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The Barrier to Internal Rotation in Amides. I. Formamide

by Torbjörn Drakenberg and Sture Forsén

Division of Physical Chemistry, The Lund Institute of Technology, Chemical Center, Lund 7, Sweden (Received June 16, 1969)

The barriers to internal rotation in ¹⁵N-formamide have been determined by proton magnetic resonance in the solvents methyl propyl ketone (MPK) and diethylene glycol dimethyl ether (diglyme). The use of ¹⁵N-enriched formamide eliminates the broadening of the proton resonances observed in ordinary formamide due to quadrupole relaxation of the ¹⁴N nucleus. The kinetic parameters were obtained from an analysis of the line shape of the ABCX-type proton resonance spectrum. Theoretical spectra were calculated by means of a computer program based on the density matrix theory of intramolecular chemical exchange in complex spin systems developed by Kaplan and Alexander. The values obtained for the activation parameters, $\Delta F \ddagger$, $\Delta H \ddagger$, and $\Delta S \ddagger$ are, in MPK solution, 17.7 kcal/mol, 18.5 kcal/mol, and 2.7 cal/deg mol; in diglyme solution, 17.8 kcal/mol, 19.0 kcal/mol, and 4.0 cal/deg mol, respectively. The barrier to internal rotation in formamide is lower than values reported for N,N-dimethylformamide by about 2–3 kcal/mol.

Introduction

The barrier to internal rotation around the C-N bond in amides has, during the last ten years, been extensively studied by nuclear magnetic resonance methods (cf. the recent reviews by Binsch¹ and Lowe²). The interest in amides is undoubtedly caused by their occurrence as building blocks in proteins and enzymes and is enhanced by the fact that the barrier to internal rotation in most amides falls in a region where magnetic resonance methods are comparatively simple to apply. Many simple amides have been repeatedly reinvestigated as a consequence of the continuous development of better measuring equipment and more refined methods for the evaluation of kinetic data from the observed spectra. As a result of these continuing efforts, the spread in reported barrier data for a given molecule has in general steadily diminished. For example, the Arrhenius energy of activation for the rotation barrier in neat N,N-dimethylformamide at present seems to converge to a value between 21 and 22 kcal/mol.³

The barrier to internal rotation in the simplest amide, formamide, is of fundamental importance as a reference point for discussions of substituent effects on the barrier in the N-C bond of amides. Furthermore, recent developments in quantum chemistry⁴ have put the rotational barrier in formamide within reach of accurate *a priori* quantum chemical calculations. Reliable data for the barrier in formamide are, however, still not available; the most reliable value of the Arrhenius energy of activation is 18 ± 3 kcal/mol reported in 1960 by Sunners, Piette, and Schneider⁵ from a study of line broadening and coalescence temperatures in the pmr spectrum of ¹⁶N-formamide. A contributing

(3) H. S. Gutowsky and C. H. Holm, J. Chem. Phys., 25, 1228
(1956); G. Fraenkel and C. Franconi, J. Amer. Chem. Soc., 82, 4428
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⁽¹⁾ G. Binsch in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968.

⁽²⁾ J. P. Lowe in "Progress in Physical Organic Chemistry," Vol. 6, S. G. Cohen, A. Streitwieser, and R. W. Taft, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968.



Figure 1. Proton nmr spectra of formamideat 60 MHz.
(a) Ordinary nmr spectrum of ¹⁴N-formamide.
(b) Double resonance spectrum of ¹⁴N-formamide with strong irradiation of the ¹⁴N resonance.
(c) Ordinary nmr spectrum of ¹⁵N-formamide.

cause to this unhappy state of the matter is that in ordinary formamide, quadrupole broadening due to ¹⁴N makes the proton nmr spectrum structureless (cf. Figure 1a). Even when the quadrupole broadening is eliminated by double irradiation at the ¹⁴N frequency (cf. Figure 1b), there still remains the problem of evaluating the rate parameters from the line shape of the complex ABC-type formamide spectrum. In the density matrix theory of the influence of exchange processes on complex spin systems developed by Kaplan⁶ and Alexander,⁷ the line shape analysis problem is formally solved. In the present work, we have applied the theory of Kaplan and Alexander to the evaluation of the barrier to internal rotation in formamide. We have, however, not employed double irradiation techniques to eliminate the ¹⁴N quadrupole broadening, but have taken an alternative approach and have performed our investigation on ¹⁵N-formamide. This compound gives a well-resolved ABCX-type proton nmr spectrum at room temperature (cf. Figure 1c), where the rate of interconversion is slow.

Experimental Section

¹⁵N-Enriched formamide containing more than 96 atom % ¹⁶N was obtained from Merck Sharp and Dohme of Canada, Ltd., Montreal. The commercial sample was used without further purification. The nmr spectra were recorded on a Varian A-60 A spectrometer equipped with a V-4341/V-6057 variable tem-

perature accessory. The amplitude of the observing rf field was approximately 0.02 mG, and the sweep rates used were 0.1 and 0.2 Hz/sec. No serious distortion of the recorded spectra due to saturation effects or excessive sweep rates was observed. A scale expansion of the recorder chart of 2 Hz/cm was used. Calibration of the spectra was performed with the usual modulation side-band technique.

Variable temperature studies were carried out on two ¹⁵N-formamide solutions: a 9.4 mol % solution of the amide in methyl propyl ketone (MPK) and a 14.1 mol % solution in diethylene glycol dimethyl ether (di-glyme).

The solution temperatures during the runs were monitored by means of a capillary, filled with a mixture of methanol and water (molar ratio 1:2), which was inserted in the center of sample tube.⁸ The temperature dependence of the difference in chemical shift between the OH and CH₃ signals in the water-methanol mixture in the capillary was calibrated in a separate experiment by means of a copper-constantan thermocouple placed inside a dummy tube containing the capillary and filled with *m*-xylene. In the solutions of ¹⁵N-formamide in diglyme, the methanol CH₃ signal of the capillary was obscured by the solvent CH₃ signal. In this case, the shift difference between the capillary OH signal and the solvent CH₃ signal was used as the "internal thermometer." The temperature dependence of this shift difference in the actual solution was calibrated in a separate experimental series by means of a copper-constantan thermocouple inserted in the annular space between the capillary and the inner wall of the sample tube. The sample temperatures obtained in this way are estimated to be accurate to $\pm 0.4^{\circ}$.

A large number of theoretical spectra were calculated on a CD 3600 computer by means of the computer program DENSMAT which has been described elsewhere.⁹ The program is based upon the density matrix theory of intramolecular exchange in complex spin systems developed by Kaplan⁶ and Alexander⁷ (cf. also Johnson¹⁰ and Binsch¹). The theoretical spectra were obtained in plotted form from a Calcomp Type plotter.

The iterative LAOCOON¹¹ calculations were carried out on a CD 3600 computer. We are grateful to Dr. S.

- (6) J. Kaplan, J. Chem. Phys., 28, 278 (1958).
- (7) S. Alexander, ibid., 37, 967, 974 (1962).

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(11) S. Castellano and A. A. Bothner-By, J. Chem. Phys., 41, 3863 (1964).

⁽⁹⁾ K.-I. Dablqvist, S. Forsén, and T. Alm, *ibid.*, in press. (A similar program has recently been developed by G. Binsch and D. A. Kleier and is available through Quantum Chemistry Program Exchange, Chemistry Dept., Indiana University, Bloomington, Ind. 47401.)



Figure 2. (a) Experimental spectrum of ¹⁶N-formamide in diglyme at 25°. The chemical shifts in Hertz from TMS. (b) Theoretical spectrum of ¹⁶N-formamide, calculated with LAOCOON III to give the best fit to the experimental one.

Castellano, Mellon Institute, for a copy of the LAOCOON 111 program.

Results and Discussion

The Nmr Spectrum of ¹⁵N-Formamide. The 60-MHz proton resonance spectrum of ¹⁵N-formamide at 25° in a 14 mol % solution in diglyme is shown in Figure 2. At this temperature the internal rotation is comparatively slow, and the nmr spectrum is of the ABCX type, X being the ¹⁵N nucleus. The hydrogen atoms will in the following be denoted according to I



ABCX spectra may be decomposed into two ABC-type subspectra, which may be denoted $a^+b^+c^+$ and $a^-b^-c^-$, respectively,¹² and in which the effective chemical shifts ν_a^+ , ν_b^+ , etc., are determined by the equations

$$\nu_{a}^{\pm} = \nu_{A} \pm \frac{1}{2} J_{AX}$$
 (1a)

$$\nu_{\rm b}^{\pm} = \nu_{\rm B} \pm \frac{1}{2} J_{\rm BX}$$
 (1b)

$$\nu_{\rm c}^{\pm} = \nu_{\rm C} \pm \frac{1}{2} J_{\rm CX}$$
 (1c)

The two *abc* subspectra in Figure 2 can be picked out by means of a repeated ABX analysis as one of the three hydrogens in both subspectra is weakly coupled to the other two. In order to obtain accurate values of the spin-coupling constants and chemical shifts, the spectra of ¹⁵N-formamide in MPK and diglyme solutions were analyzed by means of the iterative computer program LAOCOON III.¹¹ Initial values of shifts and couplings were obtained from the approximate ABXtype analysis and from the studies of ¹⁵N-formamide spectra by Sunners, *et al.*,⁵ and Bourn and Randall.¹³ The sign of all proton-proton spin couplings in formamide has been shown by Bourn, *et al.*,¹³ to be the same and to be opposite that of the directly bonded ¹⁵N-H couplings (if the ¹⁵N-H couplings are assumed to have a negative absolute sign the proton-proton couplings thus have positive sign¹⁴). The final set of parameters obtained from the iterative calculations at 25° are listed in Table I. The assignment of the ¹⁵N-formamide spectrum is based on the assumption the *trans* proton-proton coupling constant J_{BC} is larger than the *cis* coupling J_{AC} .^{5,13,14}

The degree of agreement reached between the theoretical and experimental proton resonance spectra is illustrated in Figure 2. Minor discrepancies between calculated and observed line intensities may be noted, for example, in the first two lines at low field. This is due to the fact that some lines in the experimental formamide spectrum are slightly broadened by the internal rotation already at 25° . When the finite interconversion rate is taken into consideration, the experimental spectrum can be almost perfectly reproduced.

For an accurate evaluation of the rate of internal rotation in formamide from the temperature variation of the pmr line shape it is not sufficient to know the spin-coupling and shift parameters of the spin system at one temperature; the temperature dependence of these parameters must also be taken into account. For that reason a large number of ¹⁵N-formamide spectra in MPK and diglyme solutions were recorded in the temperature interval 0 to 30°. The spectra were analyzed by means of the iterative LAO-COON III program. The temperature variation in the proton-proton spin-coupling constants was found to be statistically insignificant, with the possible exception of the coupling constant J_{AC} in MPK solution. This coupling constant was found to decrease from $1.75 \pm$ 0.05 Hz at 0° to $1.60 \pm 0.05 \text{ Hz}$ at 30°. The set of proton-proton coupling constants listed in Table I were retained unchanged in the subsequent line-shape calculations with the DENSMAT program. The chemical shifts ν_A , ν_B , and ν_C were found to vary almost linearly with temperature in the region $0-30^{\circ}$. Of the ¹⁵N-H spin couplings only the couplings to the directly bonded proton trans to the carbonyl group, i.e., J_{AX} , was found to vary significantly with temperature in both the MPK and diglyme solutions. In the temperature

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⁽¹³⁾ A. J. R. Bourn and E. W. Randall, Mol. Phys., 8, 567 (1964).

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Solvent	Mol % amide	T, °C	ΔνΑΒ	Δvac	J_{AB}	$J_{\rm AC}$	JAN	$J_{\rm BC}$	J_{BN}	JCN
Diglyme	14.1	25	21.1	-37.3	2.6	1.6	89.3	13.5	87.1	15.6
MPK	9.4	25	16.2	-57.9	2.8	1.6	90.0	13.6	87.7	15.5
Acetone	10	25	12.8	-64.9	2.9	1.7	91.0	13.5	88.0	16.4
Acetone	35	35	14.5	-50.9	2.8	1.7	89.7	13.4	86.4	16.4

Table I: Chemical Shifts and Spin-Spin Coupling Constants for 15N-Formamide^a



Figure 3. The temperature dependence of some spin-spin coupling constants and chemical shifts for ¹⁶N-formamide in diglyme.

region between 30 and 60° it was found possible to evaluate not only the rate of internal rotation in formamide but also the effective chemical shifts ν_{a}^{+} , $\nu_{\rm b}^{+}$, $\nu_{\rm c}^{+}$, $\nu_{\rm a}^{-}$, etc., from a comparison of theoretical DENSMAT spectra with experimental spectra. The parameters obtained in this way have been combined with the data obtained from the LAOCOON III calculations, and some of the results are shown in Figures 3 and 4. The differences in the effective chemical shifts $\Delta \nu_a^{+}{}_b^{+} = \nu_a^{+} - \nu_b^{+}$ and $\Delta \nu_a^{-}{}_b^{-} = \nu_a^{-} - \nu_b^{-}$ in the two abc subspectra of ¹⁶N-formamide have comparatively large influence on the calculated line shape, and, thus, on the evaluated values of the rate of interconversion, at temperatures above 60°. As may be seen from Figures 3 and 4, the values of $\Delta \nu_{a}^{+}{}_{b}^{+}$ and $\Delta \nu_{a}^{-}{}_{b}^{-}$ may be extrapolated up to at least 80° with some confidence. The same is valid for the differences $\Delta \nu_{\mathbf{a}}^{+} \mathbf{c}^{+}$, $\Delta \nu_{\mathbf{b}}^{+} \mathbf{c}^{+}$, $\Delta \nu_{\mathbf{a}}^{-} \mathbf{c}^{-}$, and $\Delta \nu_{\mathbf{b}}^{-} \mathbf{c}^{-}$. An error of a few Hertz in these differences above 60° has, however, comparatively little influence on the evaluated interconversion rates.

Evaluation of the Rate Parameters. Exchange of the protons H_A and H_B in formamide may be accomplished not only by an intramolecular rearrangement, but also



Figure 4. The temperature dependence of some spin-spin coupling constants and chemical shifts for ¹⁶N-formamide in MPK.

by intermolecular proton exchange. Both processes contribute to a broadening of the pmr spectra. As was first noted by Sunners, et al.,⁵ the rate of intermolecular proton exchange in formamide is slowed down appreciably in dilute (ca. 10 mol %) acetone solutions. A similar advantageous effect is also present in solutions of ¹⁵N-formamide in MPK and diglyme. That this is indeed so may be demonstrated in the following way. In the left half of Figure 5, a series of experimental spectra of ¹⁵N-formamide in diglyme solution at temperatures between 25 and 91.7° are shown. As may be noted in Figure 5, four C lines at low field remain unbroadened up to temperatures of about 70 to 80°. These C lines are those labeled C1 to C4 in Figures 2. As may be inferred from Figure 2 and from the spin-coupling and shift data given in Table I, the two *abc* subspectra, $a^{+}b^{+}c^{+}$ and $a^{-}b^{-}c^{-}$, in the complete ABCX spectrum of ¹⁵N-formamide, are both of the moderately strongly coupled abk type. In an ABX-type spin system it is obvious that an interchange of nuclei A and B will leave the spin states $\alpha(A)\alpha(B)$ and $\beta(A)\beta(B)$ unchanged and therefore the X transitions from the states $\alpha(A)\alpha(B)\alpha(X)$ to $\alpha(A)\alpha(B)\beta(X)$ and from $\beta(A)\beta(B)\alpha(X)$ to $\beta(A)$ - $\beta(B)\beta(X)$ will be unaffected by an *intra*molecular ex-



Figure 5. Experimental and calculated shape of the 15 N-formamide spectrum at five different temperatures. The broad signal at the arrow on the high field side of the C1 signal in spectrum e is presumably due to 14 N-formamide.

change of A and B. The same type of reasoning applies, although less rigorously, also to moderately coupled ABK spin systems. In the two subspectra of ¹⁵N-formamide in Figure 2 the lines which correspond to the transitions just discussed are C1, C2 in the $a^+b^+c^+$ subspectrum and C3, C4 in the $a^-b^-c^$ subspectrum. Intermolecular exchange of protons A and B will, however, entail a broadening also of lines C1 to C4 which makes it possible to distinguish intraand intermolecular exchange of the NH protons. In the MPK solution of ¹⁵N-formamide, as well as in the diglyme solution, the lines C1 to C4 of Figure 2 remain fairly sharp below about 80°. In the evaluation of the rate of internal rotation, the line broadenings in the C lines in excess of the small broadenings theoretically predicted with the DENSMAT program as due to the intramolecular proton exchange, have simply been treated as a lowering of the effective transverse relaxation time, T_2^{eff} , of the formamide protons. The possible errors introduced in the evaluations of the

rate constants by this approach is further discussed below.

The rate of internal rotation in ¹⁵N-formamide as a function of temperature was evaluated by means of visual fitting of theoretical line shapes to those experimentally observed. In all some 200 theoretical spectra were calculated. In general, good agreement between theoretical and experimental spectra was obtained, as is illustrated in Figure 5. At a given temperature, the value of the rate constant k = 1/rof the interconversion could mostly be demarcated to within $\pm 10\%$.

The evaluated rate constant k is plotted as log k against 1/T in Figure 3. The values for the solutions of ¹⁵N-formamide in LAPK and diglyme are seen to coincide closely. The straight line drawn in Figure 6 was obtained through a least-squares fit of the data for the diglyme solution. For clarity, the nearly co-incident line through the data for MPK solution is not shown.

Solvent	$E_{ m a}$, kcal/mol	$\log A$	∆H‡, kcal/mol	ΔS‡, cal/deg mol	ΔF^{\pm} , kcal/mol
Diglyme	19.7 ± 0.2	14.2	19.0 ± 0.2	4.0 ± 0.7	17.8 ± 0.2
MPK	19.2 ± 0.2	13.9	18.5 ± 0.2	2.7 ± 0.6	17.75 ± 0.2
Acetone	18 ± 3				

Table II: Activation Constants for Hindered Internal Rotation in ¹⁵N-Formamide^a

^a The errors as given here represent a 90% confidence interval in the least-squares deviation calculations. More realistic errors are ± 0.4 kcal/mol for E_a and ΔH^{\pm} and ± 2.0 cal/deg mol for ΔS^{\pm} . ^b Reference 5.



Figure 6. The Arrhenius plots for ¹⁵N-formamide in MPK and diglyme. O, MPK solution; Δ , diglyme solution. The solid line corresponds to $E_a = 19.7$ kcal/mol and log A = 14.2.

The experimental rate data have been analyzed as follows. The Arrhenius energy of activation, E_a , and the frequency factor, A, have been calculated in the normal way by means of the equation $k = 1/\tau = Ae^{-E_a/RT}$ from least-squares fit of $\ln k vs. 1/T$. The resulting data are presented in the first columns of Table II.

The free energy of activation, ΔF^{\pm} , enthalpy of activation, ΔH^{\pm} , and entropy of activation, ΔS^{\pm} , in the theory of the absolute reaction rate, have been calculated directly from the fundamental rate eq 2¹⁵

$$k = 1/\tau = \frac{kT}{h} e^{-\Delta F^{\pm}/RT} = \frac{kT}{h} e^{\Delta S^{\pm}/R} e^{-\Delta H^{\pm}/RT}$$
(2)

The evaluation of ΔH^{\pm} and ΔS^{\pm} is sometimes made by means of the relations

$$\Delta H^{\pm} = E_{a} - RT$$

and

$$\Delta S^{\pm} = R \ln (Ah/kT) - h$$

which follow from a combination of eq 2 with the Arrhenius equation under the assumption that E_a is temperature independent. In the direct evaluation of ΔH^{\pm} and ΔS^{\pm} from the experimental data by means of eq 2, ΔH^{\pm} and ΔS^{\pm} are assumed to be temperature independent. In the present case it is found that the values of ΔH^{\pm} obtained via E_a and directly from eq 2 differ very little since the RT term changes only a few tenths of a kilocalorie per mole over the temperature range investigated. The activation parameters ΔF^{\pm} , ΔH^{\pm} , and ΔS^{\pm} are summarized in the last columns of Table II. The standard errors

included in this table are those obtained with the too optimistic assumption that the spread in the determined τ values is entirely due to random errors. Important sources of systematical errors lie in the extrapolated values of the chemical shift between the A and B protons and in the extrapolated values of J_{AX} and J_{BX} in the temperature region 60-80°. From Figures 3 and 4 it is apparent that $\Delta \nu_{a}^{+}{}_{b}^{+}$ and $\Delta \nu_{a}^{-}{}_{b}^{-}$ tend to change less at higher temperatures. If anything, the linear extrapolation procedure adopted in this work would thus tend to overestimate the values of $\Delta \nu_{a} + {}_{b} +$ and $\Delta \nu_{a} - {}_{b} -$ at temperatures between 60 and 80°. If the actual values of these shifts are about 0.5 Hz lower than cur extrapolated values at 80°, this would mean that the value of ΔH^{\pm} in Table II is too high and should be lowered by ca. 0.4 kcal/mol. The inclusion of the broadening of the formamide proton signals due to *intermolecular* proton exchange, by means of an effective transverse relaxation time T_2^{eff} common for all transitions, is an additional source of error. In the present work the "excess" broadening due to intermolecular exchange in the sharp lines C1 to C4 can be estimated to be about 0.2 Hz at 80°. The excess broadening in the lines due to the A and B protons, which are directly involved in the intermolecular exchange, may, however, be different. In a simple spin system with two weakly coupled hydrogens A and X in which intermolecular exchange between say the A protons of different molecules takes place, the exchange broadening in the A doublet will be the same as in the nonexchanging X doublet. In a more complex spin system, this reciprocity may no longer be valid. In 15 N-formamide the proton H_c is weakly coupled to protons H_A and H_B so the assumption of reciprocity should be a comparatively good approximation. To perform a more stringent analysis one would have to know the details of the exchange process. There is no way of knowing a priori if the NH_A protons preferably exchange with other NH_A protons or preferably with NH_B protons or if the exchange of the two types of NH protons takes place completely at random. Only an extensive experimental study could make it possible to decide between

(15) S. Glasstone, K. J. Laidler, and H. Eiring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941. these alternatives. It would have been desirable to pursue the intermolecular exchange studies to higher temperatures, but unfortunately the formamide decomposes gradually as the temperature is increased above 100° . In view of the nonnegligible cost of the ¹⁶Nenriched sample, we therefore reluctantly gave up this project.

Under all circumstances, it appears preferable to include the excess intermolecular exchange broadening in the way followed in the present work rather than to neglect it entirely.

An underestimate of the excess intermolecular exchange broadening in the A and B lines of 0.2 Hz at 80°, would result in a calculated value of ΔH^{\pm} which is too high by about 0.4 kcal/mol. The systematic errors in the extrapolation of $\Delta \nu_{a} + _{b} +$ and $\Delta \nu_{a} - _{b} -$ and resulting from incorrect compensation of intermolecular proton exchange thus may tend to cancel. Our necessarily somewhat subjective estimate of the probable error in ΔH^{\pm} is ± 0.4 kcal/mol.

The free energy of activation, ΔF^{\pm} , at 298° will not be very much affected by these errors, so the probable error in ΔF^{\pm}_{298} is ± 0.2 kcal/mol, and this gives the probable error in the entropy of activation, ΔS^{\pm} , of ± 2 cal/deg mol.

The activation parameters for the MPK and diglyme solutions thus agree within the combined probable errors, and a marked solvent effect on the barriers is not apparent (cf. Table II) in contrast to the solvent effects on the nmr parameters (cf. Table I). It therefore appears justified to compare the activation parameters of formamide with those of neat N,Ndimethylformamide (DMF) for which a multitude of data are available.³ As mentioned in the Introduction, the Arrhenius energy of activation for the rotation in DMF at present seems to converge to a value between 21 and 22 kcal/mol. This value is thus some 2 to 3 kcal/mol higher than the corresponding value obtained for formamide. The difference may simply be rationalized as due to the electron-releasing and hyperconjugative effects of the methyl substituents which lead to increased stabilization to the planar or nearly planar ground state of the amide.

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Reactions of Shock-Heated Carbon Disulfide-Argon Mixtures. II.

Kinetics of the Dissociation of Carbon Disulfide

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The decomposition of shock-heated carbon disulfide diluted with argon was studied using the light emitted at 4500 Å from an upper electronic state as a monitor of the concentration. Rate data obtained in the temperature range 1900 to 3500°K, the pressure range 1 to 14.5 mm, and the mole fraction range 0.05 to 1.00, indicated that the decomposition obeys mixed order kinetics. A nonlinear statistical analysis led to a value of the rate constant for decomposition at infinite dilution in argon, k_{∞} , and that for the decomposition in pure CS₂, k_0 . These are $k_{\infty} = 10^{(15.5 \pm 0.24)} \exp(-(80.8 \pm 3.4)/RT) \text{ cm}^3 \text{ mol}^{-1} \sec^{-1}$ and $k_0 = 10^{(11.53 \pm 0.19)} \exp(-(45.2 \pm 2.2)/RT) \text{ cm}^3 \text{ mol}^{-1} \sec^{-1}$. It was concluded that, at infinite dilution, an intermediate reaction step, consistent with the transition from the ground state of CS₂ to the ³A₂ state, is required, as has been suggested by other authors. In pure CS₂ the reaction was found to be bimolecular. An induction period, observed at temperatures below 2600°K, was tentatively attributed to the time required to achieve a critical concentration of S atoms.

Introduction

Previous shock-tube studies of the dissociation of carbon disulfide diluted with $\operatorname{argon}^{1,2}$ indicated that the rate of dissociation could be expressed by

$$\frac{-\mathrm{d}[\mathrm{CS}_2]}{\mathrm{d}t} = k_{\infty}[\mathrm{CS}_2][\mathrm{Ar}] + k_{\mathrm{o}}[\mathrm{CS}_2]^2$$

Gaydon, et al.,¹ obtained the rate of dissociation by measuring the rate of appearance of CS for 0.5, 2.0, and 8.0% mixtures of CS₂ in argon at initial pressures of up to 15 mm and shock-front temperatures in the range 2250-3350°K. Under these conditions the second-order term in CS₂ appeared to correspond to a unimolecular decomposition of CS₂ in which the collision partner was another CS₂ molecule, rather than a true bimolecular reaction. By means of an iterative procedure they were able to evaluate k_{∞} , the rate constant for decomposition at infinite dilution in argon, and k_0 , the rate constant for decomposition in pure CS₂. Gaydon, et al.,¹ found $k_{\infty} =$ $10^{15.94} \exp(-81.8/RT) \text{ cm}^3 \text{ mol}^{-1} \sec^{-1}$ and $k_0 =$

In a later investigation Wagner, et al.,² studied the decomposition of $10^{-3}\%$ mixtures of CS₂ in argon at shock-front temperatures in the range $1800-3700^{\circ}$ K. Under these conditions they were able to study the unimolecular decomposition of CS₂ at effectively infinite dilution and to obtain directly a value of k_{∞} = $10^{15.65} \exp(-80.3/RT) \text{ cm}^3 \text{ mol}^{-1} \sec^{-1}$. In a subsequent investigation Wagner, et al.,³ again used $10^{-3}\%$ mixtures of CS₂ in argon but with reaction pressures up to 1500 atm, densities up to 2 $\times 10^{-3} \text{ mol cm}^{-3}$, and temperatures in the range 1950– 2800°K. In this case they obtained a value for the rate constant for the high pressure unimolecular decomposition of $10^{12.6} \exp(-87/RT) \sec^{-1}$.

Gaydon, et al.,¹ believed dissociation to occur via a spin-allowed transition to an excited singlet state. The rate-determining step would then be the transition from the ground state to the excited singlet state at a crossing point located at an energy of about 96 kcal/mol. Wagner, et al.,² however, in the light of the additional spectroscopic data available to them,⁴ showed that the dissociation more probably occurred via a spin-forbidden transition to a triplet state, the ³A₂ being considered the most likely. This state is nonlinear; hence the C_{2v} representations are used. This argument is supported by the fact that the dissociation of CO₂ occurs via a spin-forbidden singlettriplet transition.⁵

In part I,⁶ the light emission from shock-heated carbon disulfide-argon mixtures was discussed. The emission extends from 3750 to 8250 Å and appears to be continuous throughout. The emission intensity was found to be proportional to the CS₂ concentration and independent of the argon concentration. Measurements of the Arrhenius activation energy indicated that the previously unobserved ${}^{3}\Sigma_{u}{}^{+}$ state is probably responsible for the emission.

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Using some of the data obtained in these experiments, we were able to determine the rate of decomposition of CS_2 . The set of data chosen, that obtained at 4500 Å, covered the initial pressure range of 1 to 14.5 mm and a temperature range of 1900–3500°K for mole fractions of CS_2 in argon ranging from 0.05 to 1.00. An apparent induction period was observed at temperatures below 2600°K.

Experimental Section

The basic experimental apparatus was described in part I.⁶ In all cases, the emission intensity was displayed on the single sweep of an oscilloscope triggered from a velocity gauge signal. All measurements were made from photographs of the oscilloscope traces.

Results and Discussion

(a) Dissociation of CS_2 . At temperatures above 2600°K, the emission intensity rose sharply at the shock front to a maximum value and then decayed approximately exponentially to an equilibrium value (Figure 1). At lower temperatures the emission intensity again rose sharply at the front but remained essentially steady at its maximum value for a period of time before decaying (Figure 2).

If the rate of dissociation of CS_2 is expressed in its simplest form

$$\frac{d[CS_2]_3}{dt} = -k_1[CS_2]_3$$
(1)

where k_1 equals the simple unimolecular rate constant and where subscript 3 refers to conditions at time tbehind the shock front. The value of k_1 can be determined in the following manner.

Immediately behind the front, before any dissociation can take place, the intensity of the emission, I_2 , is given by

$$I_2 = I_0 [CS_2]_2 \exp(-E_{\rm a}/RT_2)$$
(2)

$$= I_0 [CS_2]_1 (\rho_2 / \rho_1) \exp(-E_a / RT_2)$$
(3)

where subscripts 1 and 2 refer to conditions before the shock and at the shock front, respectively, and where $E_{a} = 73.1$ kcal/mol, the activation energy required to populate the emitting state at 4500 Å.⁶ I_{0} is a constant independent of temperature, pressure, and mole fraction.

At a time t after the shock front, the intensity I_3 is given by

$$I_{3} = I_{0}[CS_{2}]_{3} \exp(-E_{a}/RT_{3})$$
(4)

so that

$$\frac{I_3}{I_2} = \frac{[\text{CS}_2]_3}{[\text{CS}_2]_1} \left\{ \frac{\rho_1}{\rho_2} \right\} \exp\left\{ -\frac{E_a}{R} \left\{ \frac{1}{T_3} - \frac{1}{T_2} \right\} \right\}$$
(5)

Upon taking the logarithm and differentiating with



T ₂ = 2807 °K	VELOCITY=1.73 × 105 CM SEC					
P ₂ = 195.6 mm Hg	$P_{2}/P_{1} = 4.42$					

e 1. Tracing showing the intensity-time profile steristic of a high temperature shock.



 $P_2 = 315.7 \text{ mm Hg}$ $P_2 / P_1 = 5.07$

Figure 2. Tracing showing the intensity-time profile characteristic of a lower ten perature shock. τ is equal to the induction time in laboratory coordinates.

respect to t', the time in laboratory coordinates, we obtain

$$\frac{d \ln (I_3/I_2)}{dt'} = \frac{d \ln \{ [CS_2]_3/[CS_2]_1 \}}{dt'} - \frac{E_a}{R} \frac{d(1/T_3)}{dt'} \quad (6)$$

If α is the fraction of CS₂ which has dissociated at time t, then

$$[CS_2]_3 = (1 - \alpha)(\rho_3/\rho_1)[CS_2]_1$$
(7)

Upon substituting eq 7 into eq 6 we obtain

$$\frac{\mathrm{d}\ln\left(I_{3}/I_{2}\right)}{\mathrm{d}t'} = \frac{\mathrm{d}\ln\left\{\left(1-\alpha\right)\left(\rho_{3}/\rho_{1}\right)\right\}}{\mathrm{d}t'} + \frac{E_{\mathrm{a}}}{RT_{3}}\frac{\mathrm{d}\ln T_{3}}{\mathrm{d}t'} \quad (8)$$
$$= -\frac{\mathrm{d}\alpha}{\mathrm{d}t'}\left\{\frac{1}{1-\alpha} - \frac{\mathrm{d}\ln\left(\rho_{3}/\rho_{1}\right)}{\mathrm{d}\alpha} - \frac{E_{\mathrm{a}}}{RT_{3}}\frac{\mathrm{d}\ln T_{3}}{\mathrm{d}\alpha}\right\}$$
$$(9)$$

$$\equiv -F \mathrm{d}\alpha/\mathrm{d}t' \tag{10}$$

The rate of dissociation of CS_2 (eq 1) is now related to $d\alpha/dt'$ in the following way. The left-hand side of eq 1 is changed from gas to laboratory coordinates giving

$$\frac{\mathrm{d}[\mathrm{CS}_2]_3}{\mathrm{d}t} = \left\{ \frac{\rho_1}{\rho_3} \right\} \frac{\mathrm{d}\alpha}{\mathrm{d}t'} \frac{\mathrm{d}[\mathrm{CS}_2]_3}{\mathrm{d}\alpha}$$
(11)

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and the logarithm of eq 7 is differentiated with respect to α giving

$$\frac{1}{[CS_2]_3} \frac{d[CS_2]_3}{d\alpha} = \frac{d \ln (\rho_3/\rho_1)}{d\alpha} - \frac{1}{1-\alpha}$$
(12)

Equation 12 can now be substituted into (11) to obtain

$$\frac{\mathrm{d}[\mathrm{CS}_2]_3}{\mathrm{d}t} = \frac{\rho_1}{\rho_3} \left\{ \frac{\mathrm{d}\ln (\rho_3/\rho_1)}{\mathrm{d}\alpha} - \frac{1}{1-\alpha} \right\} [\mathrm{CS}_2]_3 \frac{\mathrm{d}\alpha}{\mathrm{d}t'} \quad (13)$$

The final desired equation is then obtained by substituting the value of $d\alpha/dt'$ from eq 10 into eq 13 and rearranging

$$\frac{1}{[CS_2]_3} \frac{d[CS_2]_3}{dt} = -\frac{1}{F} \left\{ \frac{\rho_1}{\rho_3} \right\} \frac{d \ln (I_3/I_2)}{dt'} \times \left\{ \frac{d \ln (\rho_3/\rho_1)}{d\alpha} - \frac{1}{1-\alpha} \right\}$$
(14)

where

$$F = \left\{ \frac{1}{1-\alpha} - \frac{\mathrm{d}\,\ln\,(\rho_3/\rho_1)}{\mathrm{d}\alpha} - \frac{E_{\mathrm{a}}}{RT_3} \frac{\mathrm{d}\,\ln\,T_3}{\mathrm{d}\alpha} \right\} \quad (15)$$

If eq 1 is valid, then the right-hand side of eq 14 is equal to $-k_1$.

Values of d ln $(I_3/I_2)/dt'$ were obtained from measurements of the angle θ as shown in Figure 1. The values of the additional parameters required were obtained by solving the shock equation at the front and at $\alpha = 0.01$, assuming that the dissociation proceeded according to $CS_2 \rightarrow CS + 1/2S_2$. Enthalpy data were obtained from the JANAF tables. Data are given in Tables I and II.

Figure 3 shows a plot of log k_1 vs. $10^4/T$ in which there is a very large scatter in the data points. The value of k_1 , if meaningful, would represent the high pressure rate constant for unimolecular decomposition of CS₂. The lack of correlation indicates that this mechanism does not apply.

Simple bimolecular mechanisms, either first or second order in CS_2 , were then considered. For a reaction which is first order in CS_2

$$\frac{-d[CS_2]_3}{dt} = k_a[CS_2]_3[M]_3$$
(16)

where $[M]_3$ is the total gas concentration, a plot of log k_a vs. $10^4/T$ is approximately linear. For a true bimolecular reaction the equation

$$\frac{-d[CS_2]_3}{dt} = k_b[CS_2]_{3^2}$$
(17)

applies; a plot of log k_b vs. $10^4/T$, however, shows trends with mole fraction (Figure 4). It follows, therefore, that for our experimental conditions the mixed order expression

$$\frac{-\mathrm{d}[\mathrm{CS}_2]_3/\mathrm{d}t}{[\mathrm{CS}_2]_3} = k_0[\mathrm{CS}_2]_3 + k_{\infty}[\mathrm{Ar}]_3 \qquad (18)$$

Figure 3. Temperature dependence of k_1 .



Figure 4. Temperature dependence of k_b .

is likely to be valid. Using eq 14 and the fact that for dissociation close to the shock front $[M]_3 \simeq [M]_2$ and $[Ar]_3 \simeq [Ar]_2$, values of k_0 and k_{∞} can be obtained by means of a nonlinear least-squares computer calculation.⁷ This gives

$$k_{\infty} = 10^{(15.5 \pm 0.24)} \exp(-(80.8 \pm 3.4)/RT)$$

cm³ mol⁻¹ sec⁻¹

$$k_{0} = 10^{(11.53 \pm 0.19)} \exp(-(45.2 \pm 2.2)/RT)$$

$$cm^3 mol^{-1} sec^{-1}$$

where the indicated errors correspond to one standard deviation.

The rate constant k_0 was also calculated directly using a least-squares fit on the data from the pure CS₂ shocks. A value of $10^{11.44} \exp(-43.3/RT)$ cm³ mol⁻¹ sec⁻¹ with ±0.8 and ±8.5 kcal/mol for the 95% confidence intervals on the exponent of the preexponential factor and E_a was obtained.

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⁽⁷⁾ D. W. Marquandt, and R. M. Stanley, NLIN-Least Squares Estimation of Nonlinear Parameters, IBM Share Library Distribution No. S.A.D. 3093 (1964).

Table I: Shock Parameters

2	~ ~~	Velocity,	_			[Ar] × 10 ^{-s}	[CS₂] × 10 ^{−8}
Run no.	% CS1	km/sec	P_1, mm	<i>T</i> ₂ , °K	P_2/P_1	mol/cm ²	mol/cm ³
1	100	2.00	2.00	2860	11.9	0.00	128
2	100	2.00	2.50	2860	11.9	0.00	160
3 4	100	1.73	0.00	2230	11.3	0.00	365
4 5	100	2.10	1.00	2240	12.1	0.00	97.9
5	100	1.70	4.40	2300	11.4	0.00	270
7	100	1.74	3.20	2200	11.3	0.00	317
8	100	1.90	1 50	2740	11.8	0.00	209
9	100	1.33	5.50	2800	11.8	0.00	90.0
10	100	1.76	3 50	2290	11.5	0.00	042 914
11	100	1.97	3.00	2780	11.1	0.00	101
12	100	1.83	4.50	2460	11.6	0.00	280
13	100	1.73	5.00	2240	11.3	0.00	304
14	100	2.07	2.00	3030	12.0	0.00	129
15	100	1.81	4.30	2416	11.5	0.00	267
16	20	1.58	10.0	2301	5.8	2.19	54.7
17	20	1.68	4.30	2570	5.17	0.96	23.9
18	20	1.87	2.50	3081	5.31	0.57	14.3
19	20	1.58	8.10	2290	5.07	1.77	44.2
20	10	1.81	3.00	3036	4.46	0.65	7.20
21	10	1.79	3.00	2984	4.45	0.65	7.19
22	10	1.56	11.00	2330	4.30	2.29	25.5
23	10	1.48	8.00	2140	4.24	1.64	18.3
24	10	1.73	4.70	2810	4.42	1.01	11.2
20	10	1.47	9.90	2100	4.23	2.03	22.5
20	10	1.00	8.30 14 5	2440	4.33	1.74	19.4
28	10	1.83	3 00	2200	4.20	2.99	33.3 7.99
29 29	5	1 48	14.5	2200	3.88	2.05	1.22
30	5	1.65	10.4	2650	3.98	2.07	10.1
31	5	1.61	8.40	2550	3.96	1 70	8 95
32	5	1.86	3.00	3290	4.08	0.63	3.29
33	5	1.50	10.0	2220	3.88	1.98	10.5
34	5	1.80	4.70	3090	4.05	0.97	5.12
35	5	1.81	2.80	3140	4.06	0.58	3.06
36	5	1.62	8.20	2570	3.96	1.66	8.75
37	5	1.54	10.2	2350	3.91	2.04	10.7
38	5	1.55	15.0	2370	3.92	3.01	15.8
39	5	1.64	4.70	2630	3.97	0.95	5.03
40	5 F	1.87	2.60	3330	4.08	0.54	2.86
41	5 5	1.70	2.00	2940	4.03	0.54	2.82
42	5	1.40	14.5	2180	3.81	4.8/	15.1
44	5	1.00	2 50	2400	3.94 4 01	2.92	15.5
45	5	1.74	2.60	2900	4.02	0.53	2.70
46	5	1.80	5.00	3090	4.05	0.21	1.09
47	5	1.81	1.00	3110	4.06	0.21	1.09
48	5	1.86	1.00	3290	4.08	0.21	1.10
49	5	1.90	2.00	3410	4.09	0.42	2.20
50	5	1.62	3.00	2550	3.96	0.61	3.20
51	5	1.81	3.00	3140	4.06	0.62	3.28
52	5	1.59	3.00	2480	3.94	0.60	3.18
53	5	1.76	3.00	2970	4.03	0.62	3.26
04 55	5	1.87	3.00	3320	4.08	0.63	3.30
00 56	Ð	1.70	5.00	2990	4.04	1.03	5.43
57	5 5	1.04	5.00	2030 2010	0.97 4 04	1.02	5.35 5.44
58	5	1 74	5.00	2020	1.01 1.01	1.00	0.44 5.49
59	5	1.78	5 00	3030	4 04	1 03	0.42 5.44
60	5	1.78	5.00	3030	4.04	1.03	5 44
61	5	1.76	5.00	2970	4.03	1.03	5.43
62	5	1.80	5.00	3090	4.05	1.04	5.45
63	5	1.78	5.00	3050	4.05	1.03	5.44
64	5	1.77	5.00	3010	4.04	1.03	5.44

Table	II:	Kinetic	Data

'Run no.	104/ <i>T</i> , °K-1	F	d ln (I3/I2)/ dt' × 10-2	$k_1 \times 10^3$, sec ⁻¹	$k_0 \times 10^{4}$, cm ² mol ⁻¹ sec ⁻¹	$k_{\infty} \times 10^{\circ}$, cm ¹ mol ⁻¹ sec ⁻¹
1	3.50	11.4	5.46	2.60	8.31	
2	3.50	11.4	5.45	2.60	8 21	
3	4.48	19.0	2.49	0.37	7.00	
4	3.09	9.08	3.09	2 83	8 46	
5	4.35	17.9	3 55	0.63	7 27	
6	4 43	18.6	2 27	0.00	7 99	
7	3.65	10.0	J. J7	0.00	7.00	
8	3.00	12.4	4.27	1.74	7.92	
0	3.37	12.0	4.81	2.11	8.34	
9	4.07	15.6	3.30	0.83	7.39	
10	4.30	18.0	4.01	0.69	7.51	
11	3.60	12.1	2.67	1.14	7.78	
12	4.07	15.6	3.48	0.88	7.50	
13	4.47	19.0	4.32	0.64	7.32	
14	3.30	10.2	3.71	2.16	8.22	
15	4.14	16.2	4.22	0.98	7.56	
16	4.35	8.11	0.93	1.17		4.83
17	3.89	6.68	3.07	5.29		53.78
18	3.25	4.87	13.0	34.6		601
19	4.37	8.21	0.48	0.59		2.82
20	3.29	3.14	4.77	27.2		418
21	3.35	3.30	5.33	28.8		443
22	4.29	4.92	0.51	1.70		7 16
23	4.68	5.68	0.27	0.76		4 51
24	3.56	3.57	3 24	16.0		157
25	4 75	5.68	0.26	0.73		2 40
26	4 10	4 41	1 12	4.99		0.49
27	4 55	5 36	0.41	1.00		24.2
28	2.00	2.04	7.49	1.22		3.93
20	J.21 A 5A	2.04	1.44	44.0		674
29	4.04	0.04	0.34	2.19		7.56
3U 21	3.11	2.58	2.02	17.0		80.0
31	3.93	2.62	0.74	6.18		36.1
32	3.04	1.94	8.21	93.8		1500
33	4.50	3.22	0.15	1.01		5.01
34	3.24	2.09	3.98	42.3		433
35	3.19	2.14	3.67	37.9		651
36	3.90	2.64	1.07	8.76		52.4
37	4.26	3.05	0.37	2.61		12.6
38	4.22	3.01	0.36	2.59		8.48
39	3.81	2.50	0.84	7.12		74.1
40	3.00	2.01	7.76	86.3		1590
41	3.41	2.28	2.16	20.9		388
42	4.59	3.34	0.26	1.63		5.61
43	4.06	2.88	0.90	6.80		23.1
44	3.57	2.35	1.92	17.8		347
45	3.45	2.24	2.58	25.2		471
46	3.23	2.09	1.78	19.0		914
47	3.21	2.05	1.55	16.7		804
4 8	3.04	1.94	1.64	18.8		898
49	2.93	1.94	8.57	98.2		2343
50	3.92	2.71	0.54	4.35		71.3
51	3.19	2.14	8.38	86.6		1390
52	4.04	2.75	0.34	2.67		43 9
53	3.37	2.16	2.54	25.8		416
54	3.01	1.92	8.33	96 1		1533
55	3.35	2.24	4,43	43 4		410
56	3.81	2.35	0.97	7 17		70 9
57	3,33	2.13	5 64	58.9		10.4
58	3 42	2.61	2 22	20.2		002
59	3 30	2.14	5 60	50 A		317
60	3 30	2.12 9 1 <i>1</i>	0.09 207	20.4		504
61	2,00	4.14 0.04	3.8/	39,8		384
62	0.07 2.02	4.4 1 9.00	0.98	39.0		378
63	0.40 2.00	4.09	5.61	01.7		595
64	0.40 2.33	4.10 0.10	0.02	51.2		495
04	0.00	2.13	4.33	44.0		432



Figure 5. Temperature dependence of k. The lines indicate the values of k_0 and k_{∞} obtained from the nonlinear least-squares program.

Using the value of k_0 obtained from the nonlinear least-squares fit, data points for k_{∞} were obtained from eq 18. Figure 5 shows the data points for pure CS₂ with the line drawn through them representing the value of k_0 obtained by the nonlinear least-squares fit; the data points for k_{∞} are also shown, the line again representing the value obtained from the nonlinear least-squares fit. The value of k_{∞} obtained is in good agreement with the values obtained by Gaydon, *et al.*,¹ and Wagner, *et al.*² In the case of k_0 , the activation energy is in good agreement with the value of Gaydon, *et al.*,¹ but the preexponential factor is appreciably lower.

The rate constant k_{∞} has been related by previous authors^{1,2} to the collision theory expression for the rate constant for a unimolecular reaction

$$k = \left\{ \frac{PZ}{(n-1)!} \right\} \left\{ \frac{E}{RT} \right\}^{(n-1)} \exp\left\{ -\frac{E}{RT} \right\}$$
(19)

which is the product of the (collision rate) \times (the probability that the energy in the colliding pair will exceed that required to produce the transition to the new electronic state) \times (the probability that the transition will actually occur during the collision when the energy is available, *i.e.*, *P*). The collision rate, *Z*, equals 4.5×10^{14} cm³ mol⁻¹ sec⁻¹ at the mean experimental temperature of 2850°K. In this case, *E* is taken as 96 kcal/mol, the estimated energy of the crossing point of the ${}^{3}A_{2}$ state potential surface with the ground state ${}^{1}\Sigma_{g}^{+}$ potential surface.¹ The data from the present experiments are found to be consistent with n = 4 and a value of P = 0.1 and are therefore in excellent agreement with previous results.¹

It is also of interest to conjecture regarding k_0 . Even invoking the effectiveness of seven oscillators, *i.e.*, $E = (n - 3/2)RT + (45.2 \pm 2.2)$ the value of E is only 79 kcal/mol. This indicates that the reaction

$$CS_2 + CS_2 \longrightarrow CS_2 + CS + S$$
 (R1)

is not rate determining. The reaction would, therefore, appear to be truly bimolecular. Using k_0 in the true bimolecular collision theory expression

$$k_0 = PZ \exp(-E/RT) \tag{20}$$

P is found to be 10^{-3} which is not unreasonable. The reaction

$$CS_2 + CS_2 \longrightarrow 2CS + S_2$$
 (R2)

is about 94 kcal/mol endothermic and thus does not appear consistent with our measured $E_{\rm a}$ of 45 kcal/mol. It is, however, possible that reaction R1 is an over-all mechanism with an initial rate-determining step such as

$$CS_2 + CS_2 \longrightarrow CS_3 + CS$$
 (R3)

The CS_3 could then decompose rapidly by

$$CS_3 + M \longrightarrow CS_2 + S + M$$
 (R4)

Basco and Pearson⁸ have suggested that the complex CS_3 is fairly stable. Thus, it is proposed that the measured activation energy of 45 kcal/mol relates to the primary step, *i.e.*, reaction R3.

(b) Induction Period. At temperatures below 2600°K, the emission intensity traces showed a sharp rise at the front followed by a plateau where the intensity remained essentially constant. At the end of the plateau the intensity fell to an equilibrium value (Figure 2). The induction time in laboratory coordinates, τ , was taken as the interval between the front and the time at which the tangent to the region of steepest decay cuts the intensity level corresponding to the plateau. Measurements of τ were made for shocks with mole fractions, ϕ , of CS₂ from 0.05 to 0.20, shockfront pressures, P_2 , from 30 to 500 mm and shockfront temperatures, T_2 , from 2100 to 2600°K.

Certain workers, notably Levitt, et al.,⁹ in their discussion of SO₂, have linked the appearance of an induction time to the accumulation of a critical concentration of the O atom. Following this line of attack and choosing data for mole fractions of $CS_2 \leq 0.2$, the initial rate of decomposition can be approximated by

$$\frac{-d[CS_2]_3}{dt} = k_{\infty}[CS_2]_3[Ar]_3$$
(21)

It is reasonable to assume that there was a 1:1 relationship between the mcles of CS_2 decomposed and the moles of CS or S formed. Consequently, if this approach is valid, then the critical concentration of S should be given by

$$[S]_{c} \simeq k_{\infty} [CS_{2}]_{2} [Ar]_{2} \tau' \qquad (22)$$

$$\simeq k_{\infty} \rho^2 \phi (1 - \phi) \tau'$$
 (23)

(8) N. Basco and E. A. Pearson, *Trans. Faraday Soc.*, 63, 2684 (1967).
(9) B. P. Levitt and D. B. Sheen, *ibid.*, 63, 2955 (1967).



Figure 6. Plot of log $(\rho^2 \tau \phi (1 - \phi))$ vs. $10^4/T$.

where ρ is the gas density, ϕ is the mole fraction of CS_2 , $\tau' = (\rho_2/\rho_1)\tau$, and the concentrations have been approximated by the corresponding values at the shock front. Since $[S]_c$ is a constant, by definition, $1/k_{\infty} \simeq \rho^2 \phi (1-\phi)\tau$. Figure 6 shows a plot of log $(\rho^2 \phi \cdot (1-\phi)\tau)$ vs. $10^4/T$. The line drawn on the figure has a slope corresponding to E_a/R for k_{∞} . Inasmuch as the data show a reasonable scatter about this line, it is concluded that the postulated mechanism is consistent with the experimental results.

Summary and Conclusions

The decomposition of shock-heated CS_2 was monitored by measuring the rate of decay of the light emission from one of its excited states. The decomposition was found to obey the rate expression for mixed order kinetics

$$\frac{\mathrm{d}[\mathrm{CS}_2]}{\mathrm{d}t} = k_{\infty}[\mathrm{CS}_2][\mathrm{Ar}] + k_0[\mathrm{CS}_2]^2$$

with $k_{\infty} = 10^{(15.5\pm0.24)} \exp(-(80.8 \pm 3.4)/RT)$ cm³ mol⁻¹ sec⁻¹ and $k_0 = 10^{(11.53\pm0.19)} \exp(-(45.2 \pm 2.2)/RT)$ cm³ mol⁻¹ sec⁻¹. This value of k_{∞} is in excellent agreement with those previously obtained.^{1,2} The value of Gaydon, *et al.*, for k_0 differs substantially from the present result, particularly in the preexponential factor. As is noted in ref 1, however, their value of k_0 was not considered to be very trustworthy in view of experimental limitations. The low value of the activation energy in k_0 indicates that the decomposition reaction cannot be described by the one-step process

$$2CS_2 \longrightarrow CS_2 + S + CS$$

An intermediate step involving the formation of a stable CS_3 complex

$$2CS_2 \longrightarrow CS_3 + CS$$
$$CS_3 + M \longrightarrow CS_2 + S + M$$

is therefore postulated.

The observed induction times were found to be consistent with the time required to form a critical concentration of S atoms.

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Stability of Ammonium Halates in the Solid State. Kinetics and Mechanism

of the Thermal Decomposition of Ammonium Bromate

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The thermal decomposition of ammonium bromate has been studied by measuring the loss in weight. Ammonium bromate was found to be a very unstable compound; its slow self-decomposition occurred even at -5° , and it exploded above 54°. The decomposition was not complete, and the solid residue contained ammonium nitrate. The activation energy for the main process of the decomposition is 24 kcal mol⁻¹. The same value for activation energy was calculated from induction periods before explosion. The influence of various parameters such as aging, decomposition gases, and impurities on the decomposition and explosion has been also studied. The most striking effect was found in the presence of NH₈ which greatly increased the stability of ammonium bromate. It was assumed that the decomposition proceeds according to the proton-transfer mechanism.

Introduction

We have been studying for a number of years the thermal decomposition of different metallic salts of halogen oxyacids.¹⁻⁴ The purpose of these investigations is to get a general picture about the stability of the compounds and about the role of structural and physical properties in determining the stability, and to ascertain the possible mechanism of the decomposition. This research project has now been extended to ammonium compounds, which owing to the oxidizability of the cation differ in many respects from the metallic salts. Detailed kinetic investigations have been carried out so far only on the thermal decomposition of ammonium perchlorate. The ammonium halates are less stable than the ammonium perchlorate. They are all very sensitive to shock, friction, and other external influences; thus they explode at a rather low temperature. This is probably one of the reasons why detailed measurements have not been carried out on their decomposition, and only qualitative data are available concerning their stability.

The primary aim of the present work is to study the kinetics and the mechanism of the thermal decomposition of ammonium bromate (further AB) and to compare its behavior with that of ammonium chlorate and iodate.

Experimental Section

Materials. AB was obtained by the reaction

$$NaBrO_3 + NH_4Cl = NH_4BrO_3 + NaCl$$

Sodium bromate (5.35 g) was dissolved in 20 ml of water at 50°, and with constant stirring it was poured into a solution (30 ml) containing 15.1 g of ammonium chloride. The mixture was left to stand for 2 hr at 0°. The AB crystals obtained were washed with cold water and then recrystallized in 40 ml of twice distilled water. The determination

of bromate and ammonia showed an AB content of 99%.

Methods. A. The slow decomposition of AB under vacuum was followed first by measuring the pressure of the noncondensable gases formed. Other gaseous products formed during the decomposition were frozen out in a trap cooled by liquid air.

B. Since only a very slight amount of noncondensable gases was found the detailed kinetic measurements were made in a thermobalance⁵ by measuring the loss in weight of the sample. The finely powdered substance (about 50 mg) was placed in the reaction vessel by using the rotating spoon technique. The reaction vessel was immersed in a thermostatically controlled water bath and was pumped down to approximately 10^{-5} Torr before the experiments. The temperature was constant within $\pm 0.2^{\circ}$. Liquid air trap was also used in these experiments,

C. The explosion of the compound was investigated at atmospheric pressure. The substance was dropped into a glass tube heated up to the required temperature, and the gases developed before and at the moment of explosion were measured by a gas buret.

Results

Self-Decomposition of AB. Prior to kinetic investigations the self-decomposition of AB under different storing conditions was studied. A considerable weight loss had been observed even after storing at room temperature for 1 day. The extent of self-decomposi-

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- (3) F. Solymosi, Acta Chim, Acad. Sci. Hung., 57, 11, 34 (1968).
- (4) F. Solymosi and T. Bársági, Combust. Flame, 13, 262 (1969).
- (5) Z. G. Szabó and D. Király, Acta Chim. Acad. Sci. Hung., 17, 393 (1958).

⁽¹⁾ F. Solymosi and T. Bánsági, Acta Chim. Acad. Sci. Hung., 56, 337 (1968).

tion was less when the substance was kept in an open container and spread out in thin layers and much slower at -5° . In this case a 10% weight loss was observed after 18 days. A change had also occurred in the color and the composition of the sample during storage. The sample kept at room temperature had turned yellow after only 1 day. This coloring increased with time; after a few weeks, however, the sample turned white again. Chemical analysis revealed that the decrease in the AB content was due to the formation of ammonium nitrate. Some of the results are shown in Table I.

Table I: Self-Decomposition of AB

	•			
Time of th e stori ng , days	Weight loss, % (at -5°)	AB content, % (at -5°)	Weight loss, % (at 25°)	AB content, % (at 25°)
1	0.02	99.6	49.1	80.4
2	0.06		69.7	65.4
3	0.42	99.4	71.9	59.0
4	0.61		73.3	52.1
5	1.26			
6	1.77			
7	2.28	95.2		
8	3.19		77.4	47.3
10				· · · ·
11	5.11			
13				
14	7.22	94.6		
15	8.22			
18	9.25	89.7		
20	10.84			
22	12.53			· · ·
24	14.50	88.0		
28	14.98		81.2	34.3

Kinetic Investigations. A 50-mg sample of AB was used in one experiment. The slow decomposition was studied between 32 and 50°. About 56–65% of the sample decomposed into gaseous products. The solid residue contained undecomposed AB (80.7%) and ammonium nitrate (18.4%). The gaseous product consisted of mixtures of water, oxygen, nitrous oxide, and bromine. The decomposition can be characterized by the reaction equation

$$4NH_4BrO_3 = NH_4NO_3 + 2Br_2 + O_2 + N_2O + 6H_2O$$

Figure 1 shows some α -t curves. The fractional decomposition, α , was calculated on the basis of correlation

$$\alpha = \frac{w_{k} - w_{0}}{w_{k}}$$

where w = weight of the sample, $w_k =$ weight of the AB decomposed in the reaction, $w_t =$ weight of the residue of the decomposition, $w_t =$ weight measured in t time, $w_0 = w_t - w_i$, $w_k = w - w_i$.

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Figure 1. α -t curves of the decomposition of AB: 1, 44.5°; 2, 38.1°; 3, 34.0°.



Figure 2. Kinetic analysis of the decomposition of AB by the Garner equation: $1, 41.5^{\circ}$; $2, 38.1^{\circ}$.

The decomposition of AB is preceded by a considerably long time lag (τ_0), the length of which depends on the temperature. At 35.7°, the value of τ_0 exceeds 150 min.

Plotting the logarithms of the time lags against 1/T value of 24 kcal mol⁻¹ was obtained for the activation energy.

On examining the shape of the α -t curves it appears that, especially at lower temperatures, it consists of three parts: (1) short acceleration period, (2) a rather long constant rate process, and (3) deceleratory reactions The short acceleration period ($\alpha = 0.01-0.2$) obeyed the Garner relation (Figure 2)

$$\log p = k_1 t + C_1$$

The value of the activation energy was 15.9 kcal mol⁻¹. From the temperature dependence of the slope of constant rate process 24.5-kcal mol⁻¹ activation energy was calculated. The third part of the α -t curves was evaluated by the monomolecular decay equation

Table II: Kinetic Data for the Decomposition of AB

		A F	A 17		Slame of suit	1
		$(n \Rightarrow 2)$	$(n \Rightarrow 3)$	$\log n = k_{i}t$	curves	$\log \frac{1}{1-a} = k_2 t$
Temp, °C	70, min	$k_4 \times 10^8$	$k_4 \times 10^3$	$k_1 \times 10^2$	$k_a \times 10^{3}$	$k_2 \times 10^3$
32.1	165	3.72	3.08	1.6	4.51	9.31
33.0	151	4.55	3.3	2.15	5.19	9.85
34.0	178	5.55	4.27	3.5	6.18	
36.1	169	5.95	5.83	1.87	7.51	14.6
38.1	122	7.09	5.96	3.25	8.33	• • •
41.5	88	10.9	8.2	5.25	13.5	16.4
44.5	59	19.7	13.6		23.3	25.1
44.5	55	17.2	15.6	4.16	23.3	24.5
47.0	42.7	(30.5)	(25.5)	5.91	32.1	34.5
Activation energy,						
kcal mol ⁻¹	24.00	26.08	24.00	15.9	24.5	16.3
Frequency factor, \min^{-1}		$1.73 imes10^{16}$	$4.72 imes10^{14}$	$4.93 imes 10^{\circ}$	$1.72 imes 10^{16}$	4.46×10^{9}

$$\log \frac{1}{1-\alpha} = k_2 t + C_2$$

which describes the decomposition between $\alpha = 0.65$ and $\alpha = 0.95$. The activation energy was found to be 16.3 kcal mol⁻¹.

The kinetic analysis of the α -t curves was also attempted by the Avrami-Erofeyev equation

 $(-\log(1 - \alpha))^{1/n} = k_4 t + C_4$

which, especially at higher temperatures, gave reasonable straight lines between $\alpha = 0.09-0.8$ (n = 2) and $\alpha = 0.2-0.75$ (n = 3) (Figure 3). The values for the activation energy were 26 and 24 kcal mol⁻¹. Kinetic data are given in Table II.

Explosion. While at 50° the decomposition of AB took place at a measurable rate, at 54°, a "mild" explosion was observable. A very violent explosion, accompanied by flame and sound, occurred at 56°. Prior to the explosion only slight gas evolution was experienced. Using 30 mg of the sample approximately 7.5–8 ml of gas was produced; solid residue was not found after the explosion. On the basis of gas analysis the following equation describes the explosion

$$2NH_4BrO_3 = N_2 + Br_2 + O_2 + 4H_2O$$

In addition a small amount of N_2O was also formed during the explosion. From the temperature dependence of the induction periods determined between 56.0 and 75.1°, 25-kcal mol⁻¹ activation energy was obtained.

The Effect of Reaction Conditions and Foreign Substances. The stability of AB has been studied under different conditions and in the presence of various additives. Under continuous evacuation of the reaction products the decomposition commenced earlier and proceeded at faster rate and to a greater extent.

In the presence of N_2 , Br_2 , and N_2O (100 Torr) the rate of the decomposition decreased practically



Figure 3. Kinetic analysis of the decomposition of AB by the Avrami-Erofeyev equation; temp, 38.1° : 1, n = 3; 2, n = 2.



Figure 4. Decomposition of AB in the presence of different pressures of NH_3 at 42° : 1, 0 Torr; 2, 5.1 Torr, 3, 20.4 Torr; 4, 150 Torr; 5, 300 Torr; 6, 600 Torr.

to the same extent, but the loss in weight was somewhat higher. Detailed measurements have been carried out on the effect of NH_3 , and the results were plotted in Figure 4. It can be seen that at lower

Temp, °C	Pressure of gases, Torr	Weight loss, %	Undecomposed AB, %	AN formed. ^a
47	Vacuum	71.2	23.5	5.24
42	Vacuum	54.3	36.1	9.47
38.6	Vacuum	49.3	33.9	9.4
47	400 N ₂	75.3	7.76	16.7
42	600 N ₂	74.7	14.95	10.35
42	100 N ₂	66.0	27.42	6.53
42	20 NH ₂	45.2	26.22	27.85
42	100 NH ₃	20.8	36.2	50.5
42	300 NH ₃	20.55	33.5	45.8
42	600 NH ₃	4.97	2.65	2.29
42	100 Br ₂	62.9	28.82	8.06

Table III: Thermal Decomposition of AB under Vacuum and in the Presence of Different Gases

ammonia pressures only the final value of weight loss decreased; at higher pressures, however, the rate of the weight loss was also reduced.

Considering that in the decomposition of AB a solid product, ammonium nitrate, is also formed the determination of the per cent weight loss alone cannot furnish us with reliable information regarding the effect of gases. Therefore, in some cases, chemical analysis of the solid products have also been carried out, in addition to weight-loss measurements. Data are collected in Table III. It appears that at lower NH₃ pressures (up to about 300 Torr) the amount of AB transformed decreased only slightly as the reaction occurred to a greater extent in the direction of ammonium nitrate formation. Applying higher NH_3 pressure, AB is stabilized to such an extent that its reaction remains at a very low level. For the formation of ammonium nitrate it is also more favorable to perform the experiments in the presence of N_2 instead of under vacuum. The effect of Br_2 and N_2O did not differ significantly from that of N_2 . We note that ammonium bromide was found only as a contamination (<0.3%) in the solid residue. A slight rate acceleration was observed following pretreatment of the substance with HBrO₃ or HNO₃.

The above treatments and additives used influenced also the explosion of AB. The presence of NH_3 , as well as that of NH_4NO_3 , increased the induction period before the explosion. An opposite effect was experienced by the addition of $HBrO_3$ and HNO_3 . It is interesting to note that the semiconducting oxides (Fe₂O₃, CuO, NiO, ZnO, etc.), which had a striking effect on the stability of ammonium perchlorate,⁶ exerted practically no influence in the present case.

The Effect of Aging. Since AB decomposes even at room temperature, the effect of aging was studied with crystals stored at -5° . The results of these experiments are given in Figure 5. While the decomposition curves of fresh and 1-day-old samples are identical, the decomposition of the aged crystals com-



Figure 5. The effect of aging on the decomposition of AB at 47°. Age of the sample: 1, 14 days; 2, 4 days; 3, 3 days; 4, 2 days; 5, 1 day (\cdot) , fresh substance (\times) .

mences after a considerably shorter time lag. In the cases of specimens 4 or more days old the character of decomposition also changes from autocatalytic type to a deceleratory one. Consequently, the Avrami-Erofeyev equation for describing the reaction is no longer valid. Aging has also an effect on the explosive properties of AB. While fresh substances ignite at 56° those aged for 8 and 18 days deflagrate at 53 and 51°, respectively. With aging the induction period of explosion also considerably decreases as is illustrated in Figure 6; on the other hand, the activation energy calculated from the temperature dependence of the induction periods shows only a slight increase. A higher value was found only in the case of an 18-dayold substance. The effect of aging on the activation energy of the preexplosion reaction is shown in Table IV.

Microscopic Investigations. Applying a heating rate

(6) F. Solymosi and L. Révész, Z. Anorg. Allg. Chem., 322, 86 (1963); F. Solymosi and E. Krix, J. Catal., 1, 461 (1962); F. Solymosi, Combust. Flame, 9, 142 (1965).

 Table IV:
 The Activation Energy of the Preexplosion

 Reaction As Function of the Age of AB Crystals

Age of the sample, days	Activation energy, kcal mol ⁻¹
0.5	25.1
2	26.9
3	24.6
4	30.0
5	31.4
8	30.0
18	38.2



Figure 6. The effect of aging on the explosion of AB at 56°. Age of the sample: 1, fresh substance; 2, 3 days; 3, 4 days; 4, 5 days; 5, 8 days; 6, 17 days; 7, 39 days; 8, 57 days.

of 4° /min produced white spots on the surface of the crystals at 47° . As the temperature was increased, these white spots turned into a brownish color; their number gradually increased; and at 78° they completely covered the crystals. The brownish appearance vanished at 91° , and the substance turned white again. Similar changes were observed on the crystals under isothermal conditions at 42° , as well as at room temperature with the progress of the reaction. The solid residue melted at about 166° , the melting point of ammonium nitrate.

Physical Properties. The melting point of AB cannot be determined since it explodes before it melts. The reflection spectra of the substance are shown in Figure 7. The absorption edge is at 2500 Å. The low-frequency dielectric constant at 350 kc/sec is 7.501. We attempted to determine the value of the refractive index by the Becke-line method. The only conclusion to be drawn was that the refractive index of AB is greater than 1.7.

Discussion

From among the ammonium halates, the AB proved to be the most unstable compound. Its self-decomposition occurs even at -5° , and it explodes at 54°.



Due to its instability reproducible kinetic data were obtainable only under strictly controlled conditions. The most important thing was to always use samples of the same age. Similar to the ammonium chlorate and perchlorate, the decomposition does not go to completion in this case either, and about 36-40% of AB remains undecomposed. The solid residue also contains ammonium nitrate. Microscopic investigations reveal that the reaction starts at points over the crystal surface and then spreads in hemispherical zones which coalesce and completely cover the crystals.

As regards the mechanism of the decomposition, it is unlikely that the rupture of the Br-O bond in the bromate anion is the essential step of the decomposition. The dissociation energy of the Br-O bond is about 50 kcal,⁷ *i.e.*, considerably higher than that determined from kinetic data. The above process is likely to be the rate-determining step in the decomposition of the alkali bromate occurring at much higher temperatures (above 300°).⁸

Another possibility would be that the decomposition taking place according to the electron-transfer process between NH_4^+ interstitials and BrO_3^- ions

$$\mathrm{NH}_{4}^{+} + \mathrm{BrO}_{3}^{-} = \mathrm{NH}_{4} + \mathrm{BrO}_{3} \cdot \qquad (1)$$

$$NH_4 = NH_3 + H$$
 $\Delta H = 26 \pm 10 \text{ kcal}$ (2)

The BrO_3 free radical formed in the body of AB crystals will be stable because of the crystalline force field, but it can migrate to the surface by further electron-transfer processes from a neighboring BrO_3^- ion to the BrO_3 free radical. The decomposition of the BrO_3 radical on the surface and the subsequent oxidation of NH_3 form further reaction steps and result in a decomposition nucleus. The rate-determining step in this mechanism would be the initial

⁽⁷⁾ T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958, p 217.

⁽⁸⁾ J. Jach, "Fourth International Symposium on Reactivity of Solids, Amsterdam, 1964," Elsevier Publishing Co., Amsterdam, 1965, p 334.

electron-transfer process 1 since the decomposition and the interaction of the radicals formed are evidently much faster reactions. Although the electron-transfer process cannot completely be excluded, the value of the thermal activation energy $(E_{\rm T})$ required for a bandto-band electronic transition is not in agreement with it.

This value (E_{T}) was calculated from the relation

$$E_{\rm T} = E_0 \frac{K_0}{K}; \ K_0 = n^2$$

where E_0 is the optical absorption energy, K_0 and Kare the high- and low-frequency dielectric constants, respectively, and n is the refractive index. As we could not determine the refractive index of AB needed for the calculation of K_0 , that of ammonium bromide, 1.712, was used. For $E_{\rm T}$ we obtained 1.936 eV (44.6 kcal mol⁻¹), being considerably higher than that calculated from kinetic measurements.

The decomposition is most likely to take place by the proton-transfer process

$$NH_4BrO_3(s) = NH_3(s) + HBrO_3(s)$$
(3)
$$\begin{array}{c} 1 \\ 1 \\ NH_3(g) + HBrO_3(g) \end{array}$$

The HBrO₃ formed is highly unstable, thus, immediately decomposes to species that are capable of oxidizing ammonia partly on the surface of the crystals and partly in the gas phase.

The following mechanism is proposed for the decomposition of HBrO₃ and the oxidation of NH₃

$$2(\text{HBrO}_3 \longrightarrow \text{BrO}_2 + \text{OH}) \tag{4}$$

$$2(BrO_2 \longrightarrow BrO + O)$$
 (5)

$$2BrO \longrightarrow Br_2 + O_2 \tag{6}$$

$$HBrO_3 + OH \longrightarrow H_2O + BrO_3 \tag{7}$$

$$BrO_3 \longrightarrow BrO_2 + O$$
 (8a)

 $BrO_3 \longrightarrow BrO + O_2$ (8b)

$$BrO_2 \longrightarrow BrO + O$$
 (9)

$$BrO \longrightarrow 0.5Br_2 + 0.5O_2$$
 (10)

Oxygen atoms oxidize ammonia

$$3(\mathrm{NH}_3 + \mathrm{O} \longrightarrow \mathrm{NH}_2 + \mathrm{OH}) \tag{11}$$

$$3(NH_2 + O \longrightarrow NH + OH)$$
 (12)

$$3(2OH \longrightarrow H_2O + O)$$
 (13)

$$3(NH + O \longrightarrow HNO)$$
 (14)

HNO radicals may produce N₂O, on one hand

$$2HNO \longrightarrow N_2O + H_2O \tag{15}$$

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and be oxidized to HNO₃, on the other hand

$$HNO + O_2 \longrightarrow HNO_3$$
 (16)

which reacting with the undecomposed AB yields ammonium nitrate and $HBrO_3$

$$NH_4BrO_3 + HNO_3 \longrightarrow NH_4NO_3 + HBrO_3$$
 (17)

 HBrO_3 decomposes according to eq 7, 8a, 9, and 10. On summing up the above equations we come to the over-all decomposition equation

$$4NH_4BrO_3 = NH_4NO_3 + 2Br_2 + O_2 + N_2O + 6H_2O \quad (18)$$

There are several varieties of the reactions of the radicals formed in the decomposition; the formation and disproportionation of HNO_2 yielding HNO_3 and the following steps

$$NH_2 + O_2 = NO + H_2O$$
 (19)

$$2NO + O_2 = 2NO_2$$
 (20)

might also take place.

The oxidation of ammonia has been described by O atoms. It is very likely, however, that in the oxidation reactions, the oxides of bromine can also take part as was assumed for the oxides of chlorine in the case of ammonium chlorate decomposition.⁴

Unfortunately, due to the small amount of noncondensable gases evolved it was not possible to follow the decomposition by simultaneous measurements of the weight loss and the pressure of gaseous products. Consequently, it is difficult to judge the role and the importance of the gas phase reactions. From the influence of gases we can, however, conclude that reactions may proceed in gas phase also. In agreement with the ammonium chlorate and contrary to the ammonium perchlorate the sublimation of AB, *i.e.*, the evaporation of NH₃ and HBrO₃ and their condensation on the cold part of the reaction vessel, was not observed. This was probably due to the low stability of HBrO₃.

The slowest step in the decomposition of AB according to this mechanism is very likely the protontransfer process 3 itself, as other reaction steps described above occur definitely with much higher rate.

The inhibiting effect of NH_3 and accelerating one of the halogen oxyacids serve as an evidence for the proton-transfer mechanism.^{4,9} These influences were experienced here too, though NH_3 affected the rate and extent of AB decomposition only at higher pressures.

The decomposition of AB did not go to completion the reason of which probably is the same as in the case of ammonium perchlorate and chlorate,^{4,9} namely owing to the evaporation or desorption of oxidizing

(9) J. V. Davies, P. W. M. Jacobs, and A. Russel-Jones, Trans. Faraday Soc., 63, 1737 (1967).

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products of HBrO₃ decomposition the surface of the crystals is covered with NH₃ and reaction 3 is thus suppressed. This seems to be supported by the observation, that, with the progress of the decomposition, the acidity of solids first increases; then from $\alpha = 0.8$ it decreases until the cessation of the decomposition. The incomplete decomposition may be partly attributed to the formation of ammonium nitrate, which presumably occurs on the reacting surface of AB crystals.

The decomposition of AB was influenced by the other gases as well. Their effects were two directional, namely they decreased the rate of weight loss; nevertheless, they increased its extent. The apparently contradicting effect can be explained by assuming that in the presence of gases the evaporation of the oxidizing species formed and the subsequent gas phase reaction become hindered and consequently the conditions for the oxidation of NH_3 and the formation of NH_4NO_3 on the solid will be more favorable.

A Kinetic Study of the Reactions of Tetranitromethane

with Hydroxide Ion and Nitrite Ion

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Tetranitromethane (TNM) reacts with hydroxide ion to form nitroform and carbonate ions. The reactions are first order in TNM and hydroxide ion. In water, the rate constants at 30° are 0.517 ± 0.025 and 0.255 ± 0.018 l./(mol sec). The nitrite ion produced in the carbonate reaction also reacts with TNM to form nitroform. This reaction is first order in TNM and nitrite ion; at 30° in water, the rate constant is $4.53 \pm 0.33 \times 10^{-4}$ l./(mol sec). The results for the hydroxide ion reaction producing nitroform are consistent with attack on the nitrogen atom of a nitro group as the rate-determining step. The reaction of nitrite ion to produce nitroform can occur by attack on either the nitrogen atom or the oxygen atom. The rate-determining step leading to carbonate ion involves direct attack of hydroxide ion on the carbon atom of TNM.

Introduction

We have previously described the quantitative formation of nitroform from tetranitromethane (TNM) by reaction with nitrite ion.¹ A preliminary report was presented on the kinetics of this reaction as well as the reactions of TNM with hydroxide ion.² In the present paper are detailed kinetic results which suggest possible mechanisms.

The reactions of TNM with potassium hydroxide were studied by Schmidt³ under heterogeneous conditions. He reported two reactions, one leading to nitroform ion and one leading to carbonate ion

$$C(NO_2)_4 + 2OH^- = C(NO_2)_3^- + NO_3^- + H_2O$$
 (1)

$$C(NO_2)_4 + 6OH^- = CO_3^{2-} + 4NO_2^- + 3H_2O$$
 (2)

We have found that these are applicable to our data, but also that there is still a third reaction, of TNM with nitrite ion. The kinetics of this reaction in 70% ethanol have been studied.⁴ This reaction parallels reaction 1 in producing nitroform and nitrate as the primary products. The nitrite is catalytic in its effect, *i.e.*, a mole is formed for a mole consumed

$$C(NO_2)_4 + NO_2^- = C(NO_2)_3^- + N_2O_4$$
 (3)

$$N_2O_4 + 2OH^- = NO_2^- + NO_3^- + H_2O$$
 (4)

In view of the catalytic effect of nitrite produced in reaction 2 and the two modes of reaction of hydroxide, the kinetics of TNM consumption become rather complex.

Experimental Section

Apparatus. A Beckman Model DU spectrophotometer was used for all measurements of absorbance. pH measurements were made on a Beckman Model G pH meter.

(1) D. J. Glover, J. C. Dacons, D. V. Sickman, M. E. Hill, and M. J. Kamlet, U. S. Patent 3,125,606 (Mar 17, 1964).

- (2) D. J. Glover, J. Phys. Chem., 72, 1402 (1968).
- (3) E. Schmidt, Ber., 52B, 400 (1919).
- (4) M. Sh. L'vova, V. I. Slovetskii, and A. A. Fainzil'berg, Izv. Akad. Nauk SSSR, Ser. Khim., 649 (1966); Chem. Abstr., 65, 2086h (1966).

Reagents. Dioxane was purified by the method of Fieser and Fieser,⁵ except that after a first distillation from sodium, the dioxane was again distilled directly from sodium into the reaction mixture. After the first distillation, the dioxane readily formed peroxides on standing. TNM had a freezing point of 14.1° as prepared in this laboratory by Francis Taylor, Jr.

Stoichiometry at $30 \pm 0.1^{\circ}$. TNM was added to 1 l. of 62 wt % dioxane-water in a thermostated reaction vessel fitted with a stirrer, electrodes, and a siphon. The mixture was stirred for 30 sec and, after 1 min, a sample was siphoned into 25 ml of chloroform in a 50ml volumetric flask to volume (sample 25 ml). The flask was shaken and set aside. Approximately 4 Msodium hydroxide was then added at such a rate that the "pH" was kept nearly constant at "pH 6." Samples were siphoned as above at 2-min intervals near the beginning and 4-10-min intervals near the end (total time, 50 min).

Determination of Nitroform and Unreacted TNM. The samples were analyzed as follows. The layers were separated and washed in separatory funnels. The TNM was determined by the previously described procedure,⁶ while the nitroform in the aqueous extract was determined by reading directly at 350 m μ , where the molar absorbancy is 14,400.

Determination of Nitrite and Nitrate Ions. The procedure is a modification of the method developed by English.⁷

Kinetics with Nitrite Added. Usually, the inorganic reagents were weighed out and dissolved in enough water, such that when pure dioxane was added, the solution contained 62% dioxane. The reaction was started by adding a weighed amount of TNM to the stirred mixture from a weighing buret. Occasionally, the TNM was added by pipetting an aliquot of a TNMdioxane solution into such a mixture as above, containing all the dioxane except for that known to be in the TNM aliquot. The latter procedure was always used at 0°. In any event, the dioxane was distilled from sodium directly before use.

Aqueous Solutions. The aqueous stock solution of TNM was prepared by putting approximately 1 ml of TNM in a desiccator fitted with a two-hole rubber stopper for sampling and containing a beaker with 300-400 ml of water. This solution was analyzed after standing overnight by withdrawing an aliquot and adding it to hydrazine. It was again analyzed just prior to removing an aliquot for the reaction mixture. Such a solution, when removed from the desiccator, will readily lose TNM. Similarly, a stoppered TNM solution will lose TNM to the unfilled portion of the container. The saturated stock solution was approximately $5 \times 10^{-3} M$.

With either nitrite or hydroxide ion, the reagents were dissolved in water in a 10-cm spectrophotometer cell, and an aliquot of an aqueous TNM solution was added to start the reaction. The absorbance of this solution was determined vs. a solution not containing the TNM at 2-3-min intervals for about 1 hr. This corresponded to less than 1% reaction.

Hydroxide Ion Reactions. Water. $k_{\rm OH-(1)}/k_{\rm OH-(2)}$ at $30 \pm 0.1^{\circ}$ (See Conventions in Discussion). The ratio $k_{\rm OH-(1)}/k_{\rm OH-(2)}$ = ratio nitroform/carbonate found or, with the available analytical methods the ratio of nitroform found/TNM-nitroform found. This ratio was determined as follows. An aliquot of an aqueous TNM solution was pipetted into a solution of sodium hydroxide, and the absorbancy was read as quickly as possible at 350 m μ . Readings were made until the nitroform concentration remained constant. The reaction was rapid in sodium hydroxide solutions ranging from 1×10^{-2} to 1 M, but required several days in borax solution, where the hydroxide ion concentration is about $2 \times 10^{-5} M$. The data are summarized below.

Ta	hle	T

Initial TNM, M	Initial bydroxide ion, M	Nitroform, M, found	Nitroform/ carbonate
1.76×10^{-8}	$2 imes 10^{-5}$	1.18×10^{-3}	2.03
3.89×10^{-5}	1×10^{-2}	2.61×10^{-5}	2.04
3.96×10^{-5}	0.1	$2.66 imes10^{-5}$	2.05
2.72×10^{-2}	0.1	$1.81 imes 10^{-3}$	1.99
3.91×10^{-5}	1.0	$2.60 imes10^{-5}$	1.99
			Av 2.02 \pm 0.02

Stoichiometry. To determine the stoichiometry of the reaction with hydroxide, it was necessary to use a high concentration of TNM in order to obtain high concentrations of products. TNM is soluble only to a concentration of $5 \times 10^{-3} M$ in water (30°); therefore, mixtures of water and dioxane were used to increase the solubility. It was found that 62% by weight dioxane was necessary to get a solution 0.1 M in TNM.

One reaction mixture, which was $0.0485 \ M$ in TNM, showed 97% of the nitrogen accounted for throughout the reaction as nitrite ion, nitrate ion, nitroform, and unreacted TNM. A repeat of this experiment with $0.0472 \ M$ showed 99% accounted for. Starting with $0.1028 \ M$ TNM there was found 98%. In all of these experiments, the amount of nitrate formed during the reaction was equivalent to the amount of nitroform, while that of nitrite was equal to four times that of the carbon not going to nitroform. These results show that nitroform and carbonate are the only carbon-con-

⁽⁵⁾ L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 333, method a.
(6) D. J. Glover and S. G. Landsman, Anal. Chem., 36, 1690 (1964).
(7) F. L. English, Ind. Eng. Chem., Anal. Ed., 19, 850 (1947).

<i>T</i> , °C	TNM, $M \times 10^4$	Nitrite, $M \times 10^{9}$	$\mathrm{HCO}_{\mathfrak{d}}$, M	Acetate, M	Acetic acid, M	Perchlorate, M	$k_{\rm NO_3}^ imes$ 10°, 1./(mol sec)
			6	2% dioxane			
30	10.73	9.97	0.0500			0.0399	86.0
30	11.03	10.06	0.0500			0.0399	86.2
30	9.69	10.07	0.0899				91.7
30	22.52	20.16	0.0800				86.0
30	10.64	10.08		0.0449	0.0451	0.0451	85.0
30	17.66	20.12		0.0400	0.0400	0.0400	80.5
							Av 85.9 ± 2.1
0	35.00	20.63	0.0800				9.30
0	22.95	20.46	0.0800				9.57
0	9.64	10.26	0.0899				9.60
0	8.28	10.36		0.0459	0.0459	0.0459	8.72
							Av 9.30 ± 0.29
			3	0% dioxane			
30	13.36	20.13	0.0800				5.53 ± 0.10
50	8.22	10.06	0.0900				55.7 ± 2.2

	Table II:	TNM	Plus	Nitrite	Ion	in	Dioxane-Wate
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Table III: Nitrite-Catalyzed Reaction in Water $(k_{\text{HNO}_2} = 6.61 \times 10^{-4} (30^\circ))$

T, °C	TNM, $M \times 10^4$	Nitrite, $M \times 10^{10}$	pН	Initial rate, mol/(l. hr) \times 10 ⁶	Ionic strength, M^a	$k_{\rm NO_{\bullet}} \times 10^4 \rm l./(mol sec)$
30	8 71	1 992	5 52	2.58	0 0000	4 11
30	8 94	1 497	5.80	2.25	0.1000	4 67
30	9.56	1 497	6 16	2.57	0.1000	4 92
30	37.8	1.491	5.58	8.05	0 1000	3 97
30	9.93	1.377	4.24	2.25	0.0999	4.55
30	8.73	1.035	3.53	1.62	0.0995	5.00
00	0.10				010000	Av 4.53 ± 0.33
30	8.77	1.497	5.73	2.35	0.2000	4.97
30	9.14	1.501	5.71	2.73	0.1315°	5.53
30	9.35	1.497	5.70	2.57	0.1315°	5.08
10	34.1	100.0	6.30	15.7	0.1000	0.128
10	33.3	100.0	6.32	14.8	0.1000	0.124
						Av 0.126 ± 0.002
20	16.0	2.989	5.85	1.18	0.1000	0.683
20	16.6	2.981	5.53	1.19	0.1000	0.670
						Av 0.677 ± 0.020
40	3.81	1.494	5.88	3.38	0.1000	16.5
40	3.60	1.494	5.84	3.08	0.1000	15.9
						Av 16.2 ± 0.3
50	3.27	1.493	5.67	11.1	0.1000	63.1
50	3.27	1.485	5.21	9.44	0.1000	53.9
						Av 58.5 ± 4.6

 $^{\circ}$ Adjusted with sodium nitrate, except as noted. $^{\circ}$ Hydrochloric acid added to change the pH. $^{\circ}$ Potassium dihydrogen phosphate and dipotassium hydrogen phosphate in the ratio of 10:1.

taining products from TNM. No carbonate analyses were attempted at these low pH values. However, in a separate experiment with 0.15 M sodium hydroxide, 66% of the carbon not going to nitroform was recovered as carbonate. Owing to the difficulties inherent in the analysis of carbonate in this system, this carbonate analyses was again considered sufficient to accept Schmidt's report³ that only nitroform and carbonate are formed. Catalysis by Nitrite Ion. In the above experiments it was obvious that nitroform was being formed by an autocatalytic reaction² in addition to by reaction with hydroxide. That is, one of the products formed in the hydroxide reaction accelerated the further formation of nitroform. To determine the nature of the catalytic species, kinetic runs were carried out with hydroxide alone and with hydroxide with each of the reaction products. In this manner it was found that nitrite ion was responsible for the catalytic reaction, and that neither carbonate nor nitrate ion affected the rate.

Conventions. The following conventions were adopted.

 $k_{\rm NO_2}$ - represents the rate constant for reaction of TNM with nitrite ion forming nitroform, nitrate, and reforming nitrite. $k_{\rm OH^-(1)}$ represents the rate constant for the reaction of TNM with hydroxide to form nitroform and nitrate. $k_{\rm OH^-(2)}$ represents the rate constant for the reaction of TNM with hydroxide to form carbonate and nitrite.

Kinetics of the Nitrite-Catalyzed Reaction. In order to obtain useful rate data in the nitrite-catalyzed reaction, it was necessary to have the system reliably buffered. A number of the usual buffers were tried, but were not suitable because of lack of solubility in 62% dioxane. It was found, however, that a 0.1 M solution of potassium bicarbonate could be prepared and acted as a satisfactory buffer. It was also found that acetic acid-acetate buffers were satisfactory.

The rate constants for the nitrite reaction (k_{NO_2}) could be obtained without interference from the hydroxide ion reactions by adding nitrite in sufficient initial concentrations in both buffer systems. Quantitative formation of nitroform was found.¹ In Table II, it is seen that this reaction is first order in TNM and nitrite ion and independent of the buffer kind or concentration. These reactions were usually followed over about six half-lives.

In water, the nitrite-catalyzed reaction had slowed from that in 62% dioxane by nearly a factor of 200. Therefore, it was convenient to study only the initial rates (Table III). There was only a small primary salt effect as would be expected from reaction of an ion and a neutral molecule.⁸ Data in other dioxane-water concentrations (Table IV) were also obtained from initial rate studies.

Table IV: Nitrite-Catalyzed Reaction in Dioxane-Water at 30° (Ionic Strength = 0.0715 M)

% dioxane	TNM, $M \times 10^4$	Nitrite, M × 10⁴	Initial rate mol/(l. hr) × 106	k _{NO2} ⁻ × 10 ³ l./(mol sec)
3.58	10.86	9.88	2.94	0.761
10.78	5.66	9.88	1.88	0.933
20.66	9.44	7.90	5.64	2.10
40.0	1.015	5.93	3.83	17.7
49.9	1.015	1.975	3.47	48.1

Hydroxide Ion Reactions. The kinetics of the TNM-hydroxide reaction to form nitroform were studied by initial rate experiments in the absence of nitrite ion. Data for these experiments are summarized in Table V, from which it is seen that this reaction is first order in TNM and hydroxide ion.

Because carbonate ion is also formed by reaction with hydroxide ion, one can, if they are the same reaction order, obtain the ratio of the rate constants for both reactions, *i.e.*, $k_{OH^{-}(1)}$ and $k_{OH^{-}(2)}$, by measuring only the nitroform concentration at completion of reaction. The difference from the initial TNM gives the final carbonate ion concentration, and the ratio of concentrations is the ratio of rate constants. It was found that with hydroxide concentrations from $10^{-5} M$ (borax buffer) to 1 M and TNM concentrations from 3.89×10^{-5} to $2.72 \times 10^{-3} M$, the ratio of nitroform to carbonate ion formed was 2.02 ± 0.02 at 30° . Having then obtained the rate constant for nitroform production by hydroxide ion $(k_{OH^{-(1)}})$, one can readily derive the rate constant for carbonate production $(k_{OH^{-}(2)})$ as shown in Table V.

Discussion

Activation parameters for the reaction of TNM with nitrite ion and the two reactions with hydroxide ion are assembled in Table VI. In water where the reaction was run at more than two temperatures, the 10 and 50° points are used for the calculations. Data calculated at the other temperatures did not differ appreciably from these values. For the nitrite-catalyzed reaction, the enthalpy of activation increases from 11.6 to 27.9 kcal when going from 62% dioxane to water. Correspondingly, the entropy of activation becomes more positive, increasing from -25.1 to 17.8 cal/(deg mol).

The positive entropy in water could indicate loss of solvation of nitrite ion as the transition state is formed. This is also consistent with the high value of the enthalpy in water. Energy is gained by desolvation. In 62% dioxane where there is less solvation initially, the gain in energy is less and the entropy is negative.

The large differences in both enthalpy and entropy between water and 62% dioxane suggest that the transition state is well along the reaction coordinate. From the fact that the charge is dispersed in nitrite ion but more dispersed in nitroform ion, the increase in enthalpy would imply that the transition state is more like the products than the reactants. A possible mechanism is shown in reaction 5. Attack of the nitrogen atom of the nitrite ion could also be on the nitrogen atom of the nitro group and N₂O₄ would still be the product.⁹

Similarly, for the nitroform producing hydroxide ion reaction, attack is probably on the nitrogen atom of the nitro group. This would lead to the direct formation of nitrate, whereas attack on oxygen would entail a rearrangement

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		Hydroxide,		Initial rate, mol/(l. br)		kOH-(1)	kOH-(a). ^b
<i>T</i> , °C	pH	$M \times 10^{\circ}$	TNM, $M \times 10^4$	× 10⁴	$k_{OH^-(1)}$, ^a l./(mol sec)	kOH-(2)	l./(mol sec)
30	8.45	4.17	47.5	36.0	0.506 ± 0.022		
30	8.25	2.63	5.54	2.80	0.533 ± 0.025		
30	9.18	22.4	3.41	13.7	0.500 ± 0.022		
30	9.17	21.9	3.44	14.3	0.528 ± 0.025		
30	8.75	8.32	3.49	5.41	0.517 ± 0.025		
					Av 0.517 ± 0.025	2.02 ± 0.06	0.255 ± 0.018
30	8.67	6.92	3.66	4.77	0.522 (ionic strengt	h = 0.2500 M	
10	9.35	6.61	3.65	0.665	0.0766 ± 0.0036	191	
10	9.33	6.31	18.3	3.08	0.0739 ± 0.0033		
					Av 0.0753 ± 0.0036	2.56 ± 0.09	0.0295 ± 0.0027
20	9.22	11.2	3.73	3.27	0.218 ± 0.010		
20	9.24	11.8	3.63	3.27	0.212 ± 0.010		
					Av 0.215 ± 0.010	2.47 ± 0.10	0.0869 ± 0.0081
40	7.57	1.10	3.49	2.04	1.48 ± 0.07		
40	7.56	1.07	3.44	2.02	1.52 ± 0.07		
					Av 1.50 ± 0.07	2.06 ± 0.07	0.730 ± 0.061
50	7.47	1.62	3.50	7.10	3.47 ± 0.17		
50	7.47	1.62	3.44	6.62	3.31 ± 0.17		
					Av 3.39 ± 0.17	2.05 ± 0.05	1.65 ± 0.13
^a For nit	roform produ	ction. ^b For ca	arbonate product	ion.			

Table V: TNM Plus Hydroxide Ion in Water (Ionic Strength = 0.1000 M)





 $(NO_2)_3C^- + HNO_3$ (6)

Quite obviously, the reaction of hydroxide ion producing carbonate ion involves attack on the carbon of TNM

$$(NO_2)_3 \qquad \qquad \delta^- \mid \delta^- (NO_2)_4C + OH^- \longrightarrow ((NO_2) - -OH)^- \longrightarrow$$

 $((NO_2)_3C - OH) + NO_2^{-}$ $\downarrow_{fast} CO_3^{2-} (7)$

The presence of the species $(NO_2)_3C$ -OH is probably only transitory, being rapidly attacked further by hydroxide ion to produce carbonate ion.

Sequences (5) and (6) parallel accepted mechanisms for reactions of 1,1,1-trinitroalkanes with a variety of nucleophiles, *i.e.*, hydroperoxide,¹⁰ iodide,¹¹ ethoxide, and hydroxide.¹²

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(12) A. Hantzsch and A. Rinckenberger, Ber., 32, 628 (1899).

% dioxane	Activation enthalpy, kcal/mol	Activation entropy, cal/deg							
	Nitrite reaction (Tables	II and III)							
62	11.6 ± 0.2	-25.1 ± 0.7							
30	21.9 ± 0.4	3.2 ± 1.4							
0	27.9 ± 0.1	17.8 ± 0.5							
	Nitroform from hydroxide ion (Table V)								
0	16.7 ± 0.3	-4.5 ± 1.0							
Carbonate from hydroxide ion (Table V)									
0	17.7 ± 0.5	-2.9 ± 1.8							

Table VI: Activation Parameters

Analogy for reaction 7 may be found in the reaction of fluorotrinitromethane with alkoxide ions.¹³ The products are the alkyl fluorodinitromethylethers.

$$CF(NO_2)_3 + RO^-Na^+ \longrightarrow CF(NO_2)_2OR + NaNO_2$$
(8)

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Cupric Ion-Promoted Hydrolysis and Formation of Schiff Bases Derived

from Salicylaldehydes and Aliphatic Amines¹

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Hydrolysis of Schiff bases derived from aliphatic amines and salicylaldehydes proceeds by the same mechanism as hydrolysis of benzaldehyde analogs with rate-limiting carbinolamine intermediate dehydration below about pH 3 and rate-limiting carbinolamine formation above this pH. For salicylaldehydes and 2-hydroxyacetophenone, the rate increase in basic solutions is due to nucleophilic hydroxide ion attack on dipolar ion structures. Cupric ion traps the carbinolamine intermediate in the hydrolysis of salicylideneethylamine and changes the rate-limiting step in neutral solutions from formation to decomposition of complexed carbinolamine. It is suggested that this decomposition step is also rate limiting for other transition metal ion complexes and for complexed salicylaldehyde Schiff bases of amino acids. Direct evidence is provided for the absence of a kinetic template mechanism in cupric ion complexes. A neutral solution containing predominantly the mixed chelate of 5-sulfosalicylaldehyde, glycine, and cupric ion with an equivalent amount of unbound ethylamine yields first the bidentate Schiff base chelate of ethylamine and only later the thermodynamically more stable tridentate Schiff base chelate of glycine formed in a metal ion-promoted transimination reaction.

The mechanism for hydrolysis and formation of Schiff bases derived from benzaldehydes is well understood. Above about pH 3 the rate-limiting step in the hydrolysis reaction is water or hydroxide ion attack on the Schiff base to yield a carbinolamine intermediate which undergoes rapid decomposition to aldehyde and amine. Below pH 3, decomposition of the carbinolamine becomes rate limiting.^{2,3} This paper affirms that these conclusions are also applicable to Schiff bases derived from salicylaldehydes and 2-hydroxyacetophenone.

The main object of this research is to determine the role of transition metal ions in Schiff base hydrolysis and formation. Is the rate-limiting step still carbinol-amine formation in the hydrolysis reactions at pH > 3

when transition metal ions are present? Since Schiff base formation proceeds by nucleophilic attack of free amine on the carbonyl compound, what is the effect of metal ions that reduce the free amine concentration? Do metal ions serve as kinetic templates by bringing together in a complex salicylaldehydes and aliphatic amines which then somehow interact in spite of the absence of a free electron pair on the coordinated

⁽¹⁾ This paper is abstracted in part from the Ph.D. thesis of Dr. C. V. McDonnell, Jr., 1967. The research was supported by a grant from the National Science Foundation.

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CUPRIC ION-PROMOTED HYDROLYSIS OF SCHIFF BASES

nitrogen atom? This kinetic template mechanism has been suggested several times.^{4,5}

Due to the low solubility of salicylaldehyde in water some earlier studies employed mixed solvent systems.⁵ From our first spectrophotometric studies on aqueous solutions of salicylaldehyde and ethylamine, it became apparent that the buffer systems used for pH control interacted in the hydrolysis reaction both as general catalysts and by complexing with the cupric ions. In order to utilize to full advantage the pH-stat for maintaining constant pH in buffer-free systems by external addition of acid or base during the course of reaction, the more soluble 5-sulfosalicylaldehyde was employed. With a charged sulfonate group of low basicity and negligible metal ion binding capability remote from the aldehyde and hydroxy groups, this compound is ideal for studies in aqueous solutions where a salicylaldehyde type ligand is desired.

Experimental Section

Preparation of salicylideneethylamine was patterned after a published procedure.⁶ The material analyzed as the Schiff base and the spectrum in methanol is similar to that in the literature for salicylidenevaline.⁷ Crystals of bis(salicylideneethylamine)copper(II) were prepared as described, mp 150.3-150.8, lit.⁸ 151.7-151.9. Bis(salicylideneethylamine)nickel(II) was synthesized in a similar way, mp 175.5-176.0, lit.⁸ 177.2-177.6. Bis(salicylideneethylamine)zinc(II) was obtained by similar procedures and as a white powder after two recrystallizations from methanol and repeated washings of pulverized material with ether, mp 149-151°. Anal. Calcd for $C_{18}H_{20}O_2N_2Zn$: C, 59.77, H, 5.57; N, 7.74; Zn, 18.07. Found: C, 59.51; H, 5.57; N, 7.62; Zn, 18.18.

 α -Methyl-2-hydroxybenzylideneethylamine was prepared by mixing equimolar amounts of 2-hydroxyacetophenone and ethylamine in methanol to yield a yellow solution which was evaporated without heating and the product Schiff base recrystallized from ether, mp 71-73°. Anal. Calcd for $C_{10}H_{13}ON$: C, 73.58, H, 8.03; N, 8.58. Found: C, 73.48, H, 7.90; N, 8.36. The 2:1 cupric ion salt was also prepared but dissociated immediately upon placement in aqueous solutions.

The disodium salt of 5-sulfosalicylaldehyde received from Frinton Laboratories required purification. The sample was dissolved in a minimum amount of water, filtered, acidified to pH 4, and evaporated to about half its original volume. Upon cooling, the monosodium salt precipitated, after which it was collected, recrystallized several times from water, and after drying found to be greater than 98% pure by titration.

5-Sulfosalicylideneethylamine monosodium salt was prepared from the disodium salt of the aldehyde and ethylamine hydrochloride in methanol. The absence of any reaction upon mixing the disodium aldehyde

salt and free amine indicated inhibition of Schiff base formation under these conditions by the ionized phenolic group. The monosodium salt of the Schiff base was recrystallized twice from methanol and dried in vacuo over P_2O_5 . The compound did not melt, but turned brown above 220°. The nmr spectra in DMSO- d_{θ} is consistent with the structure with the unsplit imino hydrogen at 8.60 ppm and the phenolic hydrogen 13.91 ppm downfield from TMS. Anal. Calcd for C₉H₁₀O₄ NSNa: C, 43.04; H, 3.99; N, 5.58. Found: C, 42.81; H, 4.15; N, 5.70. 5-Sulfosalicylideneglycine was prepared in a similar way. Bis(5-sulfosalicylideneethylamine)copper(II) disodium salt was prepared from the Schiff base by addition of one equivalent of hydroxide ion and one-half equivalent of cupric ion to form the 2:1 complex. The complex was recrystallized from methanol until the ultraviolet absorption spectra in acidic methanol gave the values expected for the pure Schiff base. Analysis for copper by titration gave an equivalent weight 1.2% high.

The disappearance of Schiff bases and their metal complexes was followed spectrophotometrically at 272 mµ on Cary 11 or Cary 14 recording spectrophotometers usually at $5 \times 10^{-5} M$ total ligand concentration. This wavelength is near a peak in neutral unchelated and chelated complexes in aqueous solutions. Observed first-order rate constants were determined from log $(A - A_{\infty})$ vs. time plots. In those cases where the back reaction was important, rate constants were evaluated by fitting the data to the appropriate equations for reversible reactions depending upon the determined orders of the reactions.

Measurement of rapid rates with half-lives as short as 2 sec was achieved by injecting with a syringe, through a hole cut into the top of the sample cell compartment of the Cary 11 spectrophotometer, an aqueous buffered solution at the desired ionic strength into the absorption cell containing substrate in a small amount of methanol. Buffers employed at about 0.01 M concentration included chloroacetic acid, acetic acid, phosphate, triethanolamine, tris, boric acid, bicarbonate, and ethylamine.

Many rate runs and equilibrium determinations were performed at 0.2 to $1 \times 10^{-2} M$ substrate concentration on a Radiometer pH stat whose characteristics were described previously.⁹ In the results described in this paper, the pH state portrayed on a graph the amount of a standard HCl or NaOH solution added from a syringe buret to maintain a constant pH vs. time. By drawing

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a straight line through the initial portion of the rate curve, the initial molar concentration per minute, R_{stat} , of protons consumed or liberated is obtained by appropriate manipulation of units. This initial rate of molar proton consumption is not necessarily equivalent to the molar rate of substrate undergoing hydrolysis, R_{L} , but the two are related by $R_{\text{stat}} = QR_{\text{L}}$. The quantity Q must in general be determined for any system at each pH studied. The determination of Q for an important case in this research follows.

Without consideration of mechanism and merely as a material balance for protons, the hydrolysis of a neutral Schiff base SH containing an ionizable phenolic function may be written as

$$\begin{array}{ccc} \mathrm{H}^{+} + \mathrm{SH} & \longrightarrow & \mathrm{AH} + \mathrm{EH}^{+} \\ & & & & \downarrow \uparrow_{K_{2}} & & \downarrow \uparrow_{K_{A}} & & \downarrow \uparrow_{K_{E}} \\ \mathrm{S}^{-} & \mathrm{A}^{-} & \mathrm{E} \\ & & + & + \\ \mathrm{H}^{+} & \mathrm{H}^{+} & \mathrm{H}^{+} \end{array}$$

where SH, AH, and EH⁺ represent Schiff base, salicylaldehyde, and amine and K_2 , K_A , and K_E are acid ionization constants. Protonation of the imine group of the Schiff base is unimportant since all of our pH stat runs were performed at greater than 1.5 log units above its pK_a . The above scheme may be applied to Schiff bases of sulfosalicylaldehyde in this study by disregarding the negative charge on the weakly basic sulfonate group. Similarly, the negative charge due to the weakly basic carboxylate group on glycine is not counted.

For each mole of neutral Schiff base SH that is hydrolyzed, one mole of protons is consumed for the fraction of product aldehyde that is AH and the fraction of product amine that is EH⁺. To the extent that either of these products has lost a proton, the observed rate will be reduced while the observed rate will be increased by the fraction of Schiff base that is S⁻. Therefore $Q = 1 - \alpha_{A^-} - \alpha_E + \alpha_{S^-}$ where the α 's designate the fraction of each species in the indicated ionic form. The α values may be found from the known values of ionization constants in a similar way to an earlier description.⁹ Values of pK_E were taken as 10.81 for ethylammonium ion and 9.68 for glycine under the experimental conditions.¹⁰

In the presence of metal ions additional basic species will be withdrawn and we then have $Q = 1 - \alpha_{A^-} - \alpha_E + \alpha_{S^-} - \beta_{A^-} - \beta_E + \beta_{S^-}$ where the β 's represent the fraction of the designated species that are complexed by metal ions. The β values may be evaluated from metal ion formation constants. Since the formation constants for metal ions with the rapidly hydrolyzing Schiff bases are unknown, it is our practice to assume in the ethylamine system that $\beta_{S^-} = \beta_{A^-} + \beta_E$ with the result that all β terms cancel in the Q equation. The error in this assumption is not serious as long as Q values



Figure 1. Variation of the observed first-order rate constant, k_{obs} , in min⁻¹ with pH for the hydrolysis of \triangle , salicylideneethylamine; \bigcirc , 5-sulfosalicylideneethylamine; and \Box , α -methyl-2-hydroxybenzylideneethylamine.

are near unity rather than zero. In neutral solutions where most of the runs were performed on bis(5-sulfo-salicylideneethylamine), Q is unity.

All experiments were performed at $25.00 \pm 0.04^{\circ}$ and at 0.5 *M* ionic strength controlled with KCl. Even though the symbol M^{-1} is employed, second-order rate constants that represent observed first-order rate constants divided by the activity of hydrogen or hydroxide ions as calculated from the antilog of glass electrode pH meter readings and $pK_w = 14.00$ possess units of activity⁻¹ min⁻¹. These second-order rate constants may be converted to the molar concentration scale by multiplying them by 0.70, the mean ion activity coefficient of HCl and KOH in 0.5 *M* KCl.¹¹

Results

Observed first-order rate constants for the hydrolysis of 3 Schiff bases, salicylideneethylamine, 5-sulfosalicylideneethylamine, and α -methyl-2-hydroxybenzylideneethylamine, are shown in Figure 1 as a function of pH. With the exception of the ascending portion of the pHrate profile in basic solutions, the curves are typical of those observed for hydrolysis of Schiff bases derived from aliphatic amines.² The ascent in basic solutions may be accounted for by nucleophilic hydroxide ion attack on the neutral Schiff base species.

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Employing the analysis developed previously,^{2,3,12} we may account for the pH-rate profiles by the following mechanism, with the charges corresponding to those for salicylideneethylamine.

$$SH_{2}^{+} + H_{2}O + B \xrightarrow{k_{1}} IH + BH^{+}$$

$$SH_{2}^{+} + OH^{-} \xrightarrow{k_{2}} IH$$

$$SH + OH^{-} \xrightarrow{k_{3}} I^{-}$$

$$S^{-} + H_{2}O \xrightarrow{k_{4}} I^{-}$$

$$IH \xrightarrow{k_{5}} AH + E$$

$$I^{-} \xrightarrow{k_{6}} A^{-} + E$$

 $K_2 = (S^-)(H^+)/(SH)$ $K_E = (E)(H^+)/(EH^+)$

Acidic and basic species for the Schiff base are represented by SH_2^+ , SH, and S^- , for the tetrahedral carbinolamine intermediate by IH and I⁻, for the aldehyde (or ketone) by AH and A⁻, and for the amine by EH^+ and E. BH⁺ and B refer to the acidic and basic forms of general catalytic components of variable charge type. Small k's represent rate and large K's equilibrium constants.

Assuming a steady-state condition for the carbinolamine intermediate it may be shown in a straightforward fashion that the above mechanism yields for Schiff base hydrolysis an equation which is conveniently broken down into two equations, one to apply at the plateau in neutral solutions and more acidic regions and the other at the neutral plateau and more basic pH values. For acid solutions where the catalytic components are only water and hydronium ion, we obtain

$$k_{\rm obs} = \frac{k_1({\rm H}^+) + k_2 K_{\rm w}}{[({\rm H}^+) + K_1][1 + k_{-1}({\rm H}^+)/k_5]} \qquad (1)$$

and in basic solutions

 $K_1 =$

$$k_{\rm obs} = \frac{k_2 K_{\rm w}({\rm H}^+) + k_3 K_{\rm w} K_1 + k_4 K_1 K_2}{K_1({\rm H}^+) + K_1 K_2} \qquad (2)$$

By dropping terms containing (H^+) in (1) and including only such terms in (2), both equations yield $k_{obs} = k_2 K_w/K_1$ in the neutral plateau region, where K_w is the ion product constant for water, $10^{-14.00}$. Since K_1 has in all cases been determined spectrophotometrically under the same conditions, k_2 may be calculated.

According to eq 1, the acid plateau gives very nearly k_1 . In the most acidic regions (1) reduces to $k_1/[1 + k_{-1} (H^+)/k_5]$ from which the ratio k_5/k_{-1} may be determined from the points obtained in the most acidic

regions. The negative logarithm of k_5/k_{-1} gives the pH at which a change in rate-limiting step occurs from nucleophilic attack on Schiff base at high pH values to carbinolamine decomposition at lower pH values.

No general base or acid catalysis is observed in basic solutions. The plateau observed at the most basic pH is given by $(k_3K_w + k_4 K_2)/K_2$. Reasons for preferring the first of the two kinetically indistinguishable steps k_3 and k_4 are presented in the Discussion section. The k_{obs} corresponding to the average of the values for the basic and neutral plateaus occurs at pH = pK₂. Unlike pK₁, pK₂ was obtained kinetically by carefully fitting the curves in Figure 1 to the experimental points. A summary of all rate and equilibrium parameters determined for 3 Schiff bases is presented in Table I. The curves in Figure 1 are drawn with the constants listed in Table I incorporated into eq 1 and 2.

Table I: Constants from Hydrolysis and Formation ofSchiff Bases Derived from Ethylamine and5'-Sulfosalicylaldehyde (SA), Salicylaldehyde (A), and2'-Hydroxyacetophenone (MA)

	SA	Α	MA
pK₄	6.83	8.11	10.3
pK1	3.79	4.96	4.70
pK2	11.10	11.81	14.5
$k_1 \times 10^2 \min^{-1}$	69	11.8	0.165
$k_2 imes 10^{-7} \min^{-1} M^{-1}$	50	4.5	3.3
$k_{-1}/k_{b}, M^{-1}$	19	185	0.5
$k_3 imes 10^{-2} \min^{-1} M^{-1}$	51	11	0.079
$k_{-2}K_5 \times 10^4 \min^{-1} M^{-1}$	1.5		

A portion of the pH-rate profile from pH 4 to 8 was obtained spectrophotometrically for the hydrolysis of 5-sulfosalicylideneglycine. From the observed firstorder rate constants the following ratios of rate constants were calculated: $k_1/K_1 = 1.9 \times 10^5 \text{ min}^{-1} M^{-1}$ and $k_2/K_1 = 4.7 \times 10^{12} \text{ min}^{-1} M^{-2}$. It is also apparent that $k_1 > 20 \text{ min}^{-1}$ and $pK_1 < 4.0$. These values are comparable to those presented for the ethylamine Schiff base of 5-sulfosalicylaldehyde in Table I.

Up to pH 5.5 observed first-order rate constants for the disappearance of $3 \times 10^{-5} M$ bis(salicylideneethylamine)copper(II) as determined at 273 m μ are identical with those for hydrolysis of the Schiff base in absence of cupric ion, indicating that the complex immediately dissociates completely in a rapid initial step and only the hydrolysis of free Schiff base is observed. This conclusion is confirmed by the initial spectra in solutions more acid than pH 5.5 which correspond to those of free Schiff base at the same pH.

From pH 6 to 11 plots of log $(A - A_{\infty})$ vs. time were nonlinear, exhibiting two straight line portions only sometimes separated by a plateau region where the

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absorption of the intermediate could be determined. Furthermore the initial fast reaction is markedly inhibited by increasing phosphate, triethanolamine, borate, and tris(hydroxymethyl)aminomethane buffer systems while the slower second reaction exhibits general acid catalysis by at least phosphate buffer with a catalytic coefficient of 6.6 M^{-1} min⁻¹ so that at pH 7, for instance, the two reactions merge into a single one at high phosphate concentrations. Because inhibition of the initial rapid reaction is marked, some uncertainty exists in extrapolations to zero buffer concentration. In addition even at pH 7 the initial absorption curve is not that of fully complexed Schiff base but of a mixture of cupric complexed and free Schiff base.

Buffers such as triethanolamine and tris(hydroxymethyl)aminomethane strongly influence observed rates of complexed Schiff base hydrolysis. The latter buffer gives considerably slower rates than borate buffer at the same pH. The two amino buffers may form chelates expelling Schiff base, which is present in 100 times lower concentration. Studies of the cupric chelate in carbonate buffers yield rates identical with that of the free ligand at the same pH, and the initial spectra conform to that of uncomplexed Schiff base, indicating its complete expulsion from the coordination sphere of the metal ion by carbonate.

Figure 2 displays absorption spectra of bis(salicylideneethylamine)copper(II) at several times in borate buffer at pH 8.5. Though the cupric complex is reacting during the rapid scan, the curve at 1.1 min exhibits absorption peaks similar to those of the cupric Schiff base complex in methanol, but of reduced intensity. At first there is an overall decrease in absorption with a minimum value at about 15 minutes followed by an increase in absorption at longer times. The spectrum after 8 hr approaches that obtained by mixing salicylaldehyde, ethylamine, and cupric ion in a 2:2:1 ratio at the same pH and waiting about 1 day for equilibrium to be attained. The same equilibrium position about the cupric complexes of Schiff base, salicylaldehyde, and ethylamine is obtained from both directions. A similar rapid decrease with a subsequent increase in absorption was also observed in borate buffer at pH 9.4.

The spectrum at 15 min in the hydrolysis reaction shown in Figure 2 is consistent with cupric ion trapping of the weakly absorbing carbinolamine intermediate with some initial Schiff base chelate also present. Good first-order kinetics were observed over the first 15 min, with an observed rate constant of 0.38 min⁻¹ at pH 8.5. This rate increases with pH so that the initial rapid reaction may be described as nucleophilic hydroxide ion attack on complexed Schiff base to yield complexed carbinolamine

$$Cu_{1/2}S + OH^{-} \xrightarrow{\kappa_{3}} Cu$$
 (carbinolamine)

which gives $k_3 = 1.2 \times 10^5 \text{ min}^{-1} M^{-1}$. This value is about 100 times greater than that for hydroxide ion

WAVELENGTH (mµ) Figure 2. Rapidly scanned absorption spectra of 2.6 \times 10⁻⁵M bis(salicylideneethylamine)copper(II) in borate buffer at pH 8.5 showing the trapping of the carbinolamine intermediate at 15 min. Other spectra shown were taken at 1.1 and 502 min.

attack on neutral Schiff base in Table I, but 400 times slower than the k_2 rate constant for hydroxide ion attack on positively charged Schiff base.

Hydrolysis of bis(salicylideneethylamine)nickel(II) followed spectrophotometrically at $3 \times 10^{-5} M$ concentration gave two successive first-order reactions from pH 5.4 to 8.5. The second, slower reaction gave observed rate constants identical with those of the free ligand at the same pH, indicating that the initial rapid reaction is due to breakup of the nickel ion complex. The initial rapid reaction was observed when solid chelate was employed but not when a buffered solution of nickel ion was added separately to a solution containing Schiff base. Only the slower reaction of uncomplexed Schiff base hydrolysis was observed in the latter case. The rate of the initial rapid reaction of solid complex is almost proportional to the hydrogen ion activity, $k_{obs} = 1.5 \times 10^{-2} \sec^{-1} + 1.4 \times 10^{5} (\text{H}^+)$ $\sec^{-1} M^{-1}$. The hydrogen ion catalyzed rate constant is greater than that observed for breakup of the glycine complexes of nickel ion.13

Spectrophotometric observations of solutions to which had been added solid bis(salicylideneethylamine)zinc(II) at a concentration of $3 \times 10^{-5} M$ from pH

(13) A. K. S. Ahmed and R. G. Wilkins, J. Chem. Soc., 3700 (1959).



8.5 to 13.6 gave an initial rapid scan spectrum at about 1 min, which conformed to that of the Schiff base in water and rate constants that were equal within experimental error to those of uncomplexed ligand. Evidently this zinc complex dissociates at a more rapid rate than the nickel complex, and the zinc ion is not complexed to Schiff base over the pH and concentration range of our measurements.

Like the nonsulfonated analog, hydrolysis of bis(5sulfosalicylideneethylamine)copper(II) as followed at $272 \text{ m}\mu$ gave two reactions in the phosphate buffer pH 6 to 7 region. A run in borate buffer at pH 8.4 gave firstorder kinetics and no evidence of trapping of a carbinolamine intermediate. Evidently carbinolamine remains in a low steady-state concentration in this system. Initial spectra from pH-6.7 to 9.2 were identical and resembled the complex in methanol. Over this pH range, the observed pH-independent rate constant is 7×10^{-3} min⁻¹ and will be interpreted in the Discussion section. Similar results were also obstained at $3 \times 10^{-3} M$ complex in the pH-stat in the absence of buffers, where due to the higher concentration, it was necessary to consider the back reaction at the upper end of the pH range.

Schiff base formation from ethylamine and 5-sulfosalicylaldehyde was followed in the pH-stat from pH 7.0 to 7.3 where the rate-limiting step (k_{-2}) is hydroxide ion expulsion from a neutral carbinolamine intermediate. From the outlined mechanism, observed secondorder rate constants may be expressed as

$$k_{\text{obs}} = \text{rate}/T_{\text{A}}T_{\text{E}} = f_{\text{AH}}f_{\text{E}}k_{-2}K_{5}$$

where $T_{\rm A}$ and $T_{\rm E}$ represent the total molar concentrations of aldehyde and amine; $f_{\rm AH}$, the fraction of aldehyde that is neutral; and $f_{\rm E}$, the fraction of amine that is free base. Results from five experiments yield $k_{-2}K_5 = 1.5 \pm 0.1 \times 10^4 \text{ min}^{-1} M^{-1}$ where $K_5 =$ k_{-5}/k_5 . A single spectrophotometric run at pH 6.8 with $T_{\rm E}/T_{\rm A} = 25$ analyzed as a reversible first-order reaction gives a result in agreement with the above for $k_{-2}K_5$.

Schiff base formation from glycine and 5-sulfosalicylaldehyde was followed spectrophotometrically and on the pH-stat at four pH values from pH 6.8 to 7.3 to yield by an analysis similar to the above $k_{-2}K_5 = 3.4$ $\pm 0.1 \times 10^3 \text{ min}^{-1} M^{-1}$. Below pH 6.6 the reaction exhibits hydronium ion catalysis as the rate-limiting step involves k_{-1} .

Schiff base formation from $4.8 \times 10^{-3} M$ ethylamine and 5-sulfosalicylaldehyde was also followed in the pHstat in the presence of 4.8 and 9.6 $\times 10^{-4} M$ cupric ion from pH 6.6 to 7.4. Under these conditions ethylamine remains as a free ligand in solution. The first and second formation constants of 8×10^4 and 2.5 \times 10^3 , respectively, for cupric ion and 5-sulfosalicylaldehyde, interpolated from observed values on other salicylaldehydes with similar pK_a values,¹⁴ yield 1.7 to 1.9 as the average number of aldehyde molecules bound per cupric ion under the experimental conditions. The observed first-order rate constant is a sum of the reactions due to free and cupric bound aldehyde

$$rate/T_E f_E = k_{-2}K_5 f_{AH}T_A + k_M f_B T_A$$

where f_{AH} is now equal to the fraction of unbound aldehyde that is neutral and f_B is the fraction of bound aldehyde. From the results of four runs where the calculated contribution to the total rate from unbound aldehyde varies from 21 to 75%, $k_M = 1.8 \pm 0.1 \times 10^4$ M^{-1} min⁻¹ for cupric ion promoted Schiff base formation.

Experiments similar to the above were also performed with divalent nickel and zinc ions. Partly due to weaker binding of aldehyde by these metal ions the calculated rate of reaction of unbound aldehyde is comparable to the observed total reaction rate so that a definitive analysis is precluded. However, in sharp contrast to cupric ion which increases the observed second-order rate constant at pH values near 7.2, addition of nickel or zinc ions decreases this constant.

After an initial immediate decrease in pH due to binding of glycine to cupric ion in solutions containing 1:1:1 molar ratios of 5-sulfosalicylaldehyde, glycine, and cupric ions, little further change in pH was observed in the pH 6.3 to 7.8 region where about 90% of the ligands are chelated. Aliquots of these buffer-free solutions maintained at constant pH in the pH-stat were examined spectrophotometrically at various times. The absorption maximum changed from 655 m μ with ϵ 44 to 670 m μ with ϵ 80 corresponding to the spectrum obtained from a solution containing a 1:1 molar ratio of cupric ions and independently synthesized 5-sulfosalicylideneglycine. A plot of the logarithm of six observed first-order rate constants for Schiff base appearance vs. pH is linear with an approximate doubling of k_{obs} per unit increase in pH. Calculations indicate that in this system a unit rise in pH increases the binding of glycine to cupric ion so that the total amount of glycine decreases by a factor of about 5, corresponding to a doubling of the glycine anion concentration, while the change in almost fully formed chelate concentration is not significant. The two fold increase in k_{obs} and glycine anion concentration per unit rise in pH suggests that only free glycine anion reacts with chelated aldehyde. A linear plot of k_{obs} vs. glycine anion concentration that passes through the origin is obtained if a formation constant of 2.6 \times 10⁷, intermediate between the first and second formation constants of glycine with cupric ion,¹⁰ is employed to calculate the free glycinate concentration. From the slope of this plot an apparent second-order rate constant of about 3 \times 10³ M^{-1} min⁻¹ is obtained for the rate of reaction of

(14) C. Postmus, Jr., L. B. Magnusson, and C. A. Craig, Inorg. Chem., 5, 1154 (1966).



Figure 3. Spectrophotometric changes upon addition of one equivalent of ethylamine to a solution containing 1:1:1 molar ratios of 5-sulfosalicylaldehyde, glycine, and cupric ions at 10^{-2} M and pH 7.0. Numerals give hours after which spectra are taken. Spectrum in lower dashed curve is that of a solution containing 1:1:1 molar ratios of 5-sulfosalicylideneethylamine, glycine, and cupric ions while that in upper dashed curve is that of cupric ion complex of 5-sulfosalicylideneglycine.

glycinate anion with cupric chelated 5-sulfosalicylaldehyde.

When similar experiments were performed in this system with nickel replacing cupric ion, the observed first-order rate constants from pH 6.0 to 6.7 decrease with an increase in pH. Since only about one-half to three-quarters of the nickel ion is chelated, the results are more difficult to interpret than those in the cupric ion case.

In order to test further the proposal that free rather than cupric ion complexed amines react with chelated aldehyde, one equivalent of ethylamine was added to solutions containing 1:1:1 molar ratios of 5-sulfosalicylaldehyde, glycine, and cupric ions at pH 7.1 to 7.9. In the starting solution the four cupric ion binding sites are nearly filled with the pair of bidentate aldehyde and glycinate ligands while the more weakly bound monodentate ethylamine will be free in solution. The Schiff base with glycine is favored thermodynamically, and if a kinetic template mechanism is favored, it should form rapidly compared to the less stable Schiff base derived from the ethylamine free in solution. A solution containing 1:1:1 molar ratios of aldehyde, glycine, and cupric ion absorbs maximally at 655 m μ with ϵ 44; a spectrum obtained just after mixing 5-sulfosalicylideneethylamine, glycine and cupric ion at pH 7 yields an absorption maximum at 630 m μ with ϵ 64; and the 5-sulfosalicylideneglycine cupric chelate gives an absorption maximum at 670 m μ with ϵ 80, so that all three possible average complexes likely to be present in solution are distinguishable spectrophotometrically.

The progressive spectrophotometric changes observed over a period of hours on addition of one equivalent of ethylamine to a solution containing 1:1:1 molar ratios of aldehyde, glycine, and cupric ions is shown in Figure 3. These spectra were obtained in buffer-free solutions by taking aliquots from a solution maintained at constant pH on a pH-stat. During the first hour, base was added to maintain constant pH to neutralize the protons liberated upon reaction of protonated ethylamine to yield its complexed Schiff base. From the rate of addition of base, the calculated rate of attack of basic ethylamine from pH 7.1 to 7.9 is $3.2 \pm 0.4 \times 10^4$ M^{-1} min⁻¹. It is evident that during the first hour the spectra in Figure 3 approach that of the lower dashed line corresponding to a solution containing 1:1:1 molar ratios of 5-sulfosalicylideneethylamine, glycine, and cupric ions and only subsequently and more slowly does the spectrum corresponding to the thermodynamically favored cupric complex of 5-sulfosalicylideneglycine in the upper dashed curve of Figure 3 appear. At intermediate times no changes in the pH-stat occurred, but after a day the solution became basic as ethylamine was ejected from the cupric complex. The cupric complex of 5-sulfosalicylideneglycine is formed in a transimination reaction of free glycinate anion upon the complexed 5-sulfosalicylideneethylamine. Thus both the pH-stat and spectrophotometric results indicate that the early reaction is that of free ethylamine to form its thermodynamically less favored Schiff base while because most of the glycine is rendered inactive by being bound to cupric ion, it reacts more slowly to form the thermodynamically more stable tridentate Schiff base complex.

Experiments similar to the above, except for the replacement of cupric ion with nickel, yield less definite information because of less favorable absorption characteristics of the nickel ion complexes.

The overall equilibrium constant for Schiff base formation may be formulated as

$AH + E \rightleftharpoons SH + H_2O$ $K_0 = (SH)/(AH)(E)$

For the Schiff bases studied here the constant K_0 does not correspond to any pH region because in solutions so basic that the amine is in the base form E, aldehyde would also have ionized and no longer exist as AH. The above formulation is directly comparable to recorded values and the equilibrium constant at any pH may be evaluated from K_0 with the aid of furnished ionization constants. A particularly useful formulation representing the species in our solutions near pH 9 is the equilibrium $A^- + EH^+ \rightleftharpoons SH + H_2O$, $K_{\pm} = (SH)/(A^-)(EH^+)$ from which $K_{\pm} = K_0 K_E/K_A$.

For the formation of 5-sulfosalicylideneethylamit value of log $K_0 = 5.6$ is obtained from an analysis or runs for the equilibrium concentration of Schiff base II. the pH-stat from pH 7.0 to 7.6. This value may be compared with a more accurate one calculated from the observed forward and reverse reaction rates or from the kinetic parameters given for $K_5 k_{-2}$ and k_2 to give log $K_0 = 5.7$. This value is greater than that of log $K_0 =$ 4.4 reported for Schiff base formation from salicylaldehyde and ethylamine.¹⁵

The equilibrium constant for Schiff base formation from 5-sulfosalicylaldehyde and glycine was evaluated in four different ways. The equilibrium concentration of Schiff base was determined by both pH-stat and spectrophotometric methods from pH 5.7 to 7.1, from which an observed equilibrium constant at a particular pH may be calculated. Observed rate constants for formation and hydrolysis may be utilized and the kinetic parameters presented above may be employed. All four methods yield log $K_0 = 4.8 \pm 0.1$ for this system.

For the last three Schiff bases of two aldehydes and two amines log K_0 varies from 4.4 to 5.7, while for the same three compounds log $K_{\pm} = 1.8 \pm 0.1$. This latter invariant equilibrium constant suggests that the ionic formulation allows for variations in amine nucleophilicity and carbonyl compound susceptibility. This concept may be extended to the rate parameters for uncatalyzed steps in Schiff base hydrolysis of aldehydes in Table I where similar multiplicative factors appear in k_2 and K_1 and in k_3 and K_2 . Further analysis indicates that the greater part of the variation in K_0 values lies in the formation reaction, which is composed of a product of an equilibrium constant for carbinolamine addition and a rate constant for its dehydration. If partitioning of the carbinolamine intermediate to reactants and products is relatively insensitive to the particular aldehyde and amine, then the major factors determining the equilibrium constants K_0 are amine nucleophilicity and carbonyl compound susceptibility in the addition reaction to form carbinolamine, k_{-5} .

In the presence of metal ions, M, the equilibrium constant for Schiff base formation from ethylamine may be defined in a way analogous to the above $M_{1/2}A + E \rightleftharpoons M_{1/2}S + H_2O$, $K'_0 = (M_{1/2}S)/(M_{1/2}A)(E)$. By

comparison of the forward and reverse rate constants reported above for formation of 5-sulfosalicylideneethylamine in the presence of cupric ion, $\log K_0' = 6.4$ so that the presence of cupric ion in this system results in a 5 times greater equilibrium constant. If glycine were the amine, this last factor would be considerably larger for formation of a tridentate Schiff base. Stabilities of Schiff base chelates become greater relative to their decomposition complexes as the number of rings fused to the one containing the imino linkage increases.

Due to rapid hydrolysis the formation constant for metal ion binding to these Schiff bases is determinable nly with difficulty, but a value may be estimated for pric ion binding to 5-sulfosalicylideneethylamine beuse all the other equilibrium constants that compose a cyclic system have been presented. The ratio of geometric mean values of first and second formation constants for this Schiff base and 5-sulfosalicylaldehyde are given by $(\beta_{2S}/\beta_{2A})^{1/2} = K_0' K_A/K_0 K_2 = 8 \times 10^4$, a measure of the greater cupric binding strength of the Schiff base over the aldehyde. If it is assumed that the second formation constants of Schiff base and aldehyde are identical fractions of their respective first formation constants, we may estimate for the first formation constant for cupric ion binding to 5-sulfosalicylideneethylamine, $\log K_{\rm f} = \log (8 \times 10^4) + \log K_{\rm g} =$ 4.9 + 4.9 = 9.8, where K_g represents the first formation constant of cupric ion and 5-sulfosalicylaldehyde mentioned above. This result is consistent with observed breakup of the complex below pH 5.5.

Discussion

The pH-rate profiles for the ortho-hydroxy Schiff bases of ethylamine shown in Figure 1 are explicable in terms previously used to describe the hydrolysis of Schiff bases derived from substituted benzaldehydes and aliphatic amines² with the addition of the k_3 step to account for the ascent in basic solutions. This last reaction of nucleophilic hydroxide ion attack on overall neutral Schiff base is unusually effective in these cases because the predominant form of the Schiff base is a dipolar ion where the imine nitrogen bears a positive protonic charge and the ortho-hydroxy group is an anionic intramolecular hydrogen bond acceptor. The favoring of the dipolar ion over the neutral form for these ortho- and similar para-hydroxy Schiff bases is indicated by the more than one log unit greater pK_1 for the corresponding methoxy derivatives and by the relative long wavelength absorption in neutral solutions at greater than 350 m μ which may be ascribed to the quinoid-like structures that may be drawn for the dipolar ion forms.¹⁶ Thus in all cases in Table I, pK_1 refers predominantly to a phenolic ionization and pK_2 to an immonium ionization.

⁽¹⁵⁾ R. W. Green and R. J. Sleet, Aust. J. Chem., 19, 2101 (1966).

⁽¹⁶⁾ W. Bruyneel, J. J. Charette, and E. DeHoffmann, J. Amer. Chem. Soc., 88, 3808 (1966).

The ascent in basic solutions shown in Figure 1 is due to nucleophilic hydroxide ion attack on dipolar ion Schiff base (k_3) and not to the kinetically indistinguishable water attack on anionic Schiff base (k_4) for two reasons. First, as just explained, an extraordinary hydroxide ion susceptible pathway is provided by the dipolar ion structures. Second, calculated rate constants for k_4 , corresponding to the right-hand ordinate intercepts in Figure 1, are more than 50 times greater than the k_1 constants in Table I for water attack on protonated Schiff base which is unreasonable unless intramolecular general base catalysis is proposed. Neither of these arguments is applicable, however, to the basic ascent in meta-hydroxy-N-benzilidene-2aminopropane, which does not possess a quinoid-like structure, exhibits a nearly identical pK_1 with the corresponding methoxy compound, indicating first immonium then phenolic ionizations with no significant amounts of dipolar ion species, and undergoes calculated water attack on the anion less than half as rapidly as on the cation.¹⁶ We suggest that for this last compound only the k_4 rather than the k_3 step might predominate in basic solutions.

The important conclusion is that in the absence of metal ions, the Schiff bases of aliphatic amines and salicylaldehydes undergo hydrolysis and formation reactions with the same rate-limiting steps that are well established for their non-*orthe*-hydroxy counterparts. Only in solutions more acid than about pH 3 does carbinolamine decomposition become rate limiting in the hydrolysis reaction and addition to form carbinolamine become rate determining in the formation reaction. At values of pH >3, carbinolamine formation is the slow step in hydrolysis and the reverse reaction, dehydration of the carbinolamine, is the rate-limiting step in Schiff base formation.^{2,3} This conclusion is opposite to that suggested for Schiff bases derived from 3-hydroxy-pyridine-4-aldehyde.¹⁷

Trapping of the carbinolamine intermediate by cupric ion as shown in Figure 2 during the hydrolysis of salicylideneethylamine and the biphasic nature of the hydrolysis of 5-sulfosalicylideneethylamine in the presence of this metal ion indicate that carbinolamine decomposition rather than formation has become rate limiting in the presence of cupric ion. Thus the presence of cupric ion changes the rate-limiting step in the hydrolysis reactions in neutral solutions from carbinolamine formation in its absence to carbinolamine decomposition in the presence of cupric ion. Application of this conclusion to Schiff base formation in neutral solutions points up that though cupric ion appears to increase slightly the rate of formation of 5-sulfosalicylideneethylamine, the value of the rate-constant calculated for carbinolamine dehydration $(k_{-2}K_5)$ in the absence of cupric ion is not strictly comparable to the similar numerical value obtained from addition to form carbinolamine $(k_{\rm M})$ in the presence of cupric ion.

A mechanism for cupric ion-promoted ethylamine Schiff base hydrolysis and formation in neutral solutions that accounts for the increase in rate with increasing pH for the initial fast hydrolysis reaction, the pH independence of the second slower hydrolysis reaction, and the increase in rate with pH of the observed formation reaction is



The first step is the initial fast hydrolysis reaction while the last step is rate limiting for the slow hydrolysis reaction and for Schiff base formation in the presence of cupric ion. Other steps involving ionizations in the complexed carbinolamines are rapid.

The middle carbinolamine cupric ion complex is probably the main form appearing in neutral solutions. Due to coordination of the nitrogen to the metal ion in this form, expulsion of amine is hindered in the metal ion complex compared to the uncomplexed carbinolamine intermediate, accounting for the change in ratelimiting step from formation to decomposition of carbinolamine intermediate in the hydrolysis reaction. It is not necessary to observe complexed carbinolamine for a change in rate-limiting step to occur, and there is reason to expect other transition metal ions to exhibit the same rate-limiting steps as does the cupric ion system. The two fused chelate rings of salicylaldehyde Schiff bases derived from glycine need not undergo any rearrangements to form chelated carbinolamine, but the breakup of this fused ring system on decomposition of carbinolamine suggests that this step is even more apt to be rate limiting for amino acid Schiff bases in the presence of transition metal ions. Tetrahedral metal ion complexes may be able to undergo fused chelate ring breakup with the greatest facility.

⁽¹⁷⁾ T. C. French, D. S. Auld, and T. C. Bruice, Biochemistry 4, 77 (1965).

CUPRIC ION-PROMOTED HYDROLYSIS OF SCHIFF BASES

Observed first-order rate constants for Schiff base formation in solutions containing 1:1:1 ratios of 5sulfosalicylaldehyde, glycine, and cupric ion might be interpreted as examples of the kinetic template mechanism where the two disparate cupric ion bound ligands of the mixed chelate react to form the cupric chelate of the Schiff base. However, the correspondence between the observed first-order rate constants and glycinate anion concentration suggests that only free glycinate is an effective nucleophile in attacking the cupric ion bound aldehyde. Since the mixed chelate is in large excess over the free glycinate concentration, the reaction still appears first order, and the second-order rate constant obtained by dividing by the free glycinate concentration yields a value similar to that for reaction of ethylamine with chelated aldehyde. The more free basic amine in solution the greater the reaction rate.

The results of the experiment shown in Figure 3 where a solution containing predominantly the mixed chelate of 5-sulfosalicylaldehyde, glycine, and cupric ion with an equivalent amount of unbound ethylamine to yield first the thermodynamically less stable bidentate Schiff base chelate of ethylamine and only later the more stable Schiff base tridentate chelate of glycine, dramatizes the greater reactivity of unbound amine and the absence of a kinetic template mechanism in this system. In the absence of metal ions near neutral pH, both Schiff bases possess similar stabilities. Formation in the second slower reaction of the glycine Schiff base in a transimination reaction from the ethylamine Schiff base and unbound glycine in the presence of a cupric ion is an example of a thermodynamic template reaction. The mechanism of transimination in the presence of metal ion should be analogous to that implied above for Schiff base formation and hydrolysis by water and to

that suggested for ester exchange reactions in Schiff base chelates,¹⁸ with addition of a tetrahedral carbon intermediate species.

After noting an apparent zinc ion dependent pathway in Schiff base formation from salicylaldehyde and glycine and the absence of cupric and nickel ion pathways under the conditions of their study, Bai and Leussing proposed a kinetic template pathway in the presence of zinc ion.⁴ Their calculated value for nucleophilic glycine anion attack on the zinc-salicylaldehyde complex is 47 times greater than the overall rate constant for glycinate attack on neutral salicylaldehyde. However, as stressed in this paper the ratelimiting step in the latter case is carbinolamine dehydration, so that the overall rate constant is a product of a rate and equilibrium constant $(k_{-2} K_5)$ in the notation of this paper) while the rate-limiting step in the zinc ion reaction is unknown. Their cupric and nickel ion studies were performed at lower pH values than those of this work where little complex formation with salicylaldehyde is expected. Their zinc ion studies overlapped the pH region of this work where 5-sulfosalicylaldehyde is so weakly bound to zinc ion that quantitative interpretation in the pH-stat is difficult though it appears that the presence of zinc ion is inhibitory in our system with ethylamine. A zinc ion dependent pathway may be a result of its near tetrahedral disposition of donor atoms and its weaker amine binding capability. Nucleophilic attack by external amine might be less sterically hindered than in cupric and nickel ion complexes of aldehydes and the free basic amine concentration will be greatest with the metal ion that forms the weakest amine complexes.

(18) R. P. Houghton and D. J. Pointer, J. Chem. Soc., 3302 (1964).

Degradation of Graham's Salt in Presence of Water-Miscible Organic Solvents

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Graham's salt, the polymeric sodium phosphate glass, undergoes depolymerization in presence of certain watermiscible organic solvents, e.g., acetone, methyl, ethyl, n-propyl, and t-butyl alcohol, and dioxane. A 40% aqueous solution of these polar organic solvents has the same effect irrespective of the dielectric constant of the medium. The nucleophilic organic solvents catalyze the hydrolytic degradation of Graham's salt by taking part in the reaction. Kinetic results for 40% ethanol show that the energy of activation is about 16 kcal/mol, which is equal to what one would expect if 0.1 M hydrochloric acid were to induce hydrolytic degradation.

Introduction

Graham's salt, the polymeric sodium phosphate O

glass, $OH = (\stackrel{"}{P} = O)_n = H$, exists as an open-chain poly-

electrolyte. It hydrolyzes in the presence of acids.² Recently, Martens and Rieman³ mentioned in passing, and without any detailed explanation, that certain polar solvents catalyze the hydrolytic degradation of Graham's salt. Thilo⁴ found that lowering of the dielectric constant of the medium enhanced the catalytic effect of cations in causing hydrolytic degradation of Graham's salt. We⁵ observed this phenomenon while attempting the fractional precipitation of Graham's salt with the help of acetone and reached four important conclusions: (i) the degradation is negligible at low and moderate temperatures, (ii) the degradation in pure water is slight in comparison to that in presence of even a small amount of acetone, (iii) the degradation is probably not due to any increased acidity because the addition of acetone itself does not alter the pH of the solution of Graham's salt (as measured with the glass electrode) significantly, and (iv) the degradation is favored by increasing amounts of acetone.

In the present paper, a more detailed study of the phenomenon is being presented. The degradation has been observed in several other water-soluble organic solvents and a kinetic study has been made in 40% solution of ethanol.

Experimental Section

The samples of Graham's salt used in the present investigation were prepared by heating AR sodium dihydrogen phosphate (B.D.H.) in a platinum dish above 700° in a Gallenkamp muffle furnace (maintaining the temperature within $\pm 10^{\circ}$) and quenching the melt by pouring it on a stainless steel plate and quickly pressing another on it. Their weight-average molecular weights (M_w) were determined by measuring intrinsic viscosities in 0.035 N NaBr solution.⁶ As found by Strauss, et al.,⁷ intrinsic viscosity $[\eta]$ determined in this way is related to M_w determined by light-scattering measurements. Thus

$$[\eta] = 1.76 \times 10^{-5} M_{\rm w} \tag{1}$$

End group molecular weights, M_{e} , were obtained by employing the simple equation⁶

$$M_{\circ} = \frac{20,400}{a}$$
 (2)

where a is the volume of 0.1 N NaOH solution required to titrate 1.02 g of Graham's salt in the pH range of 5.5 to 8.5, the molecular weight of the monomer unit NaPO₃ being 102.

Of the samples mentioned in Table I, the one with $M_{\rm w} = 9140$ was prepared by heating NaH₂PO₄ at 700° for 6 hr and the one with $M_{\rm w} = 9950$ was prepared by heating NaH₂PO₄ at 700° for 9 hr. The values of $M_{\rm o}$ for these samples were found to be 4720 and 6370, respectively.

The following experiment was performed to study degradation in 40% aqueous solutions of six different water-miscible organic solvents: acetone, methyl, ethyl, *n*-propyl, and *t*-butyl alcohol, and dioxane. All the organic solvents were purified by using standard purification methods for each of them. A weighed amount (about 0.2 g) of a sample of Graham's salt of known molecular weight was taken in a thin glass test tube of about 10 ml capacity. Just enough solvent was added to it so that the concentration of Graham's salt in the resultant solution was exactly 10%. The

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⁽⁷⁾ U. P. Strauss, E. H. Smith, and P. L. Wineman, J. Amer. Chem. Soc., 75, 3935 (1953).

tube was then sealed off carefully and placed in an oven at $55 \pm 1^{\circ}$. After 5 hr, it was taken out of the oven, broken from the top, and its contents transferred into a centrifuge tube. The polyelectrolyte was completely precipitated by adding an excess of the organic solvent whose solution was used. The precipitate was separated by centrifugation at 0° so that no further degradation could take place. The precipitate was dried in a vacuum desiccator. Experiments with all the solvents were done simultaneously and almost similar conditions were employed in all cases. This was done so that a comparison could be made on a sound basis. Dielectric constants of the solvents were determined by a method described by Bhargava and Srivastava.⁸

Experiments done for the kinetic study in 40%aqueous solution of ethanol were similar to those described above. Six sealed tubes containing 10%solution of a particular sample of Graham's salt in 40%ethanol were placed in a preheated incubator maintained at 45°. They were taken out, one by one, after 4, 8, 16, 24, 28, and 32 hr. The contents were chilled by breaking the tubes in ice-cold ethanol and the precipitate (that is, the degraded polymer) was separated by centrifugation at 0°. The entire process was repeated at incubator temperatures of 65, 70, and 75°. The weight-average molecular weights, M_w , were determined in all cases by measuring intrinsic viscosity $[\eta]$ in 0.035 N NaBr and the number-average or endgroup molecular weight, M_{e} , by titration against sodium hydroxide.⁶ The sample used for the kinetic study had the value of $M_{\rm w} = 12,040$ and $M_{\rm e} = 9260$. It was prepared by heating NaH₂PO₄ at 800° for 12 hr and quenching the melt as mentioned earlier.

Results and Discussion

A. The Effect of the Dielectric Constant of the Medium. Table I shows the effect of the dielectric constant of the

Table I: Degradation of Graham's Salt at 55° in Presence ofDifferent Organic Solvents (Time of \supset egradation, 5 hr)

Organic solvent (40% in H:O)	Dielectric constant	M_w of undegraded material = 9140 M_w of degraded material	M_{w} of undegraded material = 9950 M_{w} of degraded material
Methyl alcohol	59.6	7570	8450
Ethvl alcohol	55.0	7410	8390
Acetone	54.6	7400	8430
n-Propyl alcohol	50.3	7410	8400
t-Butyl alcohol	43.9	7380	8410
Dioxane	43.0	7390	8350

medium in the case of two different samples of Graham's salt. A determination of the amount of phosphorus present as ring phosphates⁹ in the case of degraded and undegraded samples showed that it increased at the most by 1% after degradation. We can therefore draw two other conclusions: (1) that the composition of the water-organic solvent mixture is the main factor in inducing the degradation rather than the dielectric constant of the medium, and (2) that ring phosphates are not formed in any significant amounts during degradation.

The dielectric constant of the medium may not be totally without significance. It is likely that there is a leveling effect and below a certain value the exact value of dielectric constant is not as important as the availability of organic molecules which themselves get involved in the process of degradation.

All the organic solvents studied as catalysts favoring degradation of Graham's salt are nucleophilic agents. Their action can be visualized as an increased nucleophilic attack on P-O-P bonds. The same arguments¹⁰ which explain why solutions of Graham's salt are stable against the attack of a negatively charged nucleophile as OH^- ion in alkaline solutions will explain why suddenly the P-O-P bonds become prone to a nucleophilic attack in media of low dielectric constant. In alkaline medium, the polyelectrolyte is



Figure 1. Influence of temperature on the rate of degradation of Graham's salt in 40% aqueous solution of ethanol $(1/M_n vs. time)$: 45°, O; 65°, D; 70°, O; 75°, Δ .

(8) H. N. Bhargava and D. C. Srivastava, Kolloid Z. Z. Polym., 212, 124 (1966).

(10) F. G. R. Gimblett, "Inorganic Polymer Chemistry," Butterworth and Co. Ltd., London, 1963, Chapter 7.

⁽⁹⁾ H. N. Bhargava and D. C. Srivastava, Anal. Chim. Acta, 37, 269 (1967).

highly charged and strong negative charges on phosphorus atoms repel all nucleophilic attacks, but as soon as the dielectric constant of the medium is lowered the polyelectrolyte gets a more coiled up configuration and also loses a part of its charge density. A nucleophilic attack resulting in ultimate breakdown of P-O-P links becomes easier.

Taking acetone as an example, the nucleophilic attack on the P-O-P can be visualized as follows.

 $(-P--O-)_n$. It will, therefore, become much easier

for nucleophiles to attack P-O-P bonds.

B. Kinetics of Degradation Catalyzed by 40% v/vEthanol. Out of the several water-miscible organic solvents whose presence was found to catalyze hydrolytic degradation of Graham's salt, ethanol was chosen

Here (P) represents the rest of the chain besides the units shown. Since an unstable complex ion involving the combination of acetone and a part of the polyphosphate chain is formed as an intermediate, obviously the acetone takes part in the reaction. That increasing amounts of acetone help the process of degradation can therefore be explained on the basis of the mechanism suggested.

As mentioned earlier, the rate of attack of a negative nucleophile (like OH- ion) on a highly charged polyanion is unfavorable. This is because of the electrostatic repulsion between similar charges which greatly decreases the entropy of activation.¹¹ For a process involving the reaction of two negatively charged species, decreasing the dielectric constant would decrease the rate constant.¹¹ A classical example is the reaction of hydroxide ion with bromophenol blue.12 The rate constant decreases 200-fold by the addition of 30% ethanol to the water. However, the attack of a neutral molecule like water, acetone, or some other nucleophilic organic molecule would be expected to increase as the dielectric constant decreases.¹¹ The decrease of dielectric constant would favor ion pairing by the sodium ions with the polyphosphate anion,

for a detailed kinetic study. The choice was arbitrary and it is believed that the other solvents would behave in exactly similar manner. The conclusions drawn on the basis of the present study can be easily taken to apply in the case of the other solvents.

Graham's salt is essentially formed by condensation polymerization and has a random size distribution of molecular weights or chain-lengths.¹³ A monodisperse or random heterodisperse polymer, whose bonds are broken at random, obeys the equation¹⁴

$$1/\bar{x}_n = 1/(\bar{x}_n)_0 + kt$$
 (3)

where $(\bar{x}_n)_0$ and \bar{x}_n are the number average chain lengths at t = 0 and t, respectively. This relationship holds quite generally for random scission reactions regardless of the chemical nature or the cause of deg-

(14) C. Tanford, "Physical Chemistry of Macromolecules," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 9.

⁽¹¹⁾ A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 7.

⁽¹²⁾ E. S. Amis and V. K. La Mer, J. Amer. Chem. Soc., 61, 905 (1939).

⁽¹³⁾ F. G. R. Gimblett, "Inorganic Polymer Chemistry," Butterworth and Co. Ltd., London, 1963, Chapter 7.



Figure 2. Evaluation of the energy of activation, E. Plot of $-\ln k vs. 1/T$.

radation.¹⁶ Graham's salt should obey this equation. Figure 1 gives a plot of the reciprocal of the numberaverage molecular weight, M_n (same as M_e) against the time of degradation in hours. Within the limits of experimental error, (3) is obeyed quite well. According to Grassie and Grant,¹⁶ the slope of any line in such a plot should give the rate of the reaction for the particular temperature. Since the straight lines in Figure 1 have been obtained for the reaction at different temperatures, they also illustrate the influence of temperature on the rate of chain scission. Assuming the Arrhenius equation to hold good, they can be used for determining E, the energy of activation. In Figure 2 is shown the plot of $-\ln k vs. 1/T$ obtained. A value of Eequal to 16 kcal/mol could be deduced from it. Thilo and Wieker¹⁷ gave a value of 25 kcal for hydrolysis at pH 8 and 15 kcal for pH 1. Obviously, in 40% aqueous solution, water-miscible organic solvents such as ethanol function as well as 0.1 M hydrochloric acid.

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- (15) H. H. G. Jellinek, Pure Appl. Chem., 4, 419 (1962).
- (16) N. Grassie and E. M. Grant, European Polymer J., 2, 255 (1966).
- (17) E. Thilo and W. Wieker, Z. Anorg. Allgem. Chem., 291, 164 (1957).

Magnetic Resonance Studies of the Oxidation and Reduction of

Organic Molecules by Ionizing Radiations

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By maintaining organic compounds at low temperature (4.2°K) it is often possible to stabilize oxidation and reduction products produced by ionizing radiation. The products were observed by electron spin resonance (esr) and in some cases by electron-nuclear double resonance (endor) spectroscopy. The oxidized and reduced species observed in irradiated single crystals of thiourea derivatives, several organic disulfides, thiodiglycolic acid, glycine, glycine HCl, and two dicarboxylic acids are enumerated. Some *G* values for ion production at 4.2°K are also given. The results are discussed in terms of the following processes: electron attachment, dissociative electron attachment, intramolecular transfer of holes, and anion degradation.

Introduction

When an electron is stripped away from a neutral diamagnetic organic molecule the molecule becomes a paramagnetic radical cation. Another neutral diamagnetic molecule may attach the dissociated electron to become a paramagnetic radical anion. Both the anion and cation should be detectable by electron spin resonance spectroscopy. However, radical ions created in this fashion are usually unstable and have only a very transient existence at ordinary temperatures. In order to study these species many investigators have worked at 77°K (boiling point of liquid nitrogen at atmospheric pressure) which is sometimes sufficiently cold to stabilize and make possible the identification of the anions produced by ionizing radiation. In this laboratory it has proven more advantageous to work at 4.2°K (boiling point of liquid helium at atmospheric pressure) in order to stabilize a more primitive state of the radiation damage process. In this report we survey the results of magnetic resonance measurements made on a series of organic compounds irradiated in the form of single crystals at 4.2°K. Frequently it has been possible to stabilize both the anion and the cation formed in these compounds. The investigation utilized electron spin resonance (esr) spectroscopy primarily, but some electron nuclear double resonance (endor) measurements were made.

It will usually be satisfactory for the description of our results to assume a hamiltonian which neglects components of spin (both electron and nuclear) which are perpendicular to the applied magnetic field.¹ This leads to a system of energy levels for the electron and N interacting nuclei given by

$$E(m_i,M) = g\beta HM - \sum_i^N g_i\beta_n Hm_i + \sum_i^N A^i m_i M \quad (1)$$

where H is the magnetic field intensity, β is the Bohr magneton, β_n is the nuclear magneton, M is the magnetic quantum number of the electron $(\pm 1/2)$, m_i is the magnetic quantum number of the *i*th interacting nucleus, and g_t is its nuclear g value. The quantities g and A^{i} define the g value and the hyperfine splittings, respectively. In esr spectroscopy, electronic transitions ($\Delta M = 1$, $\Delta m = 0$) are observed, whereas in endor spectroscopy² the transitions ($\Delta M = 0, \Delta m = 1$) are detected. The g value and the hyperfine coupling which are anisotropic with respect to crystal orientation can be described by tensor quantities. In this report the principal axes of tensors are defined with respect to crystal axes designated by letters such as a, b, and c' or a', b, and c. Theoretical arguments are most succinctly made using a frame of reference defined with respect to the structural geometry of a molecule. Axes defined in this manner are designated by subscripts x, y, and z. It is often useful to compare the directions of principal axes deduced from theoretical arguments with the directions of principal axes determined experimentally. A theoretical estimate of the gtensor is given by

$$g_{jk} = g_{js} - 2 \sum_{n} \frac{\langle \psi_0 | \lambda L_j | \psi_m \rangle \langle \psi_m | L_k | \psi_0 \rangle}{E_n - E_0}$$
(2)

where $g_{fs} = 2.0023$, λ is the spin-orbit coupling parameter and L_j refers to the operator for the component of angular momentum in the *j* direction. The wave functions ψ_0 and ψ_n may be regarded as the molecular orbitals occupied by the unpaired electron in the ground state and in the *n*th excited state, respectively, and $E_n - E_0$ is the difference in energy between these states. Molecular orbitals are linear combinations of atomic orbitals. The operator λL_j , for example, is understood to mean $\Sigma_k \lambda_k L_{jk} \delta_k$ where the subscript *k* refers to a particular atom.

A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 72.
 G. Feher, *Phys. Rev.*, 103, 500 (1956).

The use of single crystals was particularly important in this investigation since we invariably dealt with at least two paramagnetic species, usually in the form of a cation and an anion. The chance of interpreting overlapping esr spectra is of course much better having single crystal data. Furthermore, for certain crystal orientations there may be sufficient difference in g value between two absorptions to allow complete separation of the spectra. Most organic free radicals have g values close to the free-spin value (2.0023) but exceptions occur in radicals in which the unpaired electron is largely localized on a heavy atom. In these radicals, spin-orbit coupling can cause significant g value variation. Considerable use was made of this effect in this investigation and the reader will note that many of the compounds studied contain sulfur or halogen atoms.

Experimental Procedures

The esr spectrometers used in this investigation operated at a microwave frequency of 24.00 and 70.10 Gc/sec and utilized superheterodyne detection. The use of superheterodyne detection makes it possible to measure paramagnetic resonance absorption at nanowatt levels of microwave power. This capability is essential for the study of radiation-induced radicals in organic systems at 4.2°K since spin-lattice relaxation times are generally long and saturation of the esr absorption occurs readily at higher power levels.

The sample cavity of the spectrometer was a cylindrical transmission type which resonated in the TE 011 mode. The dimensions of the cavity, and hence its resonant frequency, change drastically as the temperature is lowered. In order to avoid the necessity of changing the frequency of the pair of klystrons used in the superheterodyne detection system the sample cavity was made mechanically tunable as shown in Figure 1. The cavity assembly was immersed in a liquid helium dewar which was sufficiently vacuum tight so that if necessary the helium gas pressure could be reduced to the λ point. At the λ point or below microphonics generated by gas bubbles in the sample cavity can be eliminated, but this device was seldom employed, the signal-to-noise ratio being sufficiently good at 4.2°K.

The whole assembly consisting of the dewar and enclosed microwave apparatus could be removed from the spectrometer and transported to an X-ray facility. During irradiations the sample was pushed out through an axial hole in the bottom of the cavity where it was exposed to radiation passing through beryllium windows fixed in the walls of the dewar. The usual exposure time using a 250-kV, 30-mA X-ray source was 10 min. The esr absorption spectra could be recorded directly from an oscilloscope display of absorption vs. magnetic field strength. Whenever necessary the signalto-noise ratio of the signal could be enhanced using a



Figure 1. Apparatus for irradiation and measurement of crystals at 4.2°K. Cavity and dewar shown in cross section. Liquid nitrogen reservoir not shown. Legend: (a) sample rod, (b) waveguide, (c) mechanical tuning for cavity, (d) fill port, (e) discharge tube, (f) glass tubing sample guide, (g) dewar flange, (h) dewar inner wall, (i) dewar outer wall, (j) cold shield, (k) beryllium windows, (l) sample, (m) quartz fiber, (n) polyethylene mount, (o) TE 011 tunable cavity, (p) iris, (q) plunger, (r) sample during irradiation, (s) evacuation port, (t) helium.

computer of average transients. Field intensity measurements were made using a proton oscillator.

Our adaption of Feher's electron nuclear double resonance (endor) technique has been described elsewhere.³ One minor modification was required for studying samples irradiated at 4.2°K. The loop which carries the radio-frequency energy was extended through the axial hole in the bottom of the sample cavity so as not to interfere with the sample irradiation procedure. Endor is used to measure hyperfine couplings accurately when satisfactory measurements of the couplings directly from the esr spectra are impossible due either to line widths or overlapping of spectra.

Determination of G values for radical production (the number of free radicals produced per 100 electron volts of energy deposited in the sample) at 4.2° K

(3) H. C. Box, H. G. Freund, and K. T. Lilga, J. Chem. Phys., 46, 2130 (1967).

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Molecule	Formula	Oxidation product	Reduction product	<i>G</i> , 4.2°K	<i>G</i> after warming
Methylthiourea	S CH ₂ -NH-C-NH ₂	>C+_S	>C-S-		
Dibutylthiourea	S C,H3-NH-C-NH-C,H3	>C+_S	>C-S ⁻		
Benzoyldisulfide Cystine HCl Dithiodiglycolic acid Cystine HBr	$\begin{array}{c} O \ O \\ C_{6}H_{5}-C-S-S-C-C_{6}H_{5} \\ (COOH-CH(NH_{3}Cl)-CH_{2}-S-)_{2} \\ COOH-CH_{2}-S-S-CH_{2}-COOH \\ (COOH-CH(NH_{3}Br)-CH_{2}-S-)_{2} \end{array}$	-(S-S)+- -(S-S)+- -(S-S)+- Br	-(S-S) ⁻ - -(S-S) ⁻ - -(S-S) ⁻ - -(S-S) ⁻ -	2.8 3.6 3.8	0.6 0.9 2.4
Thiodiglycolic acid	COOH-CH2-S-CH2-COOH	-S+-	$-C <_{OH}^{O-}$	3 .9	1.7
Succinic acid	COOH-(CH ₂) ₂ -COOH	$-C <_{O}^{O}$	$-C <_{OH}^{O^{-}}$	3.2	2.4
Dimethylmalonic acid	COOH-C(CH ₃) ₂ -COOH	(CH ₃) ₂ COOH	$-C <_{OH}^{O^{-}}$		
Glycine	NH2-CH2-COOH	?	$-C <_{OH}^{O^-}$	1.8	1.7
Glycine HCl	NH₃Cl−CH₂−COOH	(Cl-Cl) ⁻	-C< ^{O-} _{OH}	3.8	1.2

were made for several compounds. Esr absorption measurements are subject to a number of serious In this investigation it was particularly necerrors. essary to guard against errors due to saturation of the esr absorption because, as already mentioned, spin-lattice relaxation times are much longer at 4.2°K. The microwave power was kept at the lowest possible level during G value measurements at which level there was no indication of saturation of the esr absorption. Pressed pellets of polycrystalline material were used for this part of the investigation. As a reference sample for calibrating the spectrometer's absorption a pressed pellet of polycrystalline glycylglycine which had been subjected to a known dose of irradiation at room temperature was used. The G value of glycylglycine was taken to be 2.3 although other values have been proposed.⁴ The number of roentgens exposure or dose used to prepare the reference sample could be determined by conventional methods using a Victoreen electrometer. The dose received by a sample irradiated in the cavity at room temperature was determined by comparing the esr signal from two pellets of glycylglycine, one exposed in the cavity and one exposed to a known number of roentgens. Because of the low atomic number of helium and the low density of the liquid, the additional attenuation of the X-rays with helium in the dewar was considered negligible, a conclusion which was verified experimentally. The error in the measurements of absolute Gvalue could easily be a factor of 2, but even this level of accuracy provides interesting data concerning the relative efficiency of oxidation and reduction processes in various organic compounds. Relative measurements of G values before and after warming of a given sample are more reliable and were reproducible to within about 30%.

It was helpful in warming experiments to have a paramagnetic reference sample containing a fixed number of unpaired spins. A satisfactory reference sample is afforded by Cr^{3+} ions substituted in MgO. Powdered MgO was added to a dilute aqueous solution of $Cr(NO_3)_3$. The solution was filtered and evaporated and the resultant mixture heated to 1100°. Pellets of the mixture show a single esr absorption at a g value of 1.980. Minute pellets could be affixed to the crystal sample. The absorption due to the Cr^{3+} ions, because of its low g value, usually does not obscure the absorptions due to radiation-induced free radicals in the crystal.

Results

Some typical organic molecules which have been examined for radiation damage at 4.2°K and their chemical structures are listed in the first and second columns of Table I. The nature of paramagnetic products resulting from oxidation and reduction processes are indicated in the third and fourth columns, respectively. Wherever appropriate, the locations of the

(4) W. Köhnlein and A. Müller, Phys. Med. Biol., 6, 599 (1962).

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Figure 2. The esr spectra obtained from single crystals of thiourea derivatives irradiated at 4.2 ^oK. (a) Methylthiourea with magnetic field parallel to the *a* axis; (b) methylthiourea after warming to 30 ^oK and then reccoling to 4.2 ^oK for same crystal orientation as in (a). (c) dibutylthiourea with magnetic field parallel to *b* axis.

charge density and spin density on the oxidized and reduced molecules have been shown. It should be borne in mind, of course, that strictly speaking the charge and spin densities are delocalized throughout the molecules. For some of these molecules, the net Gvalues for the paramagnetic products measured before and after warming to room temperature have been determined and are given in the last columns of Table I. These results will be described briefly before drawing our conclusions. In presenting various esr spectra an attempt has been made to introduce a consistent notation for labeling various components of each spectrum. Spectra believed to be associated with reduction processes are labeled α and those associated with oxidation processes are labeled β . The subscript zero is reserved for primary oxidation and reduction products produced from a molecule without breaking any of its chemical bonds (or without forming any new bonds). Whenever necessary, primes are used to distinguish between various primary oxidized or reduced species. Other subscripts are used as necessary to distinguish between various secondary radical absorptions associated with the oxidation or reduction processes.



Figure 3. The morphology of methylthiourea crystals showing choice of orthogonal reference axes. The a axis was chosen normal to the near face and the b axis parallel to ome edge of the face.

Thiourea Derivatives. It is convenient to discuss the spectra obtained from the thiourea derivatives first since these results are particularly simple. The esr spectrum obtained from a single crystal of methylthiourea irradiated at 4.2°K is shown in Figure 2a. Measurements are made with respect to axes fixed in the crystal as shown in Figure 3. The α_0 absorption which occurs in the region of free spin, is attributed to the negative ion of methylthiourea. The two lowfield peaks, β_0 and β'_0 , are attributed to different conformations of the positive ion. The integrated positive ion absorption equals the integrated negative ion absorption. The occurrence of chemically equivalent radicals or radical ions in different conformations is not uncommon. The conformation of cation whose absorption occurs at lower field strength in Figure 2a is the less stable of the two conformations. Slight warming of the crystal (30°K) causes the conversion of the less stable conformation into the more stable one as indicated in Figure 2b. Simple Hückel molecular orbital theory furnishes an adequate estimate of the distribution of unpaired spin density in these ions. The molecular orbital of the unpaired electron is of the form

$$\psi_0 = \sum_k C_k p_{zk} \tag{3}$$

where the p_{zk} are atomic p_z orbitals, z being the direction perpendicular to the plane of the molecule. The distribution of unpaired spin density on various atoms, given by $(C_k)^2$, is shown in Figure 4 for the anion I and cation II. The cation has the largest concentration of spin density localized on the sulfur atom. The considerable variation in g value associated with the cation absorption is due to spin-orbit coupling in

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Figure 4. Calculated spin densities in the anion I and cation II of methylthiourea. The calculations were made using the same values for the parameters as were used in ref 6.

the sulfur atom ($\lambda = -382$). The g tensor characteristics of the cation absorption can be understood by referring to eq 2. Since $L_z\psi_0 = 0$, $g_{xz} = g_{yz} = 0$ and hence the z direction corresponds to a principal axis with g_{fs} as the principal value.⁵ The most important excited state is expected to be one in which an electron from the unshared pair on the sulfur atom is promoted to a π state. The molecular orbital of the unpaired electron in this excited state is considered to be simply a sulfur $3p_x$ orbital

$$\psi_n = 3\mathbf{p}_z \tag{4}$$

where the x direction is taken orthogonal to z and to the C-S bond direction. Since $L_x\psi_{\pi} = 0$ and $L_z\psi_0 = 0$, this configuration permits an enhancement of g_{yy} only where y is the axis parallel to the C-S bond. The experimentally determined principal values of the g tensors for the cationic absorption are given in Table II. The direction cosines of the principal axes are

Table II: The Principal Values and the Direction Cosines of the Principal Axes of the g Tensors for the β'_0 and β_0 Absorptions in Irradiated Methylthiourea and for the β_0 Absorption in Irradiated Dibutylthiourea

		a	ь	c
	2.053	0.93	0.38	0.23
β'₀	2.028	0.13	-0.38	0.92
	2.003	-0.35	0.84	0.41
	2.025	0.95	0.19	-0.24
βo	2.018	0.26	-0.10	0.96
	2.001	-0.16	0.98	0.14
		a'	ь	c
	2.030	0.04	0.58	0.82
₿₀	2.015	-0.51	0.69	0.51
	2.000	0.86	0.43	0.27

given with respect to the axes a, b, and c shown in Figure 3. It should be noted that the difference in the directions of the principal axes for the two cation



Figure 5. The esr spectrum obtained from a single crystal of dibenzoyldisulfide irradiated at 4.2° K. The magnetic field was parallel to the a' axis where $a' = b \times c$.

conformations is very slight. This suggests that the conformational difference is also slight but we are unable to make any judgement as to the exact nature of the difference.

The crystal structure of methylthiourea apparently has not been determined; hence, we cannot compare the g tensor with the geometry of the molecule. However similar studies have been made on single crystals of thiourea and allylthiourea irradiated at 4.2° K.⁶ The crystal structures of these molecules have been determined. The characteristics of the g tensor for the cation absorptions in these crystals were found to be fully in accord with the foregoing analysis. Parenthetically, we note that the esr spectra of methylthiourea indicate that the crystals are triclinic.

The width of the absorption lines in Figure 2 for both ions is caused by unresolved hyperfine interactions due to the several nitrogen and hydrogen nuclei present in the molecule. Further evidence of the ionic nature of the absorbing species is obtained upon warming the crystals. The absorptions attributed to the positive and negative ions decrease concomitantly as one would expect if, at higher temperatures, holes and electrons are able to recombine. The amount of paramagnetic species left after warming to room temperature is negligible.

The absorption obtained from a single crystal of dibutylthiourea irradiated at 4.2°K is shown in Figure 2c. The spectrum is similar to that obtained from methylthiourea except that a single cation conformation is indicated. The esr results show, however, two cation absorptions related by a twofold axis of symmetry, indicating the crystals are monoclinic. So far as we are aware, no crystallographic determination of the structure of dibutylthiourea has been made although the space group has been deter-

⁽⁵⁾ P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier Publishing Co., Amsterdam, London, New York, N. Y., 1967, Appendix 3.

⁽⁶⁾ H. C. Box, E. E. Budzinski, and T. Gorman, J. Chem. Phys., 48, 1748 (1968).

mined.⁷ Using simple Hückel theory the distribution of spin densities is expected to be essentially the same as in thiourea ions. A description of the g tensor for the cation absorption for dibutylthiourea is included in Table II. Upon warming, the absorptions attributed to anion and cation in Figure 2c disappear concomitantly.

Sulfides. The ESR absorption observed in a single crystal of dibenzoyldisulfide irradiated at 4.2° K is shown in Figure 5. The two largest components of the spectrum labeled α_0 and β_0 are attributed to the negative ion



and the positive ion



respectively. The fact that the spin density is largely localized on the disulfide group in both ions is indicated by the large g shift associated with both absorptions. The unpaired electron of the disulfide anion is expected to occupy an antibonding σ molecular orbital given by

$$\psi_0 = \frac{1}{\sqrt{2}} \left(p_x - p_x' \right) \tag{5}$$

where p_x and $p_{x'}$ are 3p atomic orbitals on the sulfur atoms and x and x' are parallel to the disulfide bond. Since $L_x\psi_0 = 0$, eq 2 tells us that the x direction should be a principal axis. Experimentally, we expect the g value for this direction to approach g_{fs} . By referring to the crystal structure of dibenzoyldisulfide, which has been determined by Cole,⁸ we can deduce which absorption in Figure 5 is due to the anion. Comparing the g tensors of these two absorptions and the disulfide bond direction given in Table III we deduce that the high-field component in Figure 5 is the anion ab-

Table III: The Principal Values and the Direction Cosines of the Principal Axes of the g Tensor in Irradiated Dibenzoyldisulfide. (The Direction of the Disulfide Bond Is Also Shown.)

		a'	ь	ь
	2.014	0.724	0.514	0.460
<i>α</i> 0	2.010	0.254	-0.819	0.515
	2.004	0.642	-0.256	-0.723
	2.032	0.885	0.128	-0.447
β_0	2.019	0.183	0.789	0.587
	2.004	0.428	-0.602	0.675
S-S		0.535	-0.458	-0.709

sorption. The unpaired electron in the cation is expected to occupy a localized molecular orbital of the type

$$\psi_0 = \frac{1}{\sqrt{2}} \left(p_z + p_{z'} \right) \tag{6}$$

where p_z and $p_{z'}$ are 3p orbitals on the sulfur atoms. The nuclei of each benzoyl group lie in a plane and both planes contain the disulfide nuclei. The dihedral angle defined by this arrangement is 81°. The directions z and z' are normal to the benzoyl planes. The overall variation in g value associated with the cation absorption is larger than that associated with the anion absorption, a result which is consistent with results found in cystine di-HCl⁹ and dithiodiglycolic acid.¹⁰ The absorption attributed to the anion and cation in dibenzoyldisulfide disappear concomitantly on warming.

The interpretation of the g value characteristics associated with the ionic absorptions observed in dibenzoyldisulfide applies equally well to the principal absorptions observed in crystals of cystine di-HCl and dithiodiglycolic acid irradiated at 4.2° K. The molecules in both these crystals lie on twofold axes of rotation which bisect the disulfide bond.¹¹ The additional characteristics which this symmetry imposes on the g tensor and the hyperfine coupling associated with the ionic absorptions has been discussed elsewhere.^{9,10} Our purpose here is to describe the degradation of ions which occurs when crystals of cystine di-HCl, irradiated at 4.2° K, are gradually warmed.

The spectra shown in Figure 6 were obtained from single crystals of cystine di-DCl in which the polar hydrogen atoms of cystine were exchanged for deuterium. Deuteration serves to sharpen hyperfine patterns somewhat, but does not essentially change the character of the absorption. The α_0 absorption in Figure 6 is due to the anion

and the β_0 absorption is due to the cation

(7) The space group for dibutylthiourea was determined by Dr. Frank Cole, Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, to be $P2_1/c$ with four molecules per unit cell.

(8) F. Cole, personal communication.

(9) H. C. Box and H. G. Freund, J. Chem. Phys., 41, 2571 (1964).

(10) H. C. Box, H. G. Freund, and G. W. Frank, J. Chem. Phys., 48, 3825 (1968).

(11) L. K. Steinrauf, J. Peterson, and L. H. Jensen, J. Amer. Chem. Soc., 80, 3835 (1968); G. W. Frank, Acta Cryst., in press.



Figure 6. The esr spectra from a single crystal of cystine dideuteriochloride. The magnetic field was parallel to the c' axis where $c' = a \times b$. (a) Irradiated and observed at 4.2°K; (b) after warming to 110°K and subsequent recooling to 4.2°K; (c) endor spectrum obtained from the β_2 absorption of (b); (d) endor spectrum obtained from the α_0 absorption of (b).

The anion absorption can be observed in crystals irradiated at 77°K but not the cation absorption.¹² The two small components of the spectrum labeled β'_0 and β_1 in Figure 6a cannot be discerned for all crystal orientations since they are often overlapped by the larger components.¹³ It has been observed that upon warming the β'_0 component disappears first at which time the β_0 absorption is augmented by a corresponding amount. Therefore the β'_0 absorption is probably a less stable form of VI. The considerable variation in g value associated with the β_1 component indicates a free radical with the unpaired electron localized on sulfur. In contrast to the ions responsible for the α_0 and β_0 absorptions, the radicals responsible for the β_1 absorption occur in two orientations related by a twofold axis. The g value approaches maximum approximately parallel to the disulfide bond suggesting the radical may be

S-S-CH₂-CH(ND₃Cl)COOD VII

Upon warming cystine di-DCl to 110°K and recooling to 4.2°K, the absorption shown in Figure 6b is obtained. The principal change that has occurred is the replacement of the β_0 absorption by another which is labeled β_2 . The g tensor of the β_2 absorption is defined in Table IV. It is important to note that the radicals responsible for the β_2 absorption occur in two orientations related by a twofold axis of rotation. The endor spectrum obtained from the β_2 absorption, Figure 6c, shows that two rather large proton couplings contribute to the width of the esr absorption. **Table IV:** The Principal Values of the g Tensor and the Direction Cosines of the Principal Axes for the β_2 Absorption in Irradiated Cystine HCl

		a	ь	c'
	2.038	0.377	0.501	0.779
B 2	2.017	0.231	0.764	-0.603
	2.002	0.897	-0.407	-0.173

Based on these considerations, the β_2 absorption is ascribed to the radical

S-CH₂-CH(ND₃Cl)COOD VIII

as is discussed more fully in the following section. For completeness, the endor spectrum obtained from the α_0 absorption is shown in Figure 6d.

The esr spectrum from a single crystal of cystine di-HBr irradiated at 4.2°K is shown in Figure 7. The principal oxidized species produced in cystine HBr is different from that seen in the disulfides discussed so far in that the disulfide group is not involved. Rather the oxidized species is bromine (in the normal crystal structure bromine is undoubtedly present as the negative ion). The bromine absorption, labeled β_0 in Figure 7, is characterized by a four-line hyperfine pattern arising from the interaction of the unpaired electron with the bromine nucleus which has a spin of 3/2. Since there are two isotopes of bromine of nearly equal abundance but somewhat different magnetic moments, the esr absorption consists of two hyperfine patterns having different spacings but the same q value. There are three other major components in the absorption spectrum of Figure 7. The component labeled α_0 has a considerable g shift associated with it presumably due to spin-orbit coupling



Figure 7. The esr spectrum from a single crystal of cystine HBr irradiated at 4.2°K. The magnetic field was perpendicular to the twofold axis of symmetry exhibited by the crystal and at an angle of 30° to its morphologically long axis.¹⁴

(12) K. Akasaka, S. Ohniski, T. Suita, and I. Nitta, J. Chem. Phys., 40, 3110 (1964).

(13) The β'_0 and β_1 absorptions overlap in Figure 1 of ref 9.

in the sulfur atoms. It is anticipated, of course, that the α_0 absorption is due to the disulfide anion

although this has not been rigorously established. Variations have been discovered in the form of the crystals of cystine di-HBr grown from aqueous solution.¹⁴ These variations, though interesting, have hampered the positive identification of the paramagnetic species other than the readily identifiable bromine.

In thiodiglycolic acid, a cation is formed in which the charge and unpaired spin density is again localized primarily on the sulfide part of the molecule,^{15,16} *i.e.*

However, the sulfide part of the molecule is not involved in formation of the negative ion which is



The structure of carboxyl anions is discussed more fully below.

Carboxylic Acids. The carboxyl anion absorption is a prominent feature of the esr spectra of dicarboxylic acids irradiated at low temperature. The esr from a single crystal of succinic acid irradiated at 4.2° K is shown in Figure 8a. If the exchangeable hydrogen atom of the carboxyl group is replaced by deuterium the spectrum shown in Figure 8b is obtained. The α_0 absorption is due to the anion



XII

The unpaired electron on the carbon atom of the carboxyl group interacts with the protons of the hydrogen atoms attached to the α carbon atom to produce the four-line hyperfine pattern. From measurements on single crystals of succinic acid labeled with C¹³ it is known that the unpaired electron occupies mainly a 2p₂ carbon orbital with a small 2s admixture, z being the direction normal to the plane of the carboxyl group.¹⁷ As would be anticipated, the g value for the anion absorption is close to g_{fs} when the magnetic field is applied parallel to the z direction. The



Figure 8. The esr absorption of single crystal of succinic acid irradiated at 4.2°K. The magnetic field was parallel to the *b* axis. (a) Succinic acid absorption measured at K band; (b) succinic acid with polar hydrogens replaced by deuterium, also measured at K band; (c) succinic acid with polar hydrogen replaced by deuterium and carboxyl groups enriched (60 atom %) with C¹³ measured at V band.

anion is also observed in crystals irradiated at 77°K. However, a more primitive stage of the oxidation process is stabilized at 4.2°K. The most prominent absorption which can be associated with the oxidation process is the high g value singlet labeled β_1 in Figure 8. The considerable g value variation and the lack of any resolved hyperfine splitting in this absorption suggests a free radical in which the unpaired electron is localized on the oxygen atoms. A cation of the form



(14) The cystine dihydrobromide crystals were obtained by evaporation of aqueous solution. Apparently most of the crystals used in our experiment belong to a different space group from those described by J. Peterson, L. K. Steinrauf, and L. H. Jensen, Acta Cryst., 13, 104 (1960). Our crystals contain water of crystallization. The space group and crystal structure is being investigated by Dr. R. Parthasarathy and Mr. R. Rosenfield, Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, N. Y.

(15) H. C. Box, H. G. Freund, and E. E. Budzinski, J. Chem. Phys., 49, 3974 (1968).

(16) S. Paul, Acta Cryst., 23, 491 (1967).

(17) H. C. Box, H. G. Freund, and K. T. Lilga, J. Chem. Phys., 42, 1471 (1965); J. D. Morrison and J. M. Robertson, J. Chem. Soc., 980 (1949).

has been suggested.¹⁸ An alternative possibility is the radical



which could be formed from XIII by the dissociation of a proton.

The effect on the esr absorption of substituting C^{13} in the carboxyl group of succinic acid (60 atom %) is shown in Figure 8c. In K-band spectra (8550 G) the additional hyperfine splitting introduced into the α_0 absorption by the C¹³ nucleus results in overlapping of the α_0 and β_1 absorptions. For this reason the absorption shown in Figure 8c was recorded on the V-band spectrometer (25,000 G) since the separation between centers of the two absorptions is given approximately by $\Delta g H/2$ where Δg is the difference in g value between the two absorptions and H is the strength of the applied field. The considerable doublet hyperfine splitting introduced by the C^{13} nucleus into the α_0 absorption has been analyzed previously¹⁷ and is consistent with the structure of the proposed radical anion XII. The effect of C¹³ substitution on the β_1 absorption is minimal and the doublet splitting by the C13 nucleus is barely discernible. This result can be reconciled with either of the structures, XIII or XIV, proposed to explain the β_1 absorption.

In an attempt to understand the g tensor associated with the β_1 absorption, we consider the molecular fragment— $C <_{O}^{O}$ in (XIV). We assume this fragment has C_{2v} symmetry.¹⁹ On the basis of such symmetry the g tensor would be expected to have principal axes along, x, y, and z where x defines the C_2 rotation axis, yis in the molecular plane, and z is normal to the molecular plane. The data given in Table V for the g tensor of the β_1 absorption shows that the principal axes do correspond to these molecular axes. This result argues in favor of (XIV) as the correct interpretation. Consider a wave function of the form

$$\psi_0 = \frac{1}{\sqrt{2}} \left(p_{v'} + p_{r''} \right) \tag{7}$$

where p_y' and p_y'' are oxygen 2p functions related by C_2 . The y' direction is orthogonal to z and to the bond formed by the oxygen atom and the direction y'' is defined analogously. The finding that a principal axis with $g = g_{fs}$ lies in the x direction can be explained if we assume the wave function of the unpaired electron is of the form (7) since $L_c \psi_0 = 0$.

Clearly the integrated β_1 absorption in Figure 8 amounts

Table V: The Principal Values and the Direction Cosines of the Principal Axes Are Given for the β_1 Absorption in Succinic Acid. The Direction Cosines for the x, y, and z Axes, Fixed in the Molecule as Described in the Text, Are Also Given. There Is Another Set of Direction Cosines Related to Those Given in the Table by the Twofold Axis of Rotation about b

	a	ь	c'
2.019	0.07	0.88	0.47
2.006	0.63	-0.40	0.67
2.003	0.78	0.25	-0.58
y	0.20	0.86	0.47
2	0.66	-0.48	0.59
x	0.74	0.18	-0.66

to less than half the integrated α_0 absorption. Consequently we must look for other oxidized species. There is in fact another absorption underlying the α_0 absorption but it has not been possible to characterize it. Difficulties due to superposition of spectra are usually encountered in the study of irradiated dicarboxylic acids. In the hope of circumventing this difficulty single crystals of dimethylmalonic acid were irradiated. Dimethylmalonic acid crystallizes with the space group $I4_1/acd.^{20}$ There are 16 molecules per unit cell; onehalf of the molecule constitutes the asymmetric unit. The absorption in Figure 9a was obtained with the field applied along the tetragonal axis so that all halfmolecules were equivalently orientated with respect to the field. The acid was deuterated in the carboxyl position. Since there are no hydrogens attached to the α carbon in dimethylmalonic acid, hyperfine interactions in the carboxyl anion should be reduced to a minimum. The absorption due to the anion



is, in fact, the relatively narrow absorption designated α_0 in Figure 9a. Thus, for this dicarboxylic acid we have a somewhat less obstructed view of the broader absorption due to the oxidized species or their degradation products. As it turns out, the oxidation process for this particular dicarboxylic acid appears to lead to a specific result. The hyperfine pattern associated with the β_1 absorption in Figure 9a is fairly

^{(18) &}quot;Electron Spin Resonance and the Effects of Radiation on Biological Systems," Nuclear Science Series Report Number 43, Wallace Snipes, Ed., National Academy of Sciences, Washington, D. C., p 123.

⁽¹⁹⁾ F. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, New York, N. Y., 1963.

⁽²⁰⁾ D. J. Haas and S. A. Brenner, Acta Cryst., 20, 709 (1966).



Figure 9. The esr absorption of a single crystal of dimethylmalonic acid with the polar hydrogen atoms replaced by deuterium. The magnetic field was parallel to the fourfold axis of the crystal. (a) Irradiated and observed at 4.2° K; (b) momentarily warmed to room temperature and subsequently remeasured at 4.2° K.

well resolved for this crystal orientation. The absorption is attributed to the radical

$$(CH_3)_2C$$
—COOD

XVI

which is also observed after warming to room temperature (Figure 9b). A possible mechanism for forming this radical from oxidized dimethylmalonic acid is

$$[(CH_3)_2C(COOD)_2]^+ \longrightarrow XVI + CO_2 + D^+$$

with the deuteron probably attaching itself to a neighboring undamaged acid molecule.

Amino Acids. The esr absorption for a single crystal of glycine with the field applied along the *b* axis is shown in Figure 10. The reduced species observed in irradiated glycine is analogous to that observed in dicarboxylic acid molecules. The α_0 absorption distinguished by the doublet hyperfine pattern in Figure 10 is attributed to the negative ion







Figure 10. The esr absorption from a single crystal of glycine irradiated at 4.2° K; the absorption measured with the magnetic field applied along the *b* axis.

The g tensor for the anion absorption and the orientation of the carboxyl group in a crystal of glycine are compared in Table VI. As in the case of the thiodiglycolic acid anion and the succinic acid anion, we find one principal axis normal to the plane of the carboxyl group.²¹ The doublet hyperfine pattern is generated

Table VI: The Principal Values of the g Tensor for the α_0 Absorption in Irradiated Glyzine. The Normal to the C $<_{O}^{O}$ Plane Is Indicated by z. The Direction Cosines Are with Respect to the Crystal Axes z and b and Orthogonal to These Directions, $c' = a \times b$

		а	ь	c'
	2.0026	0.00	1.00	0.00
α_0	2.0041	0.93	0.00	0.38
	2.0048	0.38	0.00	0.93
	2	0.181	0.954	0.229

by a proton of the methylene group.²² The anion absorption overlaps another attributable to the oxidation process. However, the radical species generated by the oxidation process have not been identified. It is appropriate to point out here that in the hydrochloride salt of glycine the oxidized and reduced species are easily distinguished.²³ The oxidation process leads to the formation of Cl_2^- molecular ions. For most crystal orientations the g value of the Cl_2^- absorption is significantly larger than that of the reduced species which is



- (21) R. E. Marsh, Acta Cryst. 11, 654 (1958).
- (22) P. B. Ayscough and A. K. Roy, Trans. Faraday Soc., 64, 582 (1968).

(23) T. G. Castner and W. Kanzig, J. Phys. Chem. Solids, 3, 178 (1957);
H. C. Box, E. E. Budzinski, and H. G. Freund, J. Chem. Phys., 50, 2880 (1969).

Discussion

Our discussion of the foregoing results is divided into three parts: (1) oxidation and related processes such as intramolecular hole transfer and cation dissociation, (2) reduction and related processes such as specific electron attachment and dissociative electron attachment, and (3) possible relationships between some of our solid state results and those of radiation chemistry and radiation biology.

Oxidation. Oxidation is by definition the loss of an electron. It is well known that the oxidation caused by ionizing radiation in the primary step of the radiation damage process occurs randomly. However, holes initially created in random fashion are transferred intramolecularly to preferred sites. The results of the last section, particularly for the disulfides, thiourea and its derivatives, and glycine HCl, demonstrate this transfer. A hole located on the alkyl group of a thiourea derivative, for example, would manifest itself by strong proton hyperfine interactions. The narrowness of the cation absorption observed in planar thiourea derivatives is inconsistent with any significant hyperfine interaction. We conclude that holes created initially in the alkyl groups are transferred to the thiourea part of the molecule. The transfer of holes to the preferred sites in the compounds containing sulfur or halogens (Table I) must be substantially complete since the net cation absorption is approximately equal to that of anion. Discrepancies in stoichiometry are discussed below.

The transfer of holes to halogen ions in the amino acid hydrohalides is interesting since it shows that the transfer occurs readily between atoms ionically or covalently linked. In cystine the change of hole sites from the disulfide group in the hydrochloride salt to the bromine ion in the hydrobromide salt is probably due to the lesser electron affinity of bromine compared with chlorine. The disposition of holes in glycine HCl is partly fortuitous; the stable Cl_2^- ions can only form if pairs of Cl^- ions happen to lie in close proximity in the normal crystal structure.

At this point, some consideration should be given to the stoichiometry of ion formation. In the case of cystine di-DCl we note that the net absorption attributed to cations in Figure 6a is less than the net absorption due to anions. It is reasonable therefore to suppose that the β_1 component is associated with the oxidation process. Thus the neutral free radical VII probably results from the dissociation of oxidized cystine di-DCl.

It is clear that specific forms of oxidized molecules are often produced by ionizing radiation by virtue of the intramolecular hole transfer process. With respect to the oxidation process, what is the next step in the radiation damage process? As far as the conjugated thiourea derivatives are concerned, the esr results suggest that neutralization of the ions occurs without permanent damage to the molecules. The same conclusion applies to dibenzoyldisulfide. All the other molecules in Table I undergo considerable covalent bond rupture. In the case of cystine HCl, some further conclusions can be drawn from the esr results concerning the degradation of the oxidized species from warming experiments.

Warming of irradiated cystine di-DCl short of the transformation shown in Figure 6b causes a slight diminution of anion and cation absorptions suggesting that some recombination of electrons with cations occurs. Further warming degrades the cation and generates the radical responsible for the β_2 absorption. The latter radical is formed from one or the other half of cystine di-HCl and has its unpaired spin largely localized on the sulfur atom. The simplest interpretation of the transformation is that the disulfide bond of VI dissociates producing the cation

which is diamagnetic, and the neutral radical

which is responsible for the β_2 absorption. However, some consideration must be given to the possibility that it is the weak C-S bond which dissociates. Maximum g value for the radical (VIII) is expected to be parallel to the C-S bond.²⁴ A radical of this form is also produced in the dissociation of the anion V which occurs at still higher temperatures¹² and in the oxidation of cysteine HCl.²⁵ In both instances the C-S bond in the initial conformation of the radical is approximately in the direction of the same bond in the undamaged molecule. However in the conformation which is stable at room temperature the orientation of the bond may be quite different.²⁴ From Table IV it may be calculated that the direction of maximum g value for the β_2 absorption is approximately 34° removed from the C-S bond direction and 50° from the S-S bond direction in cystine. This consideration plus the endor evidence for hyperfine interactions involving the CH_2 protons constitutes evidence for believing it is the S-S bond rather than the C-S bond which breaks.

Akasaka¹² has documented the dissociation of the anion which occurs at temperatures well above liquid nitrogen temperature and presumably yields the anion

$$S--CH_2-CH(ND_3Cl)COOD$$

XX

as well as another conformation of VIII. The small

⁽²⁴⁾ Y. Kurita and W. Gordy, J. Chem. Phys., 34, 282 (1961).

⁽²⁵⁾ K. Akasaka, ibid., 43, 1182 (1965). H. C. Box, H. G.

Freund, and E. E. Budzinski, *ibid.*, 45, 809 (1966).

yield of neutral radicals VIII measured after warming to room temperature Table I is easily explained if we assume that neutralization of XIX and XX occurs mainly by the transfer of an electron from XX to XIX. This would result in the formation of two neutral radicals VIII in juxtaposition and recombination would be expected to occur.

The sample of cystine di-HCl serves to illustrate the study of anion degradation by esr spectroscopy. In principle it should be possible to apply the technique to any molecular crystal in which specific cations are formed by irradiation at low temperature. In practice such studies are often complicated by several factors. (1) The ionic species and their degradation products may be produced in more than one conformation. (2) The degradation of an ion into products one of which is paramagnetic may not be quantitative. In particular diminution of the ionic absorptions may be due in part to recombination of electrons with cations. (3) The anion species may also decay creating still other paramagnetic species.

It has already been noted that a predominant oxidized product is not observed in irradiated crystals of succinic acid or glycine. Ionization followed by proton dissociation was proposed as the mechanism for the formation of radical XIV in irradiated succinic acid. The overall process is one of dehydrogenation. Perhaps dehydrogenation occurs nonspecifically at various sites within the molecule producing a variety of free radicals. This seems to be the simplest way of accounting for the diverse absorptions associated with the oxidation process in succinic acid. The same explanation may apply to the results obtained from irradiated glycine where a nonspecific oxidation process is also indicated.

Reduction. Reduction is by definition the addition of an electron to a molecule. Our results show that preferred sites for electron addition are disulfide groups, the carbonyl oxygen of carboxyl groups, and the sulfur atom in C=S groups. In molecules having a disulfide group and a carbonyl group the electron attaches itself to the disulfide group. One may ask why electrons are not found attached to both groups. A somewhat naive explanation of the specificity of electron attachment is that an ionization electron meanders through the crystal gradually losing energy. Finally it loses sufficient energy so that it can be contained by the deepest of the available groups.

The oxidation process in irradiated glycine HCl crystals yields Cl_2^- ions whose absorption can be clearly distinguished from that of the anions. Moreover, the Cl_2^- ions are stable to temperatures above 100° K. Thus, the fate of reduced glycine as the crystal is warmed can be observed in a straightforward manner. Dissociation of the negative ions yields CH₂COOH and presumably ammonia²³



The radical CH₂-COOH is also produced in irradiated crystals of the free amine ε cid.²⁶

Magnetic resonance studies of radiation-induced reduction processes are often hampered by the same difficulties as were enumerated in our discussion of cation dissociation. However, there are undoubtedly many organic compounds like glycine HCl, where reduction processes could be examined profitably.

Relationship to Radiation Chemistry and Radiation Biology. A primary objective in radiation chemistry is to provide the chemical basis for understanding radiobiological effects. As far as possible, we wish to correlate our results with those of radiation chemistry. Considerable progress has been made recently by radiation chemists in analyzing the effects of ionizing radiation on amino acids in aqueous solution. For example, glycine has been studied using pulse-radiolysis techniques as well as by conventional chemical methods. From pulse-radiolysis studies the reactivity of glycine with the solvated electron can be deduced. The reactivity constant has been determined from spectroscopic measurements of the rate of disappearance of the solvated electron in deaerated solutions of glycine.²⁷ From chemical analysis of the final stable products obtained from irradiated solutions, Garrison²⁸ has inferred that dissociative electron attachment occurs which results in deamination. In our solid-state studies we have observed in a more direct fashion the attachment of the electron to glycine. From esr studies it has been possible to deduce where the electron attaches to glycine and the orbital of the resulting unpaired electron. From warmup studies it has been possible to demonstrate cirectly the dissociation of the C-N bond in glycine. Thus with respect to the reduction process, esr studies of the solid state at low temperature have provided information which is complementary to chemical studies of solutions. It is still too early to tell how well this complementarity will be preserved with other molecules. It seems probable, however, that the main radiobiological significance of low temperature esr studies is the information such studies can yield concerning radiation-induced reduction processes.

The high reactivity of molecules containing a car-

⁽²⁶⁾ H. C. Box, H. G. Freund, and E. E. Budzinski, J. Amer. Chem. Soc., 88, 658 (1966).

⁽²⁷⁾ J. V. Davies, M. Ebert, and A. J. Swallow, "Pulse Radiolysis," M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Ed., Academic Press, New York, N. Y., 1965, p 165.

⁽²⁸⁾ W. M. Garrison, Radiat. Kes. Suppl., 4, 158 (1964).

bonyl group, a disulfide group or a double-bonded sulfur (e.g., thiourea) has also been noted in pulse-radiolysis studies.²⁹ In each case our esr data provide more specific information concerning how the electron attaches to these molecules.

Considerable interest attaches to the study of radiation effects on disulfide bonds because of their essential role in determining the tertiary structure of protein. An early hypothesis was that the disulfide bond was particularly susceptible to radiation damage because of hole transfer to that bond.³⁰ On the other hand, it has been suggested that because of their high reactivity with the solvated electron the disulfide bonds in certain protein such as ribonuclease can account for most of the proteins reactivity in irradiated aqueous solutions.³¹ Our esr results obtained on small molecules, showing that disulfide bonds are favored sites for trapping holes and for electron attachment, tend to support both the foregoing suggestions.

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4, 79 (1964). E. J. Hart, S. Gordon, and J. K. Thomas, J. Phys. Chem.,
68, 127 (1964).

(30) W. Gordy, W. B. Ard, and H. Shields, Proc. Natl. Acad. Sci., U. S., 41, 983 (1955).

(31) M. Ebert and A. J. Swallow, "Solvated Electron" Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 289.

Positive and Negative Ion Formation In

Hexafluoroacetone by Electron Impact

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Positive and negative ion formation as a result of the electron bombardment of hexafluoroacetone has been studied and, from the positive ion data, a value of $\leq 4.16 \text{ eV}$ calculated for the bond dissociation energy $D(CF_3-COCF_3)$. Hexafluoroacetone is an abundant source of negative ions, the principal ions being $CF_3COCF_3^-$, $CF_3COCF_2^-$, $(CF_3)_2C^-$, CF_3CO^- , CF_3^- , CF_2^- , CFO^- and F^- . The dependence of their formation upon electron energy has been studied and a deconvolution method used to analyze the results; ionization processes have been suggested to account for the formation of most of these ions at low electron energies and electron affinities calculated for several species. $CF_3COCF_3^-$ is formed as a result of both primary and secondary electron capture and a value of $0.61 \times 10^{-16} \text{ cm}^2$ has been calculated for the electron attachment cross section for the ketone.

Introduction

Electron bombardment of a molecule may result in the formation of positive and negative ions.¹ The latter may be produced by (i) resonance attachment AB $+ e \rightarrow AB^{-}$; (ii) dissociative resonance capture, AB $+ e \rightarrow A^{-} + B$; or (iii) ion-pair formation; AB + $e \rightarrow A^{-} + B^{+} + e$.

These mechanisms usually operate at different electron energies, the resonance processes usually occurring in the 0-10 eV energy region and the ion-pair processes at energies above this.

We have examined positive and negative ion formation in hexafluoroacetone over the energy range 0-70 eV. This compound was chosen because appearance potential studies of positive ions should yield information regarding the carbon-carbon bond strength and enable comparison to be made with the analogous bond strength in acetone; in addition, preliminary studies showed several negative ions to be formed and we have examined some of these ions and their electron energy dependence.

In electron impact studies, when the source of the electrons is a heated filament, uncertainties arise in the interpretation of the experimental ionization data because of the energy spread of the thermionically-emitted electron beam. This is because the ionization thresholds become smeared-out as a result of the high-energy tail of the electron energy distribution. Morrison²

⁽¹⁾ H. S. W. Massey, "Negative Ions," Cambridge University Press, London, 1950.

⁽²⁾ J. D. Morrison, J. Chem. Phys., 39, 200 (1963).



Figure 1. Ionization efficiency curve for O^- ion formation by SO₂. Full circles, original experimental data; open circles, deconvoluted results obtained using 15 smoothing and 20 unfolding iterations.

has used analytical methods to remove the energy spread and has applied the technique to the problem of positive ions. We have applied such methods to study negative ion formation at low electron energies³ and have extended their use in this work to include hexafluoroacetone.

Experimental Section

The data were obtained using a Bendix time-offlight mass spectrometer, Model 3015. The pressure in the ion source was usually maintained below 5×10^{-6} mm in order to reduce the possibility of ion formation due to ion-molecule reactions. The energy of the ionizing electrons was read on a Solartron digital voltmeter, Model LM 1619, and the spectra recorded on a 1-mV Kent potentiometric recorder.

In both the positive and negative ion studies, the electron current was maintained constant by automatic regulation over the whole energy range investigated. Ionization curves were usually measured three to five times, the appearance potentials for negative ions being reproducible to ± 0.1 eV.

The appearance potential of the O⁻ ion from SO₂ was used as the reference for electron energy scale calibration.³⁻⁵ In a previous paper⁶ we used the S⁻ ion from CS₂ for scale calibration purposes; this is a satisfactory calibrant but we now find the O⁻ ion formed by SO₂ to be superior. Our principal reasons are that the O⁻ ion is a more intense ion and also (as can be seen in Figure 1) two resonance peaks are observed for the O⁻ ion. As a consequence, although the appearance potential of the ion at 4.2 eV is chosen for calibration purposes, the second appearance potential (6.6 eV), the positions of the peak maxima (4.9 and 7.5 eV) and the energy differences between these peak parameters serve as checks on the reliability of the calibration. For positive ion studies, argon was used to calibrate the energy scale, the method used for determining the appearance potentials being the semilogarithmic plot technique.

The electron energy distribution, which was required to be known for the deconvolution procedure, was measured using the SF_6^- ion formed by sulfur hexafluoride.^{7.8} It was found that performing 15 smoothing and 20 unfolding iterations on the basic experimental data enabled satisfactory evaluation of appearance potentials, resonance peak maxima and peak widths (at half-height) to be made.

Materials. Hexafluoroacetone was obtained by dehydration of the sesquihydrate. The impurities were fluoroform, hexafluoroethane, and carbon dioxide and these were removed by prolonged pumping on a vacuum line at -130° .

Results and Discussion

(a) Positive Ion Formation. We have measured the appearance potentials of the CF_3^+ and CF_3CO^+ ions formed from hexafluoroacetone and obtained $A(CF_3^+) = 14.26 \pm 0.10$ eV, and $A(CF_3CO^+) = 12.04 \pm 0.12$ eV.

If the ionization processes leading the formation of these ions correspond to

 $CF_3COCF_3 + e \longrightarrow CF_3^+ + COCF_3 + 2e$ (1)

$$\longrightarrow$$
 CF₃CO⁺ + CF₃ + 2e (2)

then we may use these results to evaluate the strength of the CF_3 -COCF₃ bond by means of such relations as $D(CF_3-COCF_3) \leq A(CF_3^+) - I(CF_3)$,

where $I(CF_3)$ refers to the ionization potential of the trifluoromethyl radical.

 $I(CF_3)$ has been measured directly by electron impact by two groups of workers^{9,10} and a value of 10.1 eV obtained. It has been suggested,¹¹ on the basis of reasonable values for the carbon-halogen bond strength in the trifluoromethyl halides, that this measured ionization potential is to high by about 0.8 eV.

Recently, Lifschitz and Chupka¹² have measured the

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ionization potential for the trifluoromethyl radical by a photoionization technique and have reported that $I(CF_3)$ is 9.25 ± 0.04 eV. It appears that the difference between this value and the directly measured value is largely due to the fact that the adiabatic ionization potential of the radical is much lower than the vertical ionization potential, the configuration of the CF_3^+ ion being very different from that of the radical.

If we use the direct electron impact^{9,10} value for $I(CF_3)$ in conjunction with our data for $A(CF_3^+)$ we find that $D(CF_3-COCF_3) \leq 4.16 \text{ eV}$.

There are no other values reported for the CF₃-COCF₃ bond dissociation energy in hexafluoroacetone; because of the displacement reaction observed¹³ when methyl radicals and hexafluoroacetone are present in the same system, it is likely¹⁴ that the CF₃-COCF₃ bond is about 0.1 eV weaker than the corresponding bond in acetone (which has a strength of 3.8 eV), so that $D(CF_3-COCF_3) \sim 3.7 \text{ eV}.$

Electron impact methods for measuring bond dissociation energies usually yield upper limit values because of the necessary neglect and uncertainty of the kinetic and excitation energies involved in the ionization and fragmentation processes. It may be therefore that our experimental value of ≤ 4.16 eV compared with the estimated value of 3.7 eV reflects this uncertainty. However, the trifluoroacetyl radical has been shown to be unstable,¹⁶ decomposing readily by reaction 3.

$$CF_3CO \longrightarrow CF_3 + CO$$
 (3)

Some or all of this energy difference of <0.46 eV may be used in decomposing the trifluoroacetyl radical formed in the initial ionization process; if this is so, then we may estimate a maximum value of 0.46 eV for the activation energy for reaction 3. Whittle,¹⁶ using a kinetic method, has deduced an upper limit of 0.43 eV for this reaction.

Our data for $A(CF_3CO^+)$ should, in principle, provide an unequivocal value for $D(CF_3CO-CF_3)$, however no value is available for the ionization potential of the trifluoroacetyl radical. We may estimate $I(CF_3CO)$ if we assume that $D(CF_3CO-CF_3) = 3.7 \text{ eV}$; our results indicate that $I(CF_3CO) < 8.3 \text{ eV}$. This value may be compared with the value of $8.05 \pm 0.17 \text{ eV}$ reported¹⁷ for $I(CH_3CO)$.

(b) Negative Ion Formation. O^- Ion Formation by Sulfur Dioxide. The formation of negative ions by sulfur dioxide has been investigated by several workers and the appearance potential of the O^- ion is sufficiently well established^{4,5} at 4.2 eV to be used to calibrate the energy scale.

Our experimental data for this ion are shown in Figure 1; two resonance peaks are observed which have clear maxima but uncertain appearance potentials. Deconvolution of these data, using an electron energy distribution measured using SF_6 -/ SF_6 , give the results shown by the open circles. The threshold for the

first peak is sharp and is separated from the peak maximum by 0.70 eV; this is in good agreement with the difference obtained by Kraus⁴ (using a retarding-potential-difference technique) and by Dillard and Franklin.⁵

The onset of the second resonance peak is not quite resolved; Kraus⁴ also was unable to completely separate the two peaks. The onset of the first peak and the minimum between the resonance peaks are separated by 2.4 eV in both our work and that of Kraus.

Hexafluoroacetone (HFA). In Table I we show the negative ion mass spectrum of HFA measured at nominal electron energies of 10 and 70 eV. The absence of ions such as C⁻, O⁻, and C₂⁻ from the lower energy spectrum suggests that they are formed principally by ion-pair processes. We have studied the energy dependence of formation of the ions; $CF_3COCF_3^-$, $CF_3COCF_2^-$, $(CF_3)_2C^-$, CF_3CO^- , CF_3^- , CF_2^- , CFO^- , and F⁻.

Table I: Negative Ion Mass Spectrum of Hexafluoroacetoneat Electron Energies (Uncorrected) of 10 and 70 eV

m/e	Ion	Rel. int., 10 eV	Rel. int., 70 eV
12	C-	0	3.0
16	0-	0	21.5
19	F-	751	1000
24	C2 ⁻	0	4.0
31	CF-	15.2	3.6
38	F_2^-	0	3.0
43	C ₂ F -	0	2.0
47	CFO-	25.4	18.3
50	CF_2^-	12.7	4.0
69	CF_3^-	1000	257
97	CF _a CO ⁻	10.1	17.0
147	CF ₂ COCF ₂ -	5.7	36.0
150	$(CF_3)_2C^-$	7.6	4.0
166	CF ₃ COCF ₃ -	7.6	67

It is apparent from our data (discussed below) that several of the ions (CF₃COCF₂⁻, CF₃CO⁻, CF₃⁻, CFO⁻, and F⁻) have almost identical appearance potentials ($\sim 3.1 \pm 0.1 \text{ eV}$) and their respective resonance peaks attain a maximum value at $\sim 4.2 \pm 0.1 \text{ eV}$. This suggests a common origin for these ions and we suggest that this is an electronically excited unstable state of the ketone which subsequently decomposes to form the ions mentioned

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$$CF_3COCF_3 + e \longrightarrow CF_3COCF_3^{-*} \longrightarrow CF_3COCF_2^{-} + F$$
 (4)

$$\Rightarrow CF_3CO^- + CF_3 \tag{5}$$

$$\rightarrow$$
 CF₃⁻ + COCF₃(+CO + CF₃?) (6)

$$\rightarrow$$
 CFO⁻ + CF₂ + CF₃ (7)

$$\rightarrow$$
 F⁻ + CF₂COCF₃ (8)

(i) Charge-Transfer Reactions Involving the O^- Ion. The ionization curves for several of the ions (e.g., $CF_3COCF_2^-$, CF_3^- , F^-) show inflections at energies $\sim 5 \text{ eV}$; this corresponds to the resonance peak maximum observed for the O^- ion formed by SO_2 (which was used to calibrate the electron energy scale). These inflections were not observed when SO_2 was not present in the ionization chamber; accordingly we attribute their occurrence to the charge-transfer reaction (9). This produces an unstable state of the parent ion which decomposes to yield the appropriate ions.

$$O^- + CF_3COCF_3 \longrightarrow O + CF_3COCF_3^- \longrightarrow CF_3COCF_2^- etc.$$
 (9)

It is noteworthy that, even at the low ion source pressures maintained in this work, negative ion-molecule reactions may occur to a sufficient extent to contribute noticeably to the ionization efficiency curves.

(ii) $CF_3COCF_3^{-}$. The observation of a stable molecule-ion is relatively unusual; few other such ions have been observed. Its formation must involve the electron capture process

$$CF_3COCF_3 + e \longrightarrow CF_3COCF_3^-$$
 (10)

Our data for this ion indicate two main regions of ion formation, one ~ 0 eV and the second¹⁸ commencing at about 10 eV. In earlier work,¹⁸ only the higher energy process was detected, the ion being formed as a result of secondary electron capture, the secondary electrons being produced by such positive ionization processes as CF₃COCF₃ + e \rightarrow CF₃COCF₃⁺ + 2e.

At that time, we were unable to observe ion formation at very low electron energies; however, an improved experimental technique and introduction of a 3V dry cell into the electron energy circuit so that 'negative' voltages could be obtained has enabled us to examine the primary electron capture reaction.

When hexafluoroacetone was studied at electron energies ~ 0 eV, a parent ion was observed; admission of a small quantity of sulfur hexafluoride to the ionization chamber resulted in a considerable diminution of the CF₃COCF₃⁻ ion intensity. This suggested that the electron attachment cross section for reaction 10 was much less than that for SF₆⁻ ion formation by

$$SF_6 + e \longrightarrow SF_6^- \tag{11}$$

In Figure 2, we show the data obtained for SF_6^- and



Figure 2. Ion current vs. electron accelerating energy. Full circles, SF_{6}^{-} ; open circles, $CF_{3}COCF_{3}^{-}$. Ion current scale for hexafluoroacetone 58.9 times greater than that for SF_{6} .

 $CF_3COCF_3^-$ ion formation as a function of the electron energy. A 50/50 mixture of hexafluoroacetone and sulphur hexafluoride was used; the two sets of ionization data have been normalized for convenience in presentation, the ordinate for $CF_3COCF_3^-$ being 58.9 times greater than that for SF_6^- .

Formation of the SF_6^- ion in this energy region has been used to mirror the electron energy distribution and calibrate the electron energy scale.^{7,8} It is apparent from Figure 2 that the $CF_3COCF_3^-$ and SF_6^- ions have a very similar energy dependence, both ions attaining a maximum value at the same electron energy. The ionization curve for the ketone is slightly broader in the wings than is that for the hexafluoride, this may reflect either a slightly different energy dependence for electron attachment or the experimental uncertainties in measuring the very small ion currents for the $CF_3COCF_3^-$.

Because of their similar energy dependence we consider that the relative heights of the two ion peaks may be used to indicate the relative attachment crosssections of reactions 10 and 11. If it is assumed that both ions have the same collection efficiency, then

$$\frac{\sigma_{\rm SF_6}}{\sigma_{\rm HFA}} = 58.9$$

where σ_x refers to the electron attachment cross-section of X. A value of 3.6×10^{-15} cm² has been reported¹⁹ for $\sigma_{SF_{67}}$ so that $\sigma_{HFA} = 0.61 \times 10^{-16}$ cm².

It has been observed that both sulfur hexafluoride²⁰

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and hexafluoroacetone¹⁸ form parent molecule-ions at higher electron energies as a result of secondary electron capture. We considered that competition between sulfur hexafluoride and hexafluoroacetone for secondary electrons might enable us to measure $\sigma_{\rm SF6}/\sigma_{\rm HFA}$. Accordingly, using a 39.2:1 mixture of CF₃COCF₃: SF₆, we measured the intensities of the CF₃COCF₃⁻ and SF₆⁻ ions, $I_{\rm HFA}^{-}$ and $I_{\rm SF6}^{-}$, at ten electron energy intervals over the range 15–60 eV. Our experimental data indicated that the ion current ratio, $I_{\rm SF6}^{-}/I_{\rm HFA}^{-}$ was effectively constant over the entire energy range having a value of 1.44 ± 0.06; this result yields a value for $\sigma_{\rm SF6}/\sigma_{\rm HFA}$ of 56 ± 2, which is in good accord with our directly-measured value at low electron energies.

An alternative explanation for the decrease in the $CF_3COCF_3^-$ ion current is the possibility of occurrence of the charge exchange reaction

$$CF_3COCF_3^- + SF_6 \longrightarrow CF_3COCF_3 + SF_6^-$$
 (11a)

Our data for SF_6^- formation cannot definitely distinguish between this reaction and reaction 11; however, at our ion source pressure ($\sim 5 \times 10^{-6}$ mm) although some collisions between $CF_3COCF_3^-$ and SF_6 will occur, we consider the probability of interactions occurring to a sufficient extent to account for the considerable decrease in $CF_3COCF_3^-$ ion current noted experimentally at very low SF_6 pressures ($\sim 10^{-7}$ mm) to be negligible unless the cross-section for reaction 11a is very large. The data obtained for secondary electron capture in the high energy study also suggest that reactions such as 11a may reasonably be neglected since, at these energies, other negative ion species (*e.g.*, CF_3^- , CF_3CO^-) will be present which might undergo charge transfer reactions.

$$X^- + SF_6 \longrightarrow SF_6^- + X$$



Figure 3. Ionization efficiency curve for $CF_3COCF_2^-/CF_3COCF_3$ (O) and O^-/SO_2 (\times) ion formation.



Figure 4. Deconvoluted results. $CF_3COCF_2^-/CF_3COCF_3, O; O^-/SO_2, \times$.

If such reactions occurred significantly then it would result in the ratio $\sigma_{SFe}/\sigma_{HFA}$ being greater at higher energies than at ~0 eV, whereas our experimental data show the two values to be in good agreement.

(*iii*) $CF_3COCF_2^-$. Typical experimental data and the smoothed, deconvoluted results are shown in Figures 3 and 4 together with the corresponding O⁻/SO₂ ionization curves.

Examination of the pressure dependence of the $CF_3COCF_2^-$ ion current at low electron energies showed it to be a primary ion, we may therefore neglect the possibility of the ion being formed by secondary ionic reactions.

A sharp onset at 3.10 ± 0.10 eV is observed, the resonance peak reaching a maximum at 4.20 ± 0.05 eV; the peak width at half-height is 1.35 ± 0.05 eV. The common origin of the ions formed at this energy has been discussed above and we attribute CF_3COCF_2 ion formation to reaction 4.

If a value of ~ 5.2 eV is assumed for the bond dissociation energy $D(CF_3COCF_2-F)$, (values of 5.3, 5.2, and 5.0 eV having been reported for the C-F bond strengths in CF_4 ,²¹ C_2F_6 ²², and $C_6H_5F^{23}$, respectively), then using the relation: $D(CF_3COCF_2-F) \leq A$ - $(CF_3COCF_2^-) + E(CF_3COCF_2)$, a value of ~ 2.1 eV may be estimated for the electron affinity of the perfluoroacetonyl radical.

Figure 4 shows clearly the inflection in the ionization

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Ion	A P ^a	Max ^a	\mathbf{PW}^{a}	Process
CF ₃ COCF ₃ -	0			$CF_{3}COCF_{3} + e \rightarrow CF_{3}COCF_{3}^{-}$
CF ₃ COCF ₂ -	3.10 ± 0.10	4.20 ± 0.05	1.35 ± 0.05	$CF_{3}COCF_{3} + e \rightarrow CF_{3}COCF_{3}^{-} *$
				$CF_3COCF_2^- + F$
$(CF_3)_2C^-$	5.1 ± 0.1	6.4 ± 0.1	0.6 ± 0.1	$CF_3COCF_3 + e \rightarrow (CF_3)_2C^- + 0$
$CF_{3}CO^{-}$	3.10 ± 0.05	4.1 ± 0.1	1.0 ± 0.2	$CF_3COCF_3^- * \rightarrow CF_3CO^- + CF_3$
CF_3^-	3.0 ± 0.1	4.3 ± 0.1	1.5 ± 0.2	$CF_3COCF_3^- * \rightarrow CF_3^- + CF_3CO$
	5.4 ± 0.1	6.7 ± 0.1	1.7 ± 0.1	$CF_3COCF_3 + e \rightarrow CF_3^- + CO + CF_2 + F$
	8.2 ± 0.2	8.6 ± 0.1		?
	10.5 ± 0.2	11.0 ± 0.2		?
CF_2^-	4.25 ± 0.10	5.25 ± 0.05	0.7 ± 0.1	$CF_3COCF_3 + e \rightarrow CF_2^- + F + CO + CF_3?$
CFO-	3.0 ± 0.1	uncertain	2	$CF_3COCF_3^- * \rightarrow CFO^- + CF_2 + CF_3$
	5.3 ± 0.2	6.6 ± 0.1	2.0 ± 0.1	$CF_3COCF_3 + e \rightarrow CFO^- + 2F + C_2F_3$
F-	3.1 ± 0.1	4.3 ± 0.2	1.3 ± 0.3	$CF_3COCF_3^- * \rightarrow F^- + CF_2COCF_3$
	5.7 ± 0.1	7.2 ± 0.2	1.8 ± 0.3	$CF_3COCF_3 + e \rightarrow F^- + CF_2 + CO + CF_3$
	9.0 ± 0.1			\rightarrow F ⁻ + F + CO + 2CF ₂
^a All values in eV.				

Table II: Appearance Potentials (AP), Peak Maxima, and Peak Widths at Half Height (PW) of Negative Ions Formed by Hexafluoroacetone

curve which we have considered above to be the result of the charge-transfer reaction 9.

(iv) $(CF_3)_3C^-$. Our experimental data for this ion when smoothed and deconvoluted yield the values shown in Table II. Ion formation is attributed to the reaction

$$CF_3COCF_3 + e \longrightarrow (CF_3)_2C^- + O$$
 (12)

It is noteworthy that the resonance peak is very narrow, the width at half-height being only 0.6 eV. A value of ~ 0.6 eV may be estimated for the electron affinity of $(CF_3)_2C$ if the bond strength $D(O - C(CF_3)_2)$ is assumed to be similar to that in carbon dioxide, *i.e.*, ~ 5.7 eV.

(v) CF_3CO^- . At low electron energies, this ion is formed quite abundantly but not at 70 eV; this suggests that the ion-pair process $CF_3COCF_3 + e \rightarrow$ $CF_3CO^- + CF_3^+ + 2e$ does not occur extensively. Our results for this ion are shown in Table II, and we consider reaction 5 to account for ion formation. If a value of 3.7 eV is assumed for $D(CF_3CO-CF_3)$, then our data yield a value of ≤ 0.6 eV for the electron affinity of the trifluoroacetyl radical.

(vi) CF_3^{-} . Ion formation in this case is rather complex; several appearance potentials are noted for this ion.

Initially ion formation occurred at 3.0 ± 0.1 eV and is attributed to decomposition of the electronically excited ketone by reaction 6. Because the trifluoroacetyl radical has been shown to have limited stability in the gas phase, the decomposition reaction 6 may involve the formation of CO and CF₃ as fragmentation products.

It is apparent from Figures 5 and 6 that the CF_3 ionization curve has inflections at \sim 5 eV and \sim 7.6 eV, *i.e.*, where the O⁻/SO₂ ion reaches a maximum intensity;



Figure 5. Ionization efficiency curve for CF_3 -/CF_3COCF_3, O, and O-/SO₂, \times , ion formation.

these inflections are attributed to the change transfer reaction mentioned above.

A second resonance process is observed at 5.4 eV (based upon extrapolation of the upper part of the curve). If reaction 13 is responsible for ion formation at this energy, then our data yield a value of 2.5 eV for $E(CF_3)$; this may be compared with values of $\leq 2.6 \text{ eV}^{22}$ and 1.8 eV^{24} reported for this quantity.

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Further resonance processes of very low cross section are noted at 8.2 and 10.5 eV; we cannot account for these ionization processes.

(vii) CF_2^{-} . Our data for this ion are shown in Table II; a narrow resonance peak having an onset at 4.25 ± 0.10 eV is obtained. If ion formation was due to the reaction

$$CF_3COCF_3 + e \longrightarrow CF_2^- + F + CO + CF_3$$
 (14)

then a value of $E(CF_2) \leq 3.75$ eV would be obtained; this seems improbably large. The narrow resonance peak would suggest that little excess energy was involved in the ionization process. A rearrangement reaction such as

$$CF_3COCF_3 + e \longrightarrow CF_2^- + CF_4 + CO$$
 (15)

would yield a negative value for $E(CF_2)$; we are therefore unable to assign the ionization process responsible for CF_2 -formation.

(viii) CFO⁻. This ion must be formed as the result of rearrangement; ion formation is observed initially at 3.0 ± 0.1 eV and is attributed to reaction 7. Although a sharp onset is obtained at this energy, the resonance peak is broad ($\sim 2 \text{ eV}$) and does not attain a clear maximum before a second resonance process occurs at 5.3 eV. This resonance peak is also broad and this perhaps suggests the involvement of considerable excess energy in the rearrangement.

 $CF_3COCF_3 + e \longrightarrow CFO^- + 2F + C_2F_3$ (16)

The second ionization process may correspond to



Figure 6. Deconvoluted results. CF_3^-/CF_3COCF_3 , O; O^-/SO_2 , \times .

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Figure 7. Ionization efficiency curve for $F^{-}/CF_{3}COCF_{3}$, O and O^{-}/SO_{2} , \times , ion formation.



Figure 8. Deconvoluted results. $F^{-}/CF_{3}COCF_{3}$, O; O^{-}/SO_{2} , \times .

reaction 16, *i.e.*, the C-O bond is broken and the oxygen transferred to a CF group in the rearrangement. This probably would have higher energy requirements than reaction 7 where simple fluorine transfer to CO may be involved but such assignments are tentative.

The heat of formation of the fluoroformyl radical, $\Delta H_f(\text{CFO})$, has been estimated³ to be -1.7 eV, so that our data for reaction 7 indicate $E(\text{CFO}) \sim 3.3 \text{ eV}$. A study³ of CFO⁻ ion formation by carbonyl fluoride showed E(CFO) = 2.7 eV; the resonance peak in that work was much narrower than that found in this study (~ 0.5 eV compared with ~ 2.0 eV), which may reflect the excess energy involved in the hexafluoroace-tone rearrangement.

(ix) F^{-} . Our results for this ion are summarized in Table II and typical data shown in Figures 7 and 8.

Inflections in the deconvoluted curve at ~ 5 and ~ 7.5 eV we attribute to the charge-transfer reaction involving the O⁻ ion. The first appearance potential at 3.1 \pm 0.1 eV is considered to be the result of reaction 8 discussed previously; a second process of much larger cross section occurs at 5.7 \pm 0.1 eV. If reaction 17 is responsible for the increase in the ion current at this energy, then a maximum value of 2.6 eV may be deduced for the bond dissociation energy $D(CF_2-COCF_3)$ if we assume that $D(CO-CF_3) = 0$ eV.

$$CF_3COCF_3 + e \longrightarrow F^- + CF_2 + CO + CF_3$$
 (17)

A further ionization process of very low cross-section may be seen on the tail of the second resonance peak, the onset energy being 9.0 eV.

$$CF_3COCF_3 + e \longrightarrow F^- + F + CO + 2CF_2$$
 (18)

The minimum enthalpy requirement for reaction 18 is 9.0 eV and we therefore attribute ionization to this reaction.

(c) Thermochemical Data. The following values for the heats of formation have been used in this work (in eV) CF₃COCF₃ -15.1; CF₃-5.2;²⁵ CF₂-1.6;²⁶ CF, 3.2;²⁷ F, 0.8;²⁷ CO, -1.1;²⁷ and CF₃+, 3.7.²⁸

The heat of formation of hexafluoroacetone has been estimated using the additivity rules²⁹ based upon the C-C and C-F bond contributions to the enthalpies of various fluorine-containing molecules.^{21,29}

Acknowledgment. We thank Dr. S.W. Benson of the Stanford Research Institute for comments regarding the bond dissociation energy of hexafluoroacetone.

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Rate Constants and Transient Spectra in the Gas-Phase Reactions of

Hydrogen Atoms. Substituents Effects in Monosubstituted Benzenes¹

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Transient spectra and rate constants have been obtained, using the pulse-radiolysis technique, for the gas phase reactions of hydrogen atoms with a series of monosubstituted benzenes, naphthalene, the xylenes and pyridine. Arrhenius parameters have been determined for most of these compounds by varying the temperature within the range 25–120°. The rate constants for $H + C_6H_5X$ can be correlated with the Hammett σ values of the substituents, X, and the nature of the correlation indicates that the hydrogen atom is electrophilic in these reactions.

Introduction

The transient spectra and rate constants have previously been measured in the case of hydrogen atom addition to benzene and toluene in the gas phase, and the technique of making such measurements has been described. That hydrogen atoms are produced during the pulse (microsecond) of electrons and subsequently react in a pseudo-first-order manner with the organic compound has been shown.³ We have now made similar measurements for a series of monosubstituted benzenes in $\operatorname{ord} \varepsilon r$ to determine the relationship between the observed rate constants and the Hammett σ -values of the substituent groups.

Experimental Section

A complete descript on of the basic apparatus used in this pulse-radiolysis study has been given pre-

(1) Work performed under the auspices of the United States Atomic Energy Commission.

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(3) M. C. Sauer, Jr., and B. Ward, J. Phys. Chem., 71, 3971 (1967).

viously.^{4,5} Three different types of irradiation vessels were used. The high pressure vessels used for samples containing 70-80 atm have been described.⁴ In the present work, it was found more convenient to use glass vessels designed for lower pressures. Samples of total pressure about one atm were contained in quartz cylinders 16 cm long, 40 mm i.d., with 1.5-mm walls and 1.5 mm high purity silica end-windows. Samples of about 4 atm pressure were contained in quartz cylinders 16-cm long, 20 mm i.d., with 2.5-mm walls and 3 mm high purity silica end-windows. Appropriate arms on the vessels were used for freezing the samples and sealing off under vacuum.

In the case of the high pressure vessels, the organic compound was introduced at a pressure somewhat below its vapor pressure at room temperature; then the H₂ and Ar were added. For most of the samples run in quartz vessels, the vapor pressures of the organic compounds were not sufficiently high to use this method, so liquids were introduced by using micropipets (1-20 μ l.), or by weighing quantities on the order of 1.5 to 4 mg in the case of solids. These materials were introduced to a side-arm, degassed, and distilled to the vessel. The desired amount of argon was then condensed into the vessel, and hydrogen was added on top of the 20 cm of argon (vapor pressure at liquid N₂).

Although some determinations were made at 25° using the high pressure vessels, most of the rate constants were determined at 25 to 120° and about 4 atm pressure, using the smaller quartz vessels. The thermostated oven used to heat the cell and cell holder had an Al foil window for the electron beam and a high purity silica window for the analyzing light. The temperature was known to about $\pm 5^{\circ}$.

The rate constants were determined from the known concentrations of the organic compounds, and the half-times $(t_{1/2})$ for the formation of the transients, which were obtained from straight forward analyses of the oscilloscope traces showing the optical absorption changes occurring after the electron pulses. The pulse intensity was low enough that the decay of the transients by radical-radical reactions did not appreciably affect the formation curve of the transient. The rate constant was calculated from

$$k = \frac{0.693}{t_{1/2}[X]}$$

where [X] represents the concentration of the organic compound.

Results and Discussion

Transient Spectra. The transient spectra obtained are given in Figures 1-3. Each spectrum was determined, under the conditions indicated in the legends, by measuring the optical absorption after the pulse at the maximum in the formation-decay curve. The spectra are qualitative in the sense that radicals formed



Figure 1. Absorption spectra of transient species formed by pulse radiolysis of the following mixtures. $C_6H_5CF_3$: 60°, 7 cm of $C_6H_5CF_3$, 10 cm of H_2 , 60 cm of Ar; naphthalene: 60°, 0.3 cm naphthalene, 10 cm of H_2 , 60 cm of Ar; biphenyl: 100°, 0.3 cm of biphenyl, 20 cm of H_2 , 270 cm of Ar; $(C_6H_5)C_2H_6$: 25°, 0.8 cm of $(C_6H_5)C_2H_5$, 13 atm of H_2 , 60 atm of Ar; $C_6H_5NH_2$: 60°, 2 cm of $C_6H_5NH_2$, 10 cm of H_2 , 60 cm of Ar.

by reactions other than the reaction of hydrogen atoms with the organic compound in some cases contribute to the absorption. Each spectrum has been normalized to unity at the wavelength of maximum absorption. However, under similar conditions of pulse intensity, there was a variation of a factor of three to four in the strength of the absorption for the different systems studied. The weakest absorptions were found in anisole and nitrobenzene. Possible reasons for this could be variation in absorption coefficients, reactions of hydrogen atoms other than addition to the ring, or interference of the organic compound with the production of hydrogen atoms.

In Figure 3 are shown the transient spectra which resulted when CF_4 and CF_3Cl were used as intended sources of F and Cl atoms, respectively, to observe their reactions with benzene. The spectra obtained are simpler than the corresponding spectra obtained

⁽⁴⁾ M. C. Sauer, Jr., and L. M. Dorfman, J. Amer. Chem. Soc., 87, 3801 (1965).

⁽⁵⁾ M. C. Sauer, Jr., S. Arai, and L. M. Dorfman, J. Phys. Chem., 42, 708 (1965).



Figure 2. Absorption spectra of transient species formed by pulse radiolysis of the following mixtures. Xylenes: 25°, 0.6 cm of xylene, 13 atm of H₂, 60 atm of Ar; pyridine: 25°, 1.9 cm of pyridine, 13 atm of H₂, 60 atm of Ar; C₆H₅OCH₆: 60°, 1.7 cm of C₆H₆OCH₃, 20 cm of H₂, 270 cm of Ar; C₆H₅CN: 60°, 0.7 cm of C₆H₅CN, 20 cm of H₂, 270 cm of Ar; C₆H₅NO₂: 90°, 1.5 cm of C₆H₅NO₂, 20 cm of H₂, 270 cm of Ar.

(also shown in Figure 3) by addition of H atoms to fluorobenzene and chlorobenzene. This may reasonably be ascribed to the fact that when a hydrogen atom adds to fluoro- or chlorobenzene, the addition can take place at several different positions relative to the position of the halogen on the ring. However, when a F or Cl atom adds to benzene, only one isomer can result (barring subsequent rearrangements). Formation curves for the reactions of F and Cl atoms with benzene could not be obtained, even at 1 mm of benzene. Thus, it is not clear at present whether the transients result from a very fast addition of halogen



Figure 3. Absorption spectra of transient species formed by pulse radiolysis of the following mixtures. $H + C_6H_5F$: 25°, 3 cm of C_6H_5F , 13 atm of H_2 , 60 atm of Ar; $F + C_6H_6$: 25°, 8 cm of C_6H_6 , 34 atm of CF₄; $H + C_6H_6$ Cl: 25°, 0.9 cm of C_6H_6 Cl, 7 atm of H_2 , 58 atm of Ar; Cl + C_6H_6 : 25°, 8 cm of C_6H_6 , 2.5 atm of CF-Cl, 54 atm of Ar.

atoms to the benzene, α r by ionic reactions occurring during the pulse.

Rate Constants. Values of the rate constants for the reactions of hydrogen atoms with the various organic compounds were obtained by analysis of the formation curves obtained at the wavelengths of maximum absorption. Where two peaks occurred in a spectrum, results at the two wavelengths yielded the same rate constant. Addition of the hydrogen atom to one of the carbon atoms of the ring is believed to be the predominant reaction, yielding a substituted cyclohexadienyl radical except in the case of nitrobenzene, where, as is discussed below, reaction of the hydrogen atom with the NO₂ group is believed to occur. For some combounds, the formation curves indicated an appreciable initial absorption, apparently from radical species formed during the pulse. This had no effect on the analyses of the formation curves representing the reactions of hydrogen atoms occurring after the pulse, because the rate of increase of the concentration of the resulting substituted cyclohexadienyl radical is negligibly affected by the presence

of other radicals under the low pulse intensity conditions used.

The transient formation curves were pseudo-firstorder, which was expected since the concentration of the organic compound was in all cases much greater than the concentration of hydrogen atoms formed by the pulse $(10^{-6}$ to 10^{-7} mol/l.). Also, the rate constants were not dependent on either the argon pressure or the pressure of the organic compound, although these parameters were not checked in all cases.

The results are summarized in Table I, where values are given for several compounds studied only at 25°, and Figure 4, where the rate constants are given over the temperature range from 25 to 120°. A leastsquares analysis of the data results in the straight lines shown in Figure 4, and the resulting A factors and activation energies are given in Table II. The values of log k at 100°, calculated using these parameters, are also shown in Table II, and are used in Figure 5 where log k is plotted against the Hammett σ values⁶ of the substituent group. As has been done previously in a similar study of hydrogen atom reactions in aqueous solution,⁷ both σ_p and σ_m values were plotted where the substituent has a positive σ_{p} , but only σ_p was plotted where σ_p is negative. The value for nitrobenzene has not been plotted since attack of hydrogen atoms directly on the NO₂ group appears



Figure 4. Arrhenius plots of the rate constants for the reactions H + X. Much of the scatter in the experimental data can be ascribed to the uncertainty in the temperature $(\pm 5^{\circ})$, which leads to a $\pm 1.5\%$ uncertainty in the value of 1/T, which, in view of the expanded scale, is not small.

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Table I:	Rate Constants ^a for $H + X$ at 25°				
	X	k, (l. mol ⁻¹ sec ⁻¹) \times 10 ⁸			
	p-Xylene m-Xylene p-Xylene Ethylbenzene	$\begin{array}{c} 3.5 \pm 1.0 \\ 4.4 \pm 0.9 \\ 3.5 \pm 0.7 \\ 2.0 \pm 0.4 \end{array}$			
1	Pyridine	0.8 ± 0.3			

^a Determined in "high pressure" experiments, *i.e.*, about 900 psi Ar, about 190 psi H_2 , and near the vapor pressure of the organic compound.

Table II: Arrhenius I	Parameters ^a í	for H + X	
X	log A	$E_{\rm a}$, kcal/mole	log k1000
C ₆ H ₅ CN	11.02	5.2	7.97
C ₆ H _b CF ₃	10.98	5.1	8.01
C ₆ H ₆ F	9.98	3.2	8.10
C ₆ H ₆	10.77	4.3	8.24
C ₆ H ₅ Cl	9.74	2.4	8.34
$C_6H_5NO_2$	10.71	4.0	8.38
C ₆ H ₅ OCH ₃	11.9^{b}	5.9 ⁶	8.4
C ₆ H ₅ CH ₂ Cl	10.1	3.0	8.4
$C_6H_5NH_2$	10.22	2.6	8.68
$(C_{6}H_{5})_{2}$	11.2	4.3	8.7
Naphthalene	11.93	5.1	8.95

^a Using $k = Ae^{-E_a/RT}$, where the units of A are l. mol⁻¹ sec⁻¹. These values were determined in samples containing 3.5 atm Ar, 0.3 atm H₂, and various pressures of the organic compound. The accuracies of the values of log A and E_a (columns 2 and 3) are estimated to be ± 0.5 and ± 0.8 kcal/mol, respectively, in a typical case. ^b Probably high, see Figure 4.



Figure 5. Plot of $\log k_{H+X}$ at 100° vs. Hammett σ value of substituent. The value of k for toluene is based on k_{25} ° from ref 3, and that for ethyl benzene is based on the value in Table I. Both have been "extrapolated" to 100° by assuming activation energies similar to those obtained for the other compounds.

(6) P. R. Wells, "Linear Free Energy Relationships," Academic Press, Inc., New York, N. Y., 1968. The values used are the σ° parameters (p 15) except for C₂H₅ (p 14) and C₆H₅ (p 16).
(7) M. Anbar, D. Meyerstein, and P. Neta, *Nature*, 209, 1348 (1966).

probable in view of previous studies on the reactions of H with $NO_2^{-8.9}$ and $C(NO_2)_4^{10}$ in aqueous solution. This would explain why the rate constant for nitrobenzene is larger than that for benzene in spite of the large positive value of σ for the NO₂ group. Although the deviations of the points in Figure 5 from the least squares line are appreciable, the tendency of k to decrease with increasing σ is apparent, which indicates an electrophilic character of hydrogen atoms addition to the aromatic ring. The same trend has been found in the case of reactions of hydrogen atoms with monosubstituted benzenes in aqueous solution.⁷ Although in both cases the experimental scatter is appreciable, the slopes (ρ values) of the log k vs. τ plots are essentially the same, being -0.7 in the latter work, and -0.79 in the present work. Thus, the tendency for electron withdrawing groups to decrease the rate constant and for electron donating groups to increase the rate constant is clear.

The conclusion that hydrogen atoms are electrophilic in their reaction with substituted benzenes is apparently contrary to that drawn by Cvetanovic¹¹ in the case of hydrogen atom addition to olefins, where hydrogen atoms were classified as electroneutral, as opposed to oxygen atoms, which were classified as electrophilic. (Rate constants for the addition of other radicals to olefins are also summarized and considered with respect to the conclusions one can make concerning the degree of electrophilic character.¹²) An extension of the data on the reaction of oxygen atoms with substituted benzenes¹³ would be useful in attempting to discuss the meaning of the substituent effect in the case of hydrogen atoms.

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Reaction Intermediates and Products in the Radiolysis of

Phenyl Acetate at 77°K

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The radiolysis of phenyl acetate at 77°K has been studied by product analysis and the observation of reaction intermediates. Ionic species are produced by the γ irradiation of phenyl acetate glass at 77°K and are observed by esr and optical spectroscopy. The species are easily photobleached by infrared light and change into acetyl radicals. The reaction is explained by the neutralization of phenyl acetate cation and anion. When MTHF glass containing phenyl acetate is γ -irradiated at 77°K, a doublet esr spectrum with a line separation of 22 G is obtained and is assigned to the phenyl acetate anion. When sec-butyl chloride glass containing phenyl acetate is γ -irradiated at 77°K, a doublet esr spectrum with a line separation of 14 G is obtained and is assigned to the phenyl acetate cation. The main products in the radiolysis of phenyl acetate at 77°K are anisole, phenol, and hydroxyacetophenone. The G value of anisole in the radiolysis in the polycrystalline state is twice that in the glassy state, while the G value of phenol in the polycrystalline state is half that in the glassy state.

Introduction

Product analysis and the observation of reaction intermediates have been two major methods for the study of the reaction mechanism of radiolysis. Since these two methods reveal different aspects of mechanisms, we have studied the radiolysis of phenyl acetate by both methods to elucidate its mechanism. The reactions of ionic intermediates formed by γ irradiation of phenyl acetate glass at 77°K have been observed by esr and optical spectroscopy.

Although the aluminum chloride catalyzed or photochemical Fries reaction of phenyl acetate yields only hydroxyacetophenone and phenol, anisole is one of the main products in the radiolysis of phenyl acetate

⁽¹⁰⁾ J. Rabani, W. A. Mulac, and M. S. Matheson, J. Phys. Chem., 69, 53 (1965).

in the solid phase. The mechanism of the production of anisole has been considered on the basis of the observation of reaction intermediates.

Experimental Section

Phenyl acetate ($C_6H_5OCOCH_3$) was obtained by the reaction of phenol and acetic anhydride and was found to be 99.9% pure by gas chromatographic analysis. Nitrous oxide was of high purity and was used without further purification. The 2-methyltetrahydrofuran (MTHF) was purified by distillation on a vacuum line and dried over a sodium mirror. *sec*-Butyl chloride was purified by distillation on a vacuum line.

When a sample of phenyl acetate is plunged into liquid nitrogen, it forms a clear glass. A sample is immersed in the liquid nitrogen and warmed up to some temperature higher than 77° K. When this procedure (a kind of annealing) is repeated several times, it forms a polycrystal.

Samples were irradiated with γ rays from ⁶⁰Co at a dose rate of 2.44 \times 10¹⁹ eV/g hr. Photobleaching was carried out at 77°K immersing the samples in the liquid nitrogen, and there is no possibility of a thermal bleaching. The photobleaching was carried out by a tungsten light without a filter or with a filter (VR-68).

Optical absorption spectra of irradiated glassy samples could be measured at 77° K. Optical and esr measurements were made on a Hitachi UV-VS spectrophotometer or a JES-3BX ESR spectrometer, respectively. Final products were analyzed by a Hitachi K 53 gas chromatograph with a flame ionization detector (silicone DC 710 column, 2 m long, at 155°).



Figure 1. Esr spectrum of γ -irradiated phenyl acetate glasses at 77°K. Irradiation dose, $2.4 \times 10^{19} \text{ eV/g}$. The arrow indicates signal of Mn²⁺. A, before photobleaching; B, after photobleaching with infrared light at $\lambda > 680 \text{ m}\mu$, 2 min.



Figure 2. Esr spectrum of γ -irradiated phenyl acetate glasses at 77°K. Irradiation dose, 2.4×10^{19} eV/g. The arrow indicates signal of Mn²⁺. A, before photobleaching; B, after photobleaching with infrared light at $\lambda > 680$ m μ (1 min); C_i after photobleaching sample B with visible light without filter, 2 min.

Results and Discussion

Esr and Optical Absorption Spectra. Phenyl acetate forms a glassy solid at 77°K by rapid cooling, and when irradiated with γ rays, it develops a yellowishbrown color, giving the esr spectrum A shown in Figure 1. Illumination of γ -irradiated phenyl acetate with infrared light causes spectrum A to change into spectrum B. The latter is found to be identical with that of acetyl radicals, COCH₃, produced from γ irradiation of acyl chloride.¹ Photobleaching by visible light without a filter produces the methyl radical due to the decomposition of acetyl radical (Figure 2). Methyl radicals trapped in the phenyl acetate glass are relatively stable and live longer than 5 hr at 77°K. Upon γ irradiation of phenyl acetate in the polycrystalline state, the esr spectrum and its behavior on photobleaching is the same as in the glassy state.

When MTHF solutions containing phenyl acetate at low concentrations are irradiated at 77°K with γ rays, they also develop a brown color. This color cannot be bleached with visible light. The esr spectrum of trapped electrons disappears by the addition of phenyl acetate to MTHF and a new spectrum is obtained. The spectrum is shown in Figure 3, which is obtained by subtracting the spectrum of solvent radicals. The doublet spectrum with a line separation of 22 G which appears immediately after γ irradiation

(1) S. Noda, K. Fueki, and Z. Kuri, J. Chem. Phys., 49, 3287 (1968).



Figure 3. Esr spectrum of γ -irradiated 2.4 mol % phenyl acetate in MTHF at 77°K. Irradiation dose, 1.2×10^{19} eV/g. The arrow indicates signal of Mn²⁺.



Figure 4. Est spectrum of γ -irradiated 2.5 mol % phenyl acetate in *sec*-BuCl at 77°K. Irradiation dose, 1.2 \times 10¹⁹ eV/g. The arrow indicates signal of Mn²⁺.

may be assigned to an ionic species on the basis of the general features of the spectrum of esters.²⁻⁴ Since the bond dissociation energy of $C_6H_5OCOCH_3$ is greater than its electron affinity, the dissociative electron capture $C_6H_5OCOCH_3 + e^- \rightarrow C_6H_5 + CH_3COO^$ cannot be expected in this case. The formation of molecular anion $C_6H_5OCOCH_3^-$ is suggested. In the case of γ -irradiated sec-butyl chloride (sec-Bu-Cl) glasses containing phenyl acetate, a reddish-brown color was observed, and the esr spectrum is shown in Figure 4, which is obtained by subtracting the spectrum of solvent radicals. The doublet with a line separation of 14 G may be attributable to the phenyl acetate cation, C₆H₅OCOCH₃+. In both cases, the ionic species cannot be so readily photobleached as in the case of pure phenyl acetate.

The esr spectrum obtained by γ irradiation of phenyl acetate appears to involve the phenyl acetate cation, anion, and some radicals. As mentioned already, the photobleaching of γ -irradiated phenyl acetate proceeds efficiently to produce the acetyl radical. This fact suggests the neutralization reaction between the phenyl acetate cation and anion



However, the phenoxy radical postulated in reaction 3 was not clearly detected. An acetyl radical formed in reaction 3 decomposses to the methyl radical by illumination of visible light (reaction 4). A similar phenomenon was observed in the case of acetyl radicals produced by dissociative electron attachment to acyl chloride.¹ An alternative mechanism for the production of acetyl radicals is the decomposition of excited ions produced by photoexcitation, for example







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(4) M. Nakajima and S. Satø, presented at the 11th Symposium on Radiation Chemistry, Sept 1968, Tokyo, Japan.
These mechanisms, however, may be excluded by the fact that the photobleaching of MTHF solutions containing phenyl acetate are not so effective as in the case of pure phenyl acetate, and the acetyl radical has not been found in these solutions.

The optical absorption spectrum of γ -irradiated phenyl acetate glass at 77°K has broad bands with absorption maxima near 400 and 600 m μ (Figure 5A). These bands responsible for a brown color are easily bleached with visible light. The photobleached species have peaks at 430, 630, and 720 m μ (Figure 5C). When γ -irradiated sec-BuCl glass containing



Figure 5. A, absorption spectrum of γ -irradiated phenyl acetate glass at 77°K. Irradiation dose, 7.3×10^{19} eV/g. B, the same sample as A after 10 min illumination with visible light. C, absorption spectrum of the bleached species.

phenyl acetate at 77°K is illuminated with visible light, the reddish-brown color can be less readily photobleached than in the case of γ -irradiated pure phenyl acetate and the photobleached spectrum shows peaks near 630 and 720 m μ . Therefore the photobleached peaks at 630 and 720 m μ in the γ -irradiated pure phenyl acetate may be assigned tentatively to the phenyl acetate cation. An assignment of another peak at 430 m μ is obscure at present.

Product Analysis. The yields of liquid products in the radiolysis of phenyl acetate under various experimental conditions are given in Table I. The main products in the radiolysis at 77°K are anisole (C₆H₅-OCH₃), phenol, and o-hydroxyacetophenone. p-Hydroxyacetophenone could not be observed because of its long retention time in the gas chromatography. Anisole is not found in the aluminum chloride catalyzed or photochemical Fries reaction of phenyl acetate and it is interesting to discuss the mechanism of its formation. The G value of anisole in the polycrystalline state is twice that in the glassy state, while the G value of phenol in the polycrystalline state is half that in the glassy state. In the radiolysis in the liquid phase the G value of phenol amounts to 1.5, while the yields of anisole are negligibly small. The facts that the yields of products are different in the glassy and polycrystalline state have not been reported previously except for a few examples, such as in the radiolysis of alkyl halides⁵ and isobutane.⁶ In the radiolysis of isobutane at 77°K, *i*-C₄H₉ radical is formed in the polycrystalline state, while *t*-C₄H₉ radical is formed in the glassy state.

 Table I:
 Radiolysis of Phenyl Acetate^a

		Desducts	7
Experimental conditions	Anisole	Products, o Phenol	o-Hy- droxy- aceto- phenone
77°K cryst.	0.27	0.19	0.27
77°K cryst.	0.27	0.20	0.23
77°K cryst.	0.28	0.14	0.27
77°K glass	0.14	0.38	0.21
77°K glass	0.14	0.34	0.19
77°K glass	0.12	0.27	0.20
77°K glass) photobleached	0.16	0.37	0.23
77°K glass with visible light	0.14	0.43	0.20
(10 min.)			
298°K liquid	0.02	1.54	0.22
298°K liquid	0.02	1.43	0.22
298°K liquid Additive,	0.02	1.63	0.24
298°K liquid) N2O (3 mole %)	0.02	1.50	0.23
^a Total dose, $5.9 \times 10^{22} \mathrm{eV/g}$.			

The higher yields of anisole ($C_6H_5OCH_3$) in the radiolysis of phenyl acetate in the polycrystalline state than those in the glass cannot be explained by a cage effect, because if anisole is formed *via* reactions 8 and 9 and the methyl radical can escape from the solvent cage in the glass without recombining with the phenoxy radical, the methyl radical should be observed by esr technique.

$$\begin{array}{cccc} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$$

As shown in Figure 1, however, the methyl radical is not observed after γ irradiation of phenyl acetate.

Though the photobleaching of a γ -irradiated sample with tungsten light produces methyl radicals (Figure 2), the yields of anisole and phenol are not affected by the photobleaching (Table I). Therefore, anisole would be formed by molecular detachment (reactions 10 and 11) from the excited phenyl acetate molecule

rather than the recombination of the methyl and phenoxy radicals.

$$\bigcup^{\text{OCOCH}_3} \longrightarrow \bigcup^{\text{OCOCH}_3^*} (10)$$

$$\bigcup_{i=1}^{OCOCH_3^*} \rightarrow \bigcup_{i=1}^{OCH_3} + CO$$
(11)

Then, phenol may be formed by a process independent of the formation of anisole.

Acknowledgment. The authors wish to thank Dr. A. Kawasaki of Nagoya University for the synthesis of phenyl acetate.

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Photochemistry of Complex Ions. IX. trans-Co(en)₂(NCS)Cl⁺

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Irradiation of the first ligand field band of trans- $Co(en)_2(NCS)Cl^+$ in aqueous solution at $22-24^\circ$ leads to photoaquation in very low quantum yield, with a ratio of thiocyanate to chloride aquation of 1.6. Photoredox decomposition is negligible at this wavelength. Irradiation of the first CT band leads to reaction of total quantum yield 0.013, of which 66% comprises Co^{2+} production and the remainder, aquation. The ratio of the two aquation modes is now 6.3. The thermal reaction chemistry of the complex is entirely one of chloride aquation. The results conform to qualitative photolysis rules for Co(III) ammines, and those for irradiation of the first CT band are discussed further in terms of a previously proposed homolytic bond fission mechanism. A general conclusion is that the ligand field and CT excited states are exhibiting distinctive chemistries.

Introduction

The photochemistry of Co(III) complex ammines and acidoammines conforms in a general way to the following rules.¹

Rule 1. Irradiation of the first charge-transfer (CT, or actually CTTM) band leads to redox decomposition, while that of a ligand field (L) band leads to substitution type reactions.

Rule 2. Quantum yields for redox decomposition, $\phi_{\mathbf{R}}$, are high relative to those for substitution, usually aquation, $\phi_{\mathbf{A}}$, on irradiation of the first CT and an L band, respectively.

Rule 3. Irradiation of the first CT band may lead to a ϕ_A comparable to ϕ_R , in the case of acidoammine complexes, depending on the ease of oxidation of the acido group or, alternatively, on the degree to which the presence of the acido group has produced a bathochromic shift of the CT band maximum.

As examples of rules 1 and 2, $\phi_{\rm R}$ is 0.6 to 0.9 for Co-(NH₃)₆³⁺ at 254 m μ^2 (the first CT band being at 200 m $\mu^{3.4}$), while ϕ for any reaction is less than 10⁻³ at 370 m μ and 550 m μ ,⁵ wavelengths corresponding to the first and second ligand field bands (L₁ and L₂). In the case of Co(NH₃)₅Br²⁺, $\phi_{\rm R}$ is 0.3 at 370 m μ ,⁶ this wavelength corresponding to a high extinction coefficient shoulder on the first CT band,^{3,6} while irradiation at 550 m μ , or at around the L₁ band maximum, gives only aquation with the low ϕ_A of 0.0014.⁵ Rule 3 is illustrated by this same system in that at 370 m μ , ϕ_A rises to 0.07.⁵ It may be that the aquation is sometimes of an ammonia rather than of the acido group. This is suggested by the special shifts accompanying irradiation of the CT band of Co(NH₃)₅Cl²⁺,⁷ and in a report on the 254-m μ irradiation of Co(NH₃)₅N₃²⁺.⁸

Rule 1 implies that the CT and L excited-state systems are sufficiently isolated from each other that

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(8) J. E. Endicott and M. Z. Hoffman, J. Amer. Chem. Soc., 90, 4740 (1968).

the former, in particular, is able to exhibit its own distinctive photochemistry. Internal conversions within each system are not ruled out. The photochemistry following irradiation of an L_2 band could be due to reaction from an L_1 or a d-d triplet state. The results of photosensitization studies have suggested that redox decomposition of $Co(NH_3)_{6}^{3+}$ may occur from a CT triplet state.⁹ The point is that the CT and d-d excited-state systems do not strongly intercommunicate.

Rule 2 seems not to have been provided with a detailed rationale. In particular, it is not really clear why ligand field excited states should be relatively so inert toward aquation, as compared, for example, with those of Cr(III) complexes. The problem and some *ad hoc* explanations have been discussed.¹

There does exist a mechanism of fairly long standing which accounts for rule 3, however. It was proposed that irradiation of the first CT band led to homolytic bond fission of a Co-X bond, in the case of an acidoammine complex, where X denotes the acido group in question. The proposed primary step, in the case of an acidopentaammine, was

$$Co(NH_3)_5 X^{2+} \xrightarrow{h\nu} [Co(NH_3)_5 X^{2+}]^* \longrightarrow C_C(NH_3)_5^{2+} \dots X \quad (1)$$

That fraction of excited-state species $[Co(NH_3)_bX^{2+}]^*$ escaping radiationless deactivation was thus considered to undergo Co-X bond fission to give ground-state $Co(NH_3)_5^{2+}$ and X. Cage reactions then followed, in which X might recoordinate, or might recover an electron from the complex, to escape as X⁻ ion. The resulting partially coordinated Co(III) would then attach an adjacent solvent molecule so that the net reaction would be one of aquation.

$$Co(NH_3)_{5}^{2+}...X \longrightarrow Co(NH_3)_{5}(H_2O)^{3+} + X^{-} (2)$$

Alternatively, if X escaped the above process, net redox decomposition would ensue.

$$Co(NH_3)_{5^2}^+ \dots X \longrightarrow Co(II) + 5NH_3 + X$$
 (3)

Reaction 3 does not, of course, necessarily indicate the nature of the final oxidation products.

Some of the evidence for the homolytic bond fissioncage mechanism has been summarized elsewhere.¹ One inference, of relevance to the present study, was that reaction 3 should be favored relative to (2) and the yield for (1) increased, the greater the ease of oxidation of the X group, *i.e.*, with decreasing energy for the process

$$X^{-}(aq) = X(aq) + e^{-}$$
 (4)

In conjunction with the above mechanism for CT irradiations, it was supposed that irradiation of an L band led to heterolytic bond fission (with or without solvent cooperation), so that the primary step would now be

$$\operatorname{Co}(\mathrm{NH}_3)_{\delta} \mathrm{X}^{2+} + \mathrm{H}_2 \mathrm{O} \xrightarrow{h_{\nu}} \operatorname{Co}(\mathrm{NH}_3)_{\delta}(\mathrm{H}_2 \mathrm{O})^{3+} + \mathrm{X}^{-} (5)$$

Thus aquation which occurred on irradiation of an L band was considered to derive from an entirely different mechanism than did that associated with irradiation of a CT band.

Detailed mechanistic hypotheses are notoriously controversial and difficult to establish definitively; the above is not likely to be an exception. It appeared to us, however, that it would be of significance to test the last mentioned prediction, that is, to determine whether there was any spectrospecificity to photoaquation of a Co(III) ammine. This can be done by invoking a complex of the type CoA_4XY^+ , for which two relatively similar aquation reactions are possible. Should the ratio of photoaquation of the X group to that of the Y group be spectrospecific, then a wavelength dependent mechanism would be indicated. A similar approach to Cr(III) photochemistry was successful in this respect;¹⁰ it was concluded that at least two different excited states could be precursor to aquation in the case of $Cr(NH_3)_5(NCS)^{2+}$.

The complex chosen was trans-Co(en)₂(NCS)Cl⁺. The thermal reaction chemistry of aqueous ion has been studied in detail;^{11,12} only chloride aquation occurs (the observed product being a 50–50 mixture of the isomers of Co(en)₂(H₂O)(NCS)²⁺). The spectra of both the *cis* and *trans* chloride aquation products were known, as well as those of possible thiocyanate photoaquation.^{11–13} In addition, analysis for any photoreleased thiocyanate ion would be easy.¹⁴

A second prediction could also be tested. The first CT band for $Co(NH_3)_5Cl^{2+}$ is at 228 m μ ,^{3,15} while that for $Co(NH_3)_5(NCS)^{2+}$ is at the considerably longer wavelength of 330 m μ .⁴ This shift in the location of the first CT band suggests that the energy for process (4) is lower for X = NCS⁻ than for X = Cl⁻, and, in terms of the above mechanism, is consistent with the much larger ϕ_R (0.045)⁵ for the former as compared to the latter case ($\phi_R = 0.003$),¹⁶ for irradiations around 370 m μ . The implicit assumptions are that the excited state reached through the first CT band is rather localized around the Co-X bond and that the weaker that bond is toward homolytic fission, the less likely is the thermal reverse of (1) to occur.¹⁶

Since the first CT band for trans-Co(en)₂(NCS)Cl⁺ is at 330 m μ , application of the above reasoning sug-

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(14) E. E. Wegner and A. W. Adamson, J. Amer. Chem. Soc., 88,

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gests the Cl excited state to involve primarily the Co-NCS bond. The conclusion suggested by the mechanism is, therefore, that any photoredox decomposition should center around this bond with the consequence that the predicted accompanying aquation should be primarily that of the thiocyanate group.

Experimental Section

Materials. [trans-Co(en)₂(NCS)Cl]ClO₄ was prepared according to Werner's method.¹⁷ The compound was of good spectroscopic purity; its visible and ultraviolet absorption spectrum, shown in Figure 1, agreed well with that reported for an analyzed sample.¹²

Photolysis Procedures. The light source used was an AH-6 (General Electric) high-pressure mercury arc and the general arrangement was that previously described.¹⁰ The Pyrex water jacket and collimating lenses limited the ultraviolet radiation emitted to wavelengths over about 330 m μ , and with the interposition of a Schott UG-11 glass filter, the irradiating was confined to 330-390 m μ , or to the region of the first CT band. Alternatively, the filter combination of Corning glass CS-3-69 plus CS-4-96 transmitted light between 515 and 615 m μ , or in the region of the L₁ band of the complex.

The photolyses were carried out in a 10-cm cylindrical spectrophotometer cell, using concentrations of complex such as to have essentially complete light absorption (about 0.005 M for irradiations in the CT region and 0.01 M for those in the L₁ region). The solutions were 0.1 M in perchloric acid, and their temperature 22–24°. An aliquot of the solution to be analyzed was kept in the dark, at the same temperature, so that any thermal aquation could be noted and allowed for. However, the rate constant for the thermal aquation (of chloride) is only $5 \times 10^{-8} \sec^{-1}$ at 25° ,¹¹ and since irradiation times did not exceed 2 hr, correction for such aquation was small.

The total amount of photolysis was limited to about 10% to avoid possible secondary photochemical reactions. Absorbed light intensities were determined by Reineckate actinometry.¹⁴

Analytical Procedures. The possible photolysis products, analysis for which was essential, were free chloride and thiocyanate ions, $Co(en)_2(H_2O)(NCS)^{2+}$, $Co(en)_2(H_2O)Cl^{2+}$, and Co^{2+} . It was not considered necessary to attempt to distinguish *cis* and *trans* isomers in the product aquo complexes, nor did it seem feasible to determine the nature of the final oxidation products accompanying Co^{2+} formation.

(1) Thiocyanate. Free thiocyanate ion was determined by adding an aliquot of the irradiated (or dark) solution to a fourfold volume of a reagent consisting of 0.1 *M* ferric nitrate in 0.5 *M* perchloric acid, and measuring the absorbance due to the resulting ferric thiocyanate complex (ϵ 4.3 × 10³ M^{-1} cm⁻¹ at 450 mµ).¹⁴



Figure 1. Spectrum of aqueous trans-Co(en)₂(NCS)Cl⁺.

(2) Cobalt (II). Cobaltous ion was found by forming the blue complex ion, $Co(NCS)_4^{2-}$ in a water-acetone solution and measuring the absorbance (ϵ 1.7 × 10³ at 625 mµ), according to a literature procedure.¹⁸

(3) Chloride. The cetermination of free chloride ion was based on the amount of thiocyanate ion produced by the reaction

$$Hg(SCN)_2 + 2Cl^- = HgCl_2 + 2NCS^-$$
(6)

as described by Zall and coworkers.¹⁹ The following preliminary procedure was necessary, however. A portion of the solution to be analyzed was adsorbed on a Dowex 50W-X4 ion-exchange column. The free chloride and thiocyanate ions present were eluted with water, and the thiocyanante present in the eluent decomposed by boiling the solution with hydrogen peroxide (prolonged to complete the decomposition of this last reagent). Reaction 6 is not quite complete, and allowance for this was made by means

(17) A. Werner, Ann., 1, 386 (1912).

(18) R. E. Kitson, Anal. Chen., 22, 664 (1950).

⁽¹⁶⁾ The characteristic absorption of thiocyanate complexes around this wavelength has alternatively been attributed to an internal CT absorption of the ligand (C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y., 1962, p 196; L. Di Spiro, L. Cleari, and G. De Michelis, Coordination Chem. Revi., 1, 7 (1966)) and to a ligand to metal CT transition (H. Schmidtke, "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier Publishing Co., New York, N. Y., 1968, p 509). The former interpretation makes more complex the molecular orbital description of the excited state first reached; it is still consistent with our premise that the transition is localized around the Co-NCS moiety. Also, the above rules and predictions are not affected provided the first chemical act is one of homolytic bond fission.

⁽¹⁹⁾ D. M. Zall, D. Fischer, and M. Q. Garner, *ibid.*, 28, 1665 (1956).

of a set of standardizations using known chloride containing solutions.

(4) Aquo Products. The combined amount of Co-(en)₂(H₂O)(NCS)²⁺ and Co(en)₂(H₂O)Cl²⁺ present was first found as follows. A portion of the photolyzed solution was adsorbed on the ion-exchange column, the free thiocyanate and chloride eluted with water, and the initial complex present, by means of 0.3 Mperchloric acid. The two aquo species were then jointly eluted with 3 M perchloric acid. An aliquot of this eluent was then decomposed by boiling with hydrogen peroxide, and the produced Co²⁺ determined as described above.

(5) $Co(en)_2(H_2O)(NCS)^{2+}$. Ccbalt(III) ammines are subject to rapid base hydrolysis of any acido group present, and this reaction permitted the determination of any $Co(en)_2(H_2O)(NCS)^{2+}$ present in the above eluent solution. An aliquot portion of it was made alkaline by the addition of solid potassium hydroxide, and the resulting mixture was then boiled for 3 hr, and finally reacidified with perchloric acid. The precipitated potassium perchlorate was filtered off, and the free thiocyanate present determined as described above.

(6) $Co(en)_2(H_2O)Cl^{2+}$. The above determination of $Co(en)_2(H_2O)(NCS)^{2+}$ plus that of the combined aquo products then permitted the calculation of the amount of $Co(en)_2(H_2O)Cl^{2+}$ also present in the original solution.

An independent determination was occasionally made as follows. The neutralized and filtered solution described in (5) also contained free chloride ion in amount corresponding to that of any $Co(en)_2(H_2O)$ - Cl^{2+} originally present. An aliquot portion would then be analyzed for chloride by procedure (3). However, this use of successive aliquot portions diminished the amount of sample available, and hence the accuracy of the analysis.

Results and Discussion

General Photolysis Results. The direct analytical results are given in Table I. The total quantum yield,

Table I: Photolysis of trans	-Co(en) ₂ (NCS)Cl ⁺			
	Quantum yield at 22–24°, \times 10 ²			
	330-390 mµ	515-615 mµ		
Product determined	(CT band)	(Li band)		
Total yield, ϕ_{tot}	1.31	ca. 0.01		
NCS-	$1.01 (0.77)^{a}$			
Cl-	$0.94(0.73)^{a}$			
$Co(en)_{2}(H_{2}O)(NCS)^{2+}$	0.06 (0.046)*			
$Co(en)_2(H_2O)Cl^{2+}$	$0.38(0.28)^{a}$			
Co ²⁺	$0.87 (0.66)^{a}$	<0.001		
r ^b	6.3	1.6		

^a Yields expressed as fractions, F, of the total yield. ^b The ratio, r, of yield of $Co(en)_2(H_2O)Cl^{2+}$ to that of $Co(en)_2(H_2O)-(NCS)^{2+}$.

 ϕ_{tot} , is the sum of the yields for Co²⁺ and of those for the two aquo products and is thus the yield for disappearance of the parent complex. In the case of irradiation in the region of the L₁ band, this total yield could only be estimated as about 10⁻⁴, but the sensitivity of the Co²⁺ analysis allowed an upper limit of 10⁻⁵ to be placed on the yield for redox decomposition. It was possible, moreover, to determine to 10% accuracy the ratio, r, of the yield of Co(en)₂(H₂O)-Cl²⁺ to that for Co(en)₂(H₂O)(NCS)²⁺.

The results conform generally to the rules given in the Introduction. Thus redox decomposition was essentially confined to excitation in the region of the CT band, and the quantum yield for any reaction was very low in that of the L_1 band. Rule 3 was also obeyed in that aquation contributed 33% of the total photolysis on irradiation of the first CT band.

The general predictions based on the homolytic bond fission mechanism are also confirmed. The ratio, r, of aquation modes is strongly wavelength dependent, rising from 1.6 for the region of the L_1 band to 6.3 for that of the first CT band. This last value of r, moreover, corresponds to the expected predominance of thiocyanate over chloride aquation. The results, then, add support to the premises outlined in the Introduction, namely that the photochemistries following irradiation of the L and first CT bands are characteristic of these two types of excited states. We do not, of course, rule out intersystem crossings between CT and L states; we do conclude that such processes compete with, rather than lead to, the photochemistry that follows irradiation of the CT band.

All of the above effects could simply be attributed to the reaction characteristics of hot ground-state molecules variously energized according to the wavelength of the irradiation. We regard this type of explanation as unlikely to be correct, however. It has so far seemed true of ammine type complexes that quantum yields and ratios of reaction modes do not vary much within the wavelength region of a given absorption band (see reference 1 on Co(III) and Cr(III) complexes), but remain characteristic of that band regardless of the particular wavelength chosen for the irradiation. The implication is that, following excitation, thermal equilibration, and possible internal conversions, an excited state is reached which then exhibits its particular chemistry. It thus appears to us that in the case of $trans-Co(en)_2(NCS)Cl^+$, redox decomposition and aquation of high r value describe the chemistry of a CT excited state reached by irradiation of the first CT band, and that the chemistry of the low-lying d-d excited states is one of aquation only, with a low r value.

Homolytic Bond Fission Mechanism. As noted above, the results conform to the predictions of this mech-

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trans-Co(en)₂(NCS)Cl⁺

anism. Assuming this mechanism, then, it is possible to analyze the data in somewhat more detail.

The scheme, as applied to the present system, is the following.

 $Co(NH_3)_5(NCS)^{2+}$ was that the amount of oxidized thiocyanate was only about a fourth of the Co(II) produced.^{5,20} Application of this figure of 25% oxidation to the present system suggests that path *be* should

$$\overset{0.00}{\longrightarrow} \operatorname{Co}^{2+} + \operatorname{NCS}^{-} + \operatorname{Cl}^{-} + \operatorname{oxid. prod.}$$
(7)

$$\overset{0.70}{\longrightarrow} \operatorname{Co}^{2+} + \operatorname{Cl}^{-} + \operatorname{NCS}^{-} + \operatorname{oxid. prod.}$$
(9)

$$\xrightarrow{f} Co(en)_2(H_2O)Cl^{2+}$$
(10)
(E)

Here, (B) and (C) denote the cage products of Co-Cl and Co-NCS homolytic bond fission, respectively, and a and b, c and d, and e and f, the bifurcation fractions for the first-stage and the two alternative second-stage processes.

The following material balance statements can be made, in terms of the fractions F of the total yield.

$$F_{\rm Co^{2+}} = ac + be = 0.66 \tag{11}$$

$$F_{\rm D} = ad = 0.046$$
 (12)

 $\stackrel{\smile}{\longrightarrow}$ Co(en)

$$F_{\rm E} = bf = 0.28$$
 (13)

The sum of (11) and (12), 0.66 + 0.05 = 0.71, should give $F_{\text{Cl}-}$. This is essentially the observed value of 0.73, and the agreement confirms the expectation that all released chloride terminates as Cl^- ion. Also, the sum of (11) and (13), 0.66 + 0.28 = 0.94, should give $F_{\text{NCS}-}$. The much lower observed value of 0.77 is presumably a consequence of partial oxidation of thiocyanate in step *e*. On this basis, path *be* must have a relative quantum yield of at least 0.14 (0.94– 0.77), corresponding to 100% oxidation of thiocyanation in step *e*. However, the experience in the case of be assigned essentially its maximum possible value of 0.66. The individual values for a, b, c, d, e, and fthen follow from the material balance equations and are given in parentheses in the reaction scheme above. These values seem reasonable both in showing a preponderance of Co-NCS over Co-Cl bond fission, and in giving the same ratio of paths e to f as was found for Co(NH₃)₅(NCS)^{2+,5}

The above assignment of path fractions is not unique, however. Other values follow if the degree of thiocyanate oxidation in step e is taken to be more than 25%. In summary, while the results of irradiation of the first CT band do not prove the homolytic bond fission mechanism to be correct, the mechanism does appear to provide a chemically reasonable basis for their interpretation.

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(20) Unpublished work in this laboratory.

Luminescence of 2,2',2"-Terpyridine

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2,2',2''-Terpyridine exhibits three luminescence emission bands in fluid aqueous and ethanol solutions: a violet band (maximum emission at 350 nm) in slightly acidic solution $({}^{1}\pi^{*} \rightarrow \pi)$, a blue band (maximum at approximately 440 nm) in neutral and alkaline solution $({}^{1}\pi \rightarrow n)$, and a green band (520 nm) in very acidic solution $({}^{1}\pi^{*} \rightarrow \pi)$. The presence of these bands, their fine structure, and intensities are governed by the concentration of 2,2',2''-terpyridine, pH, and solvent. These bands are correlated with the acid forms of the solute species, and assignments of the electronic transitions involved are suggested on the basis of absorption, emission, and excitation spectra, solvent effects, and luminescence lifetimes. There is evidence for conformational change in the excited singlet state $({}^{1}\pi^{*})$ of H₂Ter²⁺ in fluid solutions.

Nakamoto has published the pH-dependent ultraviolet absorption spectra and assigned the 2,2',2''terpyridine species and their configurations.¹ There has been no similar study of the pH-dependent luminescence properties of 2,2',2''-terpyridine.

The spectral properties of Ter are complicated by (a) the acid-base properties of the molecule, which can accept one or two protons over the pH range 0 to 13, and (b) the possibilities of the three different *cis-trans* isomers. Nakamoto did discuss the possible *cis-trans* conformers of terpyridine and based upon spectrophotometric studies he assigned the conformation of the basic unprotonated terpyridine molecule (Ter) as *trans-trans*, the monocation (HTer⁺) as *cis-trans*, and the dication (H₂Ter⁺) as *cis-cis*.

The nitrogen atoms in terpyridine introduce nonbonding electron pairs (n-electrons) into the molecular structure. These n-electrons may be promoted by absorption of ultraviolet-visible radiation to an antibonding- π^* molecular orbital delocalized on the pyridine ring.² Kasha^{3,4} has presented several experimental criteria to justify assigning absorption bands as $\pi^* \leftarrow n$.

It had been thought previously that fluorescence from nitrogen heterocyclics was impossible and that only phosphorescence could be observed from these molecules. The (π^*, n) excited singlet state, arising from an overlap-forbidden (absorption) transition, had a long lifetime, thus increasing the possibility of deactivation processes which result in nonradiative dissipation of the excitation energy in fluid media. Moreover, the energy difference between singlet and triplet (π^*, n) states is small, which would enhance further the intersystem crossing rate.⁵ However, *fluorescence* from a $(1\pi^*, n)$ excited state has been reported for some nitrogen heterocyclics: sym-tetrazine (1,2,4,5-tetrazine) and its dimethyl derivative,^{6,7} from a series of diazines (pyrazine, pyrimidine, and pyridazine),⁸ as well as from the N-heterocycle 9,10-diazaphenanthrene.⁹ In some of these molecules the absence of a (π^*, π) triplet between the (π^*, n) singlet and the (π^*, n) triplet greatly reduces the probability of intersystem crossing and therefore fluorescence can compete favorably with the radiationless processes because there is very little direct spin-orbit coupling between (π^*, n) singlet and (π^*, n) triplet states.⁹ More recently, Cohen and Goodman have shown that rapid internal conversion between allowed and forbidden excited (π^*, n) singlet states is responsible for the low fluorescence quantum yields of the diazines; for two of these (pyrazine and pyrimidine) the rate of internal conversion between the (π^*, n) states exceeds that for intersystem crossing despite the presence of a triplet (π^*, π) state between the excited singlet and triplet $(\pi^*, n).^8$

2,2',2''-Terpyridine forms stable chelates with many metal ions and has been used in several spectrophotometric and fluorometric analytical methods. Recently the intense violet fluorescence of the monocation of 2,-2',2''-terpyridine (HTer⁺) was employed in a sensitive analytical method for the determination of iron.¹⁰

Experimental Section

Chemicals. 2,2',2''-Terpyridine was purchased from two suppliers to check and compare properties: G. F. Smith Chemical Company and Pierce Chemical Company. The Smith product was analyzed for carbon, hydrogen, and nitrogen. *Anal.* Calcd: C, 77.24;

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H, 4.75; N, 18.01. Found: C, 77.49; H, 4.74; N, 17.87. Some yellow impurity was removed from each lot by a series of recrystallizations from petroleum ether (bp $30-60^{\circ}$). One recrystallization usually lightens the yellow color noticeably; two or more were required to obtain the (pure) white powder from most batches; melting points $90-90.5^{\circ}$ and $92-92.5^{\circ}$; lit. 88-89°. *m*-Terphenyl was purchased from Eastman Chemicals and used without further purification.

Absorption Spectra. All absorption spectra were recorded on either a Beckman Model DK-2A or on a Cary Model 14R recording spectrophotometer.

Quantitative absorption measurements were made exclusively on the Cary instrument; the low-intensity $\pi^* \leftarrow n$ absorptions were observed on this same instrument with the expanded-scale slide wire (0.0-0.1 absorbance full scale) installed.

Luminescence Spectra. A Farrand Model 104242 spectrofluorometer was used for all luminescence measurements. It was equipped with a General Electric UA-2 250-W mercury lamp, an RCA 1P28 photomultiplier tube, and an RCA WV-84C microammeter. (A xenon lamp was used to record the excitation spectra.) Emission spectra were recorded on a Hewlett-Packard Model 7035 B X-Y recorder. For all emission measurements both of the excitation monochromator slits gave effective band widths of 20 nm; the emission monochromator slits gave widths of 10 nm for the entrance beam and 5 nm for the exit beam. The sample container was a $10 \times 10 \times 48$ -mm quartz cell. All emission intensities were recorded relative to the fluorescence intensity (450 nm) of a 1.0 ppm quinine sulfate in 0.1 N sulfuric acid reference solution; 366 nm excitation was used except where noted.

Low-Temperature Luminescence Observations. Absolute ethyl alcohol was generally used as the rigid glass-forming solvent for observations at ca. 80°K. The ethanolic solutions were placed in test tubes and immersed in a liquid nitrogen bath until the rigid glass was formed. Excitation was then provided by ultraviolet hand lamps (Ultra-Violet Products, San Gabriel, Calif. Models UVL-21 and UVS-11); color and duration of emission were detected visually.

pH Measurements. pH was measured on a Corning Model 12 expanded scale pH meter. It was standardized against buffer solutions prepared from Coleman buffer tablets and also against Instrumentation Laboratory (Watertown, Mass.) phosphate and phthalate buffer solutions.

The p K_a values for H_2 Ter²⁺ have been determined as $pK_{a1} = 2.64 \pm 0.07$ and $pK_{a2} = 4.33 \pm 0.03$ by Martin and Lissfelt¹¹ and later redetermined by Nakamoto¹ as $pK_{a1} = 2.59$ and $pK_{a2} = 4.16$.

The absorption spectrum of terpyridine agreed completely with the spectra published by Nakamoto. The values $pK_{a1} = 2.6$ and $pK_{a2} = 4.2$ given by Nakamoto were used for this work. Based on these values



Figure 1. 2,2',2''-Terpyridine (ground state) concentration-pH profile. f = fraction of terpyridine present; calcd from H₂Ter²⁺ pK_{a1} = 2.6, pK_{a2} = 4.2.



Figure 2. Fluorescence spectra of 2,2',2''-terpyridine species. 1, $1.0 \times 10^{-5}M$ HTer⁺ in $10^{-4}M$ HCl at 313 nm; 2, $1.0 \times 10^{-3}M$ Ter in cyclohexane at 366 nm; 3, 1.0×10^{-3} H₂Ter²⁺ in 0.2 M HCl at 313 nm.

the fractions of (ground state) 2,2',2''-terpyridine species in solution as a function of pH were calculated and plotted in Figure 1.

Results and Discussion

An unequivocal assignment of the several luminescence bands to the emitting acid-base species of terpyridine can be made from the comparison and correlation of absorption and luminescence spectra and their variation with pH. However, assignment of emitting states and electronic transitions is somewhat less certain.

Acid-Base Species Assignments. Ultraviolet Emission Band. In slightly acidic aqueous solution (pH ca. 2 to 4), Ter emits very intense violet luminescence upon 313-nm excitation (Figure 2, Table I). The penetration of the long wavelength tail from the ultraviolet peak into the visible is responsible for its violet color. The sharp cut-off of luminescence intensity on the high-

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-
· 2.3
4.0
41.0

Table I: Comparison of the Relative Intensities of the Emission Bands of Terpyridine



Figure 3. Luminescence-pH profile for the three emission bands of 2,2',2''-terpyridine. 1, excitation, 365 nm; emission, 520 nm; 2, excitation, 313 nm; emission, 350 nm; 3, excitation, 365 nm; emission, 440 nm.

energy side of this emission band is due to self-absorption: 2,2',2''-terpyridine absorbs very strongly at wavelengths less than 350 nm.¹ Comparing the pH- I_L (350 nm) profile (Figure 3) and its correlation with the (ground state) concentration-pH profile (Figure 1) confirms that monoprotonated terpyridine, HTer⁺, is the species emitting the violet luminescence.¹⁰

The excitation spectrum for this violet emission recorded with a xenon lamp excitation source exhibits a peak at ca. 335 nm and a shoulder at ca. 280 nm. These correlate, as expected, with the absorption spectrum of monoprotonated terpyridine, HTer⁺, which has absorption peaks at approximately 330 and 280 nm.¹

Low-Energy (Green) Emission. A green emission (Figure 2) appears in very acidic aqueous solutions (pH below ca. 2) of 2,2',2''-terpyridine excited at 365 or 313 nm. The spectrum is a symmetrical Gaussianshaped curve; a single electronic transition is suggested. Variation of the intensity of this band at 520 nm is plotted vs. pH in Figure 3 and comparison with Figure 1 indicates that diprotonated terpyridine, H_2Ter^{2+} , is the emitting species.

Blue Band. In alkaline aqueous solution 2,2',2''-



Figure 4. Solvent effects on $\pi^* \leftarrow n$ absorption band of 2,2',2''-terpyridine.

terpyridine exhibits a blue luminescence. The pH-dependence of this band is also plotted in Figure 3. Comparing this pH- $I_{\rm L}$ profile and the Ter species concentration-pH profile (Figure 1) indicates that unprotonated terpyridine, Ter, is the emitting species. This same blue emission is observed also in organic solvents of low polarity *e.g.*, *n*-hexane, cyclohexane, and benzene (Figure 2).

Assignment of Excited States and Radiative Transitions. Ter is the species emitting the blue band. In this form the terpyridine has three unprotonated basic sites and six loosely held, nonbonding (n) electrons available for excitation by low energy radiation; thus, there is strong probability for $\pi^* \rightleftharpoons$ n transitions.

Low-Energy, Low-Intensity Absorption Band of Ter near 360 nm as $\pi^* \leftarrow n$. In organic solvents, a low-intensity absorption band appears (at *ca.* 360 nm) on long wavelength tail of the intense $\pi^* \leftarrow \pi$ terpyridine absorption bands (Figure 4). The singlet $\pi^* \leftarrow n$ transition is often the longest wavelength transition of the molecule containing nonbonding (n) electrons and is almost always lower in energy than singlet $\pi^* \leftarrow \pi$ transitions in N-heterocyclics. Kasha^{3,4} has presented a series of qualitative tests for assigning such low intensity absorptions as $\pi^* \leftarrow n$. The criteria were applied to this terpyridine absorption band and indicate that it results from a (spin-allowed) $\pi^* \leftarrow n$.

The molar absorptivity for the long wavelength band of terpyridine is small ($\epsilon < 100$) and is in the range for typical $\pi^* \leftarrow$ n absorption bands. Solvent effects on this long wavelength absorption band are illustrated in Figure 4 where the band is recorded in cyclohexane, nhexane, benzene, and chloroform solvents. It is most structured in cyclohexane solution; least structured, of lowest intensity, and most blue-shifted in chloroform. A blue shift is a characteristic of $\pi^* \leftarrow n$ transitions (as distinguished from $\pi^* \leftarrow \pi$ absorption bands which frequently red-shift) as solvents of increasing polarity are used. These solvent polarity shifts are presented more clearly in Figure 5, which shows the $\pi^* \leftarrow n$ band as a function of cyclohexane-ethanol solvent composition. Increasing solvent polarity shifts the (π^*, n) peaks to higher energy, broadens out the band, and also shifts the high intensity $\pi^* \leftarrow \pi$ absorption to lower energy; eventually it covers and obscures the $\pi^* \leftarrow$ n band. The same results have been found for other $\pi^* \leftarrow n$ bands—e.g., for pyridazine¹² for which the peak becomes less well pronounced and less intense during similar ethanol-hexane solvent composition changes.

The terpyridine absorption band under discussion appears as a three-peaked progression. Characteristic vibrational patterns are frequently observed for $\pi^* \leftarrow n$ absorption bands—e.g., in pyridine.^{4,13} Comparison to the absorption spectrum of *m*-terphenyl, the hydrocarbon analog of 2,2',2"-terpyridine, provides useful clues to the identity of the terpyridine band. This hydrocarbon is transparent at wavelengths greater than 350 nm in cyclohexane solvent indicating that nonbonding electrons must be present in order to observe the lowintensity 360-nm transition. The appearance of this terpyridine band is very similar to the long wavelength band in the absorption spectrum of pyridine, which has also been assigned as a $\pi^* \leftarrow$ n band.^{4,13} The pyridine $(\pi^* \leftarrow n)$ region is also a well defined low-intensity series of bands on the long wavelength tail of the $\pi^* \leftarrow \pi$ absorption spectrum. In summary, several of Kasha's criteria have been applied to the long wavelength absorption band of 2,2',2''-terpyridine, and an $\pi^* \leftarrow$ n absorption assignment is suggested by each.

Blue Luminescence of Ter as $\pi^* \rightarrow n$ Fluorescence. The blue emission of Ter appears at room temperature as a well-structured, triple-peaked emission spectrum in organic solvents. This three-peaked structure bears a good mirror image relation (Figure 6) to the low-intensity, lowest-energy triple-peaked ($\pi^* \leftarrow n$) absorption band of Ter in neutral and in alkaline solutions. If the $\pi^* \leftarrow n$ absorption assignment is accepted for this band, then the mirror image symmetry and overlap of emission and absorption spectra suggest that the emission



Figure 5. Effect of cyclohexane-ethanol solvent composition on the $\pi^* \leftarrow n$ absorption band of 2,2',2''-terpyridine. $1.0 \times 10^{-3} M$ terpyridine, 10.0-cm cells.

accompanies the reverse transition of the absorption when the molecule returns to the ground state—*i.e.*, ${}^{1}\pi^{*} \rightarrow n$.

The lifetime of this blue emission has been measured as 2 ± 1 nsec in cyclohexane and in absolute ethanol. Although this may seem extremely short for a (overlap) forbidden transition, the lifetime of the excited states of sym-tetrazine and of dimethyl-sym-tetrazine, which have both been assigned as $\pi^* \rightarrow n$ fluorescence,^{6.7} were measured (at 77°K) as 9 nsec and 4 nsec, respectively;⁶ these lifetimes are too short for phosphorescence.

The effects of solvent polarity on the $\pi^* \leftarrow$ n absorption band have been noted above. Similarly, on going from *n*-hexane to alcoholic media the emission spectrum becomes blurred—corresponding to the blurring in absorption—as expected for (π^*, n) transitions.⁶

The Ter emission spectrum was recorded in many solvents. (Each solvent was checked for any background emission.) Neither wavelength of maximum emission nor intensity of fluorescence changed significantly with solvent. The fine structure of this emissionb and decreases approximately in the following order with solvent: structure in cyclohexane > n-hexane > benzene > n-hexanol > absolute ethanol > methanol >chloroform > 1:1 ethanol-water. The absorption band exhibits the same solvent-structure relationships: structure is lost as the solvent becomes both more polar and more hydrogen-bonding. The decreased vibrational structure in the absorption spectrum indicates more solvation in the ground state, or in this case, also more hydrogen bonding to the lone electron pair on nitrogen.

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Figure 6. Absorption and emission spectra of Ter (concn ca. $10^{-3} m$).

Krishna and Goodman have considered solvent effects on $\pi^* \rightarrow$ n emission spectra.¹⁴ The absence of blue shifts on going to more polar solvents was discussed and it was pointed out that blurring in the emission spectra cannot be simply explained. In (π^*, n) excited states the lone unexcited nonboncing electron will not support a strong hydrogen bond and other factors must be involved.¹⁴

Several samples of 2,2',2''-terpyridine in absolute ethanol solution were frozen to a rigid glass at liquid nitrogen temperature. (In this medium terpyridine is in the unprotonated form, Ter.) Emission excited by radiation at 313 nm ($\pi^* \leftarrow \pi$ absorption of Ter) and at 366 nm ($\pi^* \leftarrow n$ absorption) were observed visually. Both excitation wavelengths produced a blue-white emission with no perceptible afterglow ($\pi^* \rightarrow n$ fluorescence of Ter). Moreover, both excitations also yielded a blue-green luminescence with an afterglow. This blue-green luminescence is probably phosphorescence; as discussed below, it accompanies the ${}^3(\pi^*, \pi) \rightarrow$ ground (T \rightarrow S) radiative transition.

The $T \rightarrow S$ phosphorescence of Ter in rigid medium is not surprising. Samples of the hydrocarbon *m*-terphenyl were frozen to a rigid glass in EPA (ethyl ether, isopentane, and ethyl alcohol in a ratio of 5:5:2) at liquid nitrogen temperature. Excitation at 313 nm $(\pi^* \leftarrow \pi)$ produced a blue-green luminescence with a long afterglow $(\pi^* \rightarrow \pi$ phosphorescence); excitation at 365 nm (*m*-terphenyl is transparent at this wavelength) produced no phosphorescence. These observations indicate that the Ter (π^*, π) state is at lowest energy in the triplet manifold; the blue-green Ter phosphorescence results, like that of *m*-terphenyl, from a ${}^3\pi^* \rightarrow \pi$ transition. It has been noted that *o*-phenanthroline also phosphorescence from the triplet (π^*, π) state.¹⁵

350-nm (Violet) Band of HTer⁺. The lifetime of the excited state involved in this transition was measured as 2 ± 1 nsec in fluid solution; this is consistent with a spin-allowed singlet \rightarrow singlet fluorescent transition. The excitation spectrum of the violet band indi-

cates that the emission is excited by $\pi^* \leftarrow \pi$ absorption transitions and the proximity to the absorption spectrum and the high intensity of the emission in fluid solution also lend credence to the assignment as $(\pi^* \rightarrow \pi)$ fluorescence of HTer+. There is no evidence for $\pi^* \leftarrow$ n transitions in the absorption spectrum of HTer⁺; in this species these $\pi^* \leftarrow$ n transitions have shifted to higher energy-the bands would be under the lowest energy $\pi^* \leftarrow \pi$ bands. Assignment of the violet luminescence as ${}^{1}\pi^{*} \rightarrow \pi$ is confirmed by comparison to the fluorescence spectrum of *m*-terphenyl. This hydrocarbon emits a violet fluorescence; only π -levels can be involved. Moreover, the ${}^{1}\pi^{*} \rightarrow \pi$ fluorescence of the hydrocarbon does peak at approximately the same wavelength as the 350-nm band of HTer+ and has a strikingly similar appearance.

520-nm (Green) Band of H_2Ter^{2+} . When acidified glycerol (Matheson Coleman & Bell, Spectroquality) solutions of 2,2',2''-terpyridine, *i.e.*, as H_2Ter^{2+} , were examined at room temperature (365 and 313-nm excitation) the same yellow-green luminescence (with no afterglow) was observed as in acidified aqueous solution of Ter. Upon cooling the glycerol solutions (with dry ice) to a more rigid matrix, the H_2Ter^{2+} displayed (only) a blue luminescence with no afterglow. When acidified ethanolic rigid glasses (77°K) of H_2Ter^{2+} were examined (313 and 365-nm excitation) both a blue emission with no afterglow and a blue-green emission that persisted after removal of the excitation source were observed.

There are several reasons to avoid assigning the green luminescence observed in fluid solutions of H_2Ter^{2+} as simple $\pi^* \rightarrow \pi$ fluorescence. One of these is the very large energy difference (10,200 cm⁻¹) between the lowest energy $\pi^* \leftarrow \pi$ absorption at *ca.* 340 nm (29,400 cm⁻¹) and the fluorescence peak at 520 nm (19,200 cm⁻¹) of H_2Ter^{2+} compared to the smaller but more typical energy difference (*ca.* 1,000 cm⁻¹) between the (π^* , π) absorption and fluorescence of HTer⁺. The blue fluorescence is observed in rigid media where rotation to other isomeric forms may be slow in relation to the lifetime of the singlet excited state. Nakamoto's spectra and arguments have already established that H_2Ter^{2+} probably exists in the *cis-cis* conformation in the ground state.¹

The yellow-green fluorescence in fluid solution of H_2Ter^{2+} might reasonably be attributed to a ${}^1\pi^* \rightarrow \pi$ fluorescence of another isomer of H_2Ter^{2+} , one that is formed during the lifetime of the singlet excited state in fluid solution (perhaps *cis-trans* or *trans-trans*). Thus, this form and its yellow-green fluorescence are not observed in rigid solutions.

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The blue-green luminescence with detectable afterglow in rigid media is then logically assigned as ${}^{3}\pi^{*} \rightarrow \pi$ $H_{2}\text{Ter}^{2+}$ phosphorescence. It is reasonable that the lowest triplet of $H_{2}\text{Ter}^{2+}$ would be a ${}^{3}(\pi^{*},\pi)$, just as it is for Ter; adding the protons would not likely change the ordering of the (π^{*}, n) and (π^{*}, π) triplets. Acknowledgments. We are grateful to the National Science Foundation for financial support (Grant GP-8585) and to Professor David M. Hercules and Dr. Fred E. Lytle of Massachusetts Institute of Technology, who kindly provided the lifetime measurements for the terpyridine species.

Temperature Dependence of the Phosphorescence Lifetime of

Benzene, Alkylbenzenes, and Alkyl Phenyl Ethers between 4.2 and 100°K

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The temperature dependence of the phosphorescence lifetime of benzene was measured in methylcyclohexaneisopentane (4:1 by volume), 3-methylpentane, EPA (ether, isopentane, ethanol 5:5:2 by volume), and ethanol between 4.2 and 100°K. Arrhenius plots indicate that in the region of the temperature dependence two or more paths of externally influenced nonradiative decay are contributing to the decay of the triplet state. The order of magnitude of the calculated activation energies indicates that either CH out-of-plane vibrations of the benzene molecule or vibrations of the solvent may play a role in the nonradiative externally influenced decay. The temperature dependence of the phosphorescence lifetime of isopropyl- and t-butylbenzene, and n-alkyl phenyl ethers $C_6H_5OC_nH_{2n+1}$, n = 2, 4, 6, has been measured in methylcyclohexane-isopentane (4:1 by volume) between 4.2 and 100°K. Generally, the phosphorescence lifetimes are temperature independent below about 60°K, depending on the solvent and solute, (intrinsic phosphorescence lifetimes) and temperature dependent at higher temperatures. The phosphorescence lifetimes of the alkylbenzenes are dependent upon chain length, branching, and number of alkyl substituents. The phosphorescence lifetimes of the *n*-alkyl phenyl ethers are independent of the chain length for alkyl = C_2H_5 , C_4H_9 , and C_6H_{13} . Our experiments suggest extending temperature dependence measurements to the polarization and quantum yield of emission. They suggest, furthermore, that upper limiting values of these properties may be obta ned only at temperatures well below 77°K, at least for the solvent-solute systems described here.

Introduction

In a previous paper, the temperature dependence of the phosphorescence lifetimes of benzene and alkylbenzenes in a methylcyclohexane-isopentane mixture (4:1) between 4.2 and 100°K were reported.^{2a} In this paper phosphorescence lifetime data for benzene in methylcyclohexane-isopentane (MCH-IP; 4:1 by volume), 3-methylpentane (3MP), EPA (ether, isopentane, ethanol, 5:5:2 by volume), and in ethanol will be presented. The temperature dependence of the phosphorescence lifetimes of isopropyl- and t-butylbenzene, and of the *n*-alkyl phenyl ethers $C_6H_5OC_nH_{2n+1}$, n =2, 4, 6, in MCH-IP are reported and compared with measurements of homologous compounds.2a,b Conclusions that can be drawn from the intrinsic phosphorescence lifetimes and from the temperature dependence of the phosphorescence lifetimes will be discussed in more detail.

Experimental Section

Benzene, isopropyl-, and t-butylbenzene were obtained from Matheson Coleman and Bell Co., phenetole and *n*-butyl phenyl ether from Eastman Kodak Co. *n*-Hexyl phenylether was synthesized from sodium phenolate and 1-bromo-*n*-hexane.³ All compounds were checked by gas chromatography and were found to contain less than 0.5% impurity.

Methylcyclohexane (MCH) and isopentane (IP) (Spectroquality reagen:) were obtained from Matheson Coleman and Bell Co., 3-methylpentane (3MP) (pure grade) from Phillips Fetroleum Co., EPA (mixture of

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Figure 1. Temperature dependence (°K) of the phosphorescence lifetime (sec) of benzene in ethanol $(\times; -\cdots, \cdot)$, EPA ($\Delta; ---$), 3MP ($\bigcirc; -\cdots$), and MCH-IP (+; ----).

ether, isopentane, and ethanol, 5:5:2 by volume) from American Instrument Co., and ethanol (absolute pure reagent quality, USP-NF) from U. S. Industrial Chemicals Co. MCH and IP were used as a mixture 4:1 by volume (MCH-IP). The solvents did not show absorption at wavelengths longer than 2500 Å and were used without further purification. Apparatus and procedures have been described previously.^{2a}

Temperature Dependence of the Phosphorescence Lifetime of Benzene in MCH-IP, 3MP, EPA, and Ethanol. The pattern of temperature dependence of the phosphorescence lifetime of benzene in MCH-IP, 3MP, EPA, and ethanol is very similar (Figure 1). At temperatures below about 35° K the phosphorescence lifetimes are constant and will be referred to as intrinsic (phosphorescence) lifetimes.^{2a} The temperature dependence at higher temperatures is solvent dependent. The center of this region may be characterized by the temperature $T_{1/2}^{\circ}$ K, where the lifetime has decreased to half its highest value. $T_{1/2}$ values, phosphorescence lifetimes measured at 77°K, and intrinsic phosphorescence lifetimes are listed in Table I.

The intrinsic lifetimes measured in the polar solvents, EPA and ethanol, are the same within the limits of error, while those measured in the nonpolar solvents, MCH-IP and 3MP, give a shorter lifetime. Rabalais, et al.,⁴ recently reported differences in the intrinsic

lifetimes similar to those found by Leubner (Table I) for benzene, toluene, toluene- α - d_3 , and toluene- d_8 in EPA and 3MP-IP (6:1). It is not possible to determine if this phenomenon occurs because the polar solvents form harder glasses or whether the triplet state is stabilized by the surrounding dipoles. In a recent publication, Morantz and Martin⁵ reported about solvent dependence of the phosphorescence lifetime at 77°K for phenanthene, chrysene, fluorene, carbazole, and dibenzothiophen. However, as no measurements of the temperature dependence were performed, effects described in the next paragraph cannot be excluded.

At higher temperatures the temperature dependence of the phosphorescence lifetimes is dependent on the solvent, which means that, *e.g.*, the lifetimes in EPA and ethanol, which are at lower temperatures essentially the same, differ significantly at 77°K. The determination of phosphorescence lifetimes at 77°K is further complicated by their very steep temperature dependence in this region.⁶

The measurement of the temperature dependence of the phosphorescence lifetimes should provide additional information on the possible mechanisms for the temperature-dependent, nonradiative decay of the triplet state. Thus the temperature dependence of the phosphorescence lifetimes of benzene in MCH-IP, 3MP, EPA, and ethanol have been studied in more detail.

If it is assumed that a decay process involves an activated state, then the temperature dependence of the rate constant k ($k = 1/\tau$) can be described by the Arrhenius equation (eq 1).



Figure 2. Arrhenius plots [eq 1; log $1/\tau$ vs. 1/T] for benzene in ethanol (×; -------------), EPA (Δ ; ----), 3MP (\bigcirc ; ------), and MCH-IP (+; ---------).

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n	Solvent	Av intrinsic lifetimes, sec	T range of intrinsic lifetimes	No. of measurements	Lifetime at 77°K, sec	$T^{1/2}$, ^a °K
		Benz	ene			
1	MCH-IP ^b	9.83 ± 0.15	4.6 - 32.0	15	4.29	77
2	3MP	9.92 ± 0.15	4.7-33.5	17	4.20	74
3	\mathbf{EPA}	10.91 ± 0.20	4.9-48.8	18	5.89	80
4	Ethanol	11.19 ± 0.20	6.9-32.3	10	6.86	85
		Alkylbenzenes	° Substituent			
1	$\mathrm{CH_3}^b$	8.30 ± 0.15	5.0-42.0	16	6.24	76
2	$C_2H_5^d$	7.79 ± 0.13	3.1-30.4	19	5.88	85
3	$n-C_3H_7^b$	7.46 ± 0.10	4.8-33.1	18	5.41	77
4	$iso-C_3H_7$	7.31 ± 0.15	4.8-47.8	16	0.55?	61?
5	$n-C_4H_9^b$	7.59 ± 0.10	4.8-39.5	19	2.14	73
6	t-C4H8	7.16 ± 0.14	4.5-42.3	18	0.87?	?
		<i>p</i> -Dialkylb	enzenes ^d			
1	p-(CH ₃) ₂	7.17 ± 0.10	3.0-39.8	18	6.99	88
2	p-CH ₃ , C ₂ H ₅	6.64 ± 0.20	3.2-30.1	19	6.21	92
3	$p_{-}(C_2H_5)_2$	5.97 ± 0.10	3.2-80.8	17	5.85	90
		Phenyl I	Ethers			
1	OCH ₃ ^d	3.43 ± 0.05	3.0-34.2	21	2.95	85
2	OC_2H_b	3.21 ± 0.08	5.2 - 41.0	19	2.01	83
3	OC4H9	3.21 ± 0.04	4.9-43.0	20	2.80	89
4	OC_6H_{13}	3.22 ± 0.04	21.3 - 50.5	13	2.95	89
5	OC_6H_5	0.80 ± 0.01	3.0-30.4	18	0.53	83

Table I: Intrinsic Phosphorescence Lifetimes, Lifetimes at 77°K, and $T_{1/2}$, Temperatures of Benzene, Alkyl- and *p*-Dialkylbenzenes, and Phenyl Ethers

^a See text, interpolated from plot $\tau vs. T$. ^b Reference 1. ^c Solvent for the following substances generally MCH-IP. ^d Reference 2. MCH-IP, methylcyclohexane-isopentane (4:1 by volume); 3MP, 3-methylpentane; EPA, ether-isopentane-ethanol (5:5:2) by volume).

$$\log k = -(\Delta E/2.30RT) + \text{constant}$$
(1)

Alternatively, it may be assumed that the internal radiative and nonradiative decay of the triplet state are temperature independent and represented by the intrinsic lifetime τ_0 . In this case equation 2 should apply.^{2a,7}

$$\log (1/\tau - 1/\tau_0) = -(\Delta E/2.30RT) + \text{constant}$$
 (2)

where τ represents the phosphorescence lifetime at the temperature T, °K, R is the gas constant, and ΔE is the energy of activation.

If eq 1 applies, the plot of log $(1/\tau)$ vs. 1/T should yield a straight line; if eq 2 applies, log $(1/\tau - 1/\tau_0)$ vs. 1/T. The results are shown in Figure 2 for eq 1, and in Figure 3 for eq 2.

Figure 2 indicates that the internal radiative and nonradiative decay processes are not the only processes at higher temperatures. At least one additional decay process has to play an important role.

Figure 3 shows that the decay cannot be described by two first-order decay processes. This indicates that two or more paths are contributing to the *external* nonradiative decay. In contrast to these results, Hatch, *et al.*,^{8a} reported recently a linear dependence of the phosphorescence lifetime of the temperature according to eq 2 for the systems C_6H_6 in $B_3N_3H_6$ and C_6H_{12} , and C_6D_6 in $B_3N_3H_6$ and C_6D_{12} . However, they treated $1/\tau_0$ (k_0 by their notation) as adjustable variable,^{8b} whereas here τ_0 s the experimentally obtained intrinsic lifetime. The former has not been considered in this work. Some of these differences may additionally be due to the different solvent systems used.

At temperatures over 80°K a straight line can be drawn in both cases. This indicates that either interactions between solvent and solute level out to a pseudo-first-order process or one process plays a predominant role. The energies of activation are shown in Table II. But for these energies there is an average error estimated at approximately $\pm 20\%$ because of difficulty in measuring the temperature of the sample, which results in a corresponding inaccuracy for the phosphorescence lifetime. Additional measurements would be necessary to define more accurately the temperature dependence of the phosphorescence lifetimes in the region indicated in Table II.

The nonradiative decay from an electronically excited state has been correlated either with molecular vibrations of the excited molecule⁹ or with vibrations of

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Table II:	Energies of Activation for the Temperature
Dependenc	e of the Phosphorescence Lifetime of Benzene

Solvent	$E_{1},^{a} \mathrm{cm}^{-1}$	E_{2}^{b} cm ⁻¹	Range of T, °K
MCH-IP	700	800	80-96
3MP	850	950	79-92
EPA	1900	2050	89-91
Ethanol	2200	2500	92-99
Ethanol	2200	2500	95-100

^a Equation 1 (see text). ^b Equation 2 (see text). ^c Parallel measurement. MCH-IP; methylcyclohexane-isopentane (4:1 by volume); 3MP, 3-methylpentane; EPA: ether-isopentane-ethanol (5:5:2 by volume).

the solvent.¹⁰ In MCH-IP and 3MP, nonpolar solvents with a low softening region, the activation energies are between 700 and 1000 cm⁻¹. These values are in the region of the methylene rocking vibrations of the solvent and the CH out-of-plane vibrations of benzene.¹¹ Also, this is the region of the skeletal stretch vibrations of benzene which are presumably of importance in the nonradiative decay of the triplet state.⁹

The activation energies (2000 cm^{-1}) in the polar solvents, EPA and ethanol, are significantly higher.

The infrared spectra of ether and ethanol both have a weak band in the 1900 to 2000-cm⁻¹ region, and 1950 and 1900 cm⁻¹, respectively.¹² Vibrations of benzene in the region between 1650 and 2000 cm⁻¹ are attributed to overtone and combination vibrations of fundamental (700-1000 cm⁻¹) CH out-of-plane vibrations.¹¹ CH out-of-plane vibrations have not been taken into account for the calculation of Franck-Condon factors and thus for the nonradiative decay of the triplet state of benzene.⁹ Their consideration might give a more consistent explanation for the observed energies of activation.

It should be noted that the magnitude of the activation energies obtained for MCH-IP and 3MP (700-1000 $\rm cm^{-1}$) is in good agreement with the values obtained by Hatch, et al.,8 in their solvent systems (480-1400 cm^{-1}). The values in EPA and ethanol are greater by a factor of about 2. However, also Hatch, et al., find a solvent dependence of the activation energies. The values for the constant (log of preexponential factor) in eq 1 (eq 2, respectively) are 6.37(6.95), 5.50 (5.63), 13.3 (14.4), and 14.3 (16.2) for 3MP, MCH-IP, EPA, and EtOH, respectively, for which the limits of error have been estimated to be $\pm 20\%$. Thus they range from the upper limit of Hatch, et al.,'s values (5.3) to several orders higher. The lower values are of the order of collision rates, whereas the higher values are of the order of molecular vibrations. Compared to the conclusions derived from the consideration of the activation energies (see above) this cannot be explained by only one mechanism of nonradiative decay. Different mechanisms have to be discussed for the polar and nonpolar solvents. To resolve these ambiguities, more experiments on a greater variety of systems will be necessary.

Several previous investigators have suggested that the viscosity of the solvent glass seems to be a major factor in the temperature dependence of phosphorescence lifetimes,¹³⁻¹⁸ but no coherent relationship between viscosity and the phosphorescence lifetimes has been offered. Ling and Willard¹⁹ have measured the

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viscosity of 3MP between 77.5 and 94.5° K and have obtained an energy of activation of 0.69 eV (15.9 kcal/ mol). This value is about a factor of 7 greater than that of the activation energy measured in about the same temperature range for the temperature dependence of the phosphorescence lifetime of benzene (Table II). However, it is known that the molecular relaxation processes are often not closely related to the molecular properties responsible for the macroscopic viscosity.¹⁹ Unfortunately, there do not seem to exist similar data for the other solvents used here.

It must be emphasized that the values obtained are crude and thus the indicated conclusions must necessarily be tentative. However, attempted correlations have been discussed, if only in the hope of calling attention to the problems.

Miscellaneous Investigations

In the course of this research program the temperature dependence of the phosphorescence lifetime of some branched and some *p*-dialkylbenzenes,^{2b} as well as of several alkyl phenyl ethers, has been determined. No detailed study as described for benzene has been done. The results are included in Table I for the use of others who may be interested and will be discussed briefly in the following sections.

Branched Alkylbenzenes and p-Dialkylbenzenes. Branching of the alkyl chain in the series toluene, ethyl-, isopropyl-, and t-butylbenzene, is shortening the phosphorescence lifetimes in a similar way as a homolog increase of the chain length (Table I).^{2a} n- and isopropylbenzene have, within the limits of error, the same lifetime (7.46 and 7.31 sec, respectively). However, the lifetime of t-butylbenzene (7.16 sec) is considerably shorter than that of n-butylbenzene (7.59 sec). This may be due to greater interaction of the bulky t-butyl group with the π electron system and the neighboring hydrogen atoms in comparison to the *n*-butyl group. Nonplanarity or solvent effects may contribute to this behavior also.

The intrinsic lifetimes of the p-dialkylbenzenes^{2b} are significantly shorter than those of the homolog monoalkylbenzenes (Table I). It is interesting to note that the phosphorescence lifetime of p-methylethylbenzene is about the average of the lifetimes of p-dimethyl- and p-diethylbenzene. However, in order to determine if this is an accident or not, other compounds (e.g., other p-dialkylbenzenes) should be studied.

Phenyl Ethers. The alkylbenzenes show a dependence of the intrinsic lifetimes on the nature of the chain. Therefore it seemed interesting to explore what influence would be found in the alkyl phenyl ethers. Thus the phosphorescence lifetimes of a series of *n*-alkyl phenyl ethers, $C_6H_5OC_nH_{2n+1}$, n = 2, 4, 6, were measured (Table I). Only for the change from methyl-^{2b} to ethyl phenyl ether was a significant difference between the intrinsic phosphorescence lifetimes found (Table I). Ethyl, *n*-butyl-, and *n*-hexyl phenyl ether have, within the limits of error, the same lifetimes.

The lifetimes of the phenyl ethers are shorter by a factor of 2 than those of the alkylbenzenes. In addition, they are not significantly dependent upon the alkyl chain. This indicates that the oxygen plays a major part in the nature of the triplet state and its decay. It can be visualized that the oxygen isolates the alkyl chain from the phenyl group and that resonance structures like I may play a significant role. In the framework of the Franck-Condon treatment of the nonradiative decay,⁶ a vibration involving the oxygen



could be an effective energy sink. On the other hand, it is possible that under the influence of the oxygen atom the phenyl is distorted from D_{6h} to D_{2h} symmetry. This may enhance the probability of the radiative and nonradiative $S \leftarrow T$ transitions. This might be determined by esr measurements of the molecules in the triplet state.²⁰

Another indication of the influence of the oxygen is the short lifetime of diphenyl ether² (0.80 sec) for which several mesomeric structures, e.g., IIa and IIb, involving the oxygen atom can be written. These structures involve an extended resonance system in comparison to the alkyl phenyl ethers. One might assume from the case of the alkyl phenyl ethers discussed above that the primary cause of the decay of the triplet state of the phenyl ethers are the vibrations of the phenoxy group. In the case of diphenyl ether two such groups are coupled and more active vibrations are available for the nonradiative decay than in the case of the alkyl phenyl ethers.

Discussion and Conclusion

The temperature dependence of the phosphorescence lifetimes of benzene and its derivatives in MCH-IP, 3MP, EPA, and ethanol follow a general pattern. It was not possible to describe for the systems discussed here the correlation over the whole range by a simple Arrhenius-type equation. Phosphorescence lifetimes approach constant values below about 60°K, depending upon solvent and solute. In a specific solvent these intrinsic (phosphorescence) lifetimes are considered molecular constants for the molecules examined. Since the intrinsic lifetimes are dependent upon the molecular structure and the environment, they are

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potentially useful data to study intra- and intermolecular interactions.

Arrhenius plots of the phosphcrescence lifetimes of benzene in the solvents used here yield straight lines only for temperatures over 80°K. This may be due to the major importance of one first-order decay process. Activation energies calculated from these plots are of the order of molecular vibrations of solvent and benzene molecules. A consistent explanation of these energies could involve CH out-of-plane vibrations of benzene. On the other hand, the order of magnitude of the preexponential factors suggests different decay mechanisms for the polar and nonpolar solvents. However, these conclusions are tentative and require the proof of further experimental work for confirmation.

It is commonly accepted that not the temperature, but changes in the viscosity seem to be the main factor contributing to the temperature dependence of the phosphorescence lifetime. It has been suggested that this may be due to changes in the relaxation time of the Brownian rotation and that coupling of molecular rotation with electronic motion may be of prime importance for the low viscosity rate constant.²¹ In addition, it has recently been shown²² that systematic errors in decay times may result from isotropic rotational relaxation of photo-selected emitters, even if the exciting light is unpolarized. Rotation times may be obtained, e.g., by measuring the isotropic²³ and anisotropic²⁴ rotational relaxation in rigid media using polarized photoselection. On the other hand, secondorder reactions, such as triplet-triplet annihilation and interactions of the excited molecules with solvent molecules, may increase in importance as the mobility of the molecules is increasing.

These effects become explicable for benzene and the substituted benzenes at 30 to 40°K and about 60°K, respectively, for the solvents discussed here, if one assumes that temperature dependence of the phosphorescence lifetime indicates Brownian rotation and translation. Proof for this hypothesis could be obtained by measuring the temperature dependence of the polarization of luminescence (flucrescence and phosphorescence). Additionally, such measurements can be expected to yield limiting values for the polarization of luminescence. Such data are needed to determine the relative polarization of electronic transitions and, thus, the electronic structure of molecules.²⁵

In addition to the phosphorescence lifetime, the quantum yield of emission also depends upon temperature or viscosity—however, not necessarily in the same way.¹⁴ Simultaneous measurements of both effects should give limiting values of natural lifetimes $(\tau_N)^{26,27}$ which are fundamental for comparison with theoretical calculations. It should be noted that under these assumptions neither the polarization nor the quantum yield of emission have their maximum values at 77°K for the systems discussed here. To obtain these data the measurements should be performed at 20 (liquid hydrogen) or 4.2°K (liquid helium).

In summarizing, one can say that phosphorescence lifetimes can be highly dependent upon temperature and solvent. Their influence cannot yet be predicted satisfactorily as only a few experiments have been done in this direction. Of major importance is the result that phosphorescence lifetimes measured at 77° K may be significantly shorter than the intrinsic lifetimes. It is suggested that the measurements be extended on the temperature dependence of phosphorescence lifetimes, as described here and previously, to an even greater variety of solvents and luminescing molecules. Further considerations suggest that it is highly desirable to perform parallel measurements on the temperature dependence of polarization and quantum yield of emission.

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Nuclear Magnetic Resonance Study of Liquid Crystalline Solutions of

Poly- γ -benzyl-L-glutamate in Dichloromethane and 1,2-Dichloroethane

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Nuclear magnetic resonance study on the liquid crystalline phase of solutions of poly- γ -benzyl-L-glutamate in dichloromethane and 1,2-dichloroethane and their deuterated analogs is reported. The proton second moment of the polypeptide in 1,2-dichloroethane- d_4 was calculated to be 0.11-0.14 G². When the sample was spun along an axis perpendicular to the magnetic field, all proton dipole-dipole interactions in 1,2-dichloroethane were reduced to $^{1}/_{4}$ of the original values. The ³⁶Cl spectra were analyzed according to the Redfield relaxation theory and the correlation time τ_{0} was found to be 6×10^{-12} to 8×10^{-12} sec.

In recent years it has been found that certain systems of biological interest, e.g., some lipids and peptides, form liquid crystalline phases under suitable conditions.¹ Poly- γ -benzyl-L-glutamate (PBLG) forms a liquid crystal in a number of solvents at room temperature.² The liquid crystalline solutions acquire additional ordering in a strong magnetic field such that the helical axes of the peptide are presumably parallel to the magnetic field.^{3,4} The magnetic ordering of the solution restricts the motion of the solvent molecules. The dipole-dipole and nuclear quadrupole interactions are then not averaged to zero. The nonzero interactions give rise to fine structures in the nuclear magnetic resonance (nmr) spectra of the solvent.³⁻⁶

Proton nmr spectra of CH_2Cl_2 in PBLG solutions have revealed that the dipole–dipole interaction is concentration dependent.^{3,6} Quadrupole splittings for ³⁵Cl and for deuterium in CH_2Cl_2 and CD_2Cl_2 solutions have been studied;⁵ however, the concentration dependence of the splittings and the line widths of the ³⁵Cl resonance have not been reported. Now we wish to present additional results of nmr study on PBLG solutions in CH_2Cl_2 , CD_2Cl_2 , CH_2ClCH_2Cl , and CD_2ClCD_2Cl . The line widths of the ³⁵Cl resonance are analyzed by considering the density matrix with quadrupole relaxation.

Experimental Section

The ²H, ³⁵Cl, and ¹H (for the second moment study of the polypeptide) nuclear magnetic resonances were recorded with a Varian Associates Model VF-16 wideline spectrometer at frequencies of 8.02, 6.67, and 16.00 MHz, respectively. The spectrometer was operated in the absorption mode at 25°. The line positions and line widths were measured directly from the derivative curves. A Varian C1024 time-averaging computer was employed for signal enhancement for the ³⁵Cl spectra. The number of scans for each spectrum ranged from 5 to 70. The high-resolution proton resonance spectra for solvent molecules were recorded with a Varian A-60A spectrometer at 35°.

Poly- γ -benzyl-L-glutamate (mol wt 200,000) was obtained from the Cyclo Chemical Corporation, Los Angeles, Calif. The same polypeptide (mol wt = 45,000, 99,100, 240,000) was obtained from Miles Laboratories, Inc., Elkhart, Ind. In calculating the mole fraction of the solute, the *formula* weight (that is, per peptide unit) of the polypeptide was used. The molecular weight of the polypeptide in those solutions was 200,000 except where specified.

Results

Proton Second Moment of PBLG. The broadline proton nmr of polycrystalline PBLG consists of a broad peak and a sharper peak centering at the same position. The proton spectra of PBLG in solutions of CD₂ClCD₂Cl in the liquid crystalline phase are smoother and have the shape of a "super Lorentzian" curve⁷ (broad at the base but having a sharper slope at the center). The second moment was calculated from the experimental spectrum with the trapezoid formula, using an IBM 1130 computer.⁸ The value for solid PBLG is 7.5 G². The proton second moment for the liquid crystal solutions of PBLG in 1,2-dichloroethane-d₄ varied from 0.11 to 0.14 G² when

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- (7) T. J. Flautt and K. D. Lawson, in ref 1, p 26.
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⁽²⁾ C. Robinson, Trans. Faraday Soc., 52, 571 (1956); C. Robinson, J. C. Ward, and R. B. Beevers, Discussions Faraday Soc., 25, 29 (1958).



Figure 1. The solvent proton nmr of PBLG solutions of CH_2ClCH_2Cl at 60 MHz. Spinning rate: A and B, 0 cps, C, 78 cps; D, 64 cps. Spectrum A, peptide mole fraction = 0.136; spectrum B-D, peptide mole fraction = 0.259. The computed transitions are represented by vertical lines.

the solute mole fraction was changed from 0.09 to 0.18.

High-Resolution Proton Nuclear Magnetic Resonance for Dichloromethane and 1,2-Dichloroethane. The highresolution proton nmr of CH₂Cl₂ in PBLG solutions has two peaks due to the dipole-dipole interaction of the solvent.³ Spectra of CH₂Cl₂ in solutions of polypeptides with varying degrees of polymerization showed that the dipolar splitting increased slightly with the molecular weight of the polymer. For example, the splitting for a solution of 0.10 mole fraction in PBLG was 79, 89, and 95 Hz for peptides having molecular weights 45,000, 99,100, and 240,000, respectively. For CH₂ClCH₂Cl, the proton nmr spectra are more complicated because of more interactions (Figure 1A and B). The spectra were analyzed by using a modified LAOCN3 program⁹ with an IBM 360 computer. The results showed that the two geminal dipole-dipole coupling constants are the same and the four vicinal coupling constants are equal. Whereas those constants vary with the concentration of the peptide (Figure 2), the indirect spin-spin coupling constants ($J_{pic} = 6.0$ Hz, J_{gem} unimportant) remain unchanged. Spinning of the samples along an axis perpendicular to the magnetic field produced rather complicated spectra (Figure 1C and D). The large side bands were dependent upon the spinning rate and easily recognizable. The computed results (Figure 1D) showed that the central parts of the spectra simply corresponded to systems having all dipole-dipole interactions reduced to 1/4 of those for the nonspun samples.

Deuteron Resonance for Dichloromethane- d_2 and 1,2-Dichloroethane- d_4 . The deuterium nmr spectra for CD_2Cl_2 and CD_2ClCD_2Cl in the polypeptide solutions



Figure 2. The proton dipole-dipole interaction $(\langle D \rangle = 2\Delta\nu/3)$ as functions of PBLG concentration for nonspun samples. Geminal coupling, O; vicinal coupling, \bullet .

showed two peaks due to nonzero quadrupole interaction.⁵ The variation of the deuteron quadrupole splitting with the concentration of PBLG is plotted in Figure 3.

Chlorine-35 Resonance for Dichloromethane and 1,2-Dichloroethane. The ³⁵Cl magnetic resonance spectra obtained from PBLG solutions in CH₂Cl₂ and CH₂-ClCH₂Cl showed three equally separated peaks.⁵ Two of the spectra are shown in Figure 4. The line width of the central peak was markedly narrower in comparison with the two wings. The intensity ratio of the three peaks estimated by treating the spectra as Lorentzian curves was approximately 3:4:3 for all cases. The separation was dependent upon the concentration of the peptide. It is related to the quadrupole coupling constant e^2qQ/h by¹⁰

$$\Delta \nu = \frac{3}{4} \frac{e^2 q Q}{h} \frac{1}{I(2I-1)} \langle 3 \cos^2 \theta - 1 \rangle \qquad (1)$$

for a nucleus with spin I and zero asymmetry parameter. The angle θ between the symmetry axis and the magnetic field is not constant in liquid crystal; therefore the angular part in (1) represents the motional averaged value. The data for the ³⁵Cl quadrupole splitting are plotted in Figure 5.

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Figure 3. The deuteron quadrupole splitting $(\Delta \nu)$ of CD_2Cl_2 (•) and CD_2ClCD_2Cl (0) as functions of PBLG concentration.



Figure 4. Chlorine-35 magnetic resonance of PBLG solutions of CH_2Cl_2 (spectrum A, peptide mole fraction = 0.140) and CH_2ClCH_2Cl (spectrum B, peptide mole fraction = 0.086). The resonance frequency was 6.67 MHz. The tilted base lines were due to accumulation of small dc components during the repeated scans.

Other Resonance Study. ¹⁴N and deuterium (in the NH position by exchange with CF₃COOD-chloroform solution) resonance study of PBLG has been attempted. No detectable signals were obtained even after 100 scans of computer averaging.

Discussion

The proton nmr spectrum of PBLG in CD₂ClCD₂Cl consisted of a broad, structureless peak. The lack of structure is likely due to many different inter-



Figure 5. The chlorine-35 quadrupole splitting $(\Delta \nu)$ of CH₂Cl₂(\bullet) and CH₂ClCH₂Cl (O) as functions of PBLG concentration.

actions in the complicated polypeptide molecule which give rise to completely cverlapping peaks. The "super-Lorentzian" shape of the spectra, as already mentioned, is typical for many mesomorphic systems.⁷ The second moment of the polypeptide in the liquid crystalline state was about 1.6% of that in the solid state, which is also characteristic of those systems.⁷ These features of the spectra indicate that the motion of the polypeptide in the liquid crystalline solution is not much different from that in a single-component liquid crystal.

The spectra of the solvents, namely CH₂Cl₂, CH₂-ClCH₂Cl, and their deuterated analogs, show dipoledipole and nuclear quadrupole interactions.³⁻⁶ For 1,2-dichloroethane, there are six dipole-dipole and six indirect spin-spin interaction constants for the four protons. By comparing the experimental and computed nmr spectra, it was shown that the two geminal dipole-dipole interactions had to be the same, and the four vicinal dipole-lipole interactions were likewise equal. These results imply that the rotation of the C-C bond is fast on the nmr time scale. For the indirect spin-spin interaction, the sign and magnitude for the geminal protons are unimportant because they do not affect the transition frequencies. The four vicinal spin-spin couplings were set to be equal because of fast rotation, although small variations gave similar results for the computed spectra.

The reduction of the proton dipole-dipole splitting to $^{1}/_{4}$ upon spinning was first observed by Sobajima³ for CH₂Cl₂ and CH₂Br. From that result he concluded that the molecular axes of all the solvent molecules were parallel to the magnetic field. On the other hand, Panar and Phillips⁴ argued that the reduction factor of $^{1}/_{4}$ "is precisely that expected if, prior to spinning, the time-averaged solvent dipoledipole vector and H_{0} are parallel." However, those results are not necessarily a consequence of the alignment of the proton-proton vector either along or perpendicular to the field. It is sufficient that the solvent molecules have a definite averaged orientation with respect to the polypeptide, and the polypeptide molecules slowly align in the magnetic field such that after a long time their molecular axes become parallel to the field. Weber¹¹ showed that the factor $\langle 3 \cos^2 \theta - 1 \rangle$ which appears in the formulas for dipolar and quadrupolar splittings (eq 1) in liquid crystals can be decomposed into the product of several terms. For the present case where the macroscopic ordering is perfect in a sufficiently high magnetic field

$$\langle 3 \cos^2 \theta - 1 \rangle = \frac{1}{8} (3 \cos^2 \xi - 1) \times (3 \cos^2 \delta - 1) (3 \cos^2 \gamma - 1)$$
 (2)

where ξ , δ , and γ are the angles formed by the molecular axis of the polypeptide with the magnetic field, the proton-proton vector, and the rotation axis of the solvent molecules, respectively. It is clear from (2) that the (3 cos² ξ - 1) term alone can account for the angular dependence of the system. Obviously all the vectors between the four protons in CH₂ClCH₂Cl cannot have the same direction with respect to the magnetic field, yet *every* dipolar coupling constant was reduced to $^{1}/_{4}$ upon spinning, whereas the indirect couplings did not change (Figure 1).

The ³⁵Cl spectra for both CH₂Cl₂ and CH₂Cl-CH₂Cl consisted of three transitions due to quadrupole splitting. The wings were always broader than the central peak. Pound¹² has studied the spectra of an $I = \frac{3}{2}$ nucleus and demonstrated that quadrupole relaxation would cause the central peak to saturate more easily such that the intensity ratio of the three peaks might become 4:3:4 instead of 3:4:3 for negligible saturation. In order to explain the different line widths of the three transitions, we applied the Redfield theory¹³ to an $I = \frac{3}{2}$ nuclear system with quadrupole relaxation. In a rotating framework, the absorption spectrum is proportional to the imaginary part of Tr $(\rho \mathbf{I}_{+})$, where ρ is the spin density matrix and I_+ is the nuclear raising operator.¹⁴ The equations for the pertinent matrix elements are

$$d\rho_{21}/dt = [i(\Delta + 2B) - 3/2T]\rho_{21} + (1/2T)\rho_{43} + i\sqrt{3}C \quad (3)$$

$$d\rho_{32}/dt = (i\Delta - 1/T)\rho_{32} + i2C \qquad (4)$$

$$d\rho_{43}/dt = [i(\Delta - 2B) - 3/2T]\rho_{43} + (1/2T)\rho_{21} + i\sqrt{3}C \quad (5)$$

where

 $\Delta = \omega - \omega_0 =$ sweeping frequency -

Larmor frequency

(6)

$$B = eqQ\langle 3\cos^2\theta - 1\rangle/8\hbar \ll \omega_0'$$
 (7)

$$1/T = 1/10 \cdot (eq^2 Q/\hbar)^2 \cdot \tau_{\rm c}/(1 + \omega_0^2 \tau_{\rm c}^2)$$
(8)

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Figure 6. Computed nmr spectra of an $I = \frac{3}{2}$ nuclear system with quadrupole relaxation. The parameter $B \cdot T/2$ has the values of: A, 0.4; B, 0.8; C, 1.6; and D, 3.2.

and C is a constant proportional to the population difference between adjacent energy levels.¹⁵ The relaxation terms in eq 3-5 were obtained by treating the molecules as freely tumbling with a correlation time $\tau_{\rm c}$. The solvent molecules in a liquid crystal solution actually have restricted rotations. However, the relaxation mechanism would not be affected significantly if the restriction to the free rotation is small. For the present case, the ³⁵Cl splittings (33–145 kHz) are very small compared with the quadrupole interaction constants (72.47 MHz for CH₂Cl_{2¹⁶} and 68.88 MHz for CH₂ClCH₂Cl¹⁷). Then $(3\cos^2\theta - 1)$ is in the range of 0.5×10^{-3} to 2×10^{-3} instead of zero, the difference of which is negligible for the purpose of calculating the ^{3b}Cl line width. The steady-state solution of eq 3-5 without saturation gives the result

$$Im[Tr(\rho I_{+})] = \frac{6CT(8B^{2}T^{2} + \Delta^{2}T^{2} + 4)}{(4B^{2}T^{2} - \Delta^{2}T^{2} + 2)^{2} + 9\Delta^{2}T^{2}} + \frac{4CT}{1 + \Delta^{2}T_{2}}$$
(9)

Equation 9 represents the magnetic resonance absorption of an $I = {}^{3}/{}_{2}$ nuclear system with quadrupole relaxation; the derivative curves of (9) with several different values of T are shown in Figure 6. If there is no quadrupole splitting (B = 0), the right-hand side of (9) is reduced to $10CT/(1 + \Delta^{2}T^{2})$, and it is obvious

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that T would be equal to the spin-spin relaxation time T_2 . For B = 0, the three transitions relax differently and a unique T_2 cannot be defined. Except for very small values of T, the widths of the satellites would be about 1.5 times that of the central peak, as can be seen from eq 3-5. This result can readily explain the ³⁵Cl spectra for PBLG solutions in CH₂-Cl₂. Since the splitting between the chlorine peaks is equal to B/π (eq 1 and 7), the value of T can be found by comparing the experimental and computed spectra. For CH₂Cl₂-PBLG solutions, T for chlorine is about $6 \times 10^{-6}-8 \times 10^{-6}$ sec (whereas T_2 for pure CH₂Cl₂ is 5×10^{-5} sec, as measured from the ³⁵Cl line width). The correlation time $\tau_{\rm e}$ can be calculated from (8); its value is 6×10^{-12} -8 $\times 10^{-12}$ sec. The ³⁶Cl line widths for the CH₂ClCH₂Cl solutions are similar to, but slightly broader than, those of the CH₂Cl₂ solutions for comparable concentrations of the polypeptide.

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Theory of Relaxation of the Diffuse Double Layer following

Coulostatic Charge Injection¹

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Quantitative relationships describing relaxation of the diffuse double layer (in the absence of specific adsorption) following coulostatic charge injection have been calculated using the technique of digital simulation. The variation of electric field and ion concentrations as a function of time and distance from the x_2 plane are presented for a system of interest. An empirical equation is derived which relates the basic parameters. The theoretical predictions are in accord with Anson's recent experimental results.

Recent studies by Anson, Martin, and Yarnitzky² have demonstrated double-layer relaxation following coulostatic charge injection. Newman³ has treated some of the theoretical aspects of the problem and Buck⁴ has considered the case for small perturbations where the condition

$$c_+ + c_- = 2c_{\text{bulk}} \tag{1}$$

prevails at all points in solution. Buck has also presented a thorough review of the pertinent literature in this field.

In this paper I shall present the results of Digital Simulation⁵ of double-layer relaxation for a 1:1 electrolyte in the absence of specific adsorption. The variation of electric field and ion concentrations as a function of time and distance from the x_2 plane⁶ are calculated and an empirical equation is derived which relates the basic parameters. The simulation was carried out for semiinfinite linear diffusion. Modification for spherical diffusion is presented in the Appendix. It is assumed that the diffusion coefficients

of the two ions are the same, that both ions have a common x_2 plane, and that the electrode is initially at the point of zero charge. It is further assumed that the solvent is a continuous dielectric and that there is no dielectric saturation Definition of symbols appears at the end of the paper.

A Physical Picture

When an electrode at the point of zero charge is instantaneously charged, coulostatically, an electric field is produced. If there are no mobile charge carriers

(1) This work was performed under the auspices of the United States Atomic Energy Commission.

(2) F. C. Anson, R. Martin, and C. Yarnitzky, J. Phys. Chem., 73, 1835 (1969).

(3) J. Newman, ibid., 73, 1843 [1969].

(5) S.W.Feldberg, "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, Inc., 1969 p 199.

(6) The x_2 plane is the plane of closest approach for nonspecifically adsorbed ions (see P. Delahay "Double Layer and Electrode Kinetics," Interscience Publishers, New York, N. Y., 1965).

⁽⁴⁾ R. P. Buck, Electroanal. Chem., 23, 219 (1969).



Figure 1. Variation of $\sqrt{c_+/c_{bulk}}$, $\sqrt{c_-/c_{bulk}}$, and 10 × field(x)/field (x = 0) with distance from the x_2 plane. Abscissa units = $(x - x_2) \cdot (8\pi z^2 F^2 c_{bulk}/RT\epsilon)^{1/2}$. The concentration curves will always approach unity at large x and may thus be distinguished from the field curve. Details of time, charge, and concentration are printed in each figure. This legend applies to all figures.



Figure 2.

in the dielectric medium or if the extant charge carriers have not had time to move, the electric field is constant, extending to the counter electrode. The magnitude of this field (assuming that the lines of force are all normal to the plane of the electrode) is

$$E = \frac{-4\pi q}{\epsilon} \tag{2}$$

The ions will move according to

$$f_j = \frac{FE}{RT} D_j c_j z_j + D_j \frac{\mathrm{d}c_j}{\mathrm{d}x}$$
(3)

In the beginning, $dc_j/dx = 0$; thus it is clear from eq 3 that if a positive charge is injected, the resulting negative field (eq 2) will cause the flux of negative ions to be positive (toward the electrode) and the



Figure 3.





flux of positive ions to be negative (away from the electrode). The change in charge distribution will of course effect a change in the electric field. The field will no longer be constant (eq 2) but must be calculated according to Gauss' law

$$E_{x} = \frac{-4\pi}{\epsilon} \left[q + F \int_{0}^{x} \sum_{j=1}^{n} c_{j} z_{j} \mathrm{d}x \right]$$
(4)

The variation of the electric field and the ion concentration as a function of time after charge injection are shown in Figures 1-7. The ϕ_2 potential is calculated as follows.

$$\phi_2 = \int_{x_1}^{\infty} (E_x - E_\infty) \mathrm{d}x \tag{5}$$

Inspection of Figures 1–7 shows that there are two modes of relaxation (as has been pointed out^{2,3,4}). The first comprises neutralization of the charge on the electrode. In the particular case simulated, it is virtually complete after 15 μ sec when the field at infinity has become zero (Figures 1–5). The second relaxation mode reflects the redistribution of the ions



Figure 5.



Figure 6.



Figure 7.

in the double layer as they relax to the minimum energy as defined by the Gouy-Chapman equation⁷ (Figures 5-7). It is the second, slower relaxation which is of primary interest. For the system shown here the Gouy-Chapman ϕ_2 potential, 110.6 mV ($T = 25^{\circ}$), is approached, but not attained within the time domain of the simulation.

Perhaps the critical phenomenon to note is that the concentration profile of the attracted ion (the anion when the electrode is positively charged) is not monotonic and exhibits a distinct minimum (Figure 4). The equilibrium Gouy-Chapman ion distribution, of course, exhibits no such minimum. During the second relaxation process the only observable change in the nature of the concentration profiles is the disappearance of the minimum. Two additional systems were simulated-one in which the attracted ion was immobile, *i.e.*, its diffusion coefficient was zero, and the other in which the repulsed ion was immobile. In both cases there appears to be no second relaxation. Once the neutralization is complete, the ions are in their equilibrium configuration. The concentration profiles are at all times monotonic. Thus it seems that mobility of both icns is prerequisite to the appearance of the second relaxation.

Quantitating the Relaxation Phenomena

An equation describing the first relaxation process can be derived^{3,4}

$$E_{\infty} = \frac{-4\pi q}{\epsilon} \exp\left[-\frac{4\pi t}{\epsilon} \frac{F^2}{RT} \sum_{j=1}^n D_j c_j z_j^2\right]$$
(6)

Equation 6 neglects the variation in field close to the electrode surface. In the early stages of the relaxation, however, the contribution of the field, E_{∞} , to the potential will be overwhelmingly large, *i.e.*

$$\int_{x_2}^{\infty} \frac{(E_{\rm x} - E_{\infty})}{E_{\infty}} \, \mathrm{d}x \ll 1$$

There is no analytical solution for the second relaxation process. The calculations show, however, that a plot of

$$(\phi_2)_t vs. t^{-2/3}$$

is linear once the first relaxation process is complete.⁸ The intercept of these plots is always within a per cent of the Gouy-Chapman ϕ_2 potential. Furthermore, the slopes for these plots are found to be proportional to $q^{5/6}$ when

$$\frac{q^2}{RT\epsilon c} \gtrsim 2 \tag{7}$$

From these data it is possible to write the following empirical equation

(7) See reference cited in footnote 6.

(8) The reader may wish to verify this for the data presented in Figures 1-7. The theoretical ϕ_2 potential is 110.6 mV. The resulting plot is typical subject to the limitations discussed in the paper.

$$\frac{zF}{RT}[(\phi_2)_t - (\phi_2)_{G.C.}] = 0.122 \left(\frac{q^2}{c}\right)^{t/4} \frac{t^{-2/3}}{(RT\epsilon)^{1/4} (cz^2D)^{2/4}F^{t/4}}$$
(8)

Equation 8 is valid when the condition stated in eq 7 obtains and when $E_{\infty} = 0$.

Discussion

Equation 8 should be considered as an algorithm valid from the lower limit stated in eq 7 at least up to

$$\frac{q^2}{RT\epsilon c} \approx 30 \tag{9}$$

Simulation of larger values of $q^2/(RT\epsilon c)$ requires very long computation times (e.g., hours on a CDC 6600). There is no apparent reason to assume that eq 8 is not valid for larger values of $q^2/(RT\epsilon c)$. The lower limit of validity for eq 8 can probably be explained by noting that below this limit, the surface concentration of the attracted ion is no longer much larger (at least by a factor of 10) than its bulk concentration. For very small values of $q^2/(RT\epsilon c)$ Buck's equations⁴ are applicable.

The effects predicted for large charge perturbations qualitatively agree with Buck's predictions for small charge perturbations. At long times the contribution of the first relaxation becomes small compared to the contribution of the second relaxation. Unless, however, there is a large charge perturbation, the contribution of the second relaxation is just too small to see.

Several assumptions have been made in the calculations leading to eq 8. Dielectric saturation⁹ and the discrete nature of the solvent medium have been ignored, but this is reasonable when the charge is less than 7 \times 10^{-6} C/cm² (in water) and conditions are such that the dimensions of the diffuse double layer are large compared to the molecular dimensions of the solvent. Instantaneous charging of the electrode is experimentally impossible; however, the charging process can be completed in times short relative to observation times (see discussion by Anson, et $a!.,^2$ and Newman³). Equation 8 describes the rather limited case where D_+ = D_{-} and $z_{+} = z_{-}$ (valid assumptions for KCl solutions). The digital simulation technique requires only the assumption of a continuous dielectric; thus calculations for specific cases of interest can be made.

Anson's data² for 10^{-5} C/cm² and 10^{-6} mol/cm³ KCl were interpreted according to eq 8. Plotting ϕ_2 as a function of $t^{-2/s}$ gave the predicted straight line with a slope of 6.6 \times 10⁻⁵ V sec^{-3/s}. The theoretical slope from eq 8 is 5.4 \times 10⁻¹ V sec^{-3/s}. The discrepancy may be due in part to the dielectric saturation associated with a charge of this magnitude (see eq 2 and footnote 9). Although a thorough correlation of theory and experiment remains to be done, the indications are that double-layer relaxation in the absence of specific adsorption may be explained by rather simple concepts of electrostatics, diffusion, and migration.

Acknowledgement. This problem was posed by Fred C. Anson. He, John Newman, and Richard Buck are thanked for their many helpful discussions.

Appendix

The effects of electrode and cell geometry are significant during the first relaxation period when E_{∞} is finite. During the second relaxation the field is zero except in a region very close to the electrode surface, and the potential (ϕ_2) will be independent of any practically attainable geometry.

For spherical geometry consider a test electrode of radius r_1 and with a concentric spherical counter electrode of radius r_2 . If E_{∞} is redefined as being the field just outside the diffuse double layer, at a distance δ from the electrode surface where $\delta <<< r_1$, then

$$(E_{\infty})_r = (E_{\infty})_{\delta} (r_1/r)^2$$

The potential is then expressed

$$V = (E_{\infty})_{\delta} \int_{r_1}^{r_2} \left(\frac{r_1}{r}\right)^2 dr$$
$$V = (E_{\infty})_{\delta} r_1 \left[1 - \frac{r_1}{r_2}\right]$$

and if $r_2 >> r_1$

$$V = (E_{\infty})_{\delta} r_1$$

Substituting from eq 6 will give the complete expression for V. Once the first relaxation is complete, then

$$V_t = (\phi_2)_t$$

Nomenclature

- E electric field, V cm⁻¹ q charge density on the electrode, $C cm^{-2}$ dielectric constant, $1.111 \times 10^{-12} \times 77.9 \text{ C V}^{-1} \text{ cm}^{-1}$ € for water at 25° f; F flux of *j*th species, mol cm⁻² sec⁻¹ Faraday, 96,497 C/equiv RT gas constant × temperature, 2478 V C mol⁻¹ at 25° D, diffusion coefficient of jth species, cm² sec⁻¹ Ď diffusion coefficient (= $D_1 = D_2 \dots \text{etc.}$), cm² sec⁻¹ bulk concentration of electrolyte, mol cm⁻³ С c_j concentration of *j*th species, mol cm^{-s} charge on jth species z_j see eq 5 ϕ_2 (\$\$2)G.C. equilibrium value of ϕ_2 calculated according to the Gouy-Chapman equation
- t time measured after instantaneous charge injection, sec

(9) Dielectric saturation in water becomes significant at field strengths greater than 1×10^6 V/cm (see P. Delahay, "Double Layer and Electrode Kinetics," Interscience Publishers, New York, N. Y., 1965, p 49).

Acidity of Surface Hydroxyl Groups

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Reports of hydroxyl band frequency shifts of phenols in solution indicate that the amount of shift can be related to the basicity of the solvent and the acidity of the phenol. Using this concept, the frequency shifts observed during adsorption on the hydroxyl groups of several oxide surfaces have been measured and compared with the shifts observed when several alcohols are dissolved in the same solvents. Comparison of these shifts with the known acidity constants of the alcohols enables pK_a values for the various surface hydroxyl groups to be obtained. The values found were: magnesia, 15.5; boria, 8.8; silica, 7.1; silica-alumina, 7.1; and phosphorus, -0.4.

Introduction

The nature of the hydrogen bonding interaction between alcohols or phenols and organic solvents has been the subject of numerous studies. Results obtained prior to 1959 have been well summarized by Pimentel and McClellan.¹ One of the most useful tools employed in these studies has been infrared spectroscopy. On placing a hydroxyl-containing compound in solution, the band due to the OH vibration is moved to lower frequencies due to an H-bonding interaction between solute and solvent.

Bellamy and Williams² have shown that with unhindered phenols and methanol, the perturbation of the OH band increases systematically with increasing basicity of the solvent. Also, the frequency shifts of unsubstituted phenol in a series of solvents can be plotted against the corresponding values of methanol and alkyl-substituted phenols in the same solvents to give straight lines. The slopes of these plots were "different from that of phenol and nearer to that of methanol, which is consistent with their weaker acidity." Thus, in solution at least, OH band frequency shift $(\Delta \nu)$ is a direct function of the acidity of the OH group and the basicity of the solvent.

This concept has also been discussed in the light of OH frequency shift data obtained when benzene is adsorbed on silica, magnesia, and molecular sieves,³ an increasing OH frequency shift being interpreted as being due to a more acidic OH group.

The data obtained from the work described above give only a qualitative measure of relative acidity or basicity, *i.e.*, one can only determine if a given OH group is more or less acidic than another OH group, or if a given solvent is more or less basic than another solvent. In this paper we describe the correlation between the frequency shifts observed with two phenols and methanol, and the known acidity values (pK_n) of these OH groups. With this correlation, we have used the observed OH frequency shifts on Mg-OH, B-OH, P-OH, and Si-OH surfaces to calculate the acidity of these OH groups.

Experimental Section

The solutions used were contained in a variable path length solution cell.

Spectra were taken of various concentrations of the alcohols in carbon tetrachloride. With increasing concentrations of solutes, an increasing fraction of the solute molecules are mutually hydrogen bonded to form dimeric and polymeric species. This is shown by the presence of two perturbed OH bands, the relative intensities of which change with increasing concentration of solute. The concentrations of solutes used were chosen so that essentially no mutual hydrogen bonding was detectable. These concentrations were methanol, 0.06 mol/l.; phenol, 0.10 mol/l.; and trichlorophenol, 0.05 mol/l. To these solutions various donor molecules were added and the position of the perturbed hydroxyl band(s) observed.

The oxide samples were mounted in a compensated cell so as to cancel out any gas-phase absorption bands. The experimental details for obtaining the spectra of the samples in the presence of various gases have been described previously.⁴

The following oxide surfaces were prepared. (1) Silica (Cab-O-Sil, Cabot Co.) was pressed into a selfsupporting disk and heated to 800° in air prior to using. (2) Magnesium hydroxide (J. T. Baker Chemical Co., N.F. grade) was pressed into a self-supporting disk and heated at 500° for 15 min prior to using. (3) Silica-alumina (American Cyanamid Co., Aerocat Triple A Cracking Catalyst Grade 75/85) was pressed into a self-supporting disk and heated at either 400 or 520° for 0.5 hr in air, and then at 200° *in vacuo* prior to using. (4) The phosphorus surface was prepared by treating a silica disk with PCl₃ at 120° until

⁽¹⁾ G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman and Co., San Francisco, Calif., 1959.

⁽²⁾ L. J. Bellamy and R. L. Williams, Proc. Roy. Soc., A254, 119, (1960).

⁽³⁾ M. L. Hair, "Infrared Spectroscopy in Surface Chemistry," Dekker, New York, N. Y., 1967. r 136.

⁽⁴⁾ W. Hertl and M. L. Hair, J. Phys. Chem., 72, 4676, 136 (1968).

						Silica-		
Donor	Methanol	Phenol	Trichlorophenol	Silica	Magnesia	alumina	Phosphorus	Boron
Hexane	0			30		35		27
CCl4	0			45			75	35 ± 10
CS_2	6			60				
Benzene	32			120	35	130	200	105 ± 20
Xylene	40	62	40	155	45	155	260	120
Acetaldehyde				280	75		ca. 680	260 ± 30
Trimethylmethoxy silane	134			477				
Acetone	112	131, 236	140, 290	395	105		850 ± 150	295 ± 30
Diethyl ether	142	280	345	460		430		380 ± 30
Pyridine	280	460	600, 1010	765				
Diethylamine	220, 400	ca. 650	ca. 830, 1030	ca. 900				
Triethylamine	251, 446	ca. 700	910-1030	975	350			
Ammonia				675	175		860	

Table I: Observed Hydroxyl Band Frequency Shifts (in cm⁻¹) in Solution and on Surface Groups^a

^a The frequencies of the unperturbed surface hydroxyl groups are given in Table II; for the alcohols, the unassociated hydroxyl frequencies in CCl_4 solution are methanol, 3630 cm⁻¹; phenol, 3598 cm⁻¹; and trichlorophenol, 3525 cm⁻¹.

all the silanol groups had disappeared, then hydrolyzing with water and heating the sample to 800° in air At the end of this procedure, P-OH for 1 min. groups are present as well as some silanol groups. After repeating this procedure four times, a fairly large number of P-OH groups and a small number of silanol groups remain on the surface. (5) The boron surface was prepared by treating a silica disk with BCl₃ at room temperature until all the silanol groups had disappeared. When water vapor was admitted to the cell a large fraction of the silanol groups reappeared as well as a band at 3706 cm^{-1} , which is due to the B-OH group. This procedure was repeated five times, at which point the relative intensities of the B-OH to the Si-OH ceased to change. The final intensity of the B-OH was about 2.5 times as strong as the Si-OH. The sample was then heated to 800° in air for 1 min.

Results

The results are summarized in Table I. In Figure 1, the OH frequency shifts observed for the phenols and methanol are plotted, arbitrarily, against the shifts observed for the surface Si–OH groups. Straight line relationships are obtained. These do not pass through the origin, however, since the frequency shifts on silica were measured from the gas phase, whereas those of the alcohols were measured in a solution environment. In solution the "unassociated" OH group must interact to a certain extent with the solvent, although this interaction is considerably less than the interaction with the added donors.

In some cases (e.g., phenols + acetone, methanol + amines) at least two perturbed hydroxyl bands appear, thus indicating at least two kinds of interaction. In Figure 1, the lines have been drawn through the points which we believe form a consistent series, *i.e.*, through



Figure 1. Plots of observed alcohol hydroxyl band frequency shifts in the presence of various donors against hydroxyl band frequency shifts observed when the same donors are adsorbed on silanol groups.

those perturbed bands which arise from the same type of interaction. As only one perturbed band is observed with the surface group, it is clear that the interactions in solution are much more complex than those observed when a gaseous molecule adsorbs on a surface hydroxyl group.

In Figure 2, the hydroxyl band frequency shifts observed on the various oxides are plotted against the corresponding shift observed on silica, and again straight lines are obtained. Using the relationship described above between the relative frequency shifts and the acidity of the OH groups, one can say qualitatively at this point that with the alcohols, trichlorophenol is most acidic and methanol least acidic, and



Figure 2. Plots of observed hydroxyl band frequency shifts when various donors are adsorbed on surface hydroxyl groups against the shifts observed when the same donors are adsorbed on silanol groups.

with the surface OH groups phosphorus is most acidic and magnesia least acidic (cf. slopes in Figure 1 and 2).

Discussion

If the slopes of the lines in Figure 1 are plotted against the known acidity values (pK_a) of the alcohols (Figure 3) a straight line is obtained. Since all the slopes were obtained with respect to the silanol group, the pK_a value of this group should be given by the value on the plot corresponding to a slope of 1.0. This is indicated by the labeled arrow in Figure 3 and gives a value of 7.1 ± 0.5 , which is in very good agreement with the value (about 7.0) obtained by titration.⁵ This good agreement strongly suggests that this method of calculation is valid for obtaining the acidity values of the surface hydroxyl groups.

The slopes of the plots for the surface hydroxyl band frequency shifts (Figure 2) can now be used in conjunction with the plot given in Figure 3 to obtain the $pK_{\mathbf{a}}$ values of the various surface hydroxyl groups. The values of the slopes are indicated in Figure 3 by the labeled arrows. The $pK_{\mathbf{a}}$ values to which these correspond (abscissa of Figure 3) are given in Table II, together with the frequencies of the freely vibrating

Table II: Frequencies and Observed pK_a Values of Surface Hydroxyl Groups

Oxide	Frequency (in cm ⁻¹) of freely vibrating OH group	pK_{a}	Literature pKa value for the acids (first dissociation step)
Silica	3750	7.1 ± 0.5	9.7
Magnesia	3752	15.5 ± 0.4	
Silica-alumina	3750	7.1	
Phosphorous	3670, 3700	-0.4	2.0
Boria	3706	8.8 ± 0.6	9.1



Figure 3. Plot of the line slopes for the alcohols from Figure 1 against the pK_a values for the alcohols. The arrows indicate the slopes of the lines given in Figure 2 for the various surface hydroxyl groups.

hydroxyl groups for the various metal hydroxides, and literature pK_a values for the corresponding free acids in solution (*i.e.*, silicic, phosphoric, and boric acids).

The P-OH surface shows two bands due to unperturbed hydroxyl groups. These can possibly be assigned to single OH groups attached to the phosphorus and to OH groups in a geminal configuration attached to the phosphorus. When the various gases were added to the system, the perturbed bands were very broad. This could be due either to a distribution of OH bond energies or to the presence of overlapping perturbed bands due to the two types of hydroxyl groups. The frequency shifts were measured from the lower frequency band, which was more intense. When ammonia was added to the system, no bands assignable to NH_4^+ were observed so that although the P-OH groups are much more acidic than Si-OH groups, apparently no ammonium ions are produced on the surface.

The Mg–OH band at 3752 cm^{-1} shifts to lower frequencies (ca 3700 cm^{-1}) when heated to a higher temperature than used her3. This effect has been previously reported.³

The precise frequency of the freely vibrating silanol group on the SiO₂-Al₂O: was checked by mounting a silica disk in the reference beam of the spectrophotometer. The silanol frequencies were found to be identical. The frequency shifts observed when the various gases were added appeared to be the same as the shifts observed on pure silica. This is in agreement with, and extends, the observations made previously by Basila.⁶ However, when NH₃ was added, a band attributable to NH₄⁺ was observed. Thus, although

⁽⁵⁾ R. W. Maatman, et al., J. Phys. Chem., 68, 757 (1964).

⁽⁶⁾ M. R. Basila, J. Chem. Ph 18., 35, 1151 (1961).



Figure 4. Plot of the pK_a values of the surface hydroxyl groups against the Mulliken electronegativity values.

the acidity of the OH group on this sample is the same as that observed on silica, it must be recognized that sites exist on the surface of these catalytic materials which are sufficiently acidic to protonate the ammonia molecule.

The frequency shifts observed on B-OH are slightly less than on the Si-OH group, indicating that the B-OH groups are slightly less acidic than the Si-OH groups. For a given pressure of added gas a greater *fraction* of the silanol groups are perturbed than the B-OH groups, indicating that the silanol groups are also stronger adsorption sites. It should be noted, however, that with the samples used here, the surface contains about 2.5 times as many B-OH groups as Si-OH groups so that the perturbed hydroxyl bands consist principally of perturbed B-OH groups.

This observation is somewhat surprising, as titration data on porous glass—which contains a considerable quantity of boron on its surface⁷—indicates the presence of a more acidic group ($pK_{a} \sim 5.7$) on its surface in addition to the silanol ($pK_{a} = 7$). The present data indicate that this increased acidity is probably associated with the solution interaction with Lewis acid sites rather than due to an acidic boranol group.

It is of interest to compare the pK_a values for the surface OH groups with the first dissociation step of the comparable free acid in solution (Table II). It can be seen that the surface group has a lower pK_a value than the "molecular" acid and also that there is no direct relationship between the two pK_a values. If the pK_a values for the surface hydroxyl groups are plotted against the Mulliken electronegativities $(\frac{1}{2}I + \frac{1}{2}E)$ then a good inverse relationship is revealed (Figure 4).

Acknowledgment. The authors thank Miss E. R. Herritt for assistance in the experimental work.

(7) I. Altug and M. L. Hair, J. Phys. Chem., 71, 4260 (1967).

Influence of Langmuirian Adsorption of Reactant and Product

upon Charge-Transfer Processes in Polarography

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On the basis of the diffusion layer concept, the influence of a Langmuirian adsorption of reactant and product upon voltametric curves at dropping and stationary electrodes is considered. The surface concentrations of the electroactive species affect the charge-transfer process for relatively high values of the rate constant, k_s , at the standard potential. A progressive decrease in k_s causes (i) the polarographic normal wave following the adsorption prewave to become irreversible and to shift toward increasing overvoltages in the case of predominant adsorption of the product, and (ii) the polarographic normal wave to merge with the following adsorption postwave in the case of predominant adsorption of the reactant. If the adsorption coefficients of the reactant O and of the product R are of different orders of magnitude, an appreciable difference is observed between the slopes of the normal waves given, respectively, by solutions of O and R of equal concentrations. Thus the electroactive substance preferentially adsorbed gives waves with higher slopes. If the adsorption coefficients of reactant and product are of the same order of magnitude, no pre- or postwaves are to be expected and an increase in the concentration of the reactant causes a decrease in the slope of the normal wave until the minimum slope corresponding to total irreversibility is reached. Simultaneously, the wave shifts toward increasing overvoltages.

Introduction

Since the pioneering work of Brdička¹ on the nature of adsorption waves, a great deal of work has been cevoted to the study of adsorption effects upon polarographic currents. In interpreting adsorption waves, Brdička¹ claims that the adsorbed molecules of reactant or of product are not reduced or oxidized in the normal wave but rather in the adsorption postwave or prewave. This amounts to stating that a substance, which is in the condition of being specifically adsorbed and therefore of occupying the inner Helmholtz plane, can be electroreduced or -oxidized at the outer Helmholtz plane without passing through the adsorbed state. This assumption is in contrast with several experimental findings. Thus the presence of maxima in the polarographic waves of several organic substances has been interpreted^{2,3} as due to a slow charge transfer involving the specifically adsorbed reactant. The anomalous behavior of these waves is attributable to a change in the adsorption coefficient of the reactant with applied potential.

The aim of the present note is to show the effect of the electrode coverage by reactant and product upon the rate of the charge-transfer process in the case of a Langmuirian adsorption. It will be shown that the equations for the polarographic current derived by Brdička¹ hold even when the electroactive substances exchange charges with the electrode exclusively in the adsorbed state.

Formulation of the Problem

Consider a simple redox system O-R where neither O nor R is involved in reactions other than the chargetransfer process

$$O + ne = R$$
 (1)

Under these assumptions the volume concentrations C_0 and C_R of O and R satisfy Fick's second law, which must be corrected for the convective motion due to the expansion of the drop in the case of diffusion toward a dropping electrode. Assume that the charge-transfer process is slow and involves only those molecules of O and R which are specifically adsorbed. Under these circumstances the two following boundary conditions can be written

$$D(\partial C_0/\partial x)_{z=0} = 1/A d(A \Gamma_0)/dt + k_t \Gamma_0 - k_b \Gamma_R \quad (2)$$
$$D(\partial C_R/\partial x)_{z=0} = 1/A d(A \Gamma_R)/dt -$$

 $k_{f}\Gamma_{0} + k_{b}\Gamma_{R}$ (3)

Here A is the area of the electrode surface, Γ_0 and Γ_R are the surface concentrations of O and R, respectively, D is the diffusion coefficient, which for simplicity has been considered equal for the two species, and k_t , k_b are the rate constants for the forward and backward electrode processes. Equation 2 expresses the fact that the amount of O reaching the electrode in the unit time equals the amount of C accumulating plus that reacting at the electrode surface in the same unit time. Analogous considerations can be made for eq 3 when the species R is considered. The boundary conditions (2) and (3) hold both at a stationary electrode and at a dropping

- (1) R. Brdička, Z. Elektroch m., 48, 278 (1942).
- (2) J. Koryta, ibid., 64, 23 (_960).
- (3) A. B. Ershler, G. A. Tedoradze, and S. G. Mairanovskii, Dokl. Akad. Nauk SSSR, 145, 1324 (1962).

electrode. In the former case, A is constant while in the latter the dependence of A on the electrolysis time t is expressed by the relation

$$A = A_0 t^{3/3} \tag{4}$$

where A_0 is the area of the electrode at t = 1 sec. The faradaic current due to the electrode process 1 is given by

$$i/(nF) = AD(\partial C_{\rm O}/\partial x)_{x=0} - d(A\Gamma_{\rm O})/dt =$$
$$-AD(\partial C_{\rm R}/\partial x)_{x=0} + d(A\Gamma_{\rm R})/dt =$$
$$= A(k_{\rm f}\Gamma_{\rm O} - k_{\rm b}\Gamma_{\rm R}) \quad (5)$$

It should be noted that according to the concept of charge separation and recombination introduced by Delahay,⁴ the current flowing along the external circuit does not necessarily coincide with the Faradaic current. Assuming that only the oxidized species is present in the bulk of the solution, we write

$$\begin{array}{l}
C_{\rm O} = C_{\rm O}^{*} \\
C_{\rm R} = 0
\end{array} \quad \text{for} \quad \begin{cases}
x \ge 0, t = 0 \\
x \to \infty, t > 0
\end{array}$$
(6)

The asterisk denotes bulk concentrations.

The Diffusion Layer Treatment

The diffusional problem 2, 3, and 6 will not be solved rigorously, but rather by following the approximate procedure based on the diffusion layer concept. In this connection, the mean current $\bar{\imath}$ will be derived by assuming that during electrolysis at constant potential the volume concentrations \bar{C}_0 and \bar{C}_R of the species O and R at the electrode surface remain constant. It follows that Γ_0 and Γ_R do not change with time at constant potential, provided adsorption equilibrium is achieved. Under these simplifying assumptions, integration of eq 5 over the period of electrolysis t_1 yields

$$\frac{\overline{i}}{nF} = \frac{1}{nFt_1} \int_0^{t_1} i \, \mathrm{d}t = \frac{D}{t_1} \int_0^{t_1} A\left(\frac{\partial C_0}{\partial x}\right)_{x=0} \, \mathrm{d}t - \frac{\Gamma_0}{t_1} \int_0^{t_1} \frac{\mathrm{d}A}{\mathrm{d}t} \, \mathrm{d}t \quad (7)$$

$$\frac{\overline{\imath}}{\imath F} = -\frac{D}{t_1} \int_0^{t_1} A\left(\frac{\partial C_R}{\partial x}\right)_{z=0} dt + \frac{\Gamma_R}{t_1} \int_0^{t_1} \frac{dA}{dt} dt \quad (8)$$

$$\frac{i}{nF} = \frac{1}{t_1} \int_0^{t_1} A \, \mathrm{d}t \cdot (k_t \Gamma_0 - k_b \Gamma_R) \tag{9}$$

If electrolysis is carried out at an electrode of constant area, eq 7, 8, and 9 assume the following simplified forms

$$\frac{\tilde{\imath}}{nF} = \frac{DA}{t_1} \int_0^{t_1} \left(\frac{\partial C_0}{\partial x}\right)_{x=0} \,\mathrm{d}t \tag{10}$$

$$\frac{\tilde{\imath}}{nF} = -\frac{DA}{t_1} \int_0^{t_1} \left(\frac{\partial C_{\rm R}}{\partial x}\right)_{x=0} dt \qquad (11)$$

 $\frac{i}{nF} = A \left(k_{\rm f} \Gamma_{\rm O} - k_{\rm b} \Gamma_{\rm R} \right) \tag{12}$

On the basis of the diffusion layer concept, let us place

$$\frac{D}{t_1} \int_0^{t_1} A\left(\frac{\partial C_0}{\partial x}\right)_{x=0} dt = l(C_0^* - \bar{C}_0);$$
$$\frac{D}{t_1} \int_0^{t_1} A\left(\frac{\partial C_R}{\partial x}\right)_{x=0} dt = -l\bar{C}_R \quad (13)$$

where the expression for l depends on the particular type of diffusion under study. Thus for linear diffusion

$$l = 2AD^{1/2} / (\pi^{1/2} t_1^{1/2})$$
 (14)

while for diffusion toward a dropping mercury electrode

$$l = [12D/(7\pi)]^{1/2} A_0 t_1^{1/6}$$
 (15)

A mathematical justification for the approximate relations 13-15 can be given by recalling that, in view of Duhamel's theorem, the flux $D(\partial C/\partial x)$ at x = 0 of a species obeying the diffusion equation uncomplicated by kinetic terms is related to the concentration C(O,t)of this species at the electrode surface through the equation

$$D \int_{0}^{t_{1}} \left(\frac{\partial C}{\partial x}\right)_{x=0} dt = \left(\frac{D}{\pi}\right)^{1/2} \int_{0}^{t_{1}} \frac{C^{*} - C(O,t)}{\left(t_{1} - t\right)^{1/2}} dt \quad (16)$$

for a plane electrode, and through the equation

$$\left(\frac{7\pi D}{3}\right)^{1/2} \int_0^{t_1} \left(\frac{\partial C(x,t)}{\partial x}\right)_{x=0} t^{2/2} dt = \int_0^{t_1^{7/2}} \frac{C^* - C(O,t)}{\lambda^{1/2}} d\lambda \quad (17)$$

where $\lambda = t_1^{1/a} - t^{1/a}$, for a dropping electrode. Assume that the rate of change of C(O,t) with time is much less than those of the ratio $1/(t_1 - t)^{1/2}$ in eq 16 and of the ratio $t^{4/4}/(t_1^{7/4} - t^{2/3})^{1/2}$ in eq 17. Under these conditions, which are approximately satisfied in the majority of cases, $C^* - C(0,t)$ can be brought out of the integral sign in eq 16 and 17 with sufficient confidence. By doing so we immediately obtain eq 13-15. The substantial validity of the approximate approach based on the diffusion layer concept is demonstrated by the satisfactory agreement existing between the results obtained by this approach and those obtained by rigorous numerical procedures.⁵ In particular it must be noted that the approximate procedure followed by Levich, et al.,⁶ in the treatment of diffusion-controlled adsorption at plane and dropping electrodes for different types of isotherms is perfectly equivalent to the diffusion layer approach. The boundary value problem con-

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⁽⁴⁾ P. Delahay, J. Phys. Chem., 70, 2373 (1966).

⁽⁵⁾ J. Heyrovsky and J. Kůta, "Principles of Polarography," Academic Press, New York, N. Y., 1966, pp 339-400.

⁽⁶⁾ V. G. Levich, B. I. Khaikin, and E. D. Belokolos, Élektrokhimiya, 1, 1273 (1965).

sidered in the present note reduces to that examined by the above authors when we let $k_{\rm f}$ and $k_{\rm b}$ tend to zero, *i.e.*, when no Faradaic current flows through the electrode. The approximate equation obtained by Levich and coworkers⁶ for the case of Langmuirian adsorption gives results in fairly good agreement with those derived by a rigorous numerical procedure. In fact, the accuracy of the approximate analytical solution is better than 8%.

Returning to the problem under study, it should be noted that so far we have not made any assumptions as to the nature of the adsorption isotherm relating the surface concentrations Γ_0 and Γ_R to the corresponding volume concentrations \bar{C}_0 and \bar{C}_R at the electrode surface. Consequently, any isotherm could be introduced into the equations previously derived. Since, however, we intend to consider the simultaneous adsorption of both the species O and R, it is more convenient to use the Langmuir isotherm which, unlike other commonly used isotherms (e.g., the Temkin or Frumkin isotherms) is based on the assumption that the adsorption energy of all sites is unaffected by adsorption on neighboring sites. On assuming that the propositions on which the Langmuir isotherm is based are encountered, one has

$$K_{\rm O}\bar{C}_{\rm O}(1-\theta) = \Gamma_{\rm O}/\Gamma_{\rm m}; K_{\rm R}\bar{C}_{\rm R}(1-\theta) = \Gamma_{\rm R}/\Gamma_{\rm m} \quad (18)$$

where K_0 and K_R are the adsorption coefficients of O and R, respectively, θ is the degree of coverage of the electrode and Γ_m is the maximum number of moles adsorbed per unit area of the electrode. For simplicity we shall assume that both O and R have the same value of Γ_m . Since O and R are the only species adsorbed at the electrode, the degree of coverage θ is given by

$$\theta = (\Gamma_0 + \Gamma_R) / \Gamma_m \tag{19}$$

Upon combining eq 18 and 19 the surface concentrations Γ_0 and Γ_R are readily obtained

$$\Gamma_{\rm O} = \Gamma_{\rm m} K_{\rm O} \bar{C}_{\rm O} / (1 + K_{\rm O} \bar{C}_{\rm O} + K_{\rm R} \bar{C}_{\rm R});$$

$$\Gamma_{\rm R} = \Gamma_{\rm m} K_{\rm R} \bar{C}_{\rm R} / (1 + K_{\rm O} \bar{C}_{\rm O} + K_{\rm R} \bar{C}_{\rm R}) \quad (20)$$

In view of eq 9 and 20, the mean current is expressed by the equation

$$\frac{\tilde{t}}{nF} = \frac{\frac{1}{t_{\rm I}}\int_0^{t_{\rm I}} A \, \mathrm{d}t}{1 + K_0\bar{C}_0 + K_{\rm R}\bar{C}_{\rm R}} \Gamma_{\rm m}(k_tK_0\bar{C}_0 - k_{\rm b}K_{\rm R}\bar{C}_{\rm R}) \quad (21)$$

Taking into account the well known relations between the rate constants k_f and k_b and the applied potential

$$k_{t} = k_{t}^{\circ} \exp\left[-\frac{\alpha nF}{RT}(E - E_{0})\right];$$
$$k_{b} = k_{b}^{\circ} \exp\left[(1 - \alpha)\frac{nF}{RT}(E - E_{0})\right]$$

where α is the transfer coefficient, and choosing the reference potential E_0 so as to satisfy the equality $\Gamma_m k_t^{\circ} K_0 = \Gamma_m k_b^{\circ} K_R \equiv k_s$, eq 21 becomes

$$\frac{\bar{\imath}}{nF} = \frac{1}{t_1} \int_0^{t_1} A \, \mathrm{d}t \, \frac{k_s}{1 + K_0 \bar{\mathcal{C}}_0 + K_{\mathrm{R}} \bar{\mathcal{C}}_{\mathrm{R}}} \times \left\{ \bar{\mathcal{C}}_0 \, \exp\left[-\frac{\alpha nF}{RT} \left(E - E_0 \right) \right] - \bar{\mathcal{C}}_{\mathrm{R}} \exp\left[\left(1 - \alpha \right) \frac{nF}{RT} \left(E - E_0 \right) \right] \right\}$$
(22)

In eq 22 $1/t_1 \int_0^{t_1} A \, dt$ equals A for a stationary electrode and $3/5 A_0 t_1^{2/3}$ for a dropping electrode. The reference potential E_0 , previously chosen, coincides with the standard potential of the recox couple O-R as appears from eq 22 upon setting $\bar{i} = 0$ and equating \bar{C}_0 , \bar{C}_R to the corresponding bulk concentrations. Replacement of eq 4, 13, 15, and 20 into eq 7 and 8 and rearrangement yields the following expressions for the mean current at a dropping mercury electrode

$$\frac{\tilde{\imath}}{nF} = \left(\frac{12D}{7\pi}\right)^{1/2} A_0 t_1^{1/4} (\bar{C}_0^* - \bar{C}_0) - A_0 t_1^{-1/4} \frac{\Gamma_m K_0 \bar{C}_0}{1 + K_0 \bar{C}_0 + K_R \bar{C}_R} \quad (23)$$
$$\frac{\tilde{\imath}}{nF} = \left(\frac{12D}{7\pi}\right)^{1/2} A_0 t_1^{-1/4} \bar{C}_R + A_0 t_1^{-1/4} \bar{\Gamma}_m \frac{K_R \bar{C}_R}{1 + K_0 \bar{C}_0 + K_R \bar{C}_R} \quad (24)$$

Upon combining the right-hand sides of eq 23 and 24, $\bar{C}_{\rm R}$ is readily obtained as a function of $\bar{C}_{\rm O}$

$$\bar{C}_{\rm R} = (-b + [b^2 - 4K_{\rm R}(12Dt_1/7\pi)^{1/2}c]^{1/2}/[2K_{\rm R} \times (12Dt_1/7\pi)^{1/2}]$$
(25)

where

$$b = \Gamma_{\rm m} K_{\rm R} + (12Dt_1/7\pi)^{1/2} (1 + K_{\rm O}\bar{C}_{\rm O} + K_{\rm R}\bar{C}_{\rm O} - K_{\rm R}C_{\rm O}^*)$$

and

$$c = \Gamma_{\rm m} K_{\rm O} \bar{C}_{\rm O} + (12Di_1/7\pi)^{1/2} (\bar{C}_{\rm O} - C_{\rm O}^*)(1 + K_{\rm O} \bar{C}_{\rm O})$$

Equations 22-25 express the polarographic currentpotential characteristic in an implicit form. Thus if \bar{C}_0 is given a series of values ranging from O to C_0^* , the corresponding values of \bar{C}_R are readily obtained from eq 25. The introduction of these couples of values of \bar{C}_0 and \bar{C}_R into eq 23 (or alternatively 24) and 22 leads to the couples of values of \bar{i} and $(E - E_0)$ corresponding to the same value of \bar{C}_0 and consequently to the theoretical wave form.

If the standard rate constant k_s is very high (in practice > 10 cm/sec), since \bar{i} cannot exceed the value for the diffusion limiting current, the term within the braces in eq 19 becomes negligible. Upon equating this term to zero one immediately obtains the Nernst equation, as applied to the volume concentrations of O and R at the electrode surface

$$\bar{C}_0/\bar{C}_R = \exp[nF/RT(E - E_0)] = \theta \qquad (26)$$

If K_0 tends to zero, eq 23, 24, and 26 express the well known theoretical characteristic derived by Brdička¹ and relative to a reversible process $O + ne \rightleftharpoons R$ with Langmuirian adsorption of the electrode product. This characteristic exhibits a prewave. Analogously, if we let K_R tend to zero, eq 23, 24, and 26 yield the theoretical wave form relative to a reversible process with Langmuirian adsorption of the reactant, derived by Brdička and characterized by the presence of a postwave. From the way in which eq 26 has been derived it is evident that we need not postulate the occurrence of the electrode process in the adsorbed state along the pre- or postwave and at the outer Helmholtz plane along the normal wave.

Discussion and Conclusions

The solid curves in Figure 1 represent a series of polarographic waves obtained from eq 22, 23, 24, and 25 for n = 1, $\alpha = 0.5$, $C_0^* = 10^{-6} \text{ mol/cm}^3$, $D = 10^{-5}$ cm²/sec, $t_1 = 3$ sec, $\Gamma_m = 5 \times 10^{-10}$ mol/cm², $K_0 =$ $10^4 \text{ cm}^3/\text{mol}, K_R = 10^9 \text{ cm}^3/\text{mol}$ and for different values of k_s . These curves, which illustrate the case of a predominant adsorption of the product R with respect to the reactant O are characterized by the presence of a prewave. When k_s decreases, the length of the plateau separating the prewave from the remaining part of the total wave (i.e., the so-called "normal" wave) increases while the slope of this latter part progressively diminishes reaching a limiting value for k_s $\leq 10^{-1}$ cm/sec. A further decrease in k_s leaves the slope of the normal wave unchanged but causes the wave to shift toward more negative potentials. In this connection it should be noted that in the absence of adsorption phenomena a polarographic wave reaches its minimum slope, corresponding to the total irreversibility of the electrode process, for $k_{\rm s}$ \leq 5 \times 10^{-4} cm/sec while it is practically reversible for $k_{\rm s} \geq$ 10^{-1} cm/sec. The presence of prewaves in the solid curves of Figure 1 must be ascribed to the amount of R which, after its formation from O, remains adsorbed at the surface of the dropping electrode. The contribution to the polarographic current due to this amount of R is expressed by the second term on the right-hand side of eq 24. The drawn-out shape of the curves of Figure 1 for such high values of the standard rate constant k_s as 1 cm/sec is due to the influence exerted by the surface concentration of O, and especially of R, upon the term $k_{\rm s}/(1 + K_0\bar{C}_0 + K_{\rm R}\bar{C}_{\rm R})$ in eq 22. Since this term reduces to k_s in the absence of adsorption, we can call it "apparent standard rate constant." When



Figure 1. Ratio i/i_d of the mean current i, at a given potential E, to the mean diffusion limiting current, $i_d = nFlC_0^*$, as a function of $E - E_0$. The solid curves a, b, c, d, e, and f have been derived from eq 22, 23, 24, and 25 for $C_0^* = 10^{-6}$ mol/cm³, $D = 10^{-5}$ cm²/sec, $t_1 = 3$ sec, $\Gamma_m = 5 \times 10^{-10}$ mol/cm², $K_0 = 10^4$ cm³/mol, $K_R = 10^9$ cm²/mol, n = 1, $\alpha = 0.5$, and for k_s values equal to ∞ , 10, 1, 10^{-1} , 10^{-2} , and 10^{-3} cm/sec, respectively. The dashed curves have been derived from eq 28 for the same values of C_0^* , K_0 , K_R , k_s , n, α , and $l/(i/t_1 \int_0^{t_1} A dt)$ employed in the calculation of the solid curves partially superimposed to them.

 $K_0\bar{C}_0 + K_R\bar{C}_R$ is appreciably greater than 1, the value for the apparent standard rate constant, which strongly affects the dependence of the current upon potential (see eq 22), becomes sensibly lower than the value for the true standard rate constant, k_s .

From the curves in Figure 1 it is evident that the treatment previously outlined bridges the gap between the Brdička adsorption prewaves, which are encountered in the reduction of reversible systems, and the socalled adsorption "pseudo-prewaves," which are characterized by an irreversible normal wave. According to several authors,^{7,3} the difference between Brdička prewaves and pseudo-prewaves is of a substantial nature, in the sense that the former are caused by a facilitation of the reversible electrode process due to the energy gain resulting from adsorption of products, while the latter are the result of an inhibited electrode reaction, the inhibition being caused by a surface film due to the products. This film should become compact at the plateau between the pseudo-prewave and the second wave so that the prewave should be caused by a nearly uninhibited electrolysis of reactant particles while the second wave should correspond to the discharge of the same particles inhibited by a compact layer of products. Thus Mairanovskii⁷ claims that pseudo-prewaves should not be considered as true prewaves but rather as main (normal) waves. In this sense their half-wave

⁽⁷⁾ S. G. Mairanovskii, "Catalytic and Kinetic Waves in Polarography," Plenum Press, New York, N. Y., 1968, pp 109-110.

⁽⁸⁾ R. W. Schmid and C. N. Reilley, J. Amer. Chem. Soc., 80, 2087 (1958).

potential should be close to the standard potential, E_0 , of the redox system and in no case should it be shifted with respect to E_0 in the direction opposite to that of increasing overvoltages. As a matter of fact, from Figure 1 it is apparent that such a drastic distinction between Brdička prewaves and pseudo-prewaves does not exist, since a wholly gradual passage from the former to the latter type of prewaves is observed when the true standard rate constant k_{s} decreases. The position of the half-wave potentials of the cathodic prewaves in Figure 1 on the positive side of E_0 shows that even if k_s is so low that an irreversible second wave is observed, the prewave must be considered as originated by an electrode process simultaneously facilitated by the energy gain resulting from adsorption of electrode products and inhibited by the gradual decrease in the apparent standard rate constant resulting from such an adsorption. It must be noted that the apparent standard rate constant, unlike k_s , varies along the rising portion of the total wave. In the case illustrated by Figure 1 and corresponding to the preferential adsorption of the electrode product, an increase in \bar{i}/\bar{i}_{d} causes the total amount of O and R adsorbed at the electrode surface to grow and consequently the apparent rate constant to decrease. The gradual passage from Brdička prewaves to pseudo-prewaves is confirmed by the experimental finding that in acid solutions (pH ≤ 1) the normal wave of riboflavin, which is a typical example of a substance giving a Brdička prewave, is only slightly reversible.9

There is, however, a class of pseudo-prewaves which is not adequately accounted for by the present treatment. They are due to the irreversible formation of a film of insoluble reaction products which inhibits the electrode reaction more as the current increases. The plateau of these prewaves is reached when the penetration of the reactant through the insoluble film becomes the rate-determining step. "Penetration currents" of this type have been observed during the anodic polarization of dropping mercury electrodes in the presence of compounds forming insoluble mercury salts.¹⁰⁻¹² Possible diagnostic criteria for the distinction between these prewaves and the prewaves of Figure 1, which correspond to the reversible adsorption of the electrode product R, must aim at verifying the irreversibility of film formation. A technique which can be usefully employed in this respect is chronoamperometry at a hanging mercury drop.13

The solid curves in Figure 2 represent some polarographic wave forms obtained from eq 22, 23, 24, and 25 for the same values of α , n, C_0^* , D, t_1 , Γ_m employed in Figure 1, for $K_0 = 10^9$ cm³/mol, $K_R = 10^4$ cm³/mol, and for different values of k_s . In the present case the adsorption of reactant is predominant and the waves corresponding to k_s values $\leq 10^{-1}$ cm/sec exhibit a postwave. A decrease in k_s produces a shift of the normal wave toward more negative potentials with the con-



Figure 2. Ratio $i/\bar{\iota}_d$ of the mean current $\bar{\iota}$, at a given potential E, to the mean diffusion limiting current, $\bar{\iota}_d = nFlC_0^*$, as a function of $E - E_0$. The solid curves a, b, c, d, and e have been derived from eq 22, 23, 24, and 25 for $C_0^* = 10^{-6} \text{ mol/cm}^3$, $D = 10^{-5} \text{ cm}^2/\text{sec}$, $t_1 = 3 \text{ sec}$, $\Gamma_m = 5 \times 10^{-10} \text{ mol/cm}^2$, $K_0 = 10^9 \text{ cm}^3/\text{mol}$, $K_R = 10^4 \text{ cm}^3/\text{mol}$, n = 1, $\alpha = 0.5$, and for k_s values equal to ∞ , 1, 10^{-1} , 10^{-2} , and 10^{-3} cm/sec , respectively. The dashed curves have been derived from eq 28 for the same values of C_0^* , K_0 , K_R , k_s , r, α , and $l/(1/\iota_1 \int_0^{t_1} A dt)$ employed in the calculation of the sold curves partially superimposed to them.

sequence that this wave finishes by merging with the postwave for $k_s > 10^{-1}$ cm/sec. The average slope of the normal wave does not change appreciably with decreasing k_s and only a progressive drawing out of the lower portion of the wave ($0 \leq i/i_d \leq 0.2$) is observed in passing from $k_s = \infty$ to $k_s = 10^{-1}$ cm/sec. The slope reached by the waves of Figure 2 at low k_{s} values is sensibly higher than that exhibited by the waves of Figure 1 corresponding to the same k_{\bullet} values. This fact can be easily explained by considering that in the case of Figure 2 the total amount of the substances O and R adsorbed at the electrode decreases with increasing current. Hence, contrary to the case of Figure 1, the apparent standard rate constant grows while proceeding along the polarographic wave. The steepness of the curves of Figure 2 corresponding to values of $k_{\rm s} \leq 10^{-1} \, {\rm cm/sec}$ increases with $\bar{i}/\bar{i}_{\rm d}$ up to $\bar{i}/\bar{i}_{\rm d} = 0.85$. The disappearance of the postwave when the electrode process with predominant adsorption of reactant becomes sufficiently slow $(k_s < 10^{-1} \text{ cm/sec})$ can probably explain why postwaves preceded by an irreversible normal wave have never been observed.

Several cases are known where polarographic waves due to an electrode process inhibited by adsorption of

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Figure 3. Ratio $\bar{\imath}/\bar{\imath}_d$ as a function of $E - E_0$. The solid curves a, b, c, d, and e have been derived from eq 22, 23, 24, and 25 for $C_0^* = 10^{-6} \text{ mol/cm}^3$, $D = 10^{-5} \text{ cm}^2/\text{sec}$, $t_1 = 3 \text{ sec}$, $\Gamma_m = 5 \times 10^{-10} \text{ mol/cm}^2$, $k_s = 10^{-2} \text{ cm/sec}$, n = 1, $\alpha = 0.5$ and for values of $K_0 = K_R$ equal to 10⁵, 10⁶, 10⁷, 10⁸, and 10⁹ cm³/mol, respectively. The dashed curve represents a reversible polarographic wave in the absence of adsorption. The curves a, b, c, d, and e are practically identical with those derivable from eq 29 for the same values of k_s , n, α , $l/(1/t_1 \int_0^{t_1} A dt)$ and for KC_0^* values equal to 10^{-1} , 1, 10, 10^2 , and 10^3 , respectively.

reactant have a form similar to that of the theoretical curves of Figure 2 with $k_s \leq 10^{-2}$ cm/sec.^{13,14} Thus in buffer solutions in the pH range from 4 to 10 di-(2', 2'') and di-(4', 4'')dipyridyl-1,2-ethylene give cathodic waves which, after an apparently regular start, show a sharp increase in the current.¹³ The slopes of these experimental curves are higher than those of the theoretical curves of Figure 2 but we must recall that these latter curves have been calculated for a constant value of K_0 . If we assumed that the adsorption coefficient of the reactant decreases with a shift of the applied potential toward negative values according to a given law, the theoretical curves derived from eq 22, 23, 24, and 25 would exhibit a higher slope.

If O and R have equal adsorption coefficients, the total amount of these two substances which is adsorbed at the electrode does not change appreciably with applied potential, but only the ratio Γ_0/Γ_R between their surface concentrations varies. In the present case neither prewaves nor postwaves are to be expected. Figure 3 shows a series of polarographic current-potential characteristics calculated from eq 22, 23, 24, and 25 for $C_0^* = 10^{-6} \text{ mol/cm}^3$, $D = 10^{-5} \text{ cm}^2/\text{sec}$, n = 1, $\alpha = 0.5, t_1 = 3 \text{ sec}, \Gamma_m = 5.10^{-10} \text{ mol/cm}^2, k_s = 10^{-2}$ cm/sec and for progressively increasing values of K_0 $= K_{\rm R} \equiv K$. If K is $\leq 10^6$ cm³/mol the apparent standard rate constant practically coincides with the true one, k_s , and the polarographic wave (a) which is obtained is identical with that derivable in the absence of adsorption. It must be noted that this wave is very close to the totally reversible wave $(k_s \rightarrow \infty)$ represented by the dashed curve in Figure 3. An increase in K causes a gradual decrease in the slope of the polarographic wave until, for K values in the range from 10^7 to 10^8 cm³/mol, the minimum slope corresponding to total irreversibility is reached. At this point the wave becomes centro-symmetric. A further increase in K leads only to a progressive shift of the half-wave potential, $E_{1/2}$, toward more negative values.

In the case of diffusion toward a dropping electrode, the rate of change with electrolysis time of the amounts of O and R adsorbed on the growing drop at constant potential is expressed by the second term on the righthand side of eq 23 and 24, respectively. These terms obviously cancel out in the case of diffusion toward a stationary electrode. Since it is the contribution of these terms to the current that determines the appearance of pre- and postwaves in the polarographic wave forms, voltametric curves at a stationary electrode do not exhibit pre- or postwaves. The expression for the current at a stationary electrode is obtained by combining eq 10–13 and 20

$$\bar{i}/(nF) = l(C_0^* - \bar{C}_0) = l\bar{C}_R = \frac{Ak_s}{1 + K_0\bar{C}_0 + K_R\bar{C}_R} \{\bar{C}_0\theta^{-\alpha} - \bar{C}_R\theta^{1-\alpha}\}$$
(27)

where θ is defined by eq 26. From eq 27 the theoretical characteristic is readily derived in an explicit form

$$\frac{i}{nF} = \frac{-b + [b^2 + 4AlC_0^*(K_{\rm R} - K_0)k_{\rm s}\theta^{-\alpha}]^{1/2}}{2(K_{\rm R} - K_0)}$$
(28)

Here $b = l(1 + K_0 C_0^*) + A k_s(\theta^{-\alpha} + \theta^{1-\alpha}).$

The dashed curves in Figures 1 and 2 express voltametric curves at a stationary electrode. They have been derived from eq 28 for the same values of C_0^* , k_* , K_{0}, K_{R}, α , and n employed in the calculation of the solid polarographic curves which are partially superimposed to them. Furthermore, the value of the ratio l/A used for the dashed curves is identical with the value of the analogous ratio $l/(1/t_1 \int_{a}^{t_1} A dt) = 5/3$. $\sqrt{12D/(7\pi t_1)}$ used in the calculation of the corresponding solid curves. From the figure it is evident that the effect of the adsorption of O and R on the charge-transfer process is analogous both at a stationary and at a dropping electrode. In the voltametric curves of Figure 1 corresponding to k_s values $\leq 10^{-1}$ cm/sec the polarographic prewave is replaced by an initial portion characterized by a very slow increase in the current. Within this portion the major part of the complete coverage of the electrode by the electrode product, R, is accomplished. In view of eq 27, if we set $K_0 =$ $K_{\rm R} = K$, the current-potential characteristic at a stationary electrode takes the simplified form

⁽¹⁴⁾ A. A. Podzeeva and S. I. Zhdanov, Proceedings of the 3rd International Polarographic Congress, Southampton, 1946.

$$\frac{\overline{i}}{\overline{i}_{d}} = \frac{Ak_{s}\theta^{-\alpha}}{l(1 + KC_{0}^{*}) + Ak_{s}(\theta^{-\alpha} + \theta^{1-\alpha})}$$
(29)

where $\bar{i}_{d} = nF \ lC_{0}^{*}$ is the mean diffusion limiting current; eq 29 shows that the influence of adsorption of O and R upon the behavior of the theoretical voltametric curves is determined by the value for the product KC_0^* . The curves of Figure 3, calculated for the case of diffusion toward a dropping mercury electrode, are practically identical with those derivable from eq 29 for the same value of $k_s = 10^{-2}$ cm/sec and for KC_0^* values, respectively, equal to 10^{-1} , 1, 10, 10^2 , and 10³. For $KC_0^* \ge 10$ the slope of the voltametric curves remains constant while $E_{1/2}$ continues to decrease with increasing KC_0^* . This is clearly expressed by eq 29, if we note that for sufficiently high shifts of $E_{1/2}$ from E_0 , the term $\theta^{1-\alpha}$ can be neglected with respect to $\theta^{-\alpha}$. Under these conditions eq 29 can be written in the form

$$E = E_0 - \frac{RT}{2.3\alpha nF} \log \frac{\bar{\imath}}{\bar{\imath}_d - \bar{\imath}} + \frac{RT}{2.3\alpha nF} \log \frac{Ak_s}{lKC_0^*} \quad (30)$$

This shows that a tenfold increase in C_0^* produces a shift of the half-wave potential by $60/\alpha n$ mV toward more negative values, provided the voltametric curve has reached the minimum slope corresponding to total irreversibility. If the values of K_0 and K_R differ even by a single order of magnitude, the voltametric curves which are obtained upon exchanging the values of K_0 and K_R , all other parameters remaining unaltered, are characterized by appreciably different slopes, as shown in Figure 4. Owing to the symmetry of the electrode process, such an exchange amounts to substituting R for O in the bulk of the solution.

Many experimental facts, in addition to those previously mentioned, can be adequately interpreted on the basis of the previous treatment, which can be easily extended to other adsorption isotherms as well as to the case of potential dependent adsorption coefficients. Thus many organic compounds give polarographic curves characterized by decreasing slopes and by halfwave potentials shifting toward increasing overvoltages when the concentration of the reactant increases. Such a behavior is typical of several azo compounds. The azobenzene-hydrazobenzene system in a buffer solution at pH 7.25 behaves reversibly on a dropping mercury electrode for overall concentrations of the two species \leq 10^{-5} mol/l.¹⁵ With an increase in the bulk concentration of any of the two species, the system becomes irreversible and the half-wave potentials of the waves given, respectively, by azobenzene and hydrazobenzene shift in opposite directions. Furthermore, the $E_{1/2}$ value for the wave of one of the two species is influenced by the bulk concentration of the other in accord with the



Figure 4. Ratio i/i_d as a function of $E - E_0$. The curves have been derived from eq 28 for the same values of C_0^{\bullet} , n, α , and $l/(1/t_1 \int_0^{t_1} A \, dt)$ employ d in Figures 1, 2, and 3, for $k_s =$ 10^{-3} cm/sec and for values of K_0 and K_R , in cm³/mol, respectively, equal to 10⁷, 10⁵ (curve a), 10⁵, 10⁷ (curve b), 10⁸, 10⁷ (curve c), and 10⁷, 10⁸ (curve d).

fact that the apparent standard rate constant is affected by the surface concentrations of both the forms of the redox system. Analogously the unprotonated form of actinomycin- C_1 and chloroactinomycin- C_1 give reversible cathodic waves on mercury only at concentrations $\leq 5 \times 10^{-4}$ mol/l.^{6,17} At higher concentrations of these substances inhibition effects due to adsorption cause the polarographic waves to become irreversible. Analogous phenomena are encountered at stationary electrodes. Thus, the system Tl^{III}/Tl^{I} in 1 M perchloric acid behaves reversibly at a platinum electrode, platinized for 1 sec at a current density of 1.2 A/cm³ for overall concentrations of thallium lower than 5 \times 10⁻⁵ mol/l.¹⁸ Here too an increase in the concentration of thallium produces a separation of the anodic curve of Tl¹ from the cathodic curve of Tl¹¹¹. The half-wave potentials of these voltametric curves shift toward increasing over-joltages with an increase in the bulk concentration of reactant. Owing to the great tendency of thallium to be adsorbed on platinum,¹⁹ these phenomena can be ascribed to the influence of the surface concentrations of Tl^{III} and Tl^I upon the apparent standard rate constant of the charge-transfer process $Tl^{I} \rightleftharpoons Tl^{III} + 2\vartheta$.

In concluding, the consideration of the influence exerted by the adsorption of the reactant O and of the product R upon the rate of the charge-transfer process leads to the following results. (1) If the adsorption co-

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efficients of O and R are of the same order of magnitude, an increase in the concentration of the reactant O causes a decrease in the slope of the wave until the minimum slope corresponding to total irreversibility is reached. Simultaneously the wave shifts along the potential axis toward more negative values. (2) If the adsorption coefficients of O and R are of different orders of magnitude, besides the above mentioned shift of $E_{1/2}$, an appreciable difference is observed between the slopes of the curves given, respectively, by solutions of O and R of equal concentrations. In this connection the species preferentially adsorbed gives waves with higher slopes.

Further experimental investigations are in progress in this institute in order to point out the influence of adsorption of reactant and electrode products upon polarographic and voltametric curves.

The Adsorption of Dinonylnaphthalenesulfonates

on Metal Oxide Powders¹

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The adsorption of oleophilic rust inhibitors, sodium and barium dinonylnaphthalenesulfonate, from cyclohexane solution on nickel(III) oxide and iron(III) oxide was investigated. Rate data for adsorption of sodium dinonylnaphthalenesulfonate on nickel oxide indicate a complex mechanism of adsorption. An empirical equation was found that accurately describes the data. The log of the uncovered surface plotted against log time was linear. The extrapolated time for 50% coverage was 0.36 min. Experimentally the adsorption process was irreversible. The effect of temperature in the range of 10 to 60° on the adsorption isotherm was negligible. Adsorption isotherm data for sodium dinonylnaphthalenesulfonate were of a Langmuir type. The values of a indicated a more close-packed monolayer on nickel oxide than on iron oxide. The ratio of the molecules per square centimeter for the former and the latter was 1.49. The b values indicated a rather strong interaction at the metal oxide surfaces. Monolayer concentrations were found to be essentially the same irrespective of the salt used.

Introduction

High molecular weight petroleum sulfonates and synthetic sulfonates are receiving increasing military use as corrosion inhibiting additives for lubricants and hydraulic fluids. Dinonylnaphthalenesulfonates, in addition to being excellent corrosion inhibitors, approximate the petroleum sulfonates in structure and rust inhibiting properties and it is reasonable to assume that the adsorption characteristics of the petroleum sulfonates would be similar to the synthetic sulfonates.

Although the mechanism by which alkyl aryl sulfonates function as corrosion inhibitors is still unclear, several investigators have contributed to a better understanding of the corrosion inhibition mechanism by studying parameters affecting adsorption of sulfonate. For example, the presence of water was found to promote adsorption of calcium dinonylnaphthalenesulfonate on steel.² Shropshire recently observed that the degree of adsorption of petroleum sulfonates on calcium carbonate powder was determined by the history or method of preparation of the substrate.³ Smith, Gordon, and Nelson, in a study of the adsorption of calcium dinonylnaphthalenesulfonate at the goldwhite oil interface, have reported that the adsorption is completely reversible and that the adsorbed monolayer is subject to displacement by a polyalcohol and poly(dodecyl methacrylate).⁴ Because of the multiplicity of additives in lubricating fluids, the study of competitive reactions are particularly appropriate. We have found that the rust-inhibitive activity of petroleum sulfonates is affected by the choice of solvent; this indicates that the solvent is a parameter of considerable importance.

The purpose of this study was to investigate the adsorption characteristics of sodium and barium di-

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(3) J. A. Shropshire, J. Colloid Interface Sci., 25, 389 (1967).

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⁽⁴⁾ M. L. Smith, B. E. Gordon, and R. C. Nelson, J. Phys. Chem., 69, 3833 (1965).

nonylnaphthalenesulfonates. Since these materials are used in hydraulic systems that expose the lubricant to metal oxide surfaces, submicron iron(III) oxide and nickel(III) oxide powders were chosen as substrates. A low molecular weight hydrocarbon, cyclohexane, was used as a solvent. This investigation was undertaken to (1) study the rate of adsorption, (2) study the effect of temperature and dilution on desorption of sulfonate, (3) determine the concentration of sulfonate necessary to provide monolayer coverage, and (4) establish whether the adsorbed sulfonate is physisorbed or chemisorbed.

Experimental Section

Materials. The adsorbents (Vitro Laboratories, West Orange, New Jersey) were submicron iron(III) oxide and nickel(III) oxide powders with surface areas of 28 and 30 m^2/g , respectively, as reported by the manufacturer from the BET gas adsorption method. The powders were received in sealed containers. The powders were stored and handled under a nitrogen atmosphere. Cyclohexane (J. T. Baker Chemical Co., Instra-Analyzed grade) was the solvent in the adsorption studies. Batch analysis indicated 99.98% purity with a water content of 0.006%. The absence of polar impurities was periodically confirmed by the nonspreading characteristics of the solvent on a lycopodium seed film on distilled water.

Dinonylnaphthalenesulfonic acid (R. T. Vanderbilt Company, New York, N. Y.) was a 36% solution in heptane. The acid was purified with methanol according to the method reported by Kaufman and Singleterry.⁵ The mixture readily separated into two phases; the upper phase, believed to contain resinous materials, was rejected. The sodium salt was prepared by neutralizing a solution of the acid with an excess of aqueous sodium hydroxide and subsequently backtitrating to the potentiometric end point. The solution was filtered and excess solvent removed by distillation at a reduced pressure. The salt was further purified by extracting its 2-propanol-water solution with petroleum ether. The barium salt was prepared by addition of re-precipitated barium hydroxide to a solution of the purified acid followed by back-titration to the potentiometric end point. Residual solvents were removed from the residue by several additions of cyclohexane during a distillation at reduced pressure. Both salts were dried at 60° and 15 μ . Triplicate analysis indicated that the sodium salt contained $4.73 \pm 0.01\%$ sodium (4.76% theory) and the barium salt contained $13.16 \pm 0.02\%$ barium (13.00% theory).

Adsorption Measurements. The adsorption of sulfonate on metal oxide powders was studied over the concentration range of 0.001 to 0.1%. In the adsorptive isotherm studies, 10 ml of cyclohexane-sulfonate solution was equilibrated with 500 mg of metal oxide in a small glass vial for 96 hr at room temperature. The

mixture was centrifuged; the completeness of the separation was readily ascertained by the Tyndal effect. Although the average particle size for the powder was 0.02μ , ultraviolet analysis within the short wavelength range indicated analytically clean separations. Analytical determinations of equilibrium concentrations were made at 233 and 284 mµ with a Beckman DK-2 recording spectrophotometer with matching 1-cm silica cells. Surface coverage was calculated from the equilibrium concentration data. Data are presented in Table I and Figures 1-6.

	Keg	× 10 ¹⁸
θ^b	Ni ₂ O ₂	Fe ₂ Oa
0.1-0.3	1.08	1.11
0.3-0.5	1.20	1.80
0.5-0.8	1.13	1.11
0.8-0.9	0.85	0.70
	0.57	0.58
0.9-1.0	0.73	0.86
	0.78	0.63

Table I: Calculated Adsorption Equilibrium Values^a for

Sodium DinonyInaphthalenesulfonate

^a Calculated from eq 4 in text. ^b Fractional surface area assuming a value of 1 for a monolayer.

In the study of the rate of adsorption of sodium sulfonate on nickel oxide, the initial concentration of the sulfonate was the minimum amount necessary to assure monolayer coverage on a specified amount of nickel oxide. The rate study was made at room temperature and the procedure was similar to that employed in the adsorption isotherm study. Each point in the rate curve (Figure 1) was determined from an independent sample.

The desorption study was essentially an investigation of the reversibility of the adsorption isotherm for sodium sulfonate on nickel oxide; 50 ml of 0.1984% sodium dinonylnaphthalenesulfonate in cyclohexane was equilibrated with 2.5 g of nickel(III) oxide for 24 hr; 25-ml aliquots were periodically withdrawn (8 to 16 hr) and replaced with an equal volume of pure cyclohexane. This study was made at room temperature. Concentrations of the diluted solution at equilibrium are given as a function of the number of dilutions in Figure 7. The effect of temperature on desorption or further adsorption was studied by a procedure similar to the adsorption isotherm procedure. Samples were equilibrated 2 hr at room temperature followed by 4 hr at various temperatures from 10 to 60°. The extent of the change in surface coverage was determined from identical samples kept at room temperature. The data are discussed later.

(5) S. Kaufman and C. R. Singleterry, J. Colloid Sci., 12, 456 (1957).



Figure 1. Rate of adsorption of sodium dinonylnaphthalenesulfonate on nickel oxide powder at room temperature.



Figure 2. Fraction of surface uncovered vs. log time for the adsorption of sodium dinonylnaphthalenesulfonate on nickel oxide powder.



Figure 3. Adsorption isotherms for sodium dinonylnaphthalenesulfonate on iron and nickel oxide powder.

Results and Discussion

Adsorption Rate. The rapid rate of adsorption of sodium dinonylnaphthalenesulfonate on nickel(III) oxide in cyclohexane prevented measurements at low surface coverage values. The initial measurement at 7 min indicated that 0.88 monolayer was adsorbed, whereas 4 hr was required for the completion of the monolayer. The first value is within or slightly below the knee of the rate curve (Figure 1). The fractional



Figure 4. Adsorption isotherms for barium dinonylnaphthalenesulfonate on iron and nickel oxide powder.



Figure 5. Langmuir plots for the sodium dinonylnaphthalenesulfonate isotherms on nickel and iron oxide powders.



Figure 6. Expanded adsorption isotherms for sodium and barium dinonylnaphthalenesulfonate on iron oxide powder.

monolayer coverage values are slightly misleading since at full surface coverage the molecular packing is such that the long alkyl chains must be oriented perpendicular to the metal surface; however, at lower surface coverage, random orientation of the alkyl side chains is expected. Thus, at a coverage of 0.88 monolayer, the amount of surface available for adsorption is less than expected.

Although the data could not be fitted to any rate equations, an empirical equation was found that accu-



Figure 7. Effect of dilution on the equilibrium concentration of sodium dinonylnaphthalenesulfonate in the presence of nickel oxide.

rately described the data. The logarithm of the uncovered surface was found to vary linearly with the logarithm of time. The calculated time for 50% coverage was 0.36 min for adsorption (Figure 2). A secondorder rate equation would be expected on the basis of the Langmuir adsorption theory; however, the logarithmic nature of the adsorption equation suggests a complex reaction.

The rapid asymptotic approach to a limiting value is probably associated with the low desorption rate of the sulfonate. The surface coverage obtained after 4 hr was within 0.2% of that obtained after 96 hr. In general, the rate curve resembles previously reported curves for similar materials. The rate curve for sodium dodecylbenzenesulfonate at the isooctane-steel interface⁶ was characterized by a rapid approach to a high surface coverage value; however, the asymptotic approach to a limiting value was much slower. The reverse conditions were found by Smith, Gordon, and Nelson⁴ for calcium dinonylnaphthalenesulfonate at the gold-white oil interface. Approximately 100 min was required for complete coverage but only 0.4 monolayer was rapidly asdorbed. This might indicate that the substrate plays an important role in determining adsorption rates.

Adsorption Isotherms. The adsorption isotherms for sodium and barium dinonylnaphthalenesulfonate in cyclohexane were determined on both iron(III) oxide and nickel(III) oxide. These data were normalized by a procedure similar to that used by Shropshire³ in order to correct for variations in molecular weight and for the slight variation in the surface area of the substrates. These normalized data are graphically represented in Figures 3 and 4.

The isotherms for sodium dinonylnaphthalenesulfonate and barium dinonylnaphthalenesulfonate were characterized by a monotonic approach to a limiting adsorption. Adsorption data for sodium dinonylnaphthalenesulfonate on iron and nickel oxide powders were found to follow the Langmuir equation. This is illustrated in Figure 5 where the ratio of the equilibrium concentration to the amount adsorbed is shown to be a linear function of the equilibrium concentration. The classical Langmuir equation can be expressed as

$$\frac{C}{x/m} = \frac{1}{ab} + \frac{C}{a} \tag{1}$$

where C is the equilibrium concentration, x/m is the amount adsorbed per unit area, a is the maximum adsorption possible, and b is the ratio of the rate constants for adsorption and desorption. When the area of the substrate is known, a is a measure of the surface area occupied per molecule. The value of a was found to correspond to $68.4 \text{ Å}^2/\text{molecule}$ for the sodium salt on nickel oxide and 109.1 $Å^2$ /molecule for the sodium salt on iron oxide. It can be shown that these values correspond to a monolayer coverage. Reported data for the force-area relationship of calcium dinonylnaphthalenesulfonate4-7 at the air-water interface has shown that the monomolecular film was of the liquid-expanding type. The maximum area per molecule was 200 $Å^2$; the minimum area for a tightly packed film was 125 Å² at 40 dyn/cm. It is reasonable to assume that the monovalent salt would occupy an area approximately half that of the divalent salt or an area of 62 to 100 Å² per molecule. Projections of Fisher-Hirschfelder-Taylor models of the dinonylnaphthalenesulfonate anion indicate that this assignment is reasonable. A study of the molecular models indicates that random orientation of the alkyl side chains probably predominates at low film pressures with the chains assuming a more oriented configuration with increasing pressure. Thus, the molecular packing of sodium dinonylnaphthalenesulfonate on nickel(III) oxide can be considered as close-packed, whereas the molecular packing on iron(III) oxide denotes a rather loosely packed monolayer. It is interesting to note that Smith and Allen⁸ found a similar type of behavior for the adsorption of *n*-nonadecanoic acid at the nickeland iron-cyclohexane interfaces. Molecular packing was considerably more close-packed on nickel than on iron.

The b term in the Langmuir equation expresses the ratio of the rate constants and has the dimensions of reciprocal concentration. The b value for sodium dinonylnaphthalenesulfonate was found to be 0.74×10^{-16} cm³/molecule for iron(III) oxide and 0.91×10^{-16} cm³/molecule for nickel(III) oxide. A slightly different mathematical treatment was employed to compare adsorption data for sodium dinonylnaphthalenesulfonate with that for barium dinonylnaphthalene-

- (7) F. M. Fowkes, J. Phys. Chem., 66, 1843 (1962).
- (8) H. A. Smith and K. A. Allen, ibid., 58, 449 (1954).

⁽⁶⁾ A. H. Roebuck, P. L. Gant, O. L. Riggs, and J. D. Sudburry, Corrosion, 13, 733 (1957).

sulfonate. According to Laidler,⁹ the rate of adsorption (γ_a) can be expressed as

$$\gamma_{a} = k_{1}C_{g}C_{s} \qquad (2)$$

and the rate of desorption (γ_d) as

$$\gamma_{\rm d} = k_{\rm -l} C_{\rm a} \tag{3}$$

where C_g is the equilibrium concentration in solution (molecules/cm³), C_s is the concentration of adsorption centers (sites/cm²), and C_s is the concentration of adsorbed molecules (molecules/cm²). The equilibrium condition is given by equating these two rates

$$\frac{C_{a}}{C_{g}C_{s}} = \frac{k_{1}}{k_{-1}} = K_{eq}$$
(4)

where K_{eq} is an equilibrium constant for the system. The assumption was made that C_s was equal to the maximum number of molecules adsorbed per cm² less the number of molecules adsorbed per cm² at a given equilibrium concentration. These values are presented in Table I. Equilibrium constants at low surface coverage (less than 0.8 monolayer) were greater than the values at higher surface coverages. This can probably be attributed to initial adsorption at the most active sites or to the variety of spacial configurations available to an adsorbed molecule at low surface coverage. For example, the molecule could adsorb in a flat position and interact with a large number of sites. The heat of adsorption in the flat position would be larger than expected when the molecule is in a vertical configuration. The calculated equilibrium values (K_{eq}) are of the same order of magnitude as those calculated from the Langmuir equation. The slight discrepancy can be attributed to the assumption envolved in the calculation of C_{s} .

The adsorptive behavior of the barium salt differs considerably from the sodium salt in the region below the knee of the adsorption isotherm curve. This is illustrated in the expanded adsorption isotherms of sodium and barium dinonylnaphthalenesulfonate on iron(III) oxide (Figure 6). Data for the dinonylnaphthalenesulfonates on nickel(III) oxide are not included; however, graphic representation of these data is similar to those shown in Figure 6. The greater "adsorption" of the divalent cation is difficult to explain. The larger coordination sphere of the divalent cation might allow greater interaction with surface hydroxyl groups. Another possible explanation may be related to the stability and size of the barium and sodium dinonylnaphthalenesulfonate micelles. Kaufman and Singleterry^{5,10} have reported differences in the micellar nature of these materials.

Molecular packing in the completed monolayer was found to be a function of the substrate; however, the cation does not appear to influence molecular packing. On nickel oxide, the monolayer concentrations were

 $1.12 \pm 0.02 \text{ mg} (\text{DNNS})^{-/\text{m}^2}$ and $1.07 \pm 0.04 \text{ mg}$ $(DNNS)^{-}/m^{2}$ for the sodium and barium salts, respectively. Slightly better agreement was obtained on iron oxide. The monolayer concentrations were 0.75 \pm 0.01 and 0.74 \pm 0.03 mg (DNNS)⁻/m² for the sodium and barium salts, respectively. This suggests that the monolayer might be considered as a close-packed array of anions with the cation in close proximity to provide electrical neutrality. The density of the packing indicates that the anions are in a configuration perpendicular to the surface. This configuration would allow maximum overlap of the filled p orbitals of the oxygen with vacant d orbitals of the metal atoms on a clean metal oxide surface. Interatomic distances for nickel metal are known to be 2.49 and 3.52 Å. It is interesting that the first value approximates the spacing in the sulfonate group itself. Other possible mechanisms for adsorption might include interaction of adsorbed water or surface hydroxyl groups with the coordination sphere of the cation or direct interaction of oxygen sites with the cation.

When determinations of monolayer concentration were made in relatively concentrated solutions, a slight but gradual decrease in the amount adsorbed was noted. The accuracy of these values is open to question since the sensitivity of the method decreases with increasing concentration; however, others¹¹ have noted a maximum in the adsorption isotherm for sodium dodecylbenzenesulfonate on nickel.

Effect of Temperature. The temperature dependence of the adsorption data for sodium dinonylnaphthalenesulfonate on nickel oxide was determined for possible elucidation of the interaction at the metal oxide surface. For example, if the data showed a strong dependence on temperature, it would be reasonable to attribute adsorption to van der Waals forces or other interactions such as intermolecular cohesion or hydrogen bonding to surface hydroxyl groups. (Chemically bound water appearing as hydroxyl groups on α -Fe₂O₃ surfaces is suggested by the work of Jurinak.¹²) At elevated temperatures of 45 and 60°, no detectable desorption was found at a surface coverage of 0.28 monolayer. At 60°, the amount desorbed at surface coverage of 0.95 and 1.00 monolayer was 1.1 and 1.4%, respectively. The data support a monolayer consisting essentially of chemisorbed species. The data are reasonable when the micellar nature of sodium dinonylnaphthalenesulfonate is considered. In effect, the metal oxide and micelle are both competing for adsorption of the monomer, and in the absence of a strong interaction at the

(12) J. J. Jurinak, J. Colloid Sci., 19, 477 (1964).

⁽⁹⁾ K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, p 150.

⁽¹⁰⁾ S. Kaufman and C. R. Singleterry, J. Colloid Sci., 10, 139 (1955).

⁽¹¹⁾ A. Fava and H. Eyring, J. Phys. Chem., 60, 890 (1956).

metal oxide surface, the monomer would be expected to re-enter the micelle phase.

Although the interaction at the metal oxide surface would be better evaluated by data on the isosteric heat of adsorption, the magnitude of the changes in concentration did not warrant exact calculations. Rough calculations indicated that the heat of adsorption was of the same order of magnitude as that found with chemical reactions.

Desorption Studies. The reversibility of the sodium dinonylnaphthalenesulfonate-nickel(III) oxide isotherm was investigated at room temperature (Figure 7). The initial amount of material adsorbed corresponded to full monolayer coverage and each dilution represented withdrawal of one-half of the volume of the supernatant liquid and the replacement with the same volume of clean cyclohexane. The equilibrium period was 24 hr; withdrawals were made after equilibration periods of 8 to 16 hr.

No significant desorption was found after six successive dilutions. This data indicate the absence of a significant fraction of easily desorbable sulfonate in the monolayer. Desorption undoubtedly must occur in order to reestablish equilibrium conditions; thus, the rate of desorption must be extremely slow. In order to better evaluate the rate of desorption, one equilibrium period was extended to 64 hr; however, no detectable desorption was noted.

Structural Considerations. Dinonylnaphthalenesulfonic acid is prepared by alkylation of naphthalene with nonene-1 which is made by the trimerization of propylene. Smith, et al.,4 reported that dinonylnaphthalene is greater than 95% dialkylated and that the two nonyl groups are substituted in the same ring, which is different from that containing the sulfonate group. The sulfonic acid group is probably in an α position in view of the low temperature of sulfonation. Factors affecting the structure of the alkyl side chains include (1) the method of preparation of the nonenes (6 possible branch chained isomers) and (2) isomerization. The latter reaction is known to prevail in this type of alkylation¹³ and attachment of the alkyl group would be expected at a tertiary carbon. Consideration of the structure of the nonene isomers and their most probable point of attachment indicates that the alkyl side chains are rather short and very highly branched. The structure of dinonylnaphthalenesulfonate may be more closely related to its corrosion-inhibiting ability than normally realized.

(13) A. C. Olson, Ind. Eng. Caem., 32, 833 (1960).

On the Transfer Mechanism of Uranium(VI) and Plutonium(IV) Nitrate

in the System Nitric Acid-Water/Tributylphosphate-Dodecane

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Using the single-drop method as experimental technique, the initial transfer rates of uranium(IV) and plutonium(IV) have been determined between aqueous nitrate or nitric acid and TBP dissolved in dodecane. The results of kinetic measurements have been interpreted in terms of chemical interface reactions. As soon as the metal enters the interface either in ionic or neutral form it is an interfacial complex which adds TBP molecules by degrees from the organic phase as well as nitrate anions from the aqueous phase. No evidence exists of a distinct sequence in the addition of the ligands; that means that the TBP reacts not only with the neutral metal compound but also with the ionic species. The interfacial complexes cannot be distinguished according to the phase they came from. Equilibrium is obtained by a dual transformation of the interfacial complexes either to the organic or to the aqueous phase and not by two reactions running independently in opposite directions.

Introduction

The first studies of mass transfer in the system uranium(VI)-HNO₃/TBP (tributylphosphate) diluted in hydrocarbons have been carried out by Hahn.² He followed the nonsteady-state system coming to equilibrium and found agreement with pure diffusion processes. Lewis^{3a} and then Burger^{3b} used the stirred-cell method to elucidate the transfer effects at the interface. Both authors found a steady decrease of the transfer coefficient during the approach to equilibrium. From this Burger proposed a steady change of mechanism during the process of extraction. Our work was undertaken to examine further the influence of a chemical reaction at the interface on the speed of mass transfer. The idea of a chemical resistance can be shown to be likely by setting up the chemical equation for the extraction process. Burger could not assign the resistance to a

$$UO_2^{2+} + 2NO_3 + 2TBP \longrightarrow UO_2(NO_3)_2 \cdot TBP_2$$
$$Pu^{4+} + 4NO_3^- + 2TBP \longrightarrow Pu(NO_3)_4 \cdot TBP_2$$

chemical process because the rate of mass transfer was still dependent on the stirring speed. Kinetic predictions can be examined more easily by using the initial reaction rates. This still applies to the extraction process where the state of equilibrium is caused by a superposition of the forward extraction and the reverse strip reaction.

A method particularly suited for the determination of the initial rates is the single-drop method in a technique described by Nitsch.⁴⁻⁶ The drop method has been applied already in recent years to the extraction of uranium(VI) with TBP.^{7,8} In these cases, however, the results were interpreted with hydrodynamical models and not according to chemical reaction. Furthermore, these experiments were not detailed enough with respect to concentration dependences for conclusions to be made about chemical kinetics.

Experimental Section

The solutions of TBP and dodecane were prepared by weighing distilled TBP and dodecane. The solutions were treated several times with a solution of 10%sodium carbonate and washed with distilled water. Metallic plutonium was dissolved in HCl and precipitated using H₂O₂. The precipitate was washed with 1 N HNO₃ and 2 N H₂O₂ until the washings proved to be free of chloride ions. Then the precipitate was dissolved in concentrated HNO₃ at 80–90°. Aqueous and organic solutions were prepared from the aqueous stock solution by dilution and extraction. Other chemicals used were all analytical grade.

 $\rm HNO_3$ and uranium in concentrations exceeding 10 μ mol/ml were titrated potentiometrically by a method described by Motojima and Izawa.⁹ Uranium concentrations below 10 μ mol/ml were determined by a photometric procedure¹⁰ with dibenzoylmethane. Plutonium was determined by α -counting in nitric acid solutions by a method given by Bähr and Thiele.¹¹ Figure 1 shows the basic features of the experimental

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- (10) C. A. Francois, ibid., 30, 50 (1958).

⁽¹⁾ Part of a thesis submitted by L. Finsterwalder to the Technical University of Munich in partial fulfillment of the requirements for the degree Ph.D.

 ⁽²⁾ H. T. Hahn, US-Report HW-32626 (1954); J. Amer. Chem. Soc., 79, 4625 (1957).

 ^{(3) (}a) J. B. Lewis, AERE CE/3-1366 (1956), Nature, 178, 274 (1956);
 (b) L. L. Burger, HW-62 087 (1959).

⁽⁴⁾ W. Nitsch, Dechema Monograph., 55, 1965.

⁽⁵⁾ W. Nitsch, Z. Elektrochem., 69, 884 (1965).

⁽⁶⁾ W. Nitsch, *Chem. Ing. Tech.*, **38**, 525 (1966). Nitsch investigated the extraction of carbonic acids in the system CCl_4-H_4O . He found the rate of transfer to the drops was controlled solely by a chemical reaction at the interface.

⁽⁷⁾ H. A. C. McKay and D. Rees, AERE-CIR-1199 (1953).

⁽⁸⁾ W. Knoch, and R. Lindner, Z. Elektrochem., 64, 1020 (1960).

⁽¹¹⁾ W. Bähr and D. Thiele, KFK-499, KFK-503 (1966).



Figure 1. Experimental setup.

setup similar to that of Nitsch.⁴ The primarily unloaded drops pass up or down through the loaded continuous phase. Overall mass transfer is determined by chemical analysis of a 5-cc drop sample. Transfer area is calculated assuming drops as perfect spheres. Unwanted mass transfer during formation and breakup of drops is eliminated by runs with different throughputs. The overall mass transfer per unit area is plotted vs. the reciprocal throughput and extrapolated to infinite throughput. At infinite throughput, formation time of drops is zero and, therefore, side effects are eliminated. This procedure was repeated with four different contact paths to produce a time-mass transfer plot. The initial slope of the curve represents the initial reaction rate which is entered into the double logarithmic graph.

Results and Discussion

The experimental results of the forward and reverse extraction are shown in Figures 2-5. The forward reaction of uranium (aqueous to organic), Figure 2, does not exhibit a first-order reaction with respect to the metal concentration according to the nominal eq 1

$$M_{ag}^{n+} + nX + 2TBP \longrightarrow MX_n TBP_2 \qquad (1)$$

$$MX_n TBP_2 \longrightarrow M_{aq}^{n+} + nX^- + 2TBP \qquad (2)$$

In addition, the diverging lines show an influence of the TBP concentration on the reaction order of the metal. The initial rates of the back extraction which is a dissociation described by eq 2 depend on the free TBP and nitrate concentration. The rates tend to a maximum transfer rate when either the free TBP or the nitrate concentration goes to zero. Experiments with and



Figure 2. Initial transfer rates of U(VI) from an aqueous phase of 3 N nitric acid into 20, 10, and 5% TBP.



Figure 3. Calculated and experimental transfer rates of U(VI) from an organic phase of 20, 10, and 5% TBP into an aqueous solution of 0.1, 1.5, and 3 N nitrate.



Figure 4. Calculated and experimental transfer rates of Pu(IV) from an organic phase of 20, 10, and 5% TBP into an aqueous solution of 3 N nitric acid.

without HNO_3 in the organic phase showed no significant differences because the transfer speed of HNO_3 is about one order of magnitude higher than that of the U and Pu. Thus, the HNO_3 complexed TBP in the organic phase was considered to be effectively free TBP.

Plutonium extraction experiments have been conducted at acid concentrations ranging from 0.8 to 3 N HNO₃. However, strip experiments were limited to an aqueous solution of 3 N HNO₃ in order to avoid hydrolysis and polymerization of plutonium(IV). Furthermore, experiments with an organic phase concentration exceeding approximately 0.1 M plutonium are hampered by formation of a third phase. (The similarities between the plutonium and uranium plots perhaps indicate a similar course even beyond the measurable range.)

A key to the understanding of the transfer mechanism is offered by the organic to aqueous transfer reaction which we will call the reverse reaction. According to the nominal eq 2 the initial rates should only depend on the metal concentration in the organic phase

$$v = k_{\rm a}({\rm MX}_n \,{\rm TBP}_2) \tag{3}$$

Experiments show, however, that the rate is decreased by the presence of nitrate or nitric acid in the aqueous phase and by unbound TBP in the organic phase

$$\overline{v} = k_{a}(MX_{n} TBP_{2})F^{-1}(NO_{3}^{-}, TBP) \qquad (4)$$



Figure 5. Calculated and experimental transfer rates of PuIV in 3 N nitric acid into 20, 10, and 5% TBP.



Figure 6.

In order to make the rate equation fit the experimental data, one has to assume an additional reaction opposing the reverse reaction. This opposing reaction is controlled by components of both phases, so we may conclude that this opposing reaction takes place at the interface.

Let us call the chemical species which is located at the interface an interfacial complex (IFC). Of course the IFC means, probably, several complexes with different numbers of nitrato and TBP ligands attached to the metal ion. It is possible to withdraw the IFC in two directions from the interface: one way causes transfer to the organic phase and the other to the aqueous phase.¹² It can be assumed that the IFC is the same, independent of the phase from which it has come to the interface. The opposing step starts already at the very beginning of the extraction process when still no solute is transferred to the other phase but only the interface is loaded. The reverse extraction, however, increases

(12) A. A. North and R. A. Wells, Bull. Inst. Mining Met., 702, 484 (1965).

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with buildup of solute in the initially unloaded phase. Thus the opposing step can be compared to the desorption step in a cycle of absorption and desorption at the interface. As a result, the kinetic equation of one direction must include terms describing the kinetics of the opposite direction (Figure 6).

The concentration of the IFC, an essential part of the rate equation according to this model, can be derived using a modified Langmuir's adsorption isotherm. In our case we have to take into account that the with-drawal of the IFC from the interface takes place with different probabilities f_a and f_o into the aqueous and organic phase.

The interface concentration $N_{\rm IFC}$ of the initial transfer rate considered here is obtained from the balance between entry into the interface $kc(1 - N_{\rm IFC})$ from one direction and the withdrawal from the interface into both phases $(f_a + f_o)N_{\rm IFC}$

$$N_{\rm IFC} = \frac{kc}{f_{\rm a} + f_{\rm o} + \sigma ck} \tag{5}$$

where the units are f, (1/sec); σ , effective cross-section (cm^2/mol) for entry from the aqueous or organic phase; k, probability of entrance from the aqueous or organic phase into the interface (cm/sec); and c, metal concentration in the aqueous or organic phase $[\text{mmol/cm}^3]$.

The step from the interface into the aqueous phase has to be a dissociation and the step into the organic phase an association. The probability of dissociation f_a can be regarded to be independent of TBP and nitrate concentration. Experimental results show that the probability of association, f_o , is dependent on the square of the TBP concentration

$$f_{\rm o} = \operatorname{const} \, (\mathrm{TBP})^2 (\mathrm{NO}_3^{-})^x \tag{6}$$

According to experimental results, the nitrate participates in uranium and plutonium extraction with different reaction orders x. For the uranium extraction we found a mean reaction order x = 1.75 and about x =2.5 for plutonium. This was the result of additional transfer measurements from 0.82 N and 1.5 N HNO₃ beside the 3 N HNO₃ experiments. This difference to the nominal values of 2 and 4, respectively, seems to arise from the different dissociation states of the ionic species. The disagreement with recently published exact second-order dependence of nitrate in uranium extraction may be caused by the low nitrate concentration used by those authors.¹³

Utilizing the experimental result (6) in connection with (5) yields the kinetic equation for the initial forward reaction rate: (A = area of interface)

$$\vec{v}(t=0) = \frac{1}{A} \frac{d\vec{m}}{dt} = f_0 N_{IFC} = const(TBP)^2 (NO_3^{-})^2 (N_{IFC})$$

$$= \frac{\frac{\text{const}}{f_{a}}(\text{TBP})^{2}(\text{NO}_{3}^{-})^{z}k_{a}c_{a}}{1 + \frac{\text{const}}{f_{a}}(\text{TBP})^{2}(\text{NO}_{3}^{-})^{z} + \frac{k_{a}\sigma_{a}}{f_{a}}c_{a}}$$
(7)

Correspondingly, the initial equation of the reverse reaction is

$$\overline{v}(t=0) = \frac{1}{A} \frac{\mathrm{d}m}{\mathrm{d}t} = f_{a}(N_{\rm IFC}) = \frac{k_{o}c_{o}}{1 + \frac{\mathrm{const}}{f_{a}}(\mathrm{TBP})^{2}(\mathrm{NO}_{3}^{-})^{x} + \frac{k_{o}\sigma_{o}}{f_{a}}c_{o}} \quad (8)$$

From the experimental results of the plutonium back extraction into 3 N HNO: (Figure 4) the following values for eq 8 can be derived by trial and error technique

$$\dot{v}(t=0) = \frac{8.0 \times 10^{-3} (\text{Pu})_{o}}{1 + 35.0 \text{TBP}^{2} + 7.1 (\text{Pu})_{o}} (\text{mmol/cm}^{2} \text{ sec})$$

The agreement of this empirical equation with the experimental data of plutchium is shown in Figure 4. The experimental data for uranium back extraction from the organic phase into a solution of 3 N and 1.5 N NaNO₃ (Figure 3) can be represented also in a satisfying way by eq 8 with the constants

3 N NaNO₃:
$$\overline{v}(t=o) = \frac{5.86 \times 10^{-3}(U)}{1+190(TBP)^2+10.6(U)}$$

1.5 N NaNO₃: $\overline{v}(t=o) = \frac{5.86 \times 10^{-3}c}{1+24(TBP)^2+10.6(U)}$

In the case of negligible TBP or NO_3^- concentration, eq 8 reduces to

$$\dot{\overline{v}}(t=\mathbf{o}) = \frac{k_{\mathbf{o}}c_{\mathbf{o}}}{1 + \frac{K_{\mathbf{o}}\sigma_{\mathbf{o}}}{f_{\mathbf{a}}}c_{\mathbf{o}}}$$
(9)

This maximum transfer rate has also been plotted in Figure 3 (0.01 N NO₃⁻). In the case of plutonium, this maximum rate cannot te checked experimentally because of hydrolysis. As mentioned above, a calculation of the reaction rate of th \exists forward extraction from data gained from the reverse extraction should be possible with eq 7 and would be a confirmation for the model used here.

For this calculation additional knowledge of the diffusion probabilities of entrance k and of the cross section σ is necessary. As a first approximation we put $\sigma_{aq} = \sigma_{org}$ and $k_{aq} = k_{org}$. There are reasons to do so; to become an IFC, the crganic complex necessarily has to enter the interface with its hydrophilic end. Fur-

(13) A. I. Yurtov and A. V. Nikolaev, Russ. J. Phys. Chem., 41, 705 (1967).

thermore, the cross section of the IFC will be determined more or less by the area occupied by the butyl ligands. Finally, the effective molecular weight of the ionic complex with its coordinated water should be similar to the molecular weight of the organic complex.

With these assumptions, the initial rates for the forward reaction of plutonium from $3 N \text{ HNO}_3$ can be calculated by using (7). The constants are

$$\frac{\text{const}}{f_{a}} k_{a} (\text{NO}_{3}^{-})^{x} = 280 \times 10^{-3} (\text{cm}^{7}/\text{mmol}^{2}\text{sec})$$
$$\frac{\text{const}}{f_{a}} (\text{NO}_{3}^{-})^{x} = 35.0 (\text{cm}^{6}/\text{mmol}^{2})$$
$$\frac{k_{a}\sigma_{a}}{f_{a}} = 7.1 (\text{cm}^{3}/\text{mmol})$$

The agreement with experimental data is surprisingly good as is shown in Figure 5. The extraction experiments of uranium with TBP show a reaction order for uranium exceeding 1 in the linear range (Figure 2), but our simple adsorption-desorption model yields only a first-order reaction of the metal. This deviation suggests additional to the nitrate or TBP reaction the possibility of exchange reactions between the association from the bulk phases with single IFCs such as

$$UO_{2}NO_{3}TBP^{+} + UO_{2}NO_{3}TBP_{2}^{+} \longrightarrow$$
$$UO_{2}(NO_{3})_{2}TBP_{2} + UO_{2}TBP^{++}$$
$$UO_{2}(NO_{3})_{2}TBP + UO_{2}NO_{3}TBP_{2}^{+} \longrightarrow$$
$$UO_{2}(NO_{3})_{2} + UO_{2}NO_{3}TBP^{+}$$

This additional mechanism of organic complex formation might present an explanation of the enhanced transfer velocities of uranium compared to those of plutonium. Generally speaking, exchange reactions at the interface might also be the cause for some synergisms unexplained up to now.

Acknowledgments. We are indebted to Mr. G. Höffle and T. Fritsch for experimental assistance.

Cross-Phenomenological Coefficient. XII.

Kinetic Theory of Nonlinear Transport Processes

in Nonuniform Gases

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The theory of Chapman and Cowling for nonuniform gases involving third approximation to the distribution function has been examined to understand the departures from linear phenomenological equations. It is found that terms containing products of gradients and higher order space derivatives of barycentric velocity appear in transport equations but higher powers of a single force do not occur. The second-order terms are negligible in the transport equation for mass flux as well as energy flux. Tensorial character of nonlinear transport equations obtained by Taylor-type expansion has also been examined.

Introduction

The state of a gas is characterized by the distribution function f which depends on the peculiar velocity, the radius vector, and the time t. The kinetic processes can be understood provided the time dependence of fcan be explicitly characterized.¹ For a stationary gas the distribution function is Maxwellian and is denoted by f^0 . In a nonstationary situation the distribution function can be written as²

$$f = f^{0}(1 + \phi^{(1)} + \phi^{(2)} + \dots)$$
 (1)

where $f^0 \phi^{(1)}$ and $f^0 \phi^{(2)}$ are, respectively, the second and third approximation to the distribution function. In the first approximation, $f = f^0$. Kinetic derivation of transport equations is not possible using the first

⁽¹⁾ I. Prigogine, "Nonequilibrium Statistical Mechanics," Interscience, New York, N. Y., 1962.

^{(2) (}a) S. Chapman and T. G. Cowling, "The Mathematical Theory of Nonuniform Gases," Cambridge University Press, Cambridge, 1960. Unless stated otherwise, all notations in this paper conform to this reference. (b) S. Chapman and T. G. Cowling, *Proc. Roy. Soc.*, A179, 159 (1941).

approximation. One can deduce the linear transport equations for mass flux and energy flux when f is put equal to $f^{0}(1 + \phi^{(1)})$. Such linear transport equations have considerable importance in the framework of thermodynamics of irreversible processes. When f is expressed as $f^{0}(1 + \phi^{(1)} + \phi^{(2)})$ the transport equations for mass flux are found to be nonlinear.³

In several phenomena, it is found that transport processes are nonlinear.⁴⁻⁶ From the analysis of the experimental data on thermal transpiration of gases, Hanley and Steele find that the maximum second-order effects are found in the slip region of isothermal flow.⁶ Factors responsible for deviation from linearity have been examined in recent communications.^{5,6} It is desirable to develop and examine the kinetic theory of nonlinear transport processes in order to understand the origin of second and higher order terms. This has been attempted in the present communication. The interaction of heat flow and mass flow in a nonuniform gas has been specially chosen for detailed investigation since the theory for such a case is comparatively well understood. We shall follow Chapman-Enskog theory, the limitations of which are (1) the theory is applicable to fairly dilute gases since only binary collisions are considered; (2) the applicability of the theory is limited to monoatomic gases since molecular collisions are considered to be elastic, which implies that (a) only translational energy of molecules is taken into account and that (b) only spherically symmetric molecules are to be considered; and (3) molecular collisions are described by classical mechanics.

The kinetic theory of gases containing molecules having internal states has also been developed recently.^{7,8} The Chapman-Enskog method has been used to obtain estimates for the coefficients of diffusion, thermal diffusion, and thermal conductivity for a dilute gas composed of two species of loaded sphere molecules.³ Since our object is mainly to examine and understand the factors causing departures from linear transport equations, our discussion will be confined to simple Chapman-Enskog theory.

Mass Flux and Energy Flux Using Third Approximation to Distributiom Function

The third approximation for a simple gas has been worked out by Burnett¹⁰ while that for mass flux in a mixed gas has been investigated by Chapman and Cowling. The equation for mass flux $\vec{J}_{\rm M}$ is given by

$$\vec{J}_{M} = \frac{m_{1}\rho_{2}}{\rho} \int f_{1}^{0} (1 + \phi_{1}^{(1)} + \phi_{2}^{(2)}) \vec{C}_{1} dc_{1} - \frac{m_{2}\rho_{1}}{\rho} \int f_{2}^{0} (1 + \phi_{2}^{(1)} + \phi_{2}^{(2)}) c_{2} dc_{2} \quad (2)$$

In a similar manner it can be shown that \vec{J}_{U} for a mixed gas would be given by

$$\vec{J}_{U} = \int f_{1}^{0} (1 + \phi_{1}^{(1)} + \phi_{1}^{(2)}) \left[\frac{m_{1}C_{1}^{2}}{2kT} - \frac{5}{2} \right] \vec{C}_{1} dc_{1} + \int f_{2}^{0} (1 + \phi_{2}^{(1)} + \phi_{2}^{(2)}) \times \left[\frac{m_{2}C_{2}^{2}}{2kT} - \frac{5}{2} \right] \vec{C}_{2} dc_{2} \quad (3)$$

where $\vec{J}_{U} =$ heat flux relative to mean velocity \vec{C} , ρ_{1} and $\rho_{2} =$ molecular densities of species 1 and 2, $\rho =$ molecular density of the mixture, m_{1} and $m_{2} =$ molecular masses of species 1 and 2, and dc_{1} and $dc_{2} =$ elementary volumes in the velocity space of species 1 and 2. The subscripts 1 and 2 denote the quantities corresponding to species 1 and 2. Further

$$\phi_1^{(1)} = -\vec{A}_1 \frac{\partial \ln T}{\partial \vec{r}} - n\vec{D}_1 \vec{d}_{12} - \mathbf{B}_1: \frac{\partial}{\partial \vec{r}} c_0$$

and

$$\phi_2^{(1)} = -\vec{A}_2 \frac{\partial \ln T}{\partial \vec{r}} - n\vec{D}_2 \vec{d}_{21} - \mathbf{B}_2: \frac{\partial}{\partial \vec{r}} \vec{c}_0$$

Now we will develop explicit expressions for \vec{J}_{M} and \vec{J}_{U} in terms of forces using third approximation to the distribution function. On suitable transformation, eq 2 and 3 can be written

$$\vec{J}_{M} = L_{MM}\vec{X}_{M} + L_{MU}\vec{X}_{U} + L_{MUS}\vec{X}_{U}X_{S} + L_{MMS}\vec{X}_{M}X_{S} + L_{M\epsilon U}X_{a}\vec{X}_{U} + L_{MM} \ _{a}\vec{X}_{M}X_{a} + L_{MUV}\vec{X}_{U}X_{V} + L_{MMV}\vec{X}_{M}X_{V} + L_{MPV}\vec{X}_{P}X_{V} - \left(\frac{2}{3}\frac{\rho_{1}\rho_{2}}{\rho}\right)D_{e} \ \mathrm{grad} \ X_{S} - \left(\frac{\rho_{1}\rho_{2}D_{i}}{\rho}\right)\frac{\partial}{\partial\vec{r}} \ X_{V} \quad (4)$$

and

$$\vec{J}_{U} = L_{UM}\vec{X}_{M} + L_{UU}\vec{X}_{U} + L_{UUS}\vec{X}_{U}X_{S} + L_{UMS}\vec{X}_{M}X_{S} + L_{Ua}UX_{a}\vec{X}_{U} + L_{UM}a\vec{X}_{M}X_{a} + L_{UUV}\vec{X}_{U}X_{V} + L_{UM}V\vec{X}_{M}X_{V} + L_{UP}V\vec{X}_{P}X_{V} - \frac{2}{3}kTE_{o} \text{ grad } X_{S} - kTE_{i}\frac{\partial}{\partial\vec{r}}X_{V} \quad (5)$$

where X's represent the force and L's the phenomenological coefficients in the terminology of thermody-

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$\vec{J}_{M} \text{First} \qquad \vec{X}_{M} \qquad \text{Vector} \qquad L_{MM} = \frac{nD_{1,2}}{n_{1}n_{2}} \left(\frac{\rho_{1}\rho_{2}}{\rho}\right)^{2} \cdot \frac{1}{kT}$ Second $\vec{X}_{U} \qquad \text{Vector} \qquad L_{MU} = \frac{n^{2}D_{T}}{n_{1}n_{2}} \left(\frac{\rho_{1}\rho_{2}}{\rho}\right)^{2}$ Third $X_{B}\bar{X}_{U}$ Scalar vector $L_{MUB} = \frac{\rho_{1}\rho_{2}}{\rho} \left[\frac{4}{3} D_{e} - D_{a}\right]$ Fourth $\bar{X}_{M}X_{B}$ Scalar vector $L_{MMB} = \left(\frac{\rho_{1}\rho_{2}}{\rho}\right)^{2} \cdot \frac{1}{nkT} \left[D_{b} - \frac{2}{3} D_{4}\right]$ Fifth $X_{B}\bar{X}_{U}$ Axial-vector $L_{KBU} = \frac{\rho_{1}\rho_{2}}{\rho} \cdot 2D_{e} \cdot T$ vector Sixth $X_{B}\bar{X}_{M}$ Axial-vector $L_{MUV} = \frac{\rho_{1}\rho_{2}}{\rho} \cdot 2D_{e} \cdot T$ Seventh $\bar{X}_{U}X_{V}$ Vector second- $L_{MUV} = \frac{\rho_{1}\rho_{2}}{\rho} T[D_{a} - 2D_{c}]$ order tensor Eighth $\bar{X}_{M}X_{V}$ Vector second- $L_{MMV} = \left(\frac{\rho_{1}\rho_{2}}{\rho}\right)^{2} \cdot \frac{1}{nkT} [D_{t} + D_{e} - 2D_{d}]$ Ninth $\bar{X}_{P}X_{V}$ Vector second- $L_{MPV} = \frac{\rho_{1}\rho_{2}}{\rho P} \left[D_{b}P - E_{t}\frac{n_{1}n_{2}}{n_{p}} (m_{2} - m_{1})\right]$ renth grad X_{B} Vector $-\frac{2}{3} D_{e}\frac{\rho_{1}\rho_{2}}{\rho}$	Flux	Term	Force term	Nature of the force term	Coefficient
Second \vec{X}_{U} Vector $L_{MUU} = \frac{n^2 D_T}{n_t n_2} \left(\frac{\rho_1 \rho_2}{\rho}\right)^2$ Third $X_B \vec{X}_U$ Scalar vector $L_{MUB} = \frac{\rho_1 \rho_2}{\rho} \left[\frac{4}{3} D_0 - D_n\right]$ Fourth $\vec{X}_M X_B$ Scalar vector $L_{MMB} = \left(\frac{\rho_1 \rho_2}{\rho}\right)^3 \cdot \frac{1}{nkT} \left[D_b - \frac{2}{3} D_4\right]$ Fifth $X_B \vec{X}_U$ Axial-vector $L_{KAU} = \frac{\rho_1 \rho_2}{\rho} \cdot 2D_c \cdot T$ Sixth $X_B \vec{X}_M$ Axial-vector $L_{MAM} = \frac{2Dd}{kT} \left(\frac{\rho_1 \rho_2}{\rho}\right)^3$ Seventh $\vec{X}_U X_V$ Vector second- $L_{MUV} = \frac{\rho_1 \rho_2}{\rho} T[D_a - 2D_c]$ order tensororder tensor $D_{MMV} = \left(\frac{\rho_1 \rho_2}{\rho}\right)^2 \frac{1}{nkT} [D_f + D_g - 2D_d]$ Ninth $\vec{X}_p X_V$ Vector second- $L_{MPV} = \frac{\rho_1 \rho_2}{\rho P} \left[D_b P - E_f \frac{n_1 n_2}{n\rho} (m_2 - m_1)\right]$ Tenthgrad X_B Vector $-\frac{2}{3} D_b \frac{\rho_1 \rho_2}{\rho}$ Eleventh $\frac{\partial}{\partial \vec{\tau}} X_V$ Vector $-D_i \frac{\rho_1 \rho_2}{\rho}$	\vec{J}_{M}	First	Żм	Vector	$L_{\rm MM} = \frac{n D_{1 2_{j}}}{n_{1} n_{2}} \left(\frac{\rho_{1} \rho_{2}}{\rho}\right)^{2} \cdot \frac{1}{kT}$
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Fourth $\vec{X}_{M}X_{S}$ Scalar vector $L_{MMS} = \left(\frac{\rho_{1}\rho_{2}}{\rho}\right)^{2} \cdot \frac{1}{nkT} \left[D_{b} - \frac{2}{3} D_{d} \right]$ Fifth $X_{a}\vec{X}_{U}$ Axial-vector $L_{KaU} = \frac{\rho_{1}\rho_{2}}{\rho} \cdot 2D_{c} \cdot T$ Sixth $X_{a}\vec{X}_{M}$ Axial-vector $L_{MaM} = \frac{2D_{d}}{kT} \left(\frac{\rho_{1}\rho_{2}}{\rho}\right)^{2}$ Seventh $\vec{X}_{U}X_{V}$ Vector second- $L_{MUV} = \frac{\rho_{1}\rho_{2}}{\rho}T[D_{a} - 2D_{c}]$ Seventh $\vec{X}_{M}X_{V}$ Vector second- $L_{MUV} = \frac{\rho_{1}\rho_{2}}{\rho}T[D_{a} - 2D_{c}]$ Order tensor $M_{MV} = \left(\frac{\rho_{1}\rho_{2}}{\rho}\right)^{2} \frac{1}{\eta kT} [D_{f} + D_{g} - 2D_{d}]$ Ninth $\vec{X}_{p}X_{V}$ Vector second- $L_{MPV} = \frac{\rho_{1}\rho_{2}}{\rho P} \left[D_{b}P - E_{t} \frac{n_{1}n_{2}}{n\rho} (m_{2} - m_{1}) \right]$ Tenthgrad X_{S} Vector $-\frac{2}{3} D_{o} \frac{\rho_{1}\rho_{2}}{\rho}$ Eleventh $\frac{\partial}{\partial \vec{r}} X_{V}$ Vector $-D_{i} \frac{\rho_{1}\rho_{2}}{\rho}$		Third	$X_{\mathbf{B}} \overline{X}_{\mathbf{U}}$	Scalar vector	$L_{\rm MUB} = \frac{\rho_1 \rho_2}{\rho} \left[\frac{4}{3} D_{\rm c} - D_{\rm a} \right]$
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vectorSixth $X_{\mathbf{n}} \vec{X}_{\mathbf{M}}$ Axial-vector $L_{M,\mathbf{n}M} = \frac{2D_d}{kT} \left(\frac{\rho_1 \rho_2}{\rho}\right)^2$ Sixth $X_{\mathbf{n}} \vec{X}_{\mathbf{M}}$ Axial-vector $L_{M,\mathbf{n}M} = \frac{2D_d}{kT} \left(\frac{\rho_1 \rho_2}{\rho}\right)^2$ Seventh $\vec{X}_{\mathbf{U}} X_{\mathbf{V}}$ Vector second- $L_{M,\mathbf{U}V} = \frac{\rho_1 \rho_2}{\rho} T[D_{\mathbf{n}} - 2D_{\mathbf{c}}]$ Seventh $\vec{X}_{\mathbf{M}} X_{\mathbf{V}}$ Vector second- $L_{\mathbf{M} \mathbf{W} V} = \left(\frac{\rho_1 \rho_2}{\rho}\right)^2 \frac{1}{\eta kT} [D_f + D_g - 2D_d]$ Eighth $\vec{X}_{\mathbf{M}} X_{\mathbf{V}}$ Vector second- $L_{\mathbf{M} \mathbf{W} V} = \left(\frac{\rho_1 \rho_2}{\rho}\right)^2 \frac{1}{\eta kT} [D_f + D_g - 2D_d]$ Ninth $\vec{X}_{\mathbf{p}} X_{\mathbf{V}}$ Vector second- $L_{\mathbf{M} \mathbf{P} V} = \frac{\rho_1 \rho_2}{\rho P} \left[D_{\mathbf{h}} P - E_t \frac{n_1 n_2}{n_{\rho}} (m_2 - m_1) \right]$ order tensororder tensor T Tenthgrad X_8 Vector $-\frac{2}{3} D_e \frac{\rho_1 \rho_2}{\rho}$ Eleventh $\frac{\partial}{\partial \vec{r}} X_{\mathbf{V}}$ Vector $-D_i \frac{\rho_1 \rho_2}{\rho}$		Fifth	XaXu	Axial-vector	$L_{K_{BU}} = \frac{\rho_1 \rho_2}{\rho} \cdot 2D_c \cdot T$
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Seventh $\vec{X}_{U}X_{V}$ Vector second- order tensor $L_{MUV} = \frac{\rho_{1}\rho_{2}}{\rho}T[D_{a} - 2D_{c}]$ Eighth $\vec{X}_{M}X_{V}$ Vector second- order tensor $L_{MMV} = \left(\frac{\rho_{1}\rho_{2}}{\rho}\right)^{2}\frac{1}{\eta kT}[D_{f} + D_{g} - 2D_{d}]$ Ninth $\vec{X}_{p}X_{V}$ Vector second- order tensor $L_{MPV} = \frac{\rho_{1}\rho_{2}}{\rho P}\left[D_{h}P - E_{f}\frac{n_{1}n_{2}}{n\rho}(m_{2} - m_{1})\right]$ Tenthgrad X_{8} Vector $-\frac{2}{3}D_{e}\frac{\rho_{1}\rho_{2}}{\rho}$ Eleventh $\frac{\partial}{\partial \vec{r}}X_{V}$ Vector $-D_{i}\frac{\rho_{1}\rho_{2}}{\rho}$				vector	
order tensorEighth $\vec{X}_{M}X_{V}$ Vector second- order tensor $L_{MMV} = \left(\frac{\rho_{1}\rho_{2}}{\rho}\right)^{2} \frac{1}{\eta kT} [D_{f} + D_{g} - 2D_{d}]$ Ninth $\vec{X}_{p}X_{V}$ Vector second- order tensor $L_{MPV} = \frac{\rho_{1}\rho_{2}}{\rho P} \left[D_{h}P - E_{f} \frac{n_{1}n_{2}}{n\rho} (m_{2} - m_{1}) \right]$ Tenthgrad X_{8} Vector $-\frac{2}{3} D_{o} \frac{\rho_{1}\rho_{2}}{\rho}$ Eleventh $\frac{\partial}{\partial \vec{r}} X_{V}$ Vector $-D_{i} \frac{\rho_{1}\rho_{2}}{\rho}$		Seventh	$\vec{X}_{U}X\mathbf{v}$	Vector second-	$L_{\rm MUV} = \frac{\rho_1 \rho_2}{\rho} T[D_{\rm a} - 2D_{\rm c}]$
Eighth $\vec{X}_{M}X_{V}$ Vector second- order tensor $L_{MMV} = \left(\frac{\rho_{1}\rho_{2}}{\rho}\right)^{2} \frac{1}{\eta kT} [D_{f} + D_{g} - 2D_{d}]$ Ninth $\vec{X}_{p}X_{V}$ Vector second- order tensor $L_{MPV} = \frac{\rho_{1}\rho_{2}}{\rho P} \left[D_{b}P - E_{f} \frac{n_{1}n_{2}}{n\rho} (m_{2} - m_{1}) \right]$ Tenthgrad X_{s} Vector $-\frac{2}{3} D_{o} \frac{\rho_{1}\rho_{2}}{\rho}$ Eleventh $\frac{\partial}{\partial \vec{r}} X_{V}$ Vector $-D_{i} \frac{\rho_{1}\rho_{2}}{\rho}$				order tensor	
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Ninth $\vec{X}_{p}X_{V}$ Vector second- order tensor Tenth grad X_{8} Vector $-\frac{2}{3}D_{0}\frac{\rho_{1}\rho_{2}}{\rho}$ Eleventh $\frac{\partial}{\partial \vec{r}}X_{V}$ Vector $-D_{i}\frac{\rho_{1}\rho_{2}}{\rho}$				order tensor	F 7
Tenth grad X_8 Vector $-\frac{2}{3}D_8\frac{\rho_1\rho_2}{\rho}$ Eleventh $\frac{\partial}{\partial \vec{r}}X\mathbf{y}$ Vector $-D_i\frac{\rho_1\rho_2}{\rho}$		Ninth	$\vec{X}_{\mathbf{p}}X\mathbf{v}$	Vector second-	$L_{\rm MPV} = \frac{\rho_1 \rho_2}{\rho P} \left[D_{\rm h} P - E_{\rm f} \frac{n_1 n_2}{n \rho} \left(m_2 - m_1 \right) \right]$
Tenthgrad X_8 Vector $-\frac{2}{3}D_e\frac{\rho_1\rho_2}{\rho}$ Eleventh $\frac{\partial}{\partial \vec{r}}X\mathbf{y}$ Vector $-D_i\frac{\rho_1\rho_2}{\rho}$				order tensor	
Eleventh $\frac{\partial}{\partial \vec{r}} X \mathbf{y}$ Vector $-D_i \frac{\rho_1 \rho_2}{\rho}$		Tenth	grad X_8	Vector	$-\frac{2}{3}D_{e}\frac{ ho_{1} ho_{2}}{ ho}$
		Eleventh	$\frac{\partial}{\partial \vec{r}} X_{\mathbf{V}}$	Vector	$-D_{i} \frac{\rho_{1}\rho_{2}}{\rho}$

Table I: Nature of the Coefficients and Forces in Mass and Energy Flux

namics of irreversible processes.³ For deriving eq 4 and 5, it is not necessary to express the third approximation to the distribution function explicitly. Equation 5 is new. The forces \vec{X}_{M} , \vec{X}_{U} , X_{a} , X_{V} , X_{S} , and \vec{X}_{P} are given by

$$\vec{X}_{\rm M} = -\frac{\rho}{\rho_1 \rho_2} k T n \vec{d}_{1\,2} \tag{6}$$

$$\vec{X}_{\rm U} = -\frac{{\rm grad} \ T}{T} \tag{7}$$

$$X_{\mathbf{a}} = -\frac{1}{2} \operatorname{rot} \vec{C}_{\mathbf{0}} \tag{8}$$

$$\vec{X}_P = -\frac{\operatorname{grad} P}{P} \tag{9}$$

$$X_{\rm v} = -\frac{\partial \bar{C}_0}{\partial \bar{r}} \tag{10}$$

$$X_8 = -\operatorname{div}\vec{C}_0 \tag{11}$$

where $X_{\mathbf{a}}$ is the force corresponding to the antisymmetric part of the viscous pressure tensor, $X_{\mathbf{v}}$ is the force corresponding to the nondivergent part of the symmetric viscous pressure tensor and $X_{\mathbf{s}}$ is the force corresponding to the divergent part of the viscous

tensor responsible for bulk viscosity. \vec{C}_0 is the barycentric velocity. n_1 and n_2 are the number densities of the respective components. \vec{d}_{12} is given by

$$\vec{d}_{12} = \frac{\partial n_{10}}{\partial \vec{r}} + \frac{n_1 n_2}{n_{\rho}} (m_2 - m_1) \frac{\text{grad}P}{P}$$
 (12)

The nature of the coefficients and the forces are summarized in Tables I and II.

In Tables I and II

$$D_{a} = \frac{2}{3} \frac{m_{1}m_{2}}{P_{\rho}} \frac{D_{12}}{n_{10}n_{20}} \left[\frac{7}{2} \frac{D_{T}}{T} - \frac{\partial}{\partial T} D_{T} \right];$$
$$E_{a} = \frac{2}{3} \frac{n^{2}m_{1}m_{2}D_{T}}{\rho P n_{10}n_{20}} \left[\frac{7}{2} \frac{D_{T}}{T} - \frac{\partial}{\partial T} D_{T} \right]$$

$$\begin{aligned} D_{\rm b} &= \frac{2}{3} \frac{n m_1 m_2}{P \rho} \frac{D_{1\,2} 1}{n_1 \,_0 n_2 \,_0} \left[\frac{1}{2} \frac{D_{1\,2}}{T} - \frac{0}{\partial T} D_{1\,2} \right]; \\ E_{\rm b} &= \frac{2}{3} \frac{n^2 m_1 m_{2\,1}}{\rho P} \frac{D_{\rm T}}{n_1 \,_0 n_{2\,0}} \left[\frac{7}{2} D_{1\,2} - T \frac{\partial}{\partial T} D_{1\,2} \right] \\ D_{\rm c} &= \frac{n^2 m_1 m_2}{P \rho} \frac{D_{1\,2} D_{\rm T}}{n_1 \,_0 n_{2\,0}} \frac{1}{T}; \quad E_{\rm c} &= \frac{n^2 m_1 m_2}{\rho P} - \frac{D_{\rm T}(A,A)}{n_1 \,_0 n_{2\,0}} \\ n^2 m_2 m_2 D_{\rm c} &= \frac{n^2 m_2 m_2}{\rho P} D_{\rm c} = \frac{n^2 m_2 m_2}{\rho P} \frac{D_{1\,2}}{\rho P} \frac{D_{1\,2}}{\rho P} \frac{D_{1\,2}}{\rho P} \frac{D_{1\,2}}{\rho P} \\ &= \frac{n^2 m_2 m_2}{\rho P} D_{\rm c} &= \frac{n^2 m_2 m_2}{\rho P} \frac{D_{1\,2}}{\rho P} \frac{D_{1\,2}}{\rho$$

$$D_{\rm d} = \frac{n^2 m_1 m_2}{P \rho} \frac{D_{12}}{n_{10} n_{20}}; \quad E_{\rm d} = \frac{n^2 m_1 m_2}{\rho P} \frac{D_{\rm T}}{n_{10} n_{20}}$$

Table II

Flux	Term	Force term	Nature of the force term	Coefficient
\mathcal{J}_{υ}	First	$ec{X}_{ extsf{M}}$	Vector	$L_{\rm UM} = rac{n^2}{n_1 n_2} D_{\rm T} \left(rac{ ho_1 ho_2}{ ho} ight)^2$
	Second	Χυ	Vector	$L_{\rm UU} = -\left[\lambda T + kT \frac{n^3}{n_1 n_2} \frac{D_{\rm T}^3}{D_{\rm l2}}\right]$
	Third	XsX̄υ	Scalar vector	$L_{\rm UUS} = -kT^2 \left[E_{\rm a} - \frac{4}{3} E_{\rm c} \right]$
	Fourth	$X_{\mathfrak{B}} \vec{X}_{\mathfrak{M}}$	Scalar vector	$L_{\rm UMS} = -\frac{\rho_1 \rho_2}{n\rho} \left[E_{\rm b} - \frac{2}{3} E_{\rm d} \right]$
	Fifth	$X_{a} \vec{X}_{U}$	Axial vector vector	$L_{\rm UAU} = 2E_{\rm c} {\rm k} T^2$
	Sixth	$X_{\mathbf{R}} \vec{X}_{\mathbf{M}}$	Axial -vector	$L_{\rm UAM} = -\frac{2E_{\rm d}}{n\rho} \rho_1 \rho_2$
	Seventh	$\vec{\lambda}_{\mathrm{U}} X \mathbf{y}$	Vector second- order tensor	$L_{\rm UUV} = kT^2[E_{\rm e} - 2E_{\rm o}]$
	Eighth		Vector second- order tensor	$L_{\rm UMV} = [E_{\rm f} + E_{\rm g} - 2E_{\rm d}] \frac{\rho_1 \rho_1}{n}$
	Ninth	$\vec{X}_{P}X\mathbf{v}$	Vector second-	$L_{\rm UPV} = -kT \left[E_{\rm b}P = E_{\rm f} \frac{n_1 n_2}{n_{ ho}} (m_2 - m_1) \right]$
	Tenth	grad X_8	Vector	$-\frac{2}{2}kTE_{c}$
	Eleventh	$\frac{\partial}{\partial \vec{\tau}} X \mathbf{y}$	Vector	$-kTE_{i}$

$$\begin{split} D_{e} &= \frac{2}{T} \frac{n^{2} m_{1} m_{2}}{P_{\rho}} \frac{D_{12} D_{T}}{n_{10} n_{20}} + \frac{Z_{1}(m_{1} m_{2}) D_{12}}{\rho P} \left(\mu - T \frac{\partial \mu}{\partial T}\right); \\ E_{e} &= \frac{2}{3} \frac{n^{2} m_{1} m_{2} D_{T} [A, A]}{\rho P n_{10} n_{20}} + \\ &\qquad \frac{N_{1} n (m_{2} - m_{1})}{\rho P} \left[\frac{7}{2} \mu - T \frac{\partial}{\partial T} \mu\right] \\ D_{t} &= \frac{2 D_{12} \mu}{n_{10} n_{20} P} + Z_{2} \frac{\mu \cdot D_{T}}{P}; \\ E_{t} &= \frac{2 D_{T} n \mu}{n_{10} n_{20} I^{2}} + N_{2} \frac{\mu [A, A]}{P} \\ D_{g} &= \frac{2 n^{2} m_{1} m_{2} D_{12}^{2}}{\rho P n_{10} n_{20}} + Z_{3}' \frac{\mu D_{T}}{P} + Z_{3}'' \frac{\mu D_{T}}{T}; \\ E_{g} &= \frac{2 n^{2} m_{1} m_{2}}{\rho P} \frac{D_{12} D_{T}}{n_{10} n_{20}} + N_{3}' \frac{\mu (A, A)}{P} + n_{3}'' \frac{\mu (A, A)}{T} \\ D_{h} &= Z_{4} \frac{D_{T}}{P^{2}}; \quad E_{h} &= \frac{N_{4} \mu [A, A]}{P^{2}} \\ D_{i} &= \frac{A' n (m_{2} - m_{1}) D_{12} \mu}{\rho P}; \quad E_{i} &= \frac{B' n^{2} (m_{2} - m_{1}) D_{T}}{\rho P} \end{split}$$

where $N_1 = Z_1 = 4 - 3A/2 + 3A$, A depends on the law of intermolecular force (see ref 2b,2a, p 172), Z_2 and N_2 are numerical factors and vanish for mechani-

cally similar molecules and for more general cases Z_2 and N_2 depend on concentration ratio.^{2b} Z_3' and N_3'' are related to the integral of the terms containing the coefficient of \vec{d}_{12} e in eq 7 of ref 2b. Z_4 and N_4 depend on the concentration ratio and are related to the integral of the terms containing $\partial p/\partial \vec{r}$ e in eq 7^{2b} (A, A) is the integral as defined in ref 2a, pp 144, 149. A' and B' are factors depending upon the shape and size of molecules. For a binary system with components having molecules of nearly equal mass and identical field of force, A' =0.437 and B' = 0.5. μ is the coefficient of viscosity; λ coefficient of thermal conductivity, D_{12} coefficient of diffusion, and $D_{\rm T}$ coefficient of the species 1 and 2.

An assessment of the relative magnitude of various terms in the transport equation for mass flux has been made by Chapman and Cowling.^{2b} The evaluation of relative numerical significance of various terms in the mass flux and energy flux equations for a mixture of hydrogen and helium for a mean temperature of 300° K; gradient of mass fraction ranging from 0.99 to 0.09 cm⁻¹, and grad *T* ranging from 10 to 40° cm⁻¹, confirmed the conclusion of Chapman and Enskog. The numerical results given in Table III show that in the case of heat flow, the second-order terms are much smaller so that

Term no.	Term in \vec{J}_{U}	Order of magnitude erg cm ⁻² sec ⁻¹	Term in $\vec{J}_{\sf M}$	Order of magnitude g cm ⁻² sec
1	$L_{\rm UM} \vec{X}$ M	10-5	$L_{MM} \vec{X}_{M}$	10-5
2	$L_{UU} \vec{X}_U$	10-7	$L_{MU} \vec{X}_{U}$	10-6
3	$L_{UUS} X_U X_S$	10-15	$L_{MUS}X_{U}X_{S}$	10-13
4	$L_{\rm UMS} \vec{X}_{\rm M} X_{\rm S}$	10-34	$L_{MMS} \vec{X}_M X_S$	10-33
5	$L_{UaU}X_{a}X_{U}$	10-15	$L_{MaU}X_{a}\overline{X}_{U}$	10 - 13
6	$L_{\rm UMB} \vec{X}_{\rm M} X_{\rm B}$	10-16	LMMBXMXB	10 ⁻¹²
7	$L_{UUV} \vec{X}_U X \mathbf{v}$	10-15	$L_{MUV} X U X V$	10-13
8	$L_{\rm UMV} \vec{X}_{\rm U} X_{\rm V}$	10-15	$L_{MMV} X_M X_V$	10-10
9	LUPVXPXV	10-20	LMPVXPXV	10-18
10	$\frac{2}{3}kTE_{e}$ grad X_{B}	10-17	$\frac{2}{3}D_{\rm e}{\rm grad}X_{\rm B}$	10 ⁻¹⁴
11	$-kTE_{i}\frac{\partial}{\partial x^{i}}X\mathbf{y}$	10-16	$D_{i} \frac{\partial}{\partial \vec{r}} X \mathbf{v}$	10-11

Table III: Relative Numerical Significance of Terms in Eq 4 and 6

they do not materially contribute to the heat flux. This is also true for the mass flux. Only those terms are important which are associated with the force corresponding to symmetrical nondivergent part of the viscous pressure tensor and space derivative of X_{v} . These may become important in flow through capillaries. It would appear, therefore, that linear transport equations would have a larger domain of validity although it is difficult to define precisely the domain of third approximation to the distribution function. An examination of eq 4 and 5 leads to the following conclusions. (1) $L_{MU} = L_{UM}$. This is just the Onsager relation between thermal diffusion and diffusion thermal effect. (2) All coefficients are scalar. (3) Space derivatives of forces occur in the transport equations. (4) In no $X_i X_j$ term is the tensorial order of X_i and X_j the same. (5) All the X_iX_j terms have the same tensorial order as the fluxes. (6) The secondorder symmetry^{11,12} is not obey ϵ d. (7) Nonlinearity appears on account of grad \overline{C}_0 .

The last inference also follows from Grad's method which has been used by Zhdanov, Kagan, and Sazykin to derive a general set of equations of diffusion in a multicomponent mixture.¹³ However, it is obvious that nonlinear effects start with the third approximation to the distribution function since each secondorder term has one of X_s , X_v , or X_a and all the three X_s , X_v , and X_a are the parts of grad \vec{C}_0 .

We discuss the following transport equation obtained by using Taylor's expansion¹²

$$J_{i} = \sum_{j} L_{ij} X_{j} + \frac{1}{2} \sum_{j} \sum_{k} L_{ijk} X_{j} X_{k} + \dots \qquad (13)$$

where L_{ij} and L_{ijk} are phenomenological coefficients.

Equation 13 is found to be valid in case of chemical reactions.⁸ It is obvious that equation 13 would be mathematically consistent provided X_iX_j are scalar quantities since coefficients L_{ik} and L_{ikj} are the first and second derivatives of flux with respect to forces. This difficulty does not arise in chemical reaction since the fluxes and forces are all scalar quantities.

Assuming that eq 13 is empirical, we may consider the cases: (i) both fluxes and forces are scalar as in chemical reaction; (ii) fluxes are vectorial and forces are scalar; and (iii) both fluxes and forces are vectorial.

For the first case, all coefficients would be scalar. For the second case, all the coefficients would be vectors. For the third case, coefficients would have different tensorial order depending on the nature of X_iX_j terms. When the nonlinear transport processes are examined from the view point of Curie principle,³ we can show that for an isotropic system, only those coefficients are nonzero which have zero tensorial order. Thus for the second case, eq 12 and 13 would be inapplicable for isotropic systems. Similarly, for case (iii) in case of isotropic systems, no second-order coefficients would appears if the products X_iX_j are scalar products. A similar analysis can be made for all possible cases with varying tensorial order of fluxes and forces.

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Solubilization of Benzene in Aqueous Sodium Dodecyl Sulfate Solutions

Measured by Differential Spectroscopy

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This investigation describes the use of differential absorption spectroscopy to determine the amounts of benzene dissolved in aqueous sodium dodecyl sulfate (NaDDS) solutions [as a function of concentration of the latter] and to obtain information about the region of solubilization in the micellar unit. The micellar units solubilize 0.90 mol of benzene per mol of NaDDS, a mole fraction of 0.47, over a wide range of surfactant concentration (from the cmc, 0.006, to $\sim 0.6 M$). Saturation of solutions containing >0.6 mol of NaDDS/l. with benzene results in the formation of optically isotropic gels. An activity coefficient for benzene dissolved in the hydrocarbon core of the micellar unit is computed and discussed. The spectra of benzene as a function of concentration in solvents containing molecular groups or environments similar to those in the micellar solution are reported and discussed. A quantitative comparison of these spectra with the spectrum of benzene dissolved in the micellar unit shows that only the spectra at a benzene concentration of ~ 0.5 mole fraction in *n*-alkanes, 1-dodecanol, or methanol are nearly identical with the differential spectra of benzene in the micellar unit.

Introduction

Ultraviolet (uv) absorption spectroscopy has been used previously in a qualitative manner to gain an insight into the solubilization phenomenon.^{1,2} Our objective in this investigation is to use quantitative differential uv spectroscopy to measure the amount of benzene solubilized by micellar aqueous sodium dodecyl sulfate (NaDDS) and to obtain information about the environment of solubilized benzene in the micelle.

Experimental Section

Materials. The benzene used in this experiment was a zone-refined product (purity greater than 99.9%) obtained from James Hinton (Valparaiso, Florida 32580). The solvents used were all of research grade, purity of 99.5+ mol %, and of spectrograde. The water used was doubly distilled before using as the diluent. A high-purity sodium dodecyl sulfate surfactant was used; the preparation and purification of this surfactant was described in a previous publication.³

Apparatus. The electronic absorption spectra were measured between 2800 and 2250 Å using a Cary 14 spectrophotometer. A scanning rate of 1 Å/sec and a linear dispersion of 0.3 Å/mm were used to record the spectrum. The wavelength resolving power of the Cary 14 is ~ 1 Å and the wavelength reproducibility better than ~ 0.5 Å in the spectral region measured.

Procedure. A number of NaDDS test solutions were made from a previously prepared stock solution containing ~ 0.7 mol of benzene per mol of NaDDS. The stock solution was used to minimize volume changes due to mixing and to reduce the time required to saturate solutions with benzene. To prepare saturated solutions, an excess amount of benzene was layered on the surface of 50 ml of test solution and allowed to equilibrate (approximately 1 week). Care was taken not to agitate these solutions since we wished to prevent the formation of emulsions. The equilibration process was monitored by measurements of optical density.

The differential spectra were obtained in the conventional way; the reference cell contained water saturated and overlaid with benzene. The sample cell contained aqueous surfactant solutions also overlaid with benzene. It is necessary to put an excess of benzene at the solution-air interface to make up for losses by evaporation of benzene from these saturated solutions during transfer. In general it took a day or more before saturation was re-established; a constant absorbance as a function of time signified saturation. The benzene concentration in the reference sample was determined spectroscopically. The solubility of benzene in water was found to be 24.0 mmol/l., which is in excellent agreement with that reported by others.⁴⁻⁷

Three calibrated sample cells of different path lengths were used in this study. For a given test solution a cell was selected so that the measured absorbance was between 0.2 and 1.8. Duplicate spectral measurements were made on each solution; the reproducibility of the intensities was better than 0.3%.

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Figure 1. Increase in absorbance of aqeuous solutions of sodium dodecyl sulfate saturated with benzene.

Experimental Results

Differential Spectra. Previous studies have established the cmc of NaDDS to be 6 mmol/l. in the presence of benzene.³ The uv differential spectra of benzene in aqueous solutions containing NaDDS at concentrations below the cmc indicated no increase in benzene solubility beyond that for pure water. In this case, the differential spectrum obtained is simply the instrument base line. We conclude that the benzene concentration in NaDDS solutions below the cmc is the same as for pure water, 24.0 mmol/l.

Benzene-saturated solutions of NaDDS above the cmc gave differential spectra consistent with the increased benzene solubility. Absorbances of all bands in the 2600-Å benzene system increase linearly with NaDDS concentration. Figure 1 shows the linear dependence of the 2548-Å absorbance as the NaDDS concentration increases to 0.06 mol/l. The linear increase of all bands persisted within experimental error up to 0.6 mol of NaDDS/l. At this surfactant concentration, solutions saturated with benzene form optically isotropic gels and are unsuitable for this study.

A typical differential spectrum is shown in Figure 2. Within experimental error all of the differential spectra recorded for solutions having the range of NaDDS and benzene concentrations discussed above are identical in both peak positions and band half-widths.

The maximum at 2608 ± 1 Å is the first band of the vibronically allowed progression whose other members occur at 2548, 2491, 2435, and near 2390 Å. The shoulder near 2643 Å represents a band that is not observed in the vapor and has been called the solvent-induced transition.⁸⁻¹⁰ This band can be resolved in

the spectra of benzene solutions at low temperatures.¹¹ Eastman and Rehfeld¹¹ have shown that the ratio of the maximum extinction coefficient of this band, ϵ_s , to that of the first allowed band, ϵ_v (near 2608 Å) increases with the strength of the solute–solvent interaction. For the purpose of the correlations used in the present study we have arbitrarily used ϵ_s ', the extinction coefficient of the differential spectrum at 2643 Å. This measured quantity represents the sum of contributions from the "solvent induced transition" and the tail of the broadened first vibronically allowed transition. This ratio was found to be constant for all the differential spectra of benzene dissolved in aqueous solutions containing various concentrations of NaDDS.

Spectral Measurements of Benzene in Various Polar and Nonpolar Solvents. In order to obtain information about the region of solubilization of benzene in the micellar unit, the uv spectra of benzene in various polar and nonpolar solvents were compared with its spectrum in the micellar unit. These solvents either contained molecular groups similar to those in NaDDS or represented possible environments in the micellar solution. Wavelength of the second maxima in the 2600-Å system, absorption line widths $\Delta \nu_{1/2}$, band separation $\Delta \nu_I$, molar absorptivity ϵ at the second maximum, and the integrated intensities I^{12} of these spectra are presented in Tables I and II.

Benzene dissolved in water, aqueous sodium sulfate, and aqueous sodium ethyl sulfate (NaES) solutions all give similar spectra. Various spectral values for benzene dissolved in these solvents are given in Table I. In all cases, up to the limit of benzene solubility in these solvents, Beer's law is obeyed. The amount of benzene dissolved decreases with increasing salt concentration, as shown in Figure 3. The maxima in the 2600-Å progression for benzene in these solvents are blue shifted by 8 ± 1 Å relative to the maxima observed for benzene dissolved in the micellar unit. The band half-widths and the values for $\epsilon_{\rm s}'/\epsilon_{\rm v}$ are much larger than those found for benzene in the micellar unit. Therefore the region of solubilization in the micellar unit is not the aqueous environment. These data also suggest that the amount of benzene dissolved near the micellar hydrated surface is less than the benzene concentration in the water because of the increase in salt concentration in this region. Thus we conclude that the domain of solubilization of benzene in the micellar unit does not include the hydrated micelle external surface.

The maxima in the uv spectra of benzene dissolved in

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 $\int_{2800 \text{ Å}}^{2300 \text{ Å}} \epsilon d\nu$ where ν is the reciprocal wavelength in cm⁻¹.

⁽¹¹⁾ J. W. Eastman and S. J. Rehfeld, submitted for publication in J. Phys. Chem.

⁽¹²⁾ The integrated intensity of the 2600 system is defined as I =



Figure 2. Differential ultraviolet absorption spectrum of benzene dissolved in micellar phase.

Table I: Position of the Second Maximum in the Progression of the Ultraviolet Vibrational Allowed Transition (2600-Å System) the Frequency Interval of the Progression $(\Delta \nu_I)$, the Half-Widths $(\Delta \nu_{1/2})$, Molar Absorptivity (ϵ), the Integrated Intensities (I), and the Solute-Solvent Interaction Parameter (ϵ_s'/ϵ_v) for Various Benzene Solutions (25°)

Benzene concn, mole fraction ^a	λ _{max(2)} ±1 Å	$\frac{\Delta \nu_I}{\pm 30 \text{ cm}^{-1}}$	$\Delta_{\nu}^{1/2},$ ±30 cm ⁻¹	$\epsilon \lambda_{\max(2)}$ ±4 l. (mol ⁻¹ cm ⁻¹)	I^{b} , l. (mol ⁻¹ cm ⁻¹) cm ⁻¹	es'/ev
		Solvent: D	imethyl Sulfat	e		
0.479(5.204)	2545	920	431	222	4.3	0.29
(0.0141)	2540	909	370	221	4.1	0.26
		Solvent: Met	hane Sulfonic .	Acid		
(0,1259) ^e	2543	906	463	199	4.3	0.42
(0.0325)	2543	906	463	199	4.2	0.30
	Aqueous Solu	tions of Sodium E	thyl Sulfate S	aturated with Benzer	ne	
0.5 M CH ₃ CH ₂ SO ₄ Na	2539	909	527	190	4.2	0.29
	Aqueo	us Solutions of Na	SO4 Saturated	d with Benzene		
1 095 M Na SO4	2539	909	558	190	4.3	0.31
0.480 M Na ₂ SO ₄	2539	909	558	190	4.3	0.31
0.247 M Na ₂ SO ₄	2539	910	560	190	4.2	0.32
		•	Water			
0.000 (0.024)	2539	909	530	188	4.3	0.32
	Benzene D	vissolved in Micella	ar Phase (Satu	rated with Benzene)		
0.47	2548	918	419	205 ª	4.1	0.24

^a Values in parentheses are mol of benzene per l. ^b Precision $\pm 5\%$, absolute magnitude $\pm 10\%$.¹¹ ^c This is a saturated solution. ^d Value is the average of the molar extinction coefficients at 2548 Å (Table II).

Table II: The Position of the Second Maximum in the Progression of the Ultraviolet Vibrational Allowed Transition
(2600-Å System), the Frequency Interval of the Progression ($\Delta \nu_I$), the Half-Widths ($\Delta \nu_{1/2}$), Molar Absorptivities (ϵ), the Integrated
Intensities (I), and the Solute–Solvent Interaction Parameter $(\epsilon_{s}'/\epsilon_{v})$ for Various Benzene Solutions

Benzene concn, mole fraction ^a	$\lambda_{\max(2)} \pm 1 \text{ Å}$	$\frac{\Delta \nu_I}{\pm 30 \text{ cm}^{-1}}$	$\frac{\Delta \nu^{1/2}}{\pm 30 \text{ cm}^{-1}}$	$\epsilon \lambda_{\max(2)}$ ±4 l. (mol cm) ⁻¹	I^{b} , l. (mol ⁻¹ cm ⁻¹)cm ⁻¹	€3′/€v
		Solven	t: n-Hexane			
1.0 (11.06)	2552	918	399	201	$4.1 imes 10^{5}$	0.26
0.873(9.12)	2551	915	413	204	4.1	0.24
0.525(4.78)	2548	903	400	201	4.1	0.20
0.023(0.1725)	2547	904	353	236	3.9	0.15
0.011(0.086)	2546	904	340	239	3.9	0.15
0.006(0.044)	2546	904	340	239	4.0	0.15
0.004(0.033)	2546	904	340	243	4.1	0.15
0.003(0.021)	2545	905	340	247	4.2	0.15
0.002 (0.014)	2544	904	350	267	4.0	0.14
		Solvent	t: n-Dodecane			
0.62(4.36)	2548	918	399	207	4.0	0.21
0.53 (3.38)	2548	918	400	210	4.0	0.19
		Solvent: 1-	Dodecyl Alcoh	ol		
0.79(6.67)	2551	901	414	202	4.3	0.24
0.68(4.94)	2550	901	398	203	4.0	0.21
0.46 (2.81)	2548	918	399	200	4.0	0.21
		Solver	nt: Methanol			
0.48(7.52)	2548	918	440	198	4.2	0.26
(0.014)	2543	906	330	268	4.3	0.19
alues in narentheses ar	e moles of benzen	e per liter. ⁶ Preci	sion $\pm 5\%$. abs	olute magnitude ±	10%.11	



Figure 3. Solubility of benzene in aqueous sodium sulfate and ethyl sulfuric acid sodium salt, temperature 25°.

nonaqueous solvents, dimethyl sulfate and methane sulfonic acid, are $3-5 \pm 1$ Å blue shifted relative to the maxima positions observed for benzene in the micelle. Also, the band half-widths are greater in the solvent methane sulfonic acid than in the micelle; in both of the above solvents the values of $\epsilon_{\rm s}'/\epsilon_{\rm v}$ are greater than the one obtained for the micelle. These values are given in Table I. We conclude that the major domain of solubilization of benzene is not the hydrated palisade layer, *i.e.*, between the hydrated- $CH_2-CH_2SO_4^-$ groups in the micelle surface.^{13,14}

Analysis of the uv spectra of benzene in n-hexane, n-dodecane, methanol, and 1-dodecanol, summarized in Tables I and II, demonstrates that the maxima in the 2600-Å system shift to longer wavelengths as the concentration of benzene is increased. The molar absorptivities ϵ decrease and the band half-widths and the solute-solvent interaction parameter increase with increasing benzene concentration. The position of the maxima is a function of the refractive index¹¹ and varies linearly with the mole fraction of benzene. At a benzene mole fraction of ~ 0.5 the 2nd maximum in the uv spectra in these solvents is located at 2548 ± 1 Å; the molar absorptivity ϵ_{2543} Å is 205 ± 5 l./mol cm. In Figures 4 and 5 a comparison of various spectra is shown. These include benzene in water, in *n*-hexane, in methanol, in *n*-dodecane, in 1-dodecyl alcohol, and pure liquid benzene. Also comparing the spectral parameters presented in Tables I and II with those obtained for benzene in the micelle, one finds that only the spectra of ~ 0.5 mole fraction of benzene in hydrocarbons and

(13) J. Clifford and B. A. Pethica, Trans. Faraday Soc., 60, 1483 (1964).

(14) J. Clifford, ibid., 61, 1276 (1965).



Figure 4. The 2600-Å absorption spectra of liquid benzene; benzene dissolved in *n*-hexane, water, and in micellar phase, temperature 25° .

alcohols closely resemble the spectra of benzene in the micellar unit.

The integrated intensities of the differential spectra were computed at a benzene concentration of 0.47 mole fraction. As shown in Tables I and II the value of I for the benzene dissolved in the micelle is found to be within experimental error of values of I for benzene dissolved in various solvents. Values of I for many additional solvents are reported elsewhere.¹¹

Solubility of Benzene in Micellar NaDDS. This was measured by titration of a 0.254 M NaDDS solution with benzene until further additions caused no increase in absorbance at 2548 Å in a 0.01-cm cell. The saturation concentration was found by interpolation to be 0.248 mol/l. Assuming no solubilization by monomeric NaDDS we obtain a mole fraction of benzene in the micelle of 0.475. A molar absorptivity $\epsilon_{2548\text{\AA}}$ for benzene in the micellar unit of 205 ± 4 l./mol cm was computed from Beer's law. This value agrees very well with the values 210 ± 4 l./mol cm for benzene in ndodecane at a mole fraction of 0.53 and with 201 ± 4 $l./mol \ cm$ for benzene in *n*-hexane at a mole fraction of 0.525 (Table II).

Discussion

The first direct physical evidence concerning the region of solubilization of hydrocarbon derivatives in micellar systems was the observation of Hughes, Sawyer, and Vinograd,¹⁵ that the region of solubiliza-



Figure 5. The 2600-Å absorption system of benzene dissolved in methanol, 1-dodecanol, *n*-dodecane, and in micellar phase, temperature 25°.

tion had a low electron density, as do liquid paraffins. Subsequently, Riegelman, et al.,¹ proposed that the predominant region of solubilization for ethylbenzene and for naphthalene in micellar solutions of potassium undecanoate or of dodecylamine hydrochloride is the hydrocarbon interior of the micelles. This conclusion was based on a detailed but qualitative comparison of band shapes and peak positions in the uv spectra of dilute solutions of these solutes in *n*-octane, in water, and in the micellar systems. Similar conclusions were reached also by Goerner² from a recent study of the uv spectra of various aromatic hydrocarbons solubilized in aqueous solutions of various N-alkyl quaternary ammonium bromides. As a first approximation, our results can be similarly interpreted.

A detailed examination, however, of the spectra shown in Figures 4 and 5, particularly in the region of the minimum absorption near 2590 A, shows that the average environment of solubilized benzene is appreciably different from that of a benzene molecule in a solution of *n*-alkane at 3-4 mol/l. Indeed, this is to be expected, since a micelle is a small body of nonuniform composition. The concentration of benzene in the micelle is likely also to be nonuniform within the micelle and the solubilized molecules will lie at different distances from the partially hydrated, highly

(15) E. W. Hughes, W. M. Sawyer, and J. R. Vinograd, J. Chem. Phys., 13, 131 (1945).

polar region around the exterior. The absorption spectrum observed for micellar benzene will then be a weighted average over a distribution of benzene molecules which do not occupy identical environments within the micellar unit. Similar conclusions can be drawn from the values of $\epsilon_{\rm s}'/\epsilon_{\rm v}$ at a benzene mole fraction of ~0.5 given in Tables I and II, 0.21 in aliphatic hydrocarbons, 0.24 in the micelle, and 0.26 in methanol.

On the basis of an analysis of electron spin resonance spectra for solubilized long-chain nitroxides, Waggoner, Griffith, and others¹⁶⁻¹⁸ have pointed out that their data are not consistent with a uniform environment for the solubilized molecules. They suggest, instead, that a solubilized substance should be regarded as distributed in the micelle among a number of more or less different environments among which rapid exchange occurs. Our data are not inconsistent with such a picture, though it is likely that the polar molecules investigated by Waggoner, et al., are more evenly distributed between polar and nonpolar environments than is a nonpolar solute like benzene. Indeed, in their pioneering uv studies, Riegelman, et al.,¹ pointed out that polar molecules such as substituted anilines and asymmetric highly polarizable polyaromatics such as anthracene appeared to occupy a different region of solubilization from that of ethylbenzene.

A number of investigations of solubilized substances have recently been made also by nmr techniques. These studies^{19,20} do not provide very much additional information about the region of solubilization, except that it is liquid-like. They have also given useful information about the mobility of solubilized molecules and about the dynamics of exchange between the micellar and aqueous environments.¹⁹

Finally, it may be mentioned that an activity coefficient can be calculated from the experimental solubility of benzene in micellar NaDDS. At saturation, $x\gamma = 1.00$ by definition, where x is the equilibrium mole fraction and γ is the activity coefficient. This leads to a value for γ of 2.10 for micellar benzene at 25°; this stands in strong contrast to the value of 2300 for benzene in water.²¹ The activity coefficient of infinitely dilute benzene (in *n*-heptane at 25° is 1.55²¹). A value of γ of 1.13 at 25° is obtained for a 10% solution

of benzene in n-hexadecane.²² Extrapolation by conventional methods²³ leads to an expected value of γ of \sim 1.25 to 1.10 for a solution of benzene in a normal paraffin liquid $(nC_6 \text{ to } nC_{12})$ at a concentration in the vicinity of 0.5 mole fraction benzene. This difference between the γ values for benzene in *n*-dodecane of ~ 1.1 and in the micelle 2.1 corresponds to a difference in standard free energy of about 0.4 kcal/mol; it is too large to be accounted for by the intermicellar pressure to be expected if the interfacial free energy at the micellar surface is comparable to the interfacial tension of 5 ergs cm^{-23} between benzene and the micellar solutions of NaDDS. However, if the interfacial tension were of the order of 35 ergs/cm², the value at the benzenewater interface, this would account for the difference in standard free energy.

As described above, the benzene molecules are likely to lie at different distances from the partially hydrated polar region of the micelle; therefore, the activity coefficient should reflect this averaging of environments. For example, the activity coefficient for infinitely dilute benzene in methanol and in ethanol at 25° are 7.5 and $6.0,^{21}$ respectively. Thus the value 2.1 may in part be accounted for by the averaging of environments.

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A Conductance Study of Quaternary Ammonium Halides

in Dimethyl Sulfoxide at 25°1

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Precise conductance measurements have been carried out by an ac method on solutions of quaternary ammonium halides in dimethyl sulfoxide (DMSO). The salts studied were tetramethyl- through tetra-n-heptylammonium iodides, tetramethyl- through tetra-n-butylammonium bromides, and tetrapropylammonium chloride. Single-ion conductivities were determined using tetraisoamylammonium tetraphenylborate and tetraisoamylammonium tetraisoamylborate as reference electrolytes. The order of halide ion conductances was found to be Cl > Br > I, which is the order expected for unsolvated ions. Slight association to ion pairs was found for Me4NBr and Me4NI, and approximate values for the association constants were determined. The behavior of the reference electrolytes in DMSO at dilutions less than infinite was found to be unusual and cannot be explained by current theory.

Introduction

Although the solvent properties of dimethyl sulfoxide³ indicate that this solvent should be an excellent medium for electrochemical investigation, relatively few studies of such nature have been made.⁴ In particular, only a few conductance studies have been reported,⁵⁻⁷ and data of high precision are sparse. Very few measurements have been made on quaternary ammonium halides in DMSO, which is surprising since these salts have excellent solubility characteristics in a wide variety of solvents and form a homologous series very useful for comparison purposes.

This paper reports the results of a systematic study of the conductivity of a series of quaternary ammonium halides in DMSO. Since precise transference number data for solutions of salts in DMSO are lacking, singleion conductivities have been evaluated using two reference electrolytes in an effort to provide reliable values of ion mobilities.

Experimental Section

Solvent. DMSO (Crown Zellerbach Corp.) was allowed to stand in contact with Drierite in a sealed container for several days. The liquid was then siphoned off by suction into a distilling flask and vacuum distilled from powdered 4-A molecular sieves; only the middle fraction was retained. The 3.5×120 -cm distillation column was packed with 5-mm Pyrex glass helices; the conductance of the final product was less than 2×10^{-8} mho/cm.^{6,8} On the basis of the minimum amount of water detectable in DMSO to which known amounts of water had been added, it was concluded that the water concentration in our solvent did not exceed 0.0013 M.

Purification of Salts. A check of the melting point of a salt with reported "literature" values is not a sufficient criterion of salt purity for conductance work. A salt was acceptable as "conductometrically pure" when identical conductance-concentration curves were obtained from two separate runs on a given salt with three recrystallizations being effected between runs.^{1,9} A salt was also acceptable as pure if recrystallized samples from independent lots yielded identical curves or if the conductance data were consistent with Kohlrausch's law and the results from salts shown to be conductometrically pure.¹

The reagent grade solvents used in purifying the salts were chloroform-ethyl acetate mixtures for Pr_4NI , Et_4NBr , and Pr_4NBr ; benzene for Bu_4NI and n-Am₄NI; acetone-water and acetone-benzene mixtures for Me₄NI and *i*-Am₄NI, respectively; ethyl acetate for Hex₄NI, Hept₄NI, and Bu₄NBr; methanol-ethyl acetate and methanol-benzene mixtures for Me₄NBr and Et₄NI, respectively; and acetone-ether mixtures for Pr₄NCl.

The salts were obtained from both Eastman Kodak and City Chemical Corporation. Hygroscopic salts were handled in a glove-bag. The iodides were dried *in vacuo* at temperatures below 100°. The bromides

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⁽⁸⁾ One of the reviewers has pointed out that MCB Spectrograde

and chlorides were dried following the recommendations of Unni, Elias, and Schiff.¹⁰ All salts were used within a week of purification. Although great precautions were taken in handling the chlorides, we were only able to duplicate the conductance of Pr_4NCl . The difficulty experienced with these salts can largely be attributed to their extremely hygroscopic nature.¹¹

Reference Electrolytes. Tetraisoamylammonium tetraphenylborate, $(i-Am)_4NB(C_6H_5)_4$, TAATPB, was prepared by the method of Fuoss and Hirsch.¹² It was recrystallized from acetone-benzene mixtures and dried *in vacuo* at 65° for 24 hr.

Tetraisoamylammonium tetraisoamylborate, $(i-Am)_4$ -NB $(i-Am)_4$, TAATAB,¹³ was supplied in crude form by Dr. Reynold Iwamoto of this department. It was recrystallized from acetone-demineralized water mixtures and dried *in vacuo* at 65° for 48 hr. The purity of both of these salts was established by the close agreement in their limiting equivalent conductances after successive recrystallizations.

Instrumentation and Procedure. An ac bridge similar to that described by Jones and Dike^{14,15} was used for the conductance measurements. The conductance cell was of the type used by Jenkins¹⁶ and was calibrated using dilute solutions of tetrabutylammonium bromide in DMSO.¹⁷ A conductance cell containing a pair of concentric cylinder electrodes¹⁸ which had been calibrated using standard aqueous KCl solutions¹⁹ was used for the intercomparison of cell constants. The average value which resulted from four separate intercomparisons was 0.13756 \pm 0.00004 cm⁻¹. The usual small frequency correction was applied to cell resistance measurements.

The temperature of the oil bath was controlled to $\pm 0.005^{\circ}$ and was set at $25.00 \pm 0.01^{\circ}$ with an American Instrument Co. mercruy-in-glass thermoregulator. All runs were made by the concentration method. Solutions were prepared by weight under anhydrous conditions. In order to calculate the concentrations on a molarity basis, the densities of the dilute salt solutions were assumed equal to that of the pure solvent. Density measurements made on the more concentrated solutions at the end of several runs indicated that the change in solvent density by the addition of salt was within the experimental error of the measurements and could be neglected.

Densities at 25° were determined with a 10-ml Lipkin pycnometer.²⁰ Viscosities were measured in two calibrated Cannon-Fenske viscometers; kinetic energy corrections were assumed to be negligible. Dielectric constants were determined with a Sargent Model V Chemical Oscillometer, using a series of pure organic liquids as calibration standards.²¹

We have found the following values at 25° for the physical properties of pure dimethyl sulfoxide: viscosity, 1.992 ± 0.002 cP; density, 1.0956 ± 0.0001 g/ml; dielectric constant, 46.6 ± 0.2 . These values

Table I :	Equivaler	nt Conduc	tances of	Quaternary
Ammoniur	n Iodides	ir. Dimetl	hyl Sulfox	ide ^a

10•C	Δ	104C	Λ
М	le₄NI	Et ₄ N	I
1.1220	4781	2.3201	40.001
2.0957	41.554	4.6698	39.638
3.3099	41.326	6.6872	39.399
4.1187	4 1.206	8.4258	39.225
5.1112	41.067	9.9728	39.088
6.0679	40.949	11.2382	38.981
Р	r₄NI	Bu ₄ N	NI .
1.2191	36.600	1.1309	34.823
2.2892	3€.388	2.1415	34.613
3.2374	36.235	3.0527	34.461
4.1898	36.105	3.8405	34.348
5.1265	35.986	4.5213	34.266
6.1449	35.872	5.1444	34.193
1.4853 ^b	36 .540 ⁶	1.1487 ^b	34.834 ^b
2.1045	36.420	2.3025	34.594
3.1949	36.234	3.3736	34.418
4.1061	36.108	4.2583	34.296
5.1992	35.971	5.0250	34.204
6.2162	35.859	5.7204	34.127
i-A	MaNI	<i>n</i> -Am	₄NI
1.2162	33.832	0.9771	33.689
2.2563	33.631	1.9436	33.484
3.0444	33.504	3.1950	33.279
3.7755	33.399	4.3269	33.132
4.3349	33.334	5.0119	33.053
4.8008	33.279	5.9488	32.953
		1.0629 ^b	33.678 ^b
		2.0615	33.471
		3.2191	33.284
		4.0808	33.168
		5.1590	33.045
		6.1142	32.944
<i>n</i> -]	Hex₄NI	n-Hep	t4NI
1.1324	33.057	1.1238	32.432
2.1621	32.854	2.1776	32.232
3.1651	32.695	3.1519	32.082
4.1218	32.563	4.1847	31.947
5.2527	32.435	5.2099	31.837
6.1851	32 341	6.1872	31.736
0.7709 ⁶	33.166 ^b	0.9323 ^b	32.484 ^b
1.8039	32.918	2.0130	32.257
2.5648	32.786	2.9560	32.109
3.4638	32.652	4.1014	31.957
4.3326	32.543	5.1047	31.846
5.1713	32.442	6.4238	31.712
6.0945	32.349		
" Units: C	equiv/l · A mho-	m²/equiv bInd	iantos soporo

run.

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 Table II: Equivalent Conductances of Quaternary Ammonium

 Bromides, Chlorides, and Reference Electrolytes in

 Dimethyl Sulfoxide^a

104 <i>C</i>	Δ	104 <i>C</i>	Δ
	Me ₄ NBr		Et₄NBr
1.0435	42.024	1.0952	40.539
2.0735	41.769	3.3137	40.095
3.0749	41.573	4.3666	39.947
4.0801	41.406	5.3050	39.826
5.0849	41.255	6.3459	39.703
6.1101	41.125		
1.0551	42.024 ^b	2.3512	^b 40.248 ^b
2.1130	41.765	3.4982	40.063
3.1582	41.562	4.4898	39.925
4.1694	41.392	5.2159	39.833
5.1665	41.246	6.0294	39.739
6.1495	41.113	6.9766	39.644
	Pr ₄ NBr		Bu₄NBr
1.3136	36.833	1.9379	34.908
2.5490	36.593	2.9011	34.749
3.5926	36.431	3.8270	34.616
4.4025	36.328	4.7911	34.497
5.1263	36.240	5.7025	34.393
5.9830	36.143	6.5733	34.301
		1.3309	35.034 ^b
		2.4878	34.806
		3.4968	34.649
		4.4532	34.529
		5.1914	34.444
		5.8136	34.379
	Pr ₄ NCl		ГААТАВ
0.8986	37.302	1 0384	20 739
1.9597	37.072	1 8006	20.585
3.1975	36.852	2 4978	20.000
4.2704	36.703	2.9744	20.397
5.3250	36.568	3 4377	20.336
6.3845	36.451	3 9245	20.279
7.3693	36.353	0.0210	20.210
			ТААТРВ
2.0743°	37.033°	1.3546	20.702
3.1829	36.850	2.4626	20.526
4.2915	36.691	3.4537	20.401
5.2512	36.574	4.3295	20.305
6.1962	36.467	5.0786	20.234
7.3688	36.344	5.7266	20.172
^a Units:	C, equiv/l.; A, mhos-cm ²	² equiv.	^b Indicates separate

run.

are in good agreement with those which have been reported in the literature.⁴

Results

The measured equivalent conductances and the corresponding molarities are shown in Table I for the quaternary ammonium iodides and Table II for the bromides, chlorides, and reference electrolytes. The data were analyzed with the Fuoss-Onsager equation for unassociated electrolytes in the form²²

$$\Lambda = \Lambda_0 - SC^{1/2} + EC \log C + (J - F\Lambda_0)C \quad (1)$$

which, for plotting purposes, is rearranged to the Λ' function

$$\equiv \Lambda + SC^{1/2} - EC \log C =$$

$$\Lambda_0 + (J - F\Lambda_0)C = \Lambda_0 + J'C \quad (2)$$

A plot of Λ' vs. C gives a straight line with Λ_0 as intercept and $J - F\Lambda_0$ as slope. Values of Λ_0 for the initial evaluation of the coefficients E and S for the iteration procedure were obtained from Shedlovsky extrapolations²³ of the data. Representative plots of the Λ' function are shown in Figure 1. These plots were linear for all salts over the concentration range studied. Table III lists the parameters obtained from the Fuoss-Onsager equation by a least-squares analysis of the data. The Λ_0 values are believed to be accurate to $\pm 0.05\%$.

Discussion

 Λ'

Limiting Ionic Conductance. Single-ion conductances were evaluated using tetraisoamylammonium tetra-

Table III :	Table III: Conductance Parameters for Quaternary							
Ammonium	Halides and Refer	ence Elect	rolytes in					
Dimethyl Su	Dimethyl Sulfoxide							
Salt	Δc	S	E	J'				
Me ₄ NI	42.40	56.38	81.145	161.6				
Et ₄ NI	40.86	55.61	77.256	212.6				
Pr₄NI	36.22	53.78	68.062	219.0				
Bu₄NI	35.39	52.87	63.440	189.3				
<i>i</i> -Am₄NI	34.41	52.38	60.965	231.4				
<i>n</i> -Am₄NI	34.21	52.28	60.46 0	225.3				
Hex ₄ NI	33.61	51.97	58.944	194.7				
$Hept_4NI$	32.98	51.66	57.353	247.6				
Me₄NBr	42.53	56.49	81.726	77.79				
Et ₄ NBr	41.12	55.74	77.912	219.0				
Pr₄NBr	37.45	53.90	68.643	232.8				
Bu ₄ NBr	35.65	53.00	64 .097	224.3				
Pr4NCl	37.83	54.09	69.603	203.0				
TAATAB	21.21	45.76	27.626	15.55				
ТААТРВ	21.23	45.77	27.676	158.5				

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$\lambda_0^+(I^-)^a$	λ ₀ +(Br ⁻) ^a	λ ₀ + (Lit.)	$R^{+}(\text{\AA})^{b}$	$r^+(\text{\AA})^b$
18.60	18.57		2.20	3.47
17.06	17.06		2.40	4.00
13.42	13.39		3.05	4.52
11.59	11.59	11.2^{c}	3.53	4.94
10.61 ^d			3.86	
10.41			3.93	5.29
9.79			4.18	5.61
9.18			4.45	5.89
λ₀ -			<i>R</i> −(Å)	$\tau^{-}(\text{\AA})$
10.61^{d}			3.86	
10.61^{d}			3.86	
24.40		23.9. 36'	1.68	1.81
24.06		24.2°	1.70	1.95
23.80		23.8°	1.72	2.16
	$\lambda_{0}^{+}(I^{-})^{a}$ 18.60 17.06 13.42 11.59 10.61^{d} 10.41 9.79 9.18 λ_{0}^{-} 10.61^{d} 10.61^{d} 10.61^{d} 24.40 24.06 23.80	$\lambda_0^+(I^-)^a$ $\lambda_0^+(Br^-)^a$ 18.60 18.57 17.06 17.06 13.42 13.39 11.59 11.59 10.61 ^d 9.79 9.18 λ_0^- 10.61 ^d 10.61 ^d 24.40 24.40 23.80	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table IV: Single-Ion Conductances and Ionic Radii in Dimethyl Sulfoxide

^a Units; mho-cm² equiv⁻¹. ^b R is the hydrodynamic radius; r the crystallographic. ^c Reference 5. ^d The value 10.61 for the conductance of *i*-Am₄N + is the average of the values obtained from the two reference electrolytes. ^c Reference 7b. ^f Reference 6.



Figure 1. A plot of Λ' (mhos cm² equiv⁻¹) vs. C (equiv 1.⁻¹) for reference electrolytes in DMSO.

isoamylborate as a reference electrolyte. This compound has been shown to provide values of ion mobilities that may be accurate to $\pm 0.1\%$ ²⁴ The limiting equivalent conductance for this salt was also compared with that for a second reference electrolyte, tetraisoamylammonium tetraphenylborate.

If the limiting equivalent conductance of a reference electrolyte is divided equally between its two ions, then we may obtain the value 10.61 mho-cm² equiv⁻¹ for the conductance of the tetraisoamylammonium ion, this being one-half the average limiting equivalent conductance of the two reference electrolytes employed in this study. Using this value with $\Lambda_0(i$ -Am₄NI), we derive the value 23.80 for the limiting equivalent conductance of the iodide ion. The results for the ion conductances, λ_0 , given in Table IV have been derived in a similar manner from the remaining salts. The values for a given cation in the second and third columns of this table are those derived from the iodides and bromides, respectively.

As can be seen from the data, the ionic conductance decreases with increasing number of carbon atoms in the alkyl chain, but the decrease in going from the methyl to the ethyl derivative is exceptionally small. This implies that the conductance of the Me_4N^+ ion is much too low on the basis of its dimensions. Similar behavior has been observed for this ion in nitrobenzene.²⁵ The explanation offered for this is that since the Me_4N^+ ion has a higher surface charge density than any of the other ions, it is likely to experience interaction between the charge on the ion and the dipoles of adjacent solvent molecules which leads to a reduction in its mobility.²⁶

It should be noted that the values of the conductances of the halide ions differ from the previously reported values⁵⁻⁷ by as much as 50% in one case. However, due to the greater internal consistency of our data, we believe our results should be given considerably more weight. Furthermore, the majority of available data on solutions of electrolytes in DMSO has been obtained using alkali metal salts, and these salts are difficult to obtain in a state of purity for precise conductance work.^{27,28}

Table IV also lists the hydrodynamic²⁹ and crystallo-

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Salt	$s_{ extsf{T}}$	$S_{\mathbf{E}}$	$100(S_{\rm E} - S_{\rm T})/S_{\rm T}$	åj'	åj
Me₄NI	-56.38	-59.43	+5.40	2.46	2.64
Et ₄ NI	-55.60	-55.74	+0.25	3.43	3.73
Pr ₄ NI	-53.77	-53.32	-0.83	3.88	4.32
Bu ₄ NI	-52.87	-52.18	-1.30	3.45	4.01
<i>i</i> -Am ₄ NI	-52.37	-51.03	-2.55	a	a
<i>n</i> -Am₄NI	-52.27	-50.93	-2.56	4.35	5.07
Hex4NI	-51.97	-51.07	-1.73	3.74	4.57
Hept ₄ NI	-51.65	-49.07	-4.99	5.02	6.01
Me₄NBr	-56.52	-62.55	+10.66	1.30	1.45
Et₄NBr	-55.74	-56.38	+1.14	3.53	3.83
Pr₄NBr	-53.89	-53.07	-1.52	4.14	4.59
Bu₄NBr	-52.99	-51.90	-2.05	4.16	4.74
Pr ₄ NCl	-54.08	-54.23	+0.27	3.51	3.94
Reference 30 did no	t list a value of r (Table	IV) for <i>i</i> -Am ₄ N +, and i	t is thus omitted from this t	able.	

Table V: Comparison of Theoretical (S_T) and Experimental Slopes (S_E) of Onsager's Equation and Effect of the Viscosity Correction on Ion-Size Parameters of Quaternary Ammonium Halides in Dimethyl Sulfoxide

graphic^{30,31} radii of the ions. As expected, the Stokes radii increase with increasing size of the cation, but less so for the larger ions, due, most likely, to the larger number of conformations of the alkyl chains available to reduce overall bulk. The order of the halide ion conductances in DMSO is Cl > Br > I, which is the same as that found in ethanolamine³² and acetone,³³ but the exact reverse of that found in N-methylacetamide³⁴ and several other nonaqueous solvents. The Stokes radii for these ions in DMSO are all less than the crystallographic radii, indicating that they are only slightly solvated in this solvert, if at all. Thus their relative sizes become the chief factor affecting the mobilities and the decreasing order of the conductivity of the halide ions with increasing size is easily understood.

Ion-Size Parameter. In the initial analysis of our data, it was assumed that the viscosity correction, $F\Lambda_0C$, to the conductance equation would be negligible in the concentration ranges which were covered in this work. Accordingly, values of the Fuoss-Onsager ion-size parameter, d, were calculated from the slopes of the plots of Λ' against concentration. These values of d are listed in the fifth column of Table V, and the slopes from which they were calculated are given in the fifth column of Table III.

An inspection of these values caused some concern, as they were all much smaller than would be expected from sums of crystallographic radii. The value of &for Me₄NBr, for example, is 1.30 Å, whereas the crystallographic radius of the bromide ion alone is 1.95 Å. The explanation for such discrepancies may sometimes be found by taking account of the effects on & of specific ion-solvent interactions which are not included in the continuum theory on which the conductance equations are based. The inclusion of dielectric saturation results in an increase in derived & values³⁵ and has been successfully applied for solutions of alkali metal salts in sulfolane,³⁶ where a much better correspondence between d values and crystallographic radii resulted.

Such an effect, however, is important with ions of high surface charge density, and it is difficult to believe it would be important for quaternary ammonium ions where the single positive charge is buried in a paraffin shell. It was decided, therefore, to investigate the effect of the viscosity correction on the *å* values. If this effect is included, the slope of the Fuoss-Onsager plots is actually $J - F\Lambda_0$, and in order to determine the correct value of J, the Einstein viscosity coefficient, F, must be evaluated. This, in turn, requires a value of the hydrodynamic radius, R^{22} We do have values of hydrodynamic radii calculated from the conductance data, but in view of the objections which have been raised against Stokes' law and alternatives to it,³⁷ we have elected to use the radii calculated from the molal volumes of the corresponding paraffins for the calculation of the viscosity correction. These radii are given in column six of Table IV. This treatment may actually be an over-correction, since the viscosity term is $F\Lambda C$ and not $F\Lambda_0 C$. The correction should serve, however, to give us some idea of its effect on

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the values of a calculated from J. The results are given in the sixth column of Table V.

It is seen that the correction amounts to changes in å of 0.2-0.4 Å for the smaller ions and no more than 1 Å for the largest. The situation for the tetramethylammonium salts has not been improved much; the *d*value for Me₄NBr is still less than the radius of the bromide ion, whereas the results from the iodide would imply an effective radius of the Me_4N^+ ion at contact of about 0.5 Å, which is unrealistic. Recent theoretical and experimental considerations have shown, however, that little of real physical significance may be attached to the distance of closest approach derived from $J.^{38}$ Arguments given by Gurney³⁹ also support this conclusion. For these reasons, we have reported in Table III the lumped coefficient, $J - F\Lambda_0$, in the Fuoss-Onsager equation. The uncertainties in the higher-order terms will have little effect on the intercept, Λ_0 .

Ionic Association. A good idea of the extent of ion association in a solvent may be obtained by comparing experimental and theoretical slopes of Onsager's equation.⁴⁰ A positive deviation from the Onsager limiting tangent, $-(\alpha \Lambda_0 + \beta)$, is generally attributed to ion association; the more pronounced the association, the greater the deviation.

Table V present the results of such a comparison for the quaternary ammonium halides in DMSO. We see that Me₄NI and Me₄NBr, and possibly Et₄NBr, are the most highly associated salts of those studied. The small positive deviations exhibited by Et₄NI and Pr_4NCl , though real, must be taken as evidence for virtually negligible association for these salts. The remaining salts give no indication whatever of ion association.

It is possible that some slight association to ion pairs may be partly responsible for the low values of \hat{a} for Me₄NBr and Me₄NI. For slightly associated salts, the slope of the Fuoss-Onsager equation, after correcting for viscosity, becomes $J - K_a \gamma^2 \Lambda_0$, and Fuoss has shown⁴¹ that a precision of $\pm 0.001\%$ would be required to resolve the two terms. Such precision must be regarded as unattainable with present-day techniques. If we assume a "reasonable" value for the ion-size parameter, however, we could calculate J, and from the corrected slope obtain a rough value of the association constant.

We have arbitrarily assigned a value of 4.0 Å to afor Me₄NI, in order to calculate J. Using this value of J and the experimental slope, corrected for the $F\Lambda_0$ term, we obtain a value of 2.2 for the association constant of Me₄NI in DMSO. Assigning the same value of a to Me₄NBr gives an association constant of 4.5 for this salt.

One final point deserves comment. An inspection of Figure 1 shows an extremely interesting difference between the two reference electrolytes which cannot be explained by current theory. The limiting conductances of these salts differ by only 0.02 conductance unit, and it is quite reasonable to assume that the anions have approximately equal volumes. Nevertheless, the tetraphenylborate salt has a more positive coefficient for the linear term in the conductance function than has the tetraisoamylborate derivative. The slope of the latter is smaller than that of the former by a factor of 10, as can be seen from Table III. The viscosity correction for these salts would be of the same order and therefore could not possibly account for this difference. Thus the limiting conductances of the two salts appear to be normal, but at dilutions less than infinite unexplained differences appear. Since each salt contains the same cation, this difference in two-ion encounters must be ascribed solely to the anions.

There is, of course, one important difference in the charge distribution between the two ions: in the tetraalkyl anion, the negative charge is localized on the central boron atom and insulated by a paraffin shell, whereas in the tetraphenyl anion, the negative charge is distributed over the four aryl groups. It might be argued that this would make the ion more compatible with the surrounding polar medium. Alternatively, we have seen that for slightly associated salts, the conductance equation contains a term (J')-K')C and the difference in slopes could reflect differences in the relative magnitudes of J' and K' between the two salts.⁴² Such a situation, however, would require TAATAB to be more associated than TAATPB, a conclusion which is difficult to accept if purely coulombic forces were involved in the association process.

A similar situation has been found by Skinner and Fuoss for the conductance of sodium tetraphenylborate and triisoamylbutylammonium bromide in water.⁴² They postulated that differences in association of the two salts could account for the difference in Fuoss-Onsager slopes. Even if such were the case for TAA-TPB and TAATAB in DMSO, it is not clear why association would be more favorable for TAATAB. Further work with these and other salts of similar type is being planned in an effort to determine the cause of this behavior.

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The Conductance of Dilute Solutions of Cesium

and Sodium in Methylamine

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Data are reported on the conductances of dilute solutions of cesium and sodium in liquid methylamine at -50.0, -60.0, and -70.0° . The general form of the conductance curves for the two metals differed markedly. Limiting equivalent conductances and dissociation constants for the cesium-methylamine system have been determined by the Shedlovsky extrapolation method.

Introduction

Recent studies^{1,2} have shown that the conductivities of dilute solutions of sodium and cesium in liquid ammonia are nearly the same, and the small differences which do occur may be attributed to the different conductivities of the solvated metal ions and ion-pairing. Moreover, metal-ammonia solutions exhibit a broad optical absorption band that peaks at about 1500 $m\mu$ at -45° , and the shapes of the bands are essentially the same for the different metal solutions.^{3,4} Metalamine solutions, on the other hand, exhibit two or three absorption maxima, some of which are metal dependent.⁵⁻¹¹ Recently, Hurley, Tuttle, and Golden¹² have reported experimental evidence in support of their contention that the 660-m μ band, frequently observed in metal-amine solutions other than sodium, is due to sodium contamination during the experiment. Unfortunately, to date, the optical studies of the metalamine solutions are only qualitative.

Only a limited amount of conductance data for the systems is available. Gibson and metal-amine Phipps¹³ reported the conductance data for potassium and cesium in methylamine, but their results have been questioned because of the probable presence of impurities which tended to decompose their solutions.¹⁴ Berns, Evers, and Frank¹⁴ reported data for dilute lithium-methylamine solutions at -78° in ethylenediamine. Later, Dewald and Dye¹⁵ reported conductance data for sodium, potassium, rubidium, and cesium at room temperature. Due to the instability of their metal solutions, the recent report by Hurley, et al.,¹² concerning sodium contamination, and the lack of precise temperature control, the results reported by Dewald and Dye¹⁵ should be considered preliminary in nature. However, the study did show a marked difference between the conductivities of solutions of sodium and cesium in ethylenediamine.

We are undertaking a rather comprehensive study of the properties of metal solutions. We hope to obtain data which will lead to a better understanding of the metal-nonaqueous systems. The present investigation is concerned with the conductivity of dilute solutions of cesium and sodium in methylamine at -70.0, -60.0, and -50.0° .

Experimental Section

Materials. Methylamine (Matheson 99.8%) was condensed in vacuo into a 1-l. flask containing sodium ribbon and stored at least 1 day. The methylamine was next refluxed for 24 hr while passing through a stream of purified nitrogen. The solvent was then distilled through a 1-m fractionating column packed with 2-mm helices and the middle fraction was collected. The system was designed so that the solvent did not come in contact with the atmosphere during the refluxing and fractionating stages. The methylamine was then condensed in vacuo into another trap containing sodium-potassium alloy. A dark blue solution formed immediately upon contact of the solvent with the metal alloy. The solutions always remained blue at Dry Ice temperatures (about 2 months was the longest period tested). Usually, the blue solution was stored in vacuo for 2 days after which the solvent was pro-

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	7						
Run no.	10* <i>M</i>	Δ	10• <i>M</i>	Δ	10 4 <i>M</i>	۸	
42	0.506	142	0.497	173	0.491	202	
68	0.844	124	0.829	154	0.817	187	
32	1.11	118	1.09	148	1.08	178	
28	1.17	110	1.15	143	1.14	171	
36	1.61	104	1.59	135	1.57	161	
50	3.82	84.6	3. 77	110	3.73	132	
44	5.18	79.6	5.09	98.6	5.03	120	
24	7.85	69.2	7.76	89.8	7.65	110	
38	10.0	64 .6	9.88	82.2	9.75	98.	
40	15.6	57.8	15.4	74.1	15.2	89.	
30	21.0	53.6	20.7	68.5	20.4	82.	

Table I: Conductance-Concentration Data for Solutions of Cesium in Methylamine

cessed further by following the scheme described previously for the purification of liquid ammonia.^{1,16}

Cesium (a gift from the Dow Chemical Co.) and sodium (United Mineral and Chemical Co.) were distilled twice *in vacuo* and stored in Pyrex capillaries. Breakseal tubes containing ammonium bromide (Fisher Reagent) were prepared by a method described elsewhere.¹

Apparatus and Procedure. The apparatus used in this study was similar to that described elsewhere.¹ Only electrodes of bright platinum were used in this study. The cell constants were determined by established procedures.^{1,17} Measurements were made at 600, 1000, 2000, and 4000 Hz. The conductance equipment used has been described elsewhere.^{18,19}

The procedure used in preparing the metal solutions and taking resistance measurements was identical with that which was found adequate for metal ammonia solutions.^{1,2} As observed with other metal solutions in the dilute region^{1,2,15,17} it was necessary to agitate the solution between the electrodes while determining the resistance of the solution. However, the resistance of solutions of sodium in methylamine was rather insensitive to agitation. The metal concentrations for each run (Tables I and II) were determined by procedures described elsewhere.¹

Measurements were made at -50.0 ± 0.1 , -60.0 ± 0.1 , and $-70.0 \pm 0.1^{\circ}$. The temperatures were maintained by a Harris Manufacturing Co. Model 1Le-BC2-075 convection fluid test chamber. Dow Corning No. 200 silicone fluid was used as the bath liquid.

Some remarks about the stability of metal-methylamine solutions seem warranted at this time. In an experiment, a $1.4 \times 10^{-4} M$ cesium solution was prepared and the resistance of the solution monitored for 70 hr. The resistance of the solution was found to increase at a rate of less than 1%/hr at -34° . Usually it took about 2 hr to complete the resistance measurements at the different temperatures. Hence the accuracy of the results reported herein should be within 2%. It was also observed that rate of dissolution of the metals in methylamine was much slower than we ex-

 Table II:
 Conductance-Concentration Data for Solutions of Sodium in Methylamine

	70.0°		60.0°		50.0°	
un no.	104 <i>M</i>	۸	104 <i>M</i>	Δ	104 <i>M</i>	۸
60	0.113	51.0	0.111	62.5	0.109	73.5
64	0.366	47.3	0.361	58.4	0.356	72.5
58	0.652	45.5	0.643	56.4	0.634	68 .2
56	0.828	44.2	0.818	55.5	0.806	67.7
48	1.32	42.1	1.30	54.1	1.29	65.4
62	1.56	41.7	1.54	52.7	1.51	64.7
48 62	1.32 1.56	42.1 41.7	1.30 1.54	53.5 54.1 52.7	1.29 1.51	

perienced in the case of liquid ammonia. It was necessary to dissolve the sodium in methylamine at -34° where it required approximately 1.5 hr to dissolve enough sodium to form a $1.2 \times 10^{-4} M$ solution. The slow rate of dissolution limited this study to only the dilute region.

Results and Discussion

The values of the equivalent conductance, Λ , in Kohlrausch units and the concentration, M, in moles per liter, are given in Tables I and II for cesium and sodium, respectively. The values of Λ at -50.0 ± 0.1 , -60.0 ± 0.1 , and $-70.0 \pm 0.1^{\circ}$ are plotted vs. $M^{1/2}$ in Figure 1.

The apparent limiting values of the equivalent conductance, Λ_0 , and the ion-pairing dissociation constants, K_1 , were evaluated for solutions of cesium in methylamine by using the method of Shedlovsky.²⁰ The dielectric constants^{14,21} and viscosities¹⁴ used in the Shedlovsky analysis of the cesium data were obtained by interpolation of available data. Values of 14.4, 15.3, and 16.2 were used for the dielectric constants and

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- (17) C. A. Kraus, J. Amer. Chem. Soc., 43, 749 (1921).
- (18) H. B. Thompson and M. T. Rogers, Rev. Sci. Instrum., 27, 1079 (1956).
- (19) G. E. Smith, Ph.D. Thesis, Michigan State University, 1963.
- (20) T. Shedlovsky, J. Franklin Inst., 225, 738 (1938).
- (21) H. Urich and W. Nespital, Z. Phys. Chem., B16, 221 (1932).



Figure 1. Plots of Λ vs. $M^{1/n}$ for solutions cesium and sodium in methylamine.

0.00521, 0.00631, and 0.00763 P for the viscosities at -50.0, -60.0, and -70.0° , respectively. The extended Debye-Hückel expression, employing a distance of closest approach of 5.5 Å, was used to compute the activity coefficients. Plots of the Shedlovsky analysis for the cesium data are shown in Figure 2. The various constants derived from conductance data are presented in Table II.

As shown in Figure 2, the experimental data for solutions of cesium in methylamine (for all concentrations reported in this study) can be reproduced by a conductance function having one ion-pairing dissociation constant. We would like to point out that such a fit might be fortuitous since optical spectra show the presence of two absorption bands^{5,6,22} for metal-amine systems. Previously, Dewald and Dye¹⁵ also used the Shedlovsky method to evaluate conductance data for solutions of potassium and rubidium in ethylenediamine which exhibit absorption bands other than the infrared band.⁵ These authors suggested that such a fit of the conductance data is possible if the major contributor to the conductivity of metal-primary amine solutions is the infrared absorbing species and that the contribution of other species (responsible for the other absorption bands) is small and essentially a constant fraction over the concentration range accessible to investigation.



Figure 2. Plots of the Shedlovsky analysis for cesium in methylamine.

A preliminary study²³ of the absorption spectra of solutions of cesium in methylamine $(M \simeq 10^{-3} \text{ at} - 50^{\circ})$ shows the presence of two absorption maxima, an infrared band^{5,6,7,12} and another band at about 975 m μ .²² The apparatus used in the optical study was constructed of borosilicate glass. As was shown to be the case for cesium-ethylenediamine solutions,^{5,24} no 660-m μ absorption band, character.stic of sodium contamination,¹² was observed when cesium-methylamine solutions were prepared in a clean Pyrex system. We conclude, therefore, that the effect of sodium contamination¹² on the cesium-methylamine conductance data reported in this study is probably much smaller than the 2% accuracy stated above.

The general form of the conductance curve for solutions of cesium in methylamine is similar to that which would be expected for a 1:1 electrolyte in a solvent of low dielectric constant.²⁵ The marked difference between the conductance curves of cesium and sodium in methylamine should be noted (Figure 1). Similar differences between the conductivities of solutions of cesium and sodium in ethylenediamine have been reported.¹⁵ There is alsc a marked difference between the optical spectra of sodium and cesium amine solutions,^{10,11,22} and, as in the case of metal-ethylenediamine solutions, the species responsible for the infrared absorption band is a much better conductor than the visible band species. The differences in equivalent

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- (23) R. R. Dewald, this laboratory, unpublished results.
- (24) R. R. Dewald, Ph.D. Thesis, Michigan State University, 1963.
 (25) C. A. Kraus, J. Phys. Chem., 60, 129 (1956).

conductance of primary amine solutions of cesium and sodium at corresponding concentrations must result from differences in the nature of the dissolved species rather than any electrode-solution interface phenomena. This difference in the nature of the dissolved species is also reflected in the results of kinetic studies with alkali metal-ethylenediamine systems.^{24,26,27} Preliminary kinetic studies²³ also showed that the reaction of sodium solutions with water in methylamine is markedly slower than the reaction of cesium solutions with water in methylamine. This fact suggests that different reducing species²⁷ are also present in the

different reducing species.³ are also present in the different metal-methylamine solutions. We have at this time no explanation for the anomalous conductance behavior of sodium in amine solvents. However, the Walden products, Table III, for the sodium-methyl-

System	T,°C	104kı	Λ_0	Λοη
Cs-CH ₃ NH ₂ ^a	- 50.0	1.44	249	1.3
	- 60 .0	1.43	209	1.3
	-70.0	1.38	167	1.3
Na-CH ₃ NH ₂ ª	-50.0		79	0.41
	-60.0		66	0.42
	-70.0		54	0.41
Cs–NH ₃ ^b	-33.9	48.7	1142	2.92
	-45.0	33.0	954	2.85
	-65.0	21.9	672	2.90
Na–NH3 ^c	-33.9	34.1	1127	2.88
	-45.0	24.8	927	2.77
	-65.0	18.8	645	2.79
$Cs-(CH_2NH_2)_2^d$	Room	1.44	204	3.1
$Na-(CH_2NH_2)_2^d$	Room		27	0.42
Li-CH ₃ NH ₂ ^e	-78.3	0.55	228.3	2.07
Li–NH₃′	-71.0	12.8	558.7	2.8

amine and sodium-ethylenediamine systems are the same. It should also be noted that the Walden products for sodium in methylamine are temperature independent, indicating that the conductance mechanism for this system at infinite dilution is viscosity dependent.

A log-log plot of the product of the specific conductance and viscosity vs. concentration (Figure 3) tends to correct for differences in viscosity, and is useful in comparing the different metal systems. The marked difference in the dependence of conductance on temperature between the cesium-ammonia and cesiummethylamine systems should be noted. Within experimental error, the differences in the conductances of solutions of cesium in methylamine at the three temperatures can be accounted for by the viscosity of the solvent, Figure 3, but this is not the case for cesiumammonia solutions where the dissociation constants

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Figure 3. Log-log plot of the specific conductance, κ , and viscosity, η , vs. concentration, M. Open and closed triangles: cesium in liquid ammonia at -33.9 and -65.0° , respectively, ref 2; open square: cesium in ethylenediamine at room temperature, ref 15; open circles: lithium in methylamine at -78.3° , ref 14; closed circles, cesium in methylamine at -50, -60, and -70° , this work.

were found to vary with temperatures (Table III). The dissociation constants for cesium in methylamine are predicted by Fuoss' theory²⁸ using a distance of closest approach of 5.2 ± 0.1 Å and are nearly independent of temperature (Table III). The dissociation constants for the cesium-ammonia system are somewhat larger than for solutions of cesium in methylamine and ethylenediamine (Table III), as would be expected on the basis of the higher dielectric constant of ammonia. It should also be noted that solutions of cesium in ammonia and ethylenediamine tend to be better conductors, Figure 3, and have much larger Walden products, Table III, than the cesium-methylamine system. This fact suggests that the solvent structure has influence on the mobility of the anion,²⁹ i.e., the solvated electron, or that the hydrodynamic radii of the ions in methylamine are markedly different than in ammonia or ethylenediamine. Transference number data for the metal-amine systems would be of interest.

It should be noted that the data reported by Berns, Evers, and Frank¹⁴ for the conductance of lithium in methylamine show a deviation from the usual straightline log-log plot at about 0.02 M (Figure 3). It is tempting to attribute this anomalous behavior to a systematic error introduced in their method of determining the metal concentration in the dilute region. In this study, each experimental point is based on an analysis

(26) L. H. Feldman, R. R. Dewald, and J. L. Dye, "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1963, p 163.

- (27) J. L. Dye, Accounts Chem. Res. 1, 306 (1968).
- (28) R. M. Fuoss, J. Amer. Chem. Soc., 80, 5059 (1958).
- (29) E. C. Evers and F. R. Longo, J. Phys. Chem., 70, 426 (1966).

for the amount of metal while Berns, *et al.*, employed a "method of overlapping data" to determine their metal concentrations in the dilute region. Moreover, it is difficult to understand why a lithium solution should be a better conductor than cesium in the dilute concentra-

tion region where differences should reflect the conductivities of the solvated metal ion.

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The Mutual Solubility of Anhydrous Hydrogen Fluoride

and Aliphatic Hydrocarbons

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The mutual solubilities of anhydrous hydrogen fluoride (AHF) and *n*-pentane, *n*-hexane, and *n*-heptane have been measured under equilibrium pressure conditions of the mixed vapors at five temperatures between -25° and 40° . These data, and literature data for propane, *n*- and isobutane, and octane, are compared with the corresponding data for water and hydrocarbons. Contrary to the latter, the solubilities of hydrocarbons in AHF have positive standard enthalpies, and the solubility of AHF in hydrocarbons decreases with their increasing size. The treatments of Hildebrand and Scott and of Nemethy and Scheraga for the mutual solubilities with water were examined as to their applicability to the AHF systems. A treatment following that of Prigogine and Defay for associated liquids is shown to apply better, and leads to an estimate of the fraction of monomeric hydrogen fluoride in AHF of from 0.1 to 1% at 20°.

Introduction

In the course of work on the distribution of amines and their salts between liquid anhydrous hydrogen fluoride (AHF) and liquid aliphatic hydrocarbons,¹ it became necessary to measure the mutual solubilities of the solvents. Although small, this mutual solubility can be of significance for the distribution of solutes but is also of interest in itself, since it may shed some light on the nature of AHF, about which little is as yet known.

Whereas aromatic hydrocarbons show appreciable solubility in AHF,² forming protonated species, the aliphatic ones, where such species cannot form, have rather low solubilities. Conversely, the solubility of AHF in these hydrocarbons is also quite low. Butler, Miles, and Kuhn³ studied the mutual liquid-liquid solubilities of AHF and propane, *n*-butane, and isobutane in the temperature interval 5-50°. The two liquid layers were under the mixed vapor, exerting the appropriate equilibrium pressure. Simons⁴ measured the solubility of AHF in *n*-octane by passing the vapors of boiling AHF (at atmospheric pressure) through the solvent held at temperatures in the interval 25-66° until saturation. These data can be recalculated to liquid-liquid solubilities under equilibrium pressures from the vapor pressure data for AHF.

To complete the picture, mutual liquid-liquid solubilities of AHF and *n*-pentane, *n*-hexane, and *n*-heptane have now been obtained under equilibrium pressures in the temperature interval -25 to 40° .

AHF is a polar, hydrogen bonded, and therefore a highly associated liquid. The aliphatic hydrocarbons, on the other hand, are nonpolar and not very polarizable liquids. The available theories for liquid solutions are inadequate for dealing with a mixture of such diverse substances. The extreme nonideality of the mixture is manifested by the low solubilities and the expected nonattainment of a consolute temperature below the critical gas-liquid points, as seen from the solubility vs.

(4) J. H. Simons, J. Amer. Chem. Soc., 53, 83 (1931).

⁽¹⁾ J. Soriano, J. Shamir, and Y. Marcus, to be published.

⁽²⁾ E. L. Mackor, A. Hofstra, and J. H. Van der Waals, Trans. Faraday Soc., 54, 186 (1958); C. Maclean, and E. L. Mackor, Discussions Faraday Soc., 34, 165 (1962).

⁽³⁾ E. B. Butler, C. V. Miles, and C. S. Kuhn, Ind. Eng. Chem., 38, 147 (1946).

temperature curves. Since, however, the solubilities of hydrocarbons in water—another highly associated liquid—and the excess thermodynamic functions of homogeneous mixtures of hydrocarbons and the associated lower alcohols have been discussed in terms of several theories, this is attempted in the present case too.

Experimental Section

Materials. Anhydrous hydrogen fluoride (AHF) (Matheson Co., Inc.) was purified prior to utilization by a two-step procedure. It was first frozen in liquid air and degassed to remove noncondensable gases and then vacuum distilled from a solid CO₂-trichloroethylene bath (-78°) to a liquid air bath (-190°) to get rid of H₂O. The AHF obtained had a specific conductivity of 2 \times 10⁻⁵ to 6 \times 10⁻⁵ cm ohm⁻¹.

n-Pentane, *n*-hexane, and *n*-heptane (Fluka Analytical grade) were first dried over P_2O_5 and then fractionally distilled, the middle fraction being collected for use.

Apparatus. A high-vacuum line made exclusively of Kel-F was used; the line included a manifold to which a series of five Kel-F tubes could be connected through special Kel-F valves.

Procedure. A Kel-F tube of 25 ml capacity, containing a Teflon-coated magnetic bar, was connected to the vacuum line and evacuated; about 10 g (10 ml) of AHF was then condensed into this tube and weighed. A similar volume of hydrocarbon was then distilled into the same tube and it was weighed again. The contents of the tube were agitated for 4 to 5 hr by a reciprocating external magnet at a temperature controlled to $\pm 2^{\circ}$. This period was found to be ample for attainment of equilibrium. The phases were allowed to settle down until the interface could be discerned in the translucent Kel-F tube; they were then separated in a closed system into two separate preweighed Kel-F tubes, and the weight of each phase was then determined. The tubes were then frozen and opened; the contents were diluted with a known standard NaOH solution. The excess NaOH was then titrated with standard HCl and the HF content determined. The hydrocarbon content of the HF-rich phase was thus obtained by difference but with acceptable precision.

Results

The measured solubilities are shown for *n*-pentane, *n*-hexane, and *n*-heptane in AHF in Figure 1, and of AHF in these hydrocarbons in Figure 2, as functions of the reciprocal temperature. Each point represents the average of three experiments, agreeing within $\pm 5\%$. The data of Butler, *et al.*,³ for propane and *n*-butane, converted from weight to mole fractions, are also shown for comparison. All the data can be expressed as the straight lines log $x_{\rm HR} = A_{\rm HR} + B_{\rm HR}/T$ and log $x_{\rm HF} =$ $A_{\rm HF} + B_{\rm HF}/T$, where x_i is the mole fraction of component i in the j-rich phase, where j is the second com-



Figure 1. Solubility of aliphatic hydrocarbons in AHF, expressed as mole fractions, as a function of the reciprocal temperature. Data points were obtained in this work; lines without points express literature data.

ponent. The constants A and B obtained from the data by a least-squares computation are shown in Table I for the normal hydrocarbons propane to heptane and also for isobutane.³ This table includes also the values for the data of Simons⁴ for *n*-octane, recalculated to equilibrium pressures, using the vapor pressure equation⁵ log P(Torr) = 7.37 - 1316/T. The corresponding data for the solubility of *n*-octane in AHF have not been reported.

Standard enthalpies and entropies of solution were obtained directly from the B and A values, respectively, assuming the saturated solutions to be in equilibrium with the pure liquid component, rather than with a phase containing also the other component. In view of the small solubilities, the errors introduced in this way are small. The results are also shown in Table I. A regular change of these quantities with the size of the hydrocarbons or the number C of carbon atoms is seen, in general, excepting the data for *n*-octane, where the correction to the equilibrium pressure may not be adequate. The data for isobutane are sufficiently similar to those of *n*-butane, so that in the following

(5) G. H. Simons, J. Amer. Chem. Soc., 46, 2179 (1924); W. H. Claussen and J. H. Hildebrand, *ibid.*, 56, 1820 (1934).

С	$A_{\rm HR}$	$B_{\rm HR}$	AEF	$B_{\rm HF}$	Δ <i>H</i> _{HR} °	ΔS _{HR} °	∆ <i>H</i> _{HF} °	$\Delta S_{\rm HF}^{\circ}$
3	+0.415	-605	+2.58	-1225	2780	+1.90	5650	+11.85
n4	-0.135	-570	+1.75	-1060	2620	-0.60	4880	+8.05
i4	+0.23	-630	+1.75	-1010	2890	+1.05	465 0	+8.10
5	-0.49 ± 0.02	-518 ± 12	$+0.76 \pm 0.04$	-807 ± 30	2370	-2.25	3690	+3.50
6	-0.695 ± 0.02	-497 ± 11	$+0.13 \pm 0.01$	-638 ± 25	2270	-3.20	2920	+0.60
7	-0.89 ± 0.02	-467 ± 12	-0.145 ± 0.01	-569 ± 21	2140	-4.10	2600	-0.65
8			$+0.02 \pm 0.03$	-725 ± 25			3320	+0.10
^a ∆H° ii	n cal/mol pertains to tra	unsfer from the pu	re liquid into the sat	urated solution, a	nd ∆S° in c	al/deg mo	l is $\Delta H^{\circ}/2$	$r + \ln x_i$.

Table I: Parameters for the Mutual Solubilities of Hydrocarbons and AHF^a



Figure 2. Solubility of AHF in aliphatic hydrocarbons expressed as mole fractions, as a function of the reciprocal temperature. Data points were obtained in this work; lines without points express literature data.

they are discussed along with those for the normal hydrocarbons.

Discussion

Comparison with the Mutual Solubility with Water. As the data in Figures 1 and 2 and in Table I show, the solubility of the hydrocarbons in AHF decreases with increasing size of the hydrocarbon, similarly to their behavior in water (see ref 6 for a summary of the data), but contrary to that, increases with increasing temperature. The solubility of AHF in the hydrocarbons, on the other hand, increases with temperature, as does the solubility of water,⁷ but in the range of measurement decreases with the size of the hydrocarbon, contrary to the behavior of water. Let us discuss the latter comparison first.

Hildebrand and Scott[®] applied the equation

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$$\ln a_{\rm H_{2O}} = \ln \phi_{\rm H_{2O}} + \phi_{\rm HR} \left(1 - V_{\rm H_{2O}}/V_{\rm HR}\right) + V_{\rm H_{2O}}\phi_{\rm HR}^2 \left(\delta_{\rm H_{2O}} - \delta_{\rm HR}\right)^2/RT \quad (1)$$

...

to the data of Black, Joris, and Taylor,⁷ in order to calculate $\delta_{\text{H}_{2}\text{O}}$ from the solubility data $\ln x_{\text{H}_{2}\text{O}} = \ln$ $\phi_{\rm H_{2}O}$ + ln $V_{\rm HR}/V_{\rm H_{2}O}$. In this equation $a_{\rm H_{2}O}$, the activity of water, is taken as unity since the low solubility of the hydrocarbons in water does not change its activity appreciably, ϕ_i is the volume fraction of component i, according to $\phi_i = x_i V_i / (x_{H_{2O}} V_{H_{2O}} + x_{HR})$ $V_{\rm HR}$), $x_{\rm i}$ is its mole fraction, $V_{\rm i}$ its molar volume, and $\delta_{\rm i}$ its solubility parameter, $\delta_i = (\Delta E_i^{v}/V_i)$, ΔE_i^{v} being the molar energy of vaporization. Using the known molar volumes and δ_{HR} values with the solubility data for 20°, Hildebrand^{8,9} arrived at the constant value $\delta_{H_{20}} = 24.0$ for the aliphatic hydrocarbons, fortuitiously the same as the value obtained from $(\Delta E_{H_{20}}^{v}/V_{H_{20}})^{1/2} = 23.8.$ Black, Joris, and Taylor themselves,⁷ however, concluded from the application of the same equation that even correcting for size effect¹⁰ (the second term on the right-hand side of eq 1) does not account wholly for the observed solubilities. Furthermore, the equation is found to be completely inadequate to account quantitatively for the temperature coefficient of the solubility. Thus a considerable portion of the experimental information available has escaped quantitative interpretation.

In this case there is thermodynamic and spectroscopic evidence¹¹ that water is monomeric in the dilute solutions involved, contrary to its state in the

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- (7) C. Black, G. G. Joris, and H. S. Taylor, ibid., 16, 537 (1948).
- (8) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Reinhold Publishing Corp. 1950, pp 266-268.
- (9) J. H. Hildebrand, J. Chem. Phys., 17, 1346 (1949).
- (10) J. H. Hildebrand, ibid., 15, 225 (1947).

⁽¹¹⁾ D. F. Stevenson, J. Phys. Chem. 69, 2145 (1965); W. L. Masterton and M. C. Gendrano, *ibid.*, 70, 2895 (1966); J. R. Johnson, S. D. Christian, and H. E. Affsprung, J. Chem. Soc., A, 77 (1966).

pure liquid. The inadequacy of eq 1 could therefore be even more severe for AHF, which is associated in the gaseous phase, and may thus be associated also in dilute solutions. Equation 1 takes into account the size effect—through the use of $\phi_{H_{2}O}$ in the first term instead of $x_{\rm H_{2}O}$, and the second term on the right-hand side. If AHF is associated in dilute solution, this factor should be of less importance, since the discrepancy in sizes between the associated hydrogen fluorice species and the hydrocarbon molecules is not as large as between $V_{\rm HF}$ and $V_{\rm HR}$. Furthermore, this factor is rather small in any case. The other effect that eq 1 considers, in the third term, is the resultant of the interaction energies of the two components. The mutual interaction energy, which in general is the geometric mean but could hardly be so in the present case, is collected into the empirical parameter $\delta_{\rm H_2O}$.

According to the concepts of Hildebrand,^{8,9} the increase of the solubility of water with the size of the hydrocarbon depends on the decrease of the difference $\delta_{\rm H_2O} - \delta_{\rm HR}$ as $\delta_{\rm HR}$ increases, that is, ultimately, to the increasing interaction between the two components. In order for the solubility of AHF to decrease with increasing size and $\delta_{\rm HR}$ of the hydrocarbon, $\delta_{\rm HF}$ must be smaller than $\delta_{\rm HR}$, which is evidently absurd. Therefore a term such as the last term in eq 1 cannot be the predominating one in an equation describing the solubility of AHF in hydrocarbons.

Turning now to the solubility of the hydrocarbons in the other component, which is highly associated through hydrogen-bonding, there is the recent work of Nemethy and Scheraga,⁶ who examined previous experimental data and applied their theory for hydrophobic bonding^{6,12} to the results. Their equation

$$-RT \ln x_{\rm HR} = G_{\rm HR}^{\rm E} = Y^{\circ} \Delta E_1 - E_{\rm HR-HR} - T\Delta S_{\rm conf} + Y^{\circ} (G^{\circ}_{\rm H_2O} - G^{\circ}_{\rm H_2O}) \quad (2)$$

equates the excess molar free energy of the saturated solution in equilibrium with pure liquid hydrocarbon with $-RT \ln x_{\rm HR}$, and divides it into terms pertaining to the change in free energy of the hydrocarbon (the first three terms on the right-hand side) and to that of water (the last term). The parameter Y° is the number of water molecules in the first layer around the hydrocarbon molecule (calculated from models, and equals 2C + 12; ΔE_1 , a free parameter, is the decrease in energy a water molecule with four hydrogen bonds suffers when it is situated in the first layer around the hydrocarbon; $-E_{HR-HR}$ is the energy required to break the hydrocarbon-hydrocarbon interactions in the pure liquid; ΔS_{conf} is the configurational entropy of coiling, which increases as the hydrocarbon molecules from pentane onwards change from the restricted, parallel, positions in the liquid to the more random configurations in the dilute solutions ($\Delta S_{conf} = +0.6 (C - 4)$ eu for C > 4; and $(G^{\circ}_{H_{2}O} - G^{\circ}_{H_{2}O})$ is the free energy change for one mole of water being transferred from the bulk to the first layer around the hydrocarbon. This quantity is estimated statistically,¹² and in addition to parameters necessary to fit the bulk properties of water, requires the free parameters ΔE_1 described above and ΔE_r , the rise in energy of a water molecule in the first layer which has zero to three hydrogen bonds. The parameters ΔE_1 and ΔE_r were adjusted to give a good fit of eq 2 with the experimental $x_{\rm HR}$ at one temperature, and the additional parameter $E_{\rm HR-HR}$ was adjusted in order to fit the experimental temperature coefficients of the solubility. Due to the scattering of the experimental data, this could be done only to a limited extent.

The decrease in solubility with increasing size is due mainly to the term $-E_{\text{HR}-\text{HR}}$ in eq 2, which is closely related to $\Delta E_{\rm HR}$, hence to $\delta_{\rm HR}$, and partly to the term Y^{c} ($G^{c}_{H_{2}O} - G^{o}_{H_{2}O}$), through Y^{c} the number of water molecules which suffer a change in free energy; the other terms are relatively small. The first effect should be the same for solutions of hydrocarbons in AHF, and seems to predominate there too, as the solubility in this solvent also decreases with increasing hydrocarbon size. However, whereas the term $-E_{HR-HR}$ predominates in G^{E} (making a large positive contribution), the term Y^c ($H^{c}_{H_{2}O} - H^{o}_{H_{3}O}$) must predominate in H^{E} , and make a large negative contribution, since the overall sign of H^{E} , the enthalpy of solution, is negative for hydrocarbons in water. This is explained qualitatively by the collapse of the three-dimensional structure of water with increasing temperature, hence by a decrease of the special circumstances leading to the hydrophobic bonding term, the last term on the right-hand side of eq 2. The positive enthalpy of solution of the hydrocarbons in AHF shows the absence of such special circumstances, or the absence of changes in the association of hydrogen fluoride of the kind which are important in the association of water.

Rationalization of the Mutual Solubilities. This attempt to rationalize the mutual solubilities of AHF and hydrocarbons follows the treatment of Prigogine and Defay¹³ of the excess free energies of mixtures of inert and associated liquids. The chemical potential of each component in each phase is expressed as a sum of terms for the various effects and interactions as follows.

(1) The standard state of the pure liquid is used for the standard chemical potential. Thus $(x_{\rm HR} = 1, x_{\rm HF} = 0, T, P_{\rm equil})$ is used for $\mu^{\circ}_{\rm HR}$ for both the hydrocarbon-rich phase and the dilute solution of the hydrocarbon in AHF, and similarly for $\mu^{\circ}_{\rm HF}$. The burden of the extreme nonideality observed is thus put on the other terms.

(2) The ideal partial free energy of mixing is stated in terms of mole fractions (and not volume fractions).

⁽¹²⁾ G. Nemethy and H. A. Scheraga, J. Chem. Phys., 36, 3382 (1962).

⁽¹³⁾ I. Prigogine and R. Defay, "Chemical Thermodynamics," Longmans and Green, London, 1954, pp 409-436.

С	$(V_{\rm HR} + V_{\rm HF}) \alpha/RT - \ln z^{\circ}({\rm HF})_1$	From eq 5	From eq 9
3	54.5 $\alpha/T - \ln x^{\circ}_{(\text{HF})_1} =$	-12.2 + 7400/T	-11.6 + 7400/T
n4	$60.5 \ \alpha/T \ - \ln x^{\circ}_{(\mathrm{HF})_1} =$	-8.8 + 6950/T	-9.5 + 7000/T
i4	$62.5 \ \alpha/T \ - \ \ln x^{\circ}_{(\mathrm{HF})_1} =$	-9.6 + 7000/T	-8.9 + 6900/T
5	$68.0 \ \alpha/T - \ln x^{\circ}_{(\mathrm{HF})_1} =$	-5.5 + 6200/T	-6.9 + 6550/T
6	$76.0 \ \alpha/T \ - \ln x^{\circ}_{(\mathrm{HF})_1} =$	-3.6 + 5800/T	-4.1 + 6050/T
7	$84.0 \ \alpha/T - \ln x^{\circ}_{(\mathrm{HF})_1} =$	-2.4 + 5650/T	-1.3 + 5600/T

Table II: Evaluation of the Parameters α and $x^{\circ}_{(HF)_1}$

(3) Therefore, size effects are expressed by means of the entropy effect of mixing molecules of different sizes,¹⁰ *i.e.*, the second term on the right-hand side of eq 1. This contribution to μ_i is of the form $RT[\ln (V_i/V_i) + \phi_i (1 - V_i/V_i)]$. If, through association, the effective $V_{\rm HF}$ would be larger than the nominal $V_{\rm HF} = 20$ ml/mol, this term should become smaller, and it should also be modified if shapes other than segments and chains are considered. The molar volumes of the hydrocarbons range from 89.0 ml/mol for propane to 148.0 ml/mol for heptane (see Table II).

(4) The contribution of the enthalpy of mixing to the chemical potential of component i is described by means of a term of the form $V_i x_i^2 \alpha$, where α is taken as independent of the composition. If, but for the association of AHF and the size effect, the solutions were regular, α would have the form $(\delta_{\rm HR} - \delta_{\rm HF})^2$.

(5) The contribution of the configurational entropy of the hydrocarbons from pentane on, as described by Nemethy and Scheraga,⁷ is by a term $T\Delta S_{conf} = 0.6$ (C - 4) T cal/mol for the AHF-rich phase relative to the hydrocarbon-rich phase.

(6) The association of AHF is taken into account by an activity coefficient,¹³ which relates the nominal to the actual mole fractions in the mixture. For the nonassociated component, the hydrocarbon, this is of the form $1/(x_{\rm HR} + x_{\rm HF}/\chi)$, where χ is the mean aggregation number of hydrogen fluoride in the appropriate phase, *i.e.*

$$\chi = \sum_{n} n N_{(\text{HF})_{n}} / \sum_{n} N_{(\text{HF})_{n}} = N_{\text{HF}} / \sum_{n} N_{(\text{HF})_{n}}$$
 (3)

where N is the number of moles and $(HF)_n$ is an aggregated species of AHF. For the associated component the activity coefficient is of the form $N_{(HF)_l}/x^{\circ}_{(HF)_1}$ $N_{HF} (x_{HR} + x_{HF}/\chi)$, where $(HF)_1$ is the monomer of hydrogen fluoride and $x^{\circ}_{(HF)_1}$ is the fraction of this monomer in pure AHF.

The chemical potentials are now written out as follows, the phase to which each quantity pertains being given in parenthesis.

$$\mu_{\mathrm{HR}(\mathrm{HR})} = \mu^{\circ}_{\mathrm{HR}(\mathrm{HR})} + RT \ln x_{\mathrm{HR}(\mathrm{HR})} + RT \left[\ln \left(V_{\mathrm{HR}} / V_{\mathrm{HF}} \right) + \phi_{\mathrm{HF}(\mathrm{HR})} \left(1 - V_{\mathrm{HR}} / V_{\mathrm{HF}} \right) \right] + V_{\mathrm{HR}} x_{\mathrm{HF}(\mathrm{HR})}^{2} \alpha - RT \ln \left(x_{\mathrm{HR}(\mathrm{HR})} + x_{\mathrm{HF}(\mathrm{HR})} / \chi_{\mathrm{(HR)}} \right)$$
(4a)

 $\mu_{\rm HR(HF)} = \mu^{\circ}_{\rm HR(HF)} + RT \ln x_{\rm HR(HF)} +$

$$RT[\ln (V_{\rm HR}/V_{\rm HF}) + \phi_{\rm HF(\rm HF)} (1 - V_{\rm HR}/V_{\rm HF})] + V_{\rm HR}x_{\rm HF(\rm HF)}^2 \alpha - RT \ln (x_{\rm HR(\rm HF)} + V_{\rm HR})$$

$$x_{\rm HF(HF)}/\chi_{\rm (HF)}) + T\Delta S_{\rm conf}$$
 (4b)

 $\mu_{\rm HF(HR)} = \mu^{\circ}_{\rm HF(HR)} + RT \ln x_{\rm HF(HR)} + RT [\ln (V_{\rm HF}/V_{\rm HR}) + \phi_{\rm HR(HR)} (1 - V_{\rm HF}/V_{\rm HR})] + V_{\rm HF} x_{\rm HR(HR)}^2 \alpha + RT \ln [N_{\rm (HF)_1(HR)}/$

$$x^{\circ}_{(\rm HF)}N_{\rm HF(\rm HR)}(x_{\rm HR(\rm HR)} + x_{\rm HF(\rm HR)}/\chi_{\rm (HR)})]$$
 (4c)

 $\mu_{\mathrm{HF}(\mathrm{HF})} = \mu^{\circ}_{\mathrm{HF}(\mathrm{HF})} + RT \ln x_{\mathrm{HF}(\mathrm{HF})} +$

$$RT[\ln (V_{\rm HF}/V_{\rm HR}) + \phi_{\rm HR(\rm HF)} (1 - V_{\rm HF}/V_{\rm HR})] + V_{\rm HF} x_{\rm HR(\rm HF)}^2 \alpha + RT \ln [N_{\rm (HF)_1(\rm HF)}/$$

 $x^{\circ}_{(\mathrm{HF})_{1}}N_{\mathrm{HF}(\mathrm{HF})}(x_{\mathrm{HR}(\mathrm{HF})} + x_{\mathrm{HF}(\mathrm{HF})}/\chi_{(\mathrm{HF})})]$ (4d)

At equilibrium at a given temperature and pressure $\mu_{HR(HR)} = \mu_{HR(HF)}$ and $\mu_{HF(HR)} = \mu_{HF(HF)}$ and furthermore, according to our definitions $\mu^{\circ}_{HR(HR)} = \mu^{\circ}_{HR(HF)}$ and $\mu^{\circ}_{HF(HR)} = \mu^{\circ}_{HF(HF)}$.

As a first approximation, $x_{\rm HR(HR)} \simeq 1$ and $x_{\rm HF(HF)} \simeq 1$ as is seen from the data in Figures 1 and 2, and also $N_{\rm (HF)_1(HF)}/x^{\circ}_{\rm (HF)_1}N_{\rm HF(HF)} \simeq 1$. Although the experimental solubilities were obtained at equilibrium pressures, the small compressibilities of liquids lead to a negligible error if a constant pressure is assumed, so that to a good approximation $x_{\rm HR}$ (exptl) $\simeq x_{\rm HR(HF)}$ and $x_{\rm HF}$ (exptl) $\simeq x_{\rm HF(HR)}$. Thus the following expression can be obtained from eq 4, as (4b + 4c) - (4a + 4d)

$$\ln x_{\rm HR} + \ln x_{\rm (HF)_1} + (V_{\rm HR} + V_{\rm HF})\alpha/RT - \\ \ln x_{\rm (HF)_1}^{\circ} - (V_{\rm HR} - V_{\rm HF})^2/V_{\rm HR}V_{\rm HF} + \\ \Delta S_{\rm conf}/R = 0 \quad (5)$$

in which the first four terms depend on the temperature, while the other two do not (neglecting the change of the molar volumes with temperature). They do depend, however, on the hydrocarbon, while the fourth term does not. Instead of the mole fraction of AHF in the hydrocarbon-rich phase, eq 5 involves the mole fraction of the monomer of hydrogen fluoride in this phase, which is not the same, if AHF is aggregated even in rather dilute solutions.

When the various quantities and parameters are introduced into eq 5, the results can be compared with
the experimental data. This can be done at a given temperature, but a more stringent test would be to use all the data, which are of the form $\ln x_{\rm HR} = 2.303 \cdot (A_{\rm HR} + B_{\rm HR}/T)$ and $\ln x_{\rm HF} = 2.303(A_{\rm HF} + B_{\rm HF}/T)$, as given in Table I. For this purpose it is necessary to evaluate several of the parameters in eq 5.

For evaluating $x_{(HF)_{11}}$, it is now assumed that AHF is associated in dilute solutions in hydrocarbons to the same extent as it is associated in the gas phase at an equal volume concentration. An example for similar behavior would be acetic acid, which in both cases is preponderantly dimeric.¹⁴ The dilution by the hydrocarbon is thus reckoned as a decrease of the partial pressure of hydrogen fluoride vapor. Vapor density data were obtained by Strohmeier and Briegleb¹⁵ for 26-56° and up to 57% of the saturated vapor pressure at the lower temperature (520 Torr). It is unnecessary to accept any detailed view as to the species present; it is sufficient to note that the equation¹⁶

$$N_{\rm HF} = N_{\rm (HF)_1} + 2\beta_2 N_{\rm (HF)_1}^2 + 6\beta_6 N_{\rm (HF)_1}^6 \qquad (6)$$

which may be taken as an empirical equation, expresses the experimental results¹⁵ very well. The mole numbers $N_{(\rm HF)}$ and $N_{(\rm HF)_1}$ for a given volume and temperature are given in Torr, and the coefficients β_2 and β_6 have been tabulated for several temperatures between 26 and 56°. The quantity $N_{(\rm HF)_1}/N_{\rm HF}$ can now be computed numerically as a function of $N_{\rm HF}$ for any temperature, and converted to a function of $\phi_{\rm HF}$ according to the relationship

$$\phi_{\rm HF} = c_{\rm HF} V_{\rm HF} / 1000 = N_{\rm HF} V_{\rm HF} / 1000 RT = 3.2 \times 10^{-4} N_{\rm HF} (\rm Torr) / T \quad (7)$$

where $c_{\rm HF}$ is the volume concentration in mol/l. Plots of log $N_{\rm (HF)i}/N_{\rm HF}$ as a function of $\phi_{\rm HF}$ are shown in Figure 3. It is assumed that the coefficients β_2 and β_6 hold also for concentrations higher than those for which the vapor density data were given (heavy lines in Figure 3), namely into the region of interest for the solubility measurements. This follows the observation that a given set of species and their association constants holds over the wide concentration range of $10^{-4} M$ to the pure component for solutions of alcohols in aliphatic hydrocarbons,¹⁷ which closely resemble the present system. From the extrapolated lines, the following empirical relationship was derived

$$\ln x_{(\rm HF)_{1}} = \ln x_{\rm HF} + 4.30 + 2.48 \ln (V_{\rm HR}/V_{\rm HF}) - 3200/T \quad (8)$$

Insertion of the experimental values of $A_{\rm HF}$, $A_{\rm HR}$, $B_{\rm HF}$, and $B_{\rm HR}$, the values of $\ln x_{\rm (HF)_1}$ calculated from eq 8, the values of the molar volumes, and the values of $\Delta S_{\rm conf}$ for the different hydrocarbons into eq 5 yields a set of expressions for $(V_{\rm HR} + V_{\rm HF})\alpha/RT - \ln x^{\circ}_{\rm (HF)_1}$ as functions of C and T, shown in Table II.

The quantity $\ln x^{\circ}_{(HF)i}$, the logarithm of the fraction



Figure 3. The fraction of monomeric hydrogen fluoride in AHF vapor, as a function of the volume concentration of AHF, for two temperatures. Data from ref 15, calculated with constants from ref 16, are shown as heavy lines, extrapolated beyond the range of the data as light lines. The ranges of volume concentrations which the solubility data cover for the various C numbers are shown as horizontal straight sections, their ordinate positions having no significance.

of monomeric hydrogen fluoride in pure AHF, is independent of C, but depends on T, and will be assumed to have the dependence $\ln x^{\circ}_{(\mathbf{HF})_{1}} = A_{\mathbf{x}} + B_{\mathbf{x}}/T$ (cf. eq 8). The parameter α is the sum of the homo- and heterointeraction energies per unit volume,⁸ and in order to be consistent with the form of the expressions in Table II, will be assumed to depend on the temperature as $\alpha = A_{\alpha}T + B_{\alpha}$. The major contributions to α would be the dipole-dipole interactions of (aggregated) hydrogen fluoride species (the association itself, through hydrogen bonding, has already been taken into account) and the dipole-induced dipole interaction of the hydrogen fluoride with a nearby segment of the hydrocarbon. These interactions are independent of the size of the hydrocarbon. The interaction of hydrocarbon molecules with themselves by dispersion forces, although not negligible, still is a minor contribution to α , as can be seen from their δ_{HR} values, compared with estimates of $\delta_{\rm HF}$ based on analogies with other highly polar molecules. Thus, to a reasonably good approximation, the dependence of α , or of A_{α} and B_{α} , on C can be neglected. If this is done, A_x and A_a can be evaluated from the temperature-independent term in Table II, plotted as a function of $(V_{\rm HR} + V_{\rm HF})/R$, while $B_{\rm x}$ and B_{α} are obtained similarly from the temperature-dependent term, as follows

⁽¹⁴⁾ G. Allen and E. F. Caldin, Quart. Rev., 7, 255 (1953); L. W. Reeves and W. G. Schneider, Trans. Faraday Soc., 54, 314 (1958).

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⁽¹⁷⁾ A. N. Fletcher and C. A. Heller, J. Phys. Chem., 71, 3742 (1967).

ION PAIRING IN 2:2 COMPLEX ION ELECTROLYTES

$$lpha = 0.35 \ T - 61 \ cal/ml$$

 $\ln x^{\circ}_{(HF)_1} = 30.7 \pm 1.1 - (10,700 \pm 200)/T$ (9)

The validity of this procedure is empirically shown in the last column of Table II which agrees in an acceptable manner with the data and by there being no trend away from straight lines in the above mentioned plots. Least-squares standard deviations are shown for $x^{\circ}_{(\mathrm{HF})_{1}}$.

Because of our ignorance of the interactions leading to α , it is not worthwhile to discuss this parameter further. As regards $x^{\circ}_{(HF)_{11}}$, it is of interest to note that the estimate at, e.g., 20° for $x^{\circ}_{(HF)_{1}}$ comes out to be from ca. 0.1% to 1.0% in pure AHF. This fraction may be compared with various estimates of the corresponding fraction in water. Some estimates put this fraction at a much higher figure, but some others¹⁸ present spectroscopic and nuclear magnetic resonance evidence for a fraction of monomer in liquid water of a similar magnitude as the above. The situation is similar with respect to alcohols and their solutions in aliphatic hydrocarbons. There, again, recent data point to there being only a small proportion of the monomer in the pure alcohol.^{17,19} The enthalpy of monomerization in AHF is obtained as 10,700R = 21.2kcal/mol, which is considerably lower than the 40.0 kcal/mol required in the gas phase.¹⁶ This is due to the residual interactions (dipole-dipole and dispersion) in the liquid compared to the vapor, and these are included in the parameter α .

Acknowledgment. Fruitful discussions with Dr. A. Ben-Naim are gratefully acknowledged.

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Ion Pairing in 2:2 Complex Ion Electrolytes: $[Co(NH_3)_5NO_3]SO_4$

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Conductivity data are reported for aqueous solutions of $[Co(NH_3)_5NO_2]SO_4$ in the concentration range 10^{-4} to $10^{-3} N$. The Shedlovsky method was used to calculate an ion pair dissociation constant of 2.5×10^{-3} . The pK value (2.60) is significantly larger than those of simple 2:2 sulfates, corresponding to greater association. This effect has been noted previously with salts of lower charge types. A comparison of observed pK values with those calculated using the Fuoss theory of ion-pair formation suggests that nonelectrostatic forces are of major importance in 2:1 and, particularly, in 1:1 coordination compounds.

Introduction

Recently, it has been shown that 1:1 electrolytes containing the complex cation $[Co(en)_2NCSCl]^+$ are among the few salts of this valence type to be appreciably ion paired in aqueous solution.¹ Earlier, it was found that 2:1 complex ion electrolytes such as $[Co(NH_3)_5OCOCH_3]$ (NO₃)₂ and $[Co(en)_2NH_3NO_2]$ -Cl₂ are more strongly ion paired than simple salts of the same valence type.^{2,3}

It seemed desirable to extend these studies to 2:2 complex ion electrolytes to determine whether the effect referred to above persists in salts of a higher valence type. A search of the literature failed to reveal any information on ion association in coordination compounds of this type. There is, however, a great deal of data available for simple 2:2 salts.

The method used to estimate dissociation constants

of ion pairs formed by 1:1 and 2:1 complex ion electrolytes involved measuring osmotic coefficients at concentrations up to at least 0.1 m. This approach is generally inapplicable to 2:2 complex salts because of their limited solubility in water. For this reason, we turned to conductivity studies, which yield the same information from measurements at very low concentrations. The salt chosen for this work, $[Co(NH_3)_5-NO_2]SO_4$, contains a cation which is kinetically stable to aquation⁴ and an anion which shows negligible hydrolysis.

- (1) W. L. Masterton, J. Phys. Chem., 71, 2885 (1967).
- (2) L. H. Berka and W. L. Masterton, *ibid.*, 70, 1641 (1966).
- (3) W. L. Masterton, T. I. Munnelly, and L. H. Berka, *ibid.*, 71, 942 (1967).
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Experimental Section

The compound $[Co(NH_3)_5NO_2]Cl_2$ was prepared as described by Brauer.⁵ It was converted to the sulfate salt by the method of Jörgensen.⁶ The final product was recrystallized three times from water using 95% methanol. *Anal.* Calcd for $[Co(NH_3)_5NO_2]SO_4$: H, 5.3; N, 29.4; S, 11.2. Found: H, 5.3; N, 29.5; S, 11.2.

Conductivities were measured to $\pm 0.1\%$ with an Industrial Instruments Model RC-18 bridge using a cell of the Jones type. The thermostat, held at 25 $\pm 0.02^{\circ}$, contained light mineral oil. The cell constant was determined using 10^{-3} N KCl, prepared from potassium chloride recrystallized from conductivity water. The electrodes of the cell were not platinized. Conductivities were measured at 1000 and 3000 cps and the value at infinite frequency calculated as described by Jones and Bollinger.⁷

To avoid contamination by carbon dioxide, the solutions were prepared in a glove bag filled with air which had been passed through a soda lime column. Conductivity water was produced by passing distilled water through Amberlite MB-3 deionizing resin into a Pyrex flask. The flask was placed in the glove bag and the water purged of carbon dioxide by bubbling air from the soda lime column through it. A portion of this water was withdrawn and its conductivity measured. The water remaining in the flask was weighed and a weighed sample of $[Co(NH_3)_bNO_2]SO_4$ added to give a concentration in the range 10^{-4} to 10^{-3} N. From the measured conductivities of the solution and the water, the equivalent conductance of the salt was calculated.

Preliminary experiments indicated that the conductivities of solutions of $[Co(NH_3)_5NO_2]SO_4$ increased slowly when exposed to light. For this reason, the flask in which the solution was prepared was wrapped in tin foil and the conductivity cell was masked with an opaque material.

Results

The conductivity data are given in Table I; concentrations are expressed in equivalents per liter. Equivalent conductances are estimated to be accurate to $\pm 0.1\%$.

The extent of dissociation, α , of the ion pair [Co-(NH₃)₅NO₂]SO₄ can, in principle, be calculated from the relation

$$\alpha = \frac{\Lambda}{\Lambda_0 - A(\alpha c)^{1/2}}$$
(1)

where Λ_0 is the equivalent conductance at infinite dilution and A is the Onsager slope; for a 2:2 electrolyte at 25°

$$A = 1.296\Lambda_0 + 170.6 \tag{2}$$

Once α has been determined, the equilibrium con-

104c	Λ	pK(calcd)	104c	٨
0.7288	140.1	2.61	3.011	133.1
0.7598	140.0	2.60	3.101	133.0
0.8572	139.5	2.62	3.505	132.0
1.054	138.7	2.62	3.932	131.0
1.056	138.7	2.62	4.073	130.7
1.180	138.4	2.60	4.265	130.2
1.255	138.2	2.58	4.824	129.2
1.490	137.6	2.56	5.798	127.5
1.620	136.8	2.61	6.024	126.9
1.791	136.2	2.61	6.840	125.6
1.885	136.0	2.60	7.177	125.0
2.081	135.3	2.62	7.729	124.3
2.474	134.3	2.60	10.05	121.0
2.652	134.2	2.57		
2.828	133.1	2.62		

Table I: Equivalent Conductance of [Co(NH₈)₅NO₂]SO₄

stant, K, for ion-pair dissociation can be calculated from the equation

$$K = \frac{c\alpha^2 f_{\pm}^2}{2(1-\alpha)} \tag{3}$$

The factor 2 converts from molar to equivalent concentrations; f_{\pm} is the mean activity coefficient of the salt.

In order to use eq 1-3 directly, Λ_0 must be known precisely. Since this is not the case with $[Co(NH_2)_5-NO_2]SO_4$, it is necessary to use an approach which yields Λ_0 and K simultaneously. The most exact method, that of Fuoss and Kraus,⁸ requires equivalent conductance data accurate to $\pm 0.01\%$. We have used instead the approach of Shedlovsky,⁹ which has been shown to give good results with symmetrical electrolytes having ion-pair dissociation constants of 10^{-2} or less.¹⁰ This method makes use of the equation

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \frac{c\Lambda f_{\pm}^2 S(z)}{2K(\Lambda_0)^2}$$
(4)

where

$$z = \frac{A(\Lambda c)^{1/2}}{(\Lambda_0)^{1/2}}$$
 (5)

and S(z) is a function of z, available from tables,¹¹ which is defined in such a way that

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$$\alpha = \frac{\Lambda S(z)}{\Lambda_0} \tag{6}$$

To obtain K from eq 4, a method of successive approximations is used. From a preliminary estimate of Λ_0 , tentative values are assigned to z (eq 5) and hence to S(z). The quantity $1/\Lambda S(z)$ can then be plotted against $c\Lambda f_{\pm}^2 S(z)$ to give a straight line with intercept $1/\Lambda_0$. Using this value of Λ_0 , z and S(z) are recalculated and another plot is made. This process is repeated until K, as determined from the slope (slope = $1/2K\Lambda_0^2$) by least-squares analysis, no longer changes. In practice, a single refinement in Λ_0 is ordinarily sufficient to accomplish this.

In applying eq 4 to the data in Table I, activity coefficients were calculated from the equation of Davies¹⁰

$$\log f_{\pm} = -2.0 \left[\frac{I^{1/2}}{1 + I^{1/2}} - 0.30I \right]$$
(7)

where the ionic strength, I, is equal to $2\alpha c$. A straight line was obtained up to a concentration of $3 \times 10^{-4} N$. At higher concentrations a gradual curvature became evident, indicating either a deviation from the Onsager limiting law (eq 1) or from the Davies equation.

The data in the two columns at the left of Table I were fitted to eq 4 by a least-squares technique to obtain the constants

$$\Lambda_0 = 144.9$$

 $K = 2.5 \times 10^{-3}; \ pK = 2.60$

Some idea of the precision of pK may be obtained by comparing the individual values listed in Table I. These were calculated at each concentration using eq 3, 6, and 7, with $\Lambda_0 = 144.9$. There appears to be no trend in the pK values; the average deviation is ± 0.02 . It must be kept in mind, however, that the use of a different expression for f_{\pm} might change pKby more than this amount.

Discussion

It is interest to compare the ion-pair dissociation constant of $[Co(NH_3)_5NO_2]SO_4$ to those of simple 2:2 sulfates. Davies¹⁰ has compiled pK values for several alkaline earth and transition metal sulfates of this type. They range from about 2.1 for MgSO₄ and MnSO₄ to about 2.4 for NiSO₄ and CoSO₄; all of these pK's are significantly lower than that of [Co- $(NH_3)_5NO_2$]SO₄. The dissociation constant of the ion pair formed by this complex ion electrolyte is roughly one-half that of simple sulfates of the same valence type. This effect is consistent with data reported previously for 1:1 and 2:1 salts, where the extent of association is greater for complex ion electrolytes than for simple salts.

The unusually strong ion association of coordination compounds cannot be explained solely on the basis of electrostatic factors, which predict a decrease in association with increasing ionic size. Complex cations such as $[Co(NH_3)_5NO_2]^{2+}$ can hardly be smaller than alkaline earth or transition metal cations. Nonelectrostatic forces must contribute significantly to the stability of the ion pairs formed by complex ion electrolytes.

One way to obtain a quantitative estimate of the relative contributions of electrostatic and nonelectrostatic forces in ion pairing is to study the effect of ionic charge upon the dissociation constant. The Fuoss theory,¹² which considers only electrostatic forces, predicts that

$$pK = 21.40 + 3 \log a + b/2.3 \tag{8}$$

where a is the interionic distance in the contact ion pair and b is defined by

$$b = \frac{\left|Z_1 Z_2\right| e^2}{a D k T} \tag{9}$$

Z = charge of ion, e = electronic charge, and D = dielectric constant of water.

In order to obtain a pK value of 2.60 for $[Co(NH_3)_5-NO_2]SO_4$ ($Z_1 = Z_2 = 2$), it is necessary to make a = 3.5 Å. If it is assumed that a remains constant,¹³ eq 8 can be used to calculate the pK value to be expected for a 2:1 or 1:1 complex ion electrolyte, provided only electrostatic forces are involved in the ion pair. Table II compares values of pK calculated in this manner to those observed experimentally.

Table II: Comparison of Observed and Calculated pK Values (a = 3.5 Å)

		Obsd	Calcd
2:2	$[C_0(NH_3)_5NO_2]SO_4$	2.60	(2.60)
2:1	$[C_0(NH_3)_5NO_2]Cl_2$	1.04	0.83
	$t-[Co(en)_2NH_3NO_2]Cl_2$	1.13	
	$t-[Co(en)_2NH_3NO_2](NO_3)_2$	1.30	
	$[Co(NH_3)_5OCOCH_3](NO_3)_2$	1.10	
1:1	$t-[Co(en)_2NCSCl]NO_3$	0.30	-0.07
	$t-[Co(en)_2NCSCl]Cl$	0.26	
	$t-[Co(en)_2NCSCl]I$	0.54	

Clearly, the pK values calculated for 2:1 and 1:1 complex salts on the basis of the Fuoss theory are considerably smaller than those observed.¹⁴ The ion-pair dissociation constants are 2 to 3 times smaller than those predicted on the basis of electrostatic forces

⁽¹²⁾ R. M. Fuoss, J. Amer. Chem. Soc., 80, 5059 (1958).

⁽¹³⁾ A small change in a will have relatively little effect upon pK with 2:1 or 1:1 salts. An increase in a from 3.5 to 4.0 Å changes pK by only about 0.05.

⁽¹⁴⁾ The Bjerrum theory predicts even less association than the Fuoss theory. For a 1:1 electrolyte, one would calculate from the Bjerrum theory a pK of about -1.1, corresponding to virtually no association.

alone. It would appear that nonelectrostatic forces are of major importance in ion-pair formation in complex ion electrolytes of lower charge types.

The question remains as to the nature of the nonelectrostatic factors which are responsible for the unusual stability of the ion pairs formed with these salts. One could explain why $[Co(NH_3)_5NO_2]^{2+}$ associates with anions to a greater extent than does Mg²⁺ by comparing the extent of hydration of the two ions. The Mg^{2+} ion in aqueous solution is presumably a highly hydrated species in which there are strong bonds joining the cation to water molecules. These bonds would have to be broken for Mg^{2+} to form a contact ion pair with an anion such as SO_4^{2-} . It should be somewhat easier for $[Co(NH_3)_5NO_2]^{2+}$, which must be less strongly hydrated, to form a contact ion pair. Stengle and Langford¹⁵ have used a similar argument to explain the results of nmr studies which indicate that salts of $Cr(en)_{3}^{3+}$ are extensively associated while those of $Cr(H_2O)_6^{3+}$ are not.

It is difficult to see, however, how simple hydration effects could explain the trend in dissociation constants with charge, discussed in connection with Table II. In particular, it could not explain why the pK value decreases much less than expected in going from [Co- $(NH_3)_5NO_2$]SO₄ to [Co(NH₃)₅NO₂]Cl₂, where the cation, and hence its degree of hydration, is the same. Indeed, one would expect the Fuoss theory, which assumes contact ion pairs, to apply best to salts where the cation is only weakly hydrated if at all.

The stability of an ion pair in aqueous solution would be enhanced if the cation were to promote the formation of an ice-like water structure containing cages large enough to accommodate an ion pair. Diamond,¹⁶ among others, has postulated the existence of such "solvent-structure-enforced" ion pairs to explain some of the unusual thermodynamic properties of aqueous solutions of tetraalkylammonium salts. The fact that these salts form clathrates containing a high mole ratio of water to salt tends to support such a solution structure.

It is entirely possible that complex cations may structure solvent water in a manner similar to tetraalkylammonium ions. Certain of the properties of aqueous solutions of complex ion electrolytes resemble, at least qualitatively, those of tetraalkylammonium salts. On the other hand, the only ions and molecules which have been shown to promote ice-like structures are ones containing hydrophobic groups such as alkyl radicals. It would seem surprising if an ion such as $[Co(NH_3)_5NO_2]^{2+}$, containing hydrophilic ligands, were to behave in this manner. There appears to be no evidence for such structures in the solid state; clathrates of coordination compounds, containing large numbers of water molecules, have never been reported.

In addition to the solute-solvent interactions discussed above, there is a specific type of nonelectrostatic force which could contribute to the stability of ion pairs in aqueous solution. We refer to dispersion forces between cations and anions. Dispersion interactions have been generally neglected in treating electrolyte solutions, but a simple calculation suggests that for large, highly polarizable cations they may be comparable in magnitude to electrostatic forces. As a case in point, consider cesium chloride, a salt where the parameters necessary for such a comparison are available. For the dispersion interaction between Cs^+ and Cl^- , we use the expression of Mavroyannis and Stephen¹⁷

$$U_{\rm disp} = -\frac{3a_0^{1/2}e^2\alpha_1\alpha_2}{2a^6[(\alpha_1/Z_1)^{1/2} + (\alpha_2/Z_2)^{1/2}]}$$
(10)

where $a_0 = \text{Bohr radius} = 0.5292 \times 10^{-8} \text{ cm}$; $e = \text{electronic charge} = 4.80 \times 10^{-10} \text{ esu}$; $\alpha_1, \alpha_2 = \text{polarizabilities}$ of cation and anion; $Z_1, Z_2 = \text{total number of electrons}$ in cation and anion; and a = interionic distance, Cs^+-Cl^- .

For CsCl, $\alpha_1 = 2.8 \times 10^{-24}$ cc, $\alpha_2 = 3.0 \times 10^{-24}$ cc, $Z_1 = 54$, $Z_2 = 18$. The value of *a* is estimated from hydration radii given by Conway, Desnoyers, and Smith¹⁸ to be approximately 5×10^{-8} cm. Substituting these numbers in eq 10, we obtain $U_{\rm disp} = -2 \times 10^{-14}$ erg. This is to be compared with the electrostatic interaction, uncorrected for ion-atmosphere effects, $U_{\rm el} = -e^2/Da = -6 \times 10^{-14}$ erg.

Obviously, these numbers are subject to considerable uncertainty; in particular, the dispersion interaction is extremely sensitive to the value chosen for the interionic distance (if one used crystal radii, the magnitude of $U_{\rm disp}$ would be considerably greater). However, the fact that the dispersion energy appears to be a sizeable fraction of the electrostatic energy suggests that it cannot be ignored in treating the thermodynamics of solutions of CsCl or similar salts.

At present, the parameters for eq 10 are not available for complex ion electrolytes. However, preliminary measurements made in this laboratory indicate that the polarizabilities of complex cations derived from cobalt(III) are from 5–10 times as great as that of Cs^+ . These ions are presumably somewhat larger than Cs^+ , but the net effect will almost certainly be to increase the magnitude of the dispersion interaction. It would appear that dispersion forces between an anion and a complex cation are large enough to explain the unusual stability of ion pairs in these systems. They could also explain the fact that the ion-pair dissociation constant does not increase as

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much in going from a 2:2 to a 2:1 or 1:1 salt as simple electrostatic theory would predict. The dispersion contribution to K, unlike the electrostatic contribution, would be essentially independent of charge.

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Low-Concentration Solutions of Hydrogen and Deuterium in a-Hafnium

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The pressures of hydrogen and deuterium in equilibrium with their solutions in α -hafnium have been measured in an ultrahigh-vacuum system, over the temperature interval from 275 to 845° and for atom ratios from $\sim 5 \times 10^{-5}$ to $\sim 5 \times 10^{-4}$. The solutions were found to follow Sievert's law. Constant relative partial molal enthalpies of -8.60 kcal/g-atom and -8.77 kcal/g-atom were determined for hydrogen and deuterium, respectively. Also the relative partial molal entropies were proved to be essentially independent of temperature. The entropy data lead to the exclusion of strict localization of hydrogen and deuterium in the tetrahedrally coordinated interstitial sites within the lattice.

Introduction

In previous articles,¹⁻³ the equilibrium conditions between hydrogen and deuterium in the gaseous phase and their solutions in α -Ti and α -Zr were examined. The experimental techniques developed for these measurements (ultrahigh-vacuum equipment, omegatron mass spectrometer, lanthanum hexaboride coated filaments, samples formed by metal powder directly pressed to the thermocouple wire, heating by externally induced eddy currents) permitted very low concentrations to be considered and a wide range of pressures and temperatures to be explored.

In all cases Sievert's law was found to be obeyed and constant relative partial molal enthalpies were observed; only minor differences were found to distinguish the deuterium from the hydrogen solutions and strictly similar behavior was shown by both metals.

The partial molal entropy of dissolved gases proved to be essentially independent of temperature, which contradicts the general assumptions that dissolved atoms occupy the tetrahedral interstices in the metal lattice and that their motion is a purely vibrational one (Einstein oscillators). Entropy values seem to reveal a larger mobility of dissolved species. This is in accordance with many heat capacity data which show the need for a diffusional (or translational) hydrogen contribution, 4^{-6} and with recent results of proton resonance techniques.^{7,8}

Such behavior could probably be accounted for in the simplest way by assuming a protonic model. In fact, protonic models have been proposed for metallic hydrides for a long⁹ time, and a "screened proton" model has been advanced quite recently to interpret the solubility of hydrogen in transition metals and alloys.¹⁰ It is possible that a "narrow band" model might be more appropriate, as something intermediate between the Einstein oscillator and the free proton model of Fowler and Smithells, but in any case, the search for an adequate model has to be considered as an open problem.¹¹

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Due to these general implications, it appeared useful to extend our measurements to other exothermic occluders. The extension of measurements to hafnium is justified both by the possibility of useful comparisons with other metals in its group and by the relatively scarce literature existing on this metal. Besides the beautiful work of Sidhu, *et al.*, who studied the structure of the hydrides of Ti, Zr, and Hf using the neutron diffraction technique,^{12,13} work has been done in this field by Espagno, *et al.*,^{14,15} but always concerning hafnium hydrides with high hydrogen contents.

The only investigation concerning the low hydrogen content α phase, was carried out by Edwards and Veleckis,¹⁶ while as far as we are aware, no comparable data are available for the hafnium-deuterium system.

Experimental Section

The ultrahigh-vacuum system, equipment, techniques, and procedures were the same as previously reported.¹

Two different metal samples were used for hydrogen and deuterium measurements, of 944 and 931 mg, respectively.

The major impurity in the hafnium powder employed was zirconium ($\sim 2\%$ by weight), and an appropriately corrected molecular weight was used in calculating the atomic concentrations of the dissolved gases. Other impurities were as follows (in ppm) Al, <25; Cr, <10; Cu, <40; Fe, <270; Mg, <10; Mn, <10; Mo, <10; Ni, <10; Pb, <5; Si, <40; Sn, <10; Ti, <10; V, <5; W, <50; Zn, <50.

After the initial high-temperature treatment of the samples at 1000°, they were submitted to thermal stabilization at 800° for 24 hr and under a vacuum better than 10^{-9} Torr.

As in the case of titanium and zirconium, an auxiliary titanium sample was employed in order to evaluate more accurately the quantities of gases introduced and to purify them further.

Spectroscopically pure hydrogen and 99.5% deuterium were used. Hydrogen-sorbed quantities were 3.16; 6.24; 9.24; 12.48; 15.49; 18.47; 20.38; and 21.95 cm³ Torr. Deuterium sorbed quantities were 5.84; 8.76; 11.67; 14.60; 16.83; 20.42; 23.35 cm³ Torr.

The equilibrium temperatures ranged from 288 to 845° for hydrogen and from 275 to 759° for deuterium. The equilibrium pressures were measured by using the mass spectrometer tuned on mass 2 for hydrogen and on mass 4 for deuterium.

In the case of deuterium, the HD partial pressure resulting from equilibration was always found to be below 2%. Due to this very low HD concentration and to the ideal solution behavior of the system, no allowance has been made for the presence of hydrogen when studying the $D_2-\alpha$ -Hf system.

The attainment of the equilibrium conditions was

controlled by comparing the pressures obtained with increasing and decreasing temperatures, and the stability of the samples was checked by comparing the data obtained before and after a complete set of measurements.

Results and Discussion

The equilibrium pressures P for different concentrations C of dissolved species at different temperatures T, within the ranges previously indicated, were found to follow, for both hydrogen and deuterium, a relationship of the form

$$\ln P = A + \ln C^n + B\frac{1}{T} \tag{1}$$

The parameters A, B, and n were determined through best fitting of the complete set of data for each gas (128 and 113 experimental points for H₂ and D₂, respectively), by a least-squares method.

The values found for n were $n_{\rm H_2} = 1.97$ and $n_{\rm D_2} = 1.96$ so that it was considered that the above relationship was satisfactorily indicative of a close approach to the Sievert law (n = 2) in accordance with the results previously found for solutions of the same gases in α -Ti and α -Zr.

A new fitting of the data using a relationship directly assuming a Sievert model leads to the equations

$$\ln P_{\rm H2} = 9.611 \ (\pm \ 0.034) \ + \\ \ln \left(\frac{N_{\rm H}}{N_{\rm Hf}}\right)^2 \ - \ 8652 \ (\pm 11) \ \frac{1}{T}$$
(2)

 $\ln P_{\rm D2} = 10.160 \ (\pm \ 0.025) \ +$

$$\ln\left(\frac{N_{\rm D}}{\rm N_{Hf}}\right)^2 - 8830 \ (\pm 18) \ \frac{1}{T} \quad (3)$$

where P is expressed in atmospheres, T in °K, and the concentrations of dissolved species are expressed as atomic ratios ($N_{\rm Hf}$ is the number of metal atoms in the hafnium sample, $N_{\rm H}$ and $N_{\rm D}$ are the numbers of hydrogen or deuterium atoms in solution).

The very good fit of the experimental data is shown in Figures 1 and 2, where the straight lines, each corresponding to a different quantity of dissolved gas, have been drawn according (2) and (3).

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Figure 1. Equilibrium pressure as a function of temperature in the $H_{2-\alpha}$ -Hf system. Weight of the sample, 944 mg. Sorbed quantities (in cm³ Torr at 25°): a, 3.16; b, 6.24; c, 9.24; d, 12.48; e, 15.49; f, 18.47. The lines corresponding to 20.38 and 21.95 cm³ Torr have been omitted for clarity of the graph.



Figure 2. Equilibrium pressure as a function of temperature in the $D_{2^{-}\alpha}$ -Hf system. Weight of the sample, 931 mg. Sorbed quantities (in cm³ Torr at 25°): a, 5.84; b, 8.76; c, 11.67; d, 14.60; e, 16.83; f, 20.42. The line corresponding to 23.35 cm³ Torr has been omitted for clarity of the graph.

The errors reported in (2) and (3) are the quadratic mean errors in the determination of the two parameters. They appear to be too low when compared with our accuracy in temperature measurements (which was estimated $\pm 0.5\%$), so that we consider them as indicative of the inner self-consistency of the two sets of measurements rather than of the true experimental error.

The equilibrium condition between the solute and the gas is

$$\bar{G}_{(a)} = \frac{1}{2} G^{\circ}_{(g)} + RT \ln P$$
(4)

where $\bar{G}_{(\alpha)}$ is the partial free energy per g-atom dissolved in α -Hf and $G^{\circ}_{(g)}$ is the standard molal free energy of the gas.

This condition may be written

$$\ln P = -\frac{2}{R} \left[\bar{S}_{(\alpha)} - \frac{1}{2} S^{\circ}_{(g)} \right] + \frac{2}{R} \left[\bar{H}_{(\alpha)} - \frac{1}{2} H^{\circ}_{(g)} \right] \frac{1}{T} \quad (5)$$

where $\bar{H}_{(\alpha)}$, $\bar{S}_{(g)}$ are the partial enthalpy and the partial entropy per g-atom c issolved in α -Hf, and $H^{\circ}_{(g)}$, $S^{\circ}_{(g)}$ are the standard molal enthalpy and entropy, respectively.

Comparison between ec 5 and eq 2 and 3 gives the relative partial molal entropy (partial molal entropy of soution) and the relative partial molal enthalpy (partial molal enthalpy of solution), for hydrogen

$$(\Delta S)_{\rm H_2} = \bar{S}_{\rm H(\alpha)} - \frac{1}{2} S^{\circ}_{\rm H_2(g)} = - [9.55 + R \ln (N_{\rm H}/N_{\rm Hf})] \, {\rm eu/g-atom} \quad (6)$$

$$(\Delta H)_{\rm H_2} = \bar{H}_{\rm H(\alpha)} - \frac{1}{2} H^{\circ}_{\rm H_2(g)} = -8597 \, {\rm cal/g-atom}$$
(7)

and for deuterium

$$(\Delta S)_{D_2} = \bar{S}_{D(\alpha)} - \frac{1}{2} S^{\circ}_{D_{2(g)}} = -$$

[10.10 + R ln (N_D/N_{Hf})] eu/g-atom (8)

$$(\Delta H)_{\rm D_2} = \bar{H}_{\rm D(\alpha)} - \frac{1}{2} H^{\circ}_{\Gamma_2(g)} = - 8774 \ {\rm cal/g-atom}$$
(9)

Both hydrogen and det terium present a strictly constant ΔH , for a temperature interval of more than 500° and for concentrations ranging over more than one order of magnitude (from less than 5×10^{-5} to about 5×10^{-4} in atom ratios). Furthermore, the ΔH values for the two gases differ from each other by no more than a few per cent, so that in this respect, hafnium behaves like other metals in the group.

The enthalpies of solution, however, are much lower in this case than for titan um and zirconium; the value obtained for the hydrogen solution is in good accordance with the value of 8990 cal/g-atom found by Edwards and Veleckis.¹⁶ Also these authors found that ΔH did not show any variation with temperature within the experimental error and remained constant with concentration up to the concentration at which the α - δ transition occurs.

The entropies of solution, as well, appear to be constant over the whole of the explored range of temperatures and show only smal. differences between hydrogen and deuterium.

If the standard partial entropies of the dissolved species are defined with reference to the standard concentrations $N_{\rm H} = N_{\rm Hf}$ and $N_{\rm D} = N_{\rm Hf}$, the following expressions are obtained

$$\bar{S}^{\circ}_{H(\alpha)} = \frac{1}{2} S^{\circ}_{H_{2}(g)} - 9.55 \pm 0.25 \text{ eu/g-atom}$$
 (10)

$$\bar{S}^{\circ}{}_{D(\alpha)} = \frac{1}{2} S^{\circ}{}_{D_2(g)} - 10.10 \pm 0.25 \text{ eu/g-atom}$$
(11)

where the indicated error does not refer to the fitting of the data by the adopted law but has been independently estimated by approximately evaluating the possible extent of experimental errors in the temperature and pressure measurements.

Their dependence on temperature, calculated using tabulated standard entropies of normal hydrogen and deuterium,^{17,18} is shown in Figure 3.

Even in the case of hafnium, as was previously found for titanium and zirconium, the partial molal entropies of dissolved species are appreciably higher for deuterium than for hydrogen. Furthermore, these entropy values show a continuous increase from Ti to Zr to Hf. This increase is particulary high when passing from Zr to Hf (~ 2.5 eu/g-atom, as compared to ~ 0.5 eu/g-atom when passing from Ti to Zr); it seems likely that such a large increase in entropy is related to the very appreciable decrease in the enthalpy of solution which occurs between these two metals.

It may be observed at this point that from the data of Edwards and Veleckis for the hydrogen solution in α -Hf, one obtains at 500° a standard partial entropy $\bar{S}^{\circ}_{H(\alpha)} = 8.04$ eu/g-atom, as compared to $\bar{S}^{\circ}_{H(\alpha)} = 9.38$ eu/g-atom which was found in our measurements at the same temperature. This is a satisfactory agreement, since the measurements of Edwards and Veleckis were effected at concentrations which range one order of magnitude above the highest concentrations here explored. This relatively small difference in the standard partial entropies could well be due to the very different experimental conditions and measuring techniques, but it could also mean that, by increasing the concentration, some restrictions are introduced in the mobility of dissolved hydrogen.

It was shown² that the standard partial entropy of a dissolved species corresponds to its vibrational entropy when it is localized at the tetrahedrally coordinated interstitial sites which are present in the hcp lattice of α -hafnium. By assuming such a localization and considering the vibrations to be isctropic, the Einstein



Figure 3. Standard partial entropy of hydrogen and deuterium dissolved in α -hafnium, as a function of temperature.



Figure 4. Einstein characteristic temperatures for hydrogen and deuterium dissolved in α -hafnium, as calculated by assuming localized isotropic vibrators. The dashed line, corresponding to the Einstein temperatures for hydrogen divided by $\sqrt{2}$ should give the Einstein temperatures for deuterium if purely vibrational motions were involved.

characteristic temperature may be calculated using the equation

$$\frac{1}{3} S^{\circ}{}_{(\alpha)} = R \left[\frac{\theta_{\rm E}}{T} \left(e^{\theta_{\rm E}/T} - 1 \right)^{-1} - \ln \left(1 - e^{-\theta_{\rm E}/T} \right) \right]$$
(12)

The results are shown in Figure 4, where the calculated $\theta_{\rm E}$ is plotted as a function of T for both hydrogen and deuterium.

Even in this case, as in the previously studied solutions of the same gases in Ti and Zr, the Einstein temperature is far too low to correspond to a strictly localized oscillator. Furthermore, it largely depends on temperature, so that the dissolved species may not be considered as confined to the tetrahedral interstices, but probably moves almost freely within the metal lattice. Further indication in this sense is given by the fact that the differences between hydrogen and deuterium do not correspond to a ratio $\sqrt{2}$, as should be observed in the case of localized oscillators. In fact, due to the largely different masses, the metal atoms could be considered at rest in their equilibrium position, and the vibration of the dissolved atoms could be considered almost independent from each other, due to the low concentrations here examined. Finally, larger partial entropies are found with hafnium than with zirconium, while the lattice parameters are lower for hafnium than for zirconium.

In conclusion, if the data now obtained for hafnium are considered together with the previously obtained data for titanium and zirconium, quite a homogeneous picture emerges which leads to the exclusion of the strict localization of hydrogen and deuterium dissolved at very low concentrations in the α -phase of the metals of this group.

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Mixed Ionic Solvent Systems. III. Mechanism

of the Extraction

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Mixed ionic solvent systems, consisting of high molecular weight alkylammonium carboxylates in suitable diluents, extract inorganic salts reversibly from aqueous solutions, forming metal carboxylates and alkylammonium salts of the inorganic anion. Analysis of extraction data for $MgCl_2$ and $CaCl_2$ leads to the conclusion that the extracted species are monomeric in the organic phase. All species are associated with several unused extractant molecules.

Introduction

A preliminary account has been given of a "mixed ionic" solvent extraction system in which both ionic components of an inorganic salt can be extracted reversibly from aqueous solution and subsequently removed by contact with water.¹ Because of the considerable potential of such systems in practical applications, a further study has been made of the physical chemistry of some typical mixed ionic systems, with the goal of achieving some understanding of the nature of the extractant system and the mechanism of operation.

A typical system involves an alkylammonium carboxylate dissolved in a hydrocarbon diluent. The extraction of magnesium chloride, for example, occurs according to the equation

$$Mg^{2+} + 2Cl^{-} + 2R_4N^+R'COO^- \iff \overline{Mg(R'COO)_2} + 2R_4NCl \quad (1)$$

where the bars indicate species in the organic phase.

We have determined the distribution of magnesium and calcium chlorides between water and typical mixed ionic systems under various conditions. The data have been examined by the method of slope analysis and lead to a consistent picture of the behavior of these systems.

Experimental Methods

The data used in this study were partially reported previously.¹ For the study of this system by the methods of slope analysis we have extended the data down into regions of lower concentration, using the same methods as before.

Mixed ionic solvent systems were prepared in most cases simply by mixing the desired amine and acid and diluting with the diluent to the desired concentration. In the case of quaternary systems, the quaternary ammonium chloride and the acid were mixed, diluted, and then contacted with a slight excess of dilute sodium hydroxide to convert the acid to the corresponding anion. The organic phase was washed with water several times to remove the sodium chloride formed in this conditioning step.

Samples were shaken for 1 hr and then separated in a centrifuge. Both organic and aqueous samples were subsequently analyzed.

Most experiments were performed with tracer chlorine-36 using counting times adjusted to produce a $\pm 2\%$ maximum standard deviation in the net count. Equivalence of extraction of cation and anion was checked with magnesium chloride in one system by running duplicate experiments, determining magnesium by atomic absorption spectrometry in one case, and determining chloride with chlorine-36 tracer in the other.

The distribution of the organic extractants into the aqueous phases was examined in a number of cases in order to make certain that losses into the aqueous phases were negligible. The carboxylate component was determined by examination of the carbonyl infrared absorption after extraction into carbon tetrachloride, while the amine component was determined spectrophotometrically after extraction of the picrate salt into chloroform.

Data on aggregate formation were obtained with a Mechrolab osmometer Model No. 301. In order to conform as closely as possible to the conditions of the extraction studies, water-saturated toluene was used as the reference solvent, and solutions of benzil in that reference solvent were used as standards.

Experimental Data

Aggregation and Association of the Extracted Species. One of the common methods for determining the nature of extracting species in liquid-liquid systems is the method of slope analysis. In this procedure, the effect

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of certain variables on the equilibrium is determined, and the desired information is obtained by suitable manipulation of the equilibrium expressions and plotting of data.

For the distribution of magnesium chloride, two general situations are possible.

If the magnesium carboxylate (denoted by MgA_2) and the alkylammonium chloride (denoted by CCl) are associated in the organic phase, the general equation for the distribution of magnesium chloride is

$$Mg^{2+} + 2Cl^{-} + \frac{\frac{v}{t} + 2}{p} ([CA]_{p}) = 1$$

$$\frac{1}{t} \overline{([MgA_{2} \cdot 2CCl]_{t} \cdot vCA)} \quad (2)$$

where v is the number of unreacted extractant molecules associated with the extracted species and t is the degree of aggregation of that species. The equilibrium constant for the reaction is

$$K_{1} = \frac{\left([MgA_{2} \cdot 2CCl]_{t} \cdot vCA \right)^{1/t}}{\left([CA]_{p} \right)} \frac{v/t + 2}{p} a_{MgCl_{2}}$$
(3)

If the magnesium chloride concentration in the organic phase is kept low, the CA concentration is essentially a constant and, taking the logarithms of eq 3, we get

$$\frac{1}{t}\log(\overline{[MgA_2 \cdot 2CC1]_t \cdot vCA}) = \log a_{MgC1_2} + \log K_1' \quad (4)$$

The actual concentration of the species following the log term on the left side of (4) is simply equal to 1/t times the analytical concentration of magnesium chloride in the organic phase, represented by $(MgCl_2)$. Making this substitution, and noting that $a_{MgCl_2} = 4(m\gamma)^3$

$$\log (\mathrm{MgCl}_2) = 3t \log (m \cdot \gamma)_{\mathrm{MgCl}_2} + \log K_1^{\prime\prime}$$
 (5)

where *m* is the aqueous molality of magnesium chloride. Thus eq 5 is in the slope-intercept form and if $(MgCl_2)$ is plotted against $m \cdot \gamma$ on a log-log plot, the resulting line will have a slope of 3t. The minimum possible slope will be 3.0 if no aggregation occurs in the organic phase.

If the extracted magnesium and chloride species are not associated with each other in the organic phase, the general equation for magnesium chloride distribution will be

$$Mg^{2+} + 2Cl^{-} + \left[\frac{\frac{2y}{r} + \frac{z}{q} + 2}{p}\right]\overline{([CA]_{p})} \Longrightarrow$$
$$\frac{1}{q}\overline{([MgA_{2}]_{q} \cdot zCA)} + \frac{2}{r}\overline{([CC1]_{r} \cdot yCA)} \quad (6)$$

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Taking logarithms we get

$$\frac{1}{q} \overline{\log\left([\mathrm{MgA}_2]_q \cdot z\mathrm{CA}\right)} + \frac{2}{r} \overline{\log\left([\mathrm{CCl}]_a \cdot y\mathrm{CA}\right)} = \log\left(m\gamma\right)^3_{\mathrm{MgCl}_1} + K_2' \quad (7)$$

Equivalence of magnesium and chloride in the organic phase requires that

$$r/\overline{2([\mathrm{CCl}]_r \cdot y\mathrm{CA})} = q([\mathrm{MgA}_2]_q \cdot z\mathrm{CA}) = (\mathrm{MgCl}_2)$$
 (8)

where $(MgCl_2)$ is again the analytical magnesium chloride concentration in the organic phase. Using this equation in (7) we get

$$\log \overline{(\mathrm{MgCl}_2)} = \frac{3qr}{2q+r} \log (m \cdot \gamma)_{\mathrm{MgCl}_2} + \log K_2^{\prime\prime} (9)$$

Thus by plotting the log of the analytical concentration of magnesium chloride in the organic phase against the log of $m \cdot \gamma$ for magnesium chloride, the slope of the plot has the value of 3qr/2q + r. The minimum slope which can occur, when no aggregation occurs, *i.e.*, r = q = 1, is 1.0.

In Figure 1, the data for magnesium chloride distribution with four different solvent systems are plotted



Figure 1. Magnesium chloride distribution between water and alkylammonium 2-ethylundecanoates in toluene. Slopes of straight-line portions given on curves. Open points, chlorine-36 tracer data; solid points, atomic absorption data.

against the quantity $m \cdot \gamma$ for magnesium chloride. Activity coefficient values were obtained from Robinson and Stokes.² The four systems consisted of 0.5 *M* 2-ethylundecanoic acid plus 0.5 *M* amine in toluene. The amines were: primary, 1-amino-2,2 dihexyloctane; secondary, N-dodecyl-2-ethylhexylamine; tertiary, trioctylamine; quaternary, trioctylmethylammonium ion.

The validity of eq 8 is demonstrated for the quaternary system by the agreement of points obtained by determination of both magnesium and chloride. For the other amine systems, adherence to eq 8 was determined by examination of the soluble loss of the extractant and the aqueous pH. Deviations from eq 8 can arise from distribution of one of the extracted species (magnesium or chloride) into the aqueous phase to a greater extent than the other. If the difference in distribution is significant compared to the actual magnesium or chloride level in the organic phase, eq 8 does not hold. For all the systems studied here, these differences were negligible.

Another source of failure of eq 8 is through hydrolysis of one of the extracted species. For example, hydrolysis of the magnesium carboxylate would form magnesium hydroxide; hydrolysis of the alkylammonium chloride would give HCl. Formation of either of these inorganic hydrolysis products would reduce the organic phase concentration of magnesium or chloride ion, respectively, and lead to an excess of the other. pH measurements on the aqueous phases in the primary amine systems were always less than 8.3, which is equivalent to $2 \times 10^{-5} M$ hydroxide ion. This represents a negligible hydrolysis. No measurements were made on the other amines, but since aliphatic amines are of comparable base strengths in aqueous solution, the extent of their hydrolysis should be comparable to the primary amine.

The interesting feature of Figure 1 is that all four systems studied have the same slope of the straight-line portion of each curve, and the slope is approximately 1.0. Equation 5, which suggests a minimum slope of 3.0, obviously does not hold for this system, and we conclude that the magnesium and chloride are present as separate species. Assuming then that eq 9 is the valid equation for the distribution of magnesium chloride, the resulting slope (1.0) must equal 3qr/2q + r. Values of q = 1 and r = 1 are the only integral solutions to this equation. That is, both the magnesium carboxylate and the alkylammonium chloride exist as unaggregated monomers. This situation holds in the straight-line region, below an organic phase concentration of about 0.02 M magnesium chloride for the quaternary and primary amine, and below about 0.03 M for the secondary and tertiary amines.

Similar results were obtained for calcium chloride extraction by the quaternary and primary ammonium systems, and the data are shown in Figure 2. The



10-1

Figure 2. Distribution of magnesium and calcium chlorides between water and alkylammonium 2-ethylundecanotates in toluene: 0.48 M Aliquat $3368:EUD: \triangle$, $CaCl_2; \Box$, $MgCl_2;$ 0.50 M Primene JM-T:EUD: \blacktriangle , $CaCl_2; \blacksquare$, $MgCl_2$. Slopes of straight-line portions are all 1.).

 $m\gamma$ for acueous MgCl₂.

10-2

(MgCl₂) or (CaCl₂), M.

10-1

10-3

corresponding magnesium chloride data are included here for comparison. In the low concentration region the calcium chloride curves also exhibit a slope of 1, indicating that the extraction mechanism is the same as for magnesium chloride. It is interesting to note that the distribution of these two salts in the quaternary system is roughly the same, while in the primary system, the calcium exhibits a significantly greater distribution toward the organic phase than the magnesium.

Association of the Extracted Species with Unused Extractant. The preceding data have all been taken at a constant extractant concentration, and at sufficiently low loadings that the extractant concentration is essentially constant throughout a given experiment. In order to obtain information about the participation of the extractant in the extraction mechanism, additional experiments were cone in which the extractant concentration was varied. These data are shown in Figure 3 for magnesium chloride in the quaternary ammonium system.

Now, if in eq 6 the organic concentration of magnesium chloride is held constant, we get, upon taking logarithms of the equilibrium expression

$$\log \overline{([CA]_p)} = -\frac{3p}{\frac{2y}{r} + \frac{z}{q} + 2} \log (m \cdot \gamma)_{MgCl_2} + \log K_2^{\prime\prime\prime}$$
(10)

Corresponding values of $ri\gamma$ and extractant concentration can be obtained at ϵ ny given organic magnesium

⁽²⁾ R. A. Robinson, and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Academic Press, Inc., London, 1959.



Figure 3. Effect of extractant concentration on distribution of magnesium chloride between water and Aliquat 336S: EUD. Extractant concentrations: \Box , \blacksquare , 0.48 *M* (filled points, chlorine-36 data; open points, atomic absorption data); \triangle , 0.29 *M*; \Diamond , 0.10 *M*. Slopes of straight-line portions of lines are 1.0.



Figure 4. Relation between extractant (CA) concentration and aqueous magnesium chloride activity for constant organic composition. Extractant is Aliquat 336S-EUD in toluene. Slopes of lines are both -1.0; \bullet , $\overline{(MgCl_2)} = 5.0 \times 10^{-3} M$; \blacksquare , $\overline{(MgCl_2)} = 3.0 \times 10^{-3} M$.

chloride concentration from the data in Figure 3. A log-log plot of the extractant concentration vs. the quantity $m\gamma$ will then have slopes which contain the variables y, z, r, p, and q as shown in eq 10. Such a plot is given in Figure 4 for two concentrations of magnesium chloride in the organic phase, $5.0 \times 10^{-3} M$ and $3.0 \times 10^{-3} M$. The slopes of both plots are about -1.0.

Table I contains the data obtained by vapor pressure osmometry to determine the degree of aggregation of the extractant molecules. Data are given for the quaternary amine system at two temperatures, 37° and 25° . The aggregation does not seem to vary greatly with temperature, being equivalent to about a trimer for both temperatures studied. If we use the values

Nominal concn, <i>m</i>	Molarity	T, °C	Aggregation no., p = nominal molality/ observed molality
0.10	0.09	25	3.2
0.39	0.28	25	3.2
0.90	0.46	25	3.0
0.10	0.09	37	3.2
0.39	0.28	37	3.2
0.90	0.46	37	3.4
^a Trioctylmeth	vlammonium	2-ethylundecanoat	e in toluen

system equilibrated with water.

q = 1, r = 1, and p = 3 for the extraction of magnesium chloride, the slope of -1.0 gives, from eq 10

slope =
$$-\frac{3p}{\frac{2y}{r} + \frac{z}{q} + 2} = -1.0; \ 2y + z = 7$$
 (11)

Explicit values of y and z are not obtained from eq 11, but even so, these calculations suggest that the association of unreacted extractant with the extracted species is quite significant.

Discussion

The extraction of metal cations into organic solvent systems of low polarity normally involves replacing the water in the coordination sphere of the cation by donor groups of a hydrophobic nature, such as alcohols, amines, etc. In the case of the magnesium and calcium cations, the stoichiometric requirement of two carboxylate ions per cation could account for up to four of the coordination positions of these cations. Further coordination may be due to additional carboxylate ions of the "unused" extractant, or possibly even to water which remains in the coordination shell. Since the carboxylates involved are branched, the steric hindrance might be sufficient to limit the coordination to two of these species per cation.

In a previous paper,³ it was shown that at high concentrations of amine hydrochlorides in toluene, the amine salts were invariably aggregated. Yet, in the mixed solvent systems studied here, the same amine hydrochlorides are not noticeably aggregated at similar concentrations. This result is presumably due to the presence of unused alkylammonium carboxylate which is available for association with the inorganic-organic ion pairs. Neither the cation carboxylate nor the ammonium salt can be involved in an association with the other since the mechanism indicates no association of the two inorganic extracted ions. The "solvent"

(3) R. R. Grinstead and J. C. Davis, J. Phys. Chem., 72, 1630 (1968).

then is not just a hydrocarbon but a mixture of "solvating" species within a toluene diluent. The exact nature of this interaction can only be speculated upon, but must involve a close association of the alkylammonium carboxylate with either the metal ion carboxylate or the alkylammonium chloride or both. It is not possible to determine from our data the extent of association for the individual species, but, if we assume for example, equal association with the magnesium and chloride species, then x and y in eq 11 will each be approximately 2. A value of p = 4 would increase the association numbers to about 3 each. Thus, on the average, each magnesium and chloride ion is associated with 2 or 3 extractant molecules in addition to the stoichiometric requirement. It should be pointed out here that the above arguments for association apply only to quaternary amine systems, for no data were obtained for other amines.

It should also be clear that the discussion applies only to systems in which the organic phase contains only small concentrations of inorganic species. Since it is possible to reach rather high organic loading levels of inorganic salts, the amount of unused extractant available for association cannot in these cases conform to the figures given above. Similarly, although association of metal ion and halide ion species does not exist at low organic loadings, it may at higher levels corresponding to the curved portions of the log-log plots.

One of the most important features of the distribution data is the wide variation in extraction among the amine types. There are two possible explanations for this behavior, both of which may be valid. In the first place, recalling the basic reaction for extraction by the mixed ionic solvent (eq 1) we see that for a particular aqueous concentration, the position of equilibrium will be influenced by the relative free energies of the two amine salts, the carboxylate and the chloride. If we replace a given alkylammonium component by another for which the chloride salt is relatively more stable with respect to the carboxylate, the equilibrium will shift to the right; *i.e.*, the extraction will be more complete.

Barrow and Yerger⁴⁻⁶ have shown that the extent of reaction of an amine and acetic acid to form the salt is relatively independent of the type of amine. In comparison, amine hydrochloride formation is very dependent on the amine type.³ Thus the amine itself might be expected to have a considerable effect on the overall distribution by shifting the equilibrium to the

right through a relative increase in the hydrochloride stability as compared to the carboxylate stability. Admittedly, the cause of the great variation in amine hydrochloride stability in toluene is due to aggregation while in the mixed ionic systems the hydrochlorides are monomers. However, the ease of aggregation in toluene is also a reflection of the need for solvation, and those amine hydrochlorides which were found to aggregate most readily in toluene can be expected to most readily accept and be stabilized by the unused extractant in the mixed ionic solvent systems. The unreacted solvent then could stabilize some amine hydrochlorides more than others, essentially by stabilizing the least sterically hindered in preference to the more sterically hindered amines. The fact that the stability of amine hydrochlorides in toluene is in the order $1^{\circ} >$ $2^{\circ} > 3^{\circ}$ and that the order of ease of salt extraction in the mixed solvent is the same suggests that such an argument is not unreasonable.

The quaternary ammonium compound provides a special case. The argument involving completeness of reaction with acids is inapplicable, since quaternary salts are completely ionized; *i.e.*, salt formation is complete. A more fruitful explanation is to be found in the fact that quaternary ammonium salts have considerably larger dipole moments than any of the other three types.⁷ This is a consequence of the larger separation of charge which must exist, and also of the fact that no dissipation of the dipole can occur through hydrogen bonding of the ammonium ion to the anion. The quaternary salt is thus in greater need of solvation, which it can obtain by extraction of a metal salt. The quaternary ammonium chloride which is formed may not provide a great deal of reduction of the dipole moment. However, it should be sterically easier for the unused extractant to combine with these new species than to combine with itself; *i.e.*, formation of the inorganic salts allows for greater stabilization by association with the unused extractant.

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- (5) E. A. Yerger and G. M. Barrow, *ibid.*, 77, 4474 (1955).
- (6) E. A. Yerger and G. M. Barrow, *ibid.*, 77, 6206 (1955).
- (7) K. Bauge and J. W. Smith, J. Chem. Soc., A, 616 (1966).

⁽⁴⁾ G. M. Barrow and E. A. Yerger, J. Amer. Chem. Soc., 76, 5211 (1954).

Dielectric Relaxation Study of Some Pure Liquids

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The dielectric constants and losses of liquid diphenyl ether, dibutyl ether, N,N'-dimethylaniline, and N,N'-diethylaniline have been measured at two frequencies (9.72 and 31.82 GHz) in the microwave range and at three different temperatures. The calculated values of thermodynamic and distribution parameters indicate the possibilities of (i) more than one relaxation mechanism and (ii) bond formation in the cases of liquid dimethyland diethylanilines. The relaxation times for these anilines showed frequency dependence as well.

Introduction

The present work essentially deals with the dielectric relaxation study of diphenyl ether, dibutyl ether, N,N'-dimethylaniline, and N,N'-ciethylaniline as pure liquids. Extensive data are already available in the literature for the diphenyl ether molecule $^{1-7}$ and, as such, this work would hardly add anything to the existing situation. The purpose for the study of this molecule is therefore mainly to test the reliability of experimental technique adopted by the author and see if the results obtained tally with those already reported. The other molecules have, in general, been studied in a number of nonpolar solvents but not many data seem to be available for their study in liquid state. It was therefore thought that this work may provide some more information for determining their molecular behavior.

Experimental Section

Chemicals. All the liquids were imported from Dr. Theodor Schuchardt, München, West Germany, with the specifications: diphenyl ether, pure grade; dibutyl ether, pure grade; N,N'-dimethylaniline, AR Grade, free from monomethylaniline; and N,N'-diethylaniline, pure grade.

These chemicals were used without any further purification except N,N'-diethylaniline, which was distilled under vacuum and dried before use. Their physical constants, if compared with the literature values shown in Table I, indicate the extent of their purity.

Static Dielectric Constant, Density, Refractive Index, and Viscosity Measurements. The static dielectric constant values were determined by the help of a dielectrometer,⁸ designed and fabricated by the author, working on the principle of heterodyne beat method. The density was measured with a pycnometer (capacity ~12 ml) which could be dipped inside a thermostatic bath having an accuracy of $\pm 0.03^{\circ}$.

The values of refractive indices (for sodium D-line) were measured at different temperatures by a Hilger-Abbey refractometer having an arrangement for the circulation of temperature-controlled water through a jacket enclosing the experimental liquid. The viscosity values were measured by the Ubbelohde viscometer, duly calibrated with conductivity water. The entire viscometer was kept inside a thermostatic bath with a glass window through which the time of fall was noted. The instrument had an accuracy of 0.01%. The viscosity of the unknown was found by the formula

$$\eta = \eta_0 \frac{dt}{d_0 t_0}$$

where η is the viscosity of the unknown and η_0 is that of water at the given temperature, while d and d_0 are their densities; t and t_0 are the efflux times for the unknown and water, respectively, at the same temperature.

The experimentally observed values of the parameters mentioned above are shown in Table I along with their literature values.

Dielectric Constant and Loss Measurements. These measurements were made at two frequencies, 9.72 and 31.82 GHz. Figure 1 gives the block diagram of the arrangement used. The entire assembly for the X-band (9.72 GHz), manufactured by Microwave Instruments Ltd., consisted of a reflex klystron as energy source, a wavemeter for the measurement of frequency, wave guides for transmitting the energy and a traveling probe (S.W.D.) for detecting the energy. The output from the standing wave detector was fed to the galvanometer (sensitivity: 22×10^{-9} A) provided with a lamp and scale arrangement. A

W. E. Vaughan and C. P. Smyth, J. Phys. Chem., 65, 98 (1961).
 K. Higasi, "Dipole, Molecule and Chemistry," a monograph series of the Research Institute of Applied Electricity, No. 13, 1965, p 21.

⁽³⁾ K. Higasi, "Dielectric Relaxation and Molecular Structure," a monograph series of the Research Institute of Applied Electricity, No. 9 1961, p 21.

⁽⁴⁾ D. M. Roberti, O. F. Kalman, and C. P. Smyth, J. Amer. Chem. Soc., 82, 3523 (1960).

⁽⁵⁾ Reference 3, p 9.

⁽⁶⁾ F. Hufnagel, G. Klages, and P. Knobloch, Z. Naturforsch., 17a, 96 (1962).

⁽⁷⁾ J. E. Anderson and C. P. Smyth, J. Chem. Phys., 42, 473 (1965).

⁽⁸⁾ P. K. Sharma and K. K. Srivastava, Oyo Denki Kenkyusho Iho, 16, 53 (1964).

Table I

	-Static	dielectric constant—		ty, g/ml	R	efractive index		osity, cP
<i>T</i> ,°C	Obsd	Lit.	Obsd	Lit.	Obsd	Lit.	Obsd	Lit.
				Diphenyl Et	her			
30	3.660	3.61ª	1.0669	1.0661 ^d	1.5760	1.5762 ^d	2.92	1.78°
40	3.593	at 40°	1.0584	at 30°	1.5711	at 30°	2.39	at 60°
50	3.517		1.0499		1.5670		1.95	
				Dibutyl Et	her			
30	3.116		0.7612	0.75976 ^d	1.3950	1.39906 ^d	0.58	0.602^{d}
40	3.029	Not available	0.7528	at 30°C	1.3900	at 15° (for	0.50	at 30°
50	2.952		0.7439		1.3867	He yellow line)	0.45	
			:	N,N'-Dimethyla	niline			
30	4.998		0.9495		1.5530		1.13	1.16 ^d
40	4.864	4.910	0.9415	0.94804ª	1.5481	1.5523ª	0.96	at 30°
50	4.722	at 20°	0.9329	at 30°	1.5431	at 32.5°	0.83	
				N,N'-Diethylar	niline			
30	5.037	Not available	0.9263	0.9348 ^d	1.5362	1.5 4 105ª	1.61	0.783ª
40	4.877		0.9181	at 20°	1.5311	at 22.3°	1.30	at 75.5
50	4.729		0.9102		1.5267		1.09	

^a J. H. Calderwood and C. P. Smyth, J. Amer. Chem. Soc., 78, 1295 (1956). ^b A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, U. S. Government Printing Office, 1951. ^c W. E. Vaughan, W. S. Lovell, and C. P. Smyth, J. Chem. Phys., 36, 535 (1962). ^a J. Timmermans, "Physicochemical Constants of Pure Organic Compounds," Elsevier Press, New York, N. Y., 1950.



Figure 1. Block diagram for microwave measurements.

mica window was used to separate the top part of the wave guide, forming the dielectric cell, into which was put the experimental liquid. This cell was enclosed by an outer jacket through which temperaturecontrolled water was circulated. The measurements in the J band (31.82 GHz) were carried out⁹ by using a klystron (EM1/R9546) and a frequency meter, Type PRD 538. The micrometer-driven plunger arrangements for both the frequency ranges were fabricated at the workshop of Allahabad University. The accuracy of measurement was $\pm 2\%$ for ϵ' and $\pm 5\%$ for ϵ'' .

Theory of Measurements and Results

The values of dielectric constants and losses were determined by the method developed by Heston, Franklin, Hennelly, and Smyth¹⁰ for low loss liquids. The experimental procedure of this method, for a shortcircuit case, is as follows. With the liquid in the cell and the plunger at the cell window, the traveling probe is set to a minimum power position. The shorting plunger is then turned upward, increasing the depth of the liquid, and the output of the standing wave detector (probe position fixed) is noted. The distance between successive minima is equal to $\lambda_d/2$. For low loss materials, the dielectric constant is given by

$$\epsilon' = \left(\frac{\lambda_0}{\lambda_d}\right)^2 + \left(\frac{\lambda_0}{\lambda_c}\right)^2 \tag{1}$$

where λ_c is the cut-off wavelength, λ_0 is the free space wavelength, and λ_d is the wavelength in the dielectric filled guide of the cell.

The dielectric loss is determined by bringing the plunger down to the mica window so that the liquid length is zero. The field pattern in the standing wave detector is then recorded by moving the probe, and the width at twice minimum power points Δx_0 is determined. The inverse voltage standing wave ratio ρ_0 is calculated by relation

$$\rho_0 = \frac{\pi \Delta z_{\gamma}}{\lambda_{\rm g}} \tag{2}$$

where λ_g is the wavelength in the airfilled wave guide. The value of ρ_0 , obtained from eq 2, is corrected for

⁽⁹⁾ These measurements were carried out in the laboratory of Prof. Krishna Ji of Allahabad University, India.

⁽¹⁰⁾ W. M. Heston, A. D. Franklin, E. J. Hennelly, and C. P. Smyth, J. Amer. Chem. Soc., 72, 3443 (1950).

the approximation involved in deriving the relation.¹¹ Next, the plunger is kept at different positions in steps of $\lambda_d/2$ and the standing wave pattern is recorded by moving the probe of the standing wave detector. The width at twice minimum power points is determined in each case. The values of ρ_n for each plunger position are found by applying the relation (2) alongwith necessary corrections, as stated above. The slope $d\rho_n/dn$ is then determined by plotting a $\rho_n vs. n$ curve, showing a linear relationship. The dielectric loss factor ϵ'' is finally determined by the relation

$$\epsilon^{\prime\prime} = \frac{2}{\pi} \left(\frac{\lambda_0}{\lambda_d} \right)^2 \frac{\lambda_g}{\lambda_d} \left(\frac{\mathrm{d}\rho_n}{\mathrm{d}n} \right) \tag{3}$$

The values of ϵ' and ϵ'' , for the two frequencies and different temperatures, have been tabulated in Table II.

Fable II				
	9.72	GHz		GHz
T,°C	e'	•"	•'	٤"
		Diphenyl Et	her	
30	3.35	0.38		
40	3.32	0.33	3.07	0.44
50	3.32	0.30		
		Dibutyl Eth	her	
30	3.03	0.22	2.49	0.36
40	2.78	0.26	2.49	0.37
50	2.76	0.25	2.49	0.34
	N,	N'-Dimethyla	ninline	
30	3.39	0.42	2.93	0.27
40	3.67	0.47	2.93	0.31
5 0	4.08	0.51	3.03	0.60
	1	I,N'-Diethyla	niline	
30	2.78	0.31	2.66	0.24
40	2.74	0.23	2.69	0.27
50	2.83	0.16	2.60	0.12
	_			

Distribution Parameter and Relaxation Time. The values of distribution parameter (α) and macroscopic relaxation time (τ) are obtained by the help of a Cole-Cole¹² plot of ϵ'' against ϵ' for different frequencies and temperatures. Figures 2-6 illustrate that these plots for all the experimental liquids represent an arc of a circle intersecting the abscissa axis at the values of ϵ_{∞} and ϵ_0 , and having their centers lying below the abscissa axis. ϵ_0 is the static dielectric constant and the value of ϵ_{∞} is obtained by squaring the refractive index value.

The diameter drawn through the center from the ϵ_{α} makes an angle $\alpha \pi/2$ with the ϵ' axis. Tan $\alpha \pi/2$ is determined from the plots and α is calculated.



Figure 2. Cole-Cole arc plot for diphenyl ether at 40°. Open circles, this work; closed circles, ref 1.



Figure 3. Cole-Cole arc plot for diphenyl ether at 30 and 50°.



Figure 4. Cole-Cole arc plot for dibutyl ether at 30, 40, and 50°.

Knowing α , the macroscopic relaxation time τ is found by the relation

$$\frac{v}{u} = (\omega \tau)^{1-\alpha} \tag{4}$$

(11) A. R. Von Hippel, "Dielectric Materials and Applications," The Technology Press of M.I.T., 1954, Chapter II, p 86.

(12) K. S. Cole and R. H. Cole, J. Chem. Phys., 9, 341 (1941).



Figure 5. Cole-Cole arc plot for dimethylaniline at 30, 40, and 50°.



Figure 6. Cole-Cole arc plot for diethylaniline at 30, 40, and 50°.

where v is the distance on the Cole–Cole plot between ϵ_0 and the experimental point, u is the distance between that point and ϵ_{∞} , and ω is the angular frequency. Further, the Powles internal field correction is applied and the molecular relaxation time τ_0 is calculated from the macroscopic relaxation time τ by the relation¹³

$$\tau_{\circ} = \frac{2\epsilon_0 + \epsilon_{\infty}}{3\epsilon_0} \tau \tag{5}$$

T,°C	Distribution parameter α	$\begin{array}{c} \mathbf{Macroscopic} \\ \mathbf{relaxation} \\ \mathbf{time,} \\ \mathbf{\tau} \ \times \ 10^{12} \ \mathrm{sec} \end{array}$	Microscopic relaxation time, ro × 10 ¹² sec
	Dipl	henyl Ether	
30	0.34	5.0	4.4
40	0.35	4.1	3.6
50	0.33	2.7	2.4
	Dib	outyl Ether	
30	0.30	5.7	5.0
40	0.25	4.7	4.2
50	0.25	4.2	3.6
	N,N'-D	Dimethylaniline	
30	0.59	46.1	38.2
40	0.55	14.0	11.6
50	0.34	4.7	3.9
	N,N'-1	Diethylaniline	
30	0.52	354.0	290.3
40	0.54	475.8	390.1
50	0.71	1231. 7	1022.3

Table IV

1

Table III

	Free energy of activation kcal/mol		Entro activ	ppy of ation (mol	Enthalpy of activation kcal/mol		
',°C	ΔF_{ϵ}	ΔF_{η}	ΔSε	ΔS_{η}	ΔH_{ϵ}	ΔH	
			Diphenyl	Ether			
30	2.07	5.64	10.75	-5.76			
40	2.04	5.70	10.52	-5.47	5.33	3.99	
50	1.87	5.76	10.73	-5.48			
			Dibutyl	Ether			
30	2.16	4.71	0.81	-7.37			
40	2.13	4.78	0.85	-7.34	2.41	2.48	
50	2.14	4.87	0.82	-7.41			
		N	N'-Dimet	h yla nilin e			
30	3.41	4.93	59.78	-6.82			
40	2.81	5.00	59.81	-6.83	21.53	2.86	
50	2.22	5.07	59.76	-6.85			
	~	1	N,N'-Dieth	ylaniline			
30		5.23		-4.69			
40		5.33		-4.64		3.81	
50		5.39		-4.91			

These values of α , τ , and τ_0 for the experimental liquids at different temperatures have been shown in Table III.

Thermodynamic Parameters. These parameters have been calculated by the help of Eyring's equations¹⁴⁻¹⁶

- (13) J. G. Powles, J. Chem. Phys., 21, 633 (1953).
- (14) H. Eyring, ibid., 4, 283 (1936).
- (15) A. E. Stearn and H. Eyring, *ibid.*, 5, 113 (1937).

(16) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941, pp 544-551.

$$\tau = \frac{h}{kT} e^{\Delta F_e/RT} \tag{6}$$

and

$$\eta = \frac{hN}{V} e^{\Delta F_{\eta}/RT} \tag{7}$$

where the notations all have their usual significance. ΔF_{ϵ} and ΔF_{η} are the free energies of activation for dipole relaxation and viscous flow. These values are related to the enthalpy of activation and entropy of activation by the relations

$$\Delta F_{\epsilon} = \Delta H_{\epsilon} - T \Delta S_{\epsilon} \tag{8}$$

and

$$\Delta F_{\eta} = \Delta H_{\eta} - T \Delta S_{\eta} \tag{9}$$

Equations 6 and 7 indicate that the plots of log (τT) vs. 1/T and log η vs. 1/T should give approximately a linear relationship (see Figures 7-11) with slopes equal to $\Delta H_{\epsilon}/R$ and $\Delta H_{\eta}/R$, respectively, from which ΔH_{ϵ} and ΔH_{η} are calculated.

Also, from eq 6 and 7, one gets

$$\Delta F_{\epsilon} = 2.303 \ RT \log\left(\frac{kT\tau}{h}\right) \tag{10}$$

and

$$\Delta F_{\eta} = 2.303 \ RT \log\left(\frac{V}{hN} \eta\right) \tag{11}$$

where V is taken to be the molar volume and is found from the density measurements. Knowing τ , η , and T, one can evaluate ΔF_{ϵ} and ΔF_{η} and subsequently ΔS_{ϵ} and ΔS_{η} from eq 8 and 9. Table IV lists the values of all these parameters.

Discussion

Diphenyl Ether. Figure 2 shows the Cole-Cole plot for this molecule at 40° . For comparison's sake, the



Figure 7. Log η and log $(\tau \times T)$ vs. (1/T) for diphenyl ether.



Figure 8. Log η and log $(\tau \times T)$ vs. (1/T) for dibutyl ether.



Figure 9. Log η and log $(\tau \times T)$ vs. (1/T) for dimethylaniline.

literature values of ϵ' and ϵ'' for diphenyl ether at 40°, observed by Vaughan and Smyth¹ have also been plotted on the same curve. Open circles correspond to the values determined by the author whereas the closed circles refer to the values observed by Vaughan and Smyth. All the points fall fairly well on the Cole-Cole plot which indicates, if nothing else, at least the reliability of the present experimental data. Similar plots for the same molecule at temperatures 30 and 50° have been shown in Figure 3. Although it has been shown that relaxation of diphenyl ether involves two distinct mechanisms,^{3,4,7} the data fit a Cole-Cole plot closely at 30, 40, and 50°. The values of distribution parameter (α), found from these plots hardly indicate any observable trend with temperature.



Figure 10. Log $(\tau \times T)$ vs. (1/T) for dimethylaniline, where the relaxation time (τ) corresponds to 31.82 GHz.



Figure 11. Log η and log ($\tau \times T$) vs. (1/T) for diethylaniline.

These values are $0.34/30^{\circ}$, $0.35/40^{\circ}$, and $0.33/50^{\circ}$ as against $0.21/40^{\circ}$, reported by Vaughan and Smyth.¹ Slightly higher values obtained by the author may be due to a different method adopted for the determination of α . Maybe a plot of $\ln |v/u| vs$. $\ln \omega$ would bring the α values down but it could not be checked as the measurements for ϵ' and ϵ'' were carried out only at two frequencies.

The relaxation time for liquid diphenyl ether, as reported by Smyth, *et al.*,² is 5.1 psec whereas the author found a value of 5.0 psec at 30° .

The literature value³ for free energy of activation (ΔF_{ϵ}) is 2.20 kcal/mol at 40° whereas the present work at 40° gives a value of 2.04 kcal/mol. Roberti, Kalman, and Smyth⁴ found ΔH_{ϵ} and ΔH_{τ} to be 1.9 kcal/mol and 3.8 kcal/mol for diphenyl ether in Nujol. These values for pure liquid have been found to be 5.33 and 3.99 kcal/mol, respectively. Even by orthodox methods,⁵ the value for ΔH_{ϵ} comes out to be 5.21 kcal/mol at 40°.

Dibutyl Ether. No data on relaxation study seem to be available in the literature for this molecule. The ϵ' and ϵ'' values for the three temperatures represent the Cole-Cole plot fairly well (See Figure 4). The point corresponding to 9.72 GHz/30° falls far beyond the curve, which may be an experimental error. The values of distribution parameter α also indicate the usual trend with temperature. The macroscopic relaxation time τ calculated for both the frequencies (9.72 GHz and 31.82 GHz) showed a difference of only 5%. Their average values, therefore, have been inserted in Table III. These values are, $5.7 \text{ psec}/30^{\circ}$, 4.7 psec/40°, and 4.2 psec/50°. The relaxation times for the same molecule in different solvents, e.g., benzene, cyclohexane, carbon tetrachloride, heptane, decalin, and Nujol, have also been determined in the same laboratory.¹⁷ This value in benzene has been found to be 6.5 psec at 25° and shows an almost regular variation with the viscosity of the medium giving $\tau = 14.2$ psec for Nujol, having the largest viscosity coefficient. The viscosity of dibutyl ether at 30° is 0.58 cP, which is almost the same as that of benzene (0.57 cP). Obviously, the small difference in the two relaxation times hardly indicates any observable difference involved between the two systems. Also, considering the molecular volumes of dibutyl ether, diphenyl ether, and benzophenone, one finds that they have almost similar values of 170.9, 159.5, and 170 cc, respectively, but the relaxation times of dibutyl ether and benzophenone in benzene are 6.5 psec and 18.7 psec,¹⁸ respectively. This is possibly due to the fact that the butyl group sweeps a lesser area of solvent molecules while relaxing as compared to the phenyl group.

N,N'-Dimethylaniline. In this case also, a perusal of Figure 5 reveals that the experimentally determined values of ϵ' and ϵ'' at different temperatures represent the Cole-Cole arc fairly well. The values of distribution parameter α are found to be quite large, thus indicating the possibility of more than one relaxation mechanism. These values are $0.59/30^{\circ}$, $0.55/40^{\circ}$, and $0.34/50^{\circ}$, which show the usual trend with temperature. Whereas the molecular relaxation times for these temperatures are 38.2, 11.6, and 3.9

⁽¹⁷⁾ This work has been done in this laboratory in collaboration with J. K. Vij and is shortly to be communicated for publication.

⁽¹⁸⁾ Reference 2, p 21.

psec, Garg and Smyth,19 however, found a value of 28 psec for pure liquid. Other details of their work are not available since their findings have not been published. Grubb and Smyth, in their paper,20 reported the measurements performed by Dr. K. Fish which do not agree with those reported here. It appears that the main source of discrepancy is the method adopted for calculations. The author feels that for low-loss substances, the method of Heston, et al.,10 (adopted in this paper) gives more reliable results than that of Surber²¹ (adopted by the authors²⁰) which gives accurate results for medium- and high-loss substances. Also, as low a value for α (0.02) as reported in the paper²⁰ should not account for the molecule having a relaxation mechanism suggested by Smyth.¹⁹ Chitoku²² also reported the values of the average relaxation time for this molecule in benzene and dioxane which are 14.5 and 30.4 psec at 20° but the distribution parameters, obtained by him for these solvents, are zero for both the cases. On comparing the viscositites of pure N,N'-dimethylaniline and dioxane, one finds that these are almost of the same order, having values equal to 1.13 cP at 30° and 1.28²³ cP at 20°, respectively. Higasi, et al.,²² already suggested the formation of bonds between aminohydrogen atoms in aniline and an oxygen atom of dioxane molecule which leads to a high relaxation time in dioxane.

Another factor noticed for this molecule is about its large variation in the relaxation time found at experimental frequencies. The τ_0 values, mentioned above and noted in Table III, correspond to the frequency 9.72 GHz, whereas the values calculated for 31.82 GHz, using eq 4 and 5, are 84.6 psec/ 30° , 59.8 psec/40°, and 11.5 psec/50°. On comparing Figures 9 and 10, one finds that a log (τ T) vs. 1/T plot is a perfect straight line if τ values correspond to 9.72 GHz but it is not true if the values of τ , obtained for 31.82 GHz, are used (Figure 10). No adequate explanation can be given at this stage with the limited data available but it appears that in this case, $\tau_{\rm m}$ seems to be dependent on the frequency of observation, whereas this quantity is assumed to be constant for the validity of Cole–Cole's rule. $\tau_{\rm m}$ is the most probable relaxation time corresponding to the frequency that gives the greatest value of ϵ'' .

N,N'-Diethylaniline. The study of liquid N,N'diethylaniline indicates its unusual behavior in many ways. For example, the distribution parameter and the relaxation time increase with increasing temperature (see Table III and Figure 11). The molecular relaxation times for the liquid have been found to be 290.3 psec/30°, 390.1 psec/40°, and 1022.3 psec/50°. The literature²² values for the same substance in benzene and dioxane are 33.2 psec and 47.4 psec at 20°. Like that of N,N'-dimethylaniline, the relaxation time for this substance also shows frequency dependence. However, the concentration of almost all the experimentally observed points into a small region of a Cole-Cole plot leads one to suspect the experimental inaccuracy involved to distinguish one point from the other in this range of frequency (see Figure 6). It is therefore felt that measurements at still lower frequencies are very essential in this case.

Thermodynamic Parameters. These parameters have been calculated for all the substances under study at different temperatures and the results are shown in Table IV. The values of ΔF_{ϵ} , ΔH_{ϵ} , and ΔS_{ϵ} have not been calculated for N,N'-diethylaniline because of the uncertainty involved, but it is expected that ΔS_{ϵ} for this molecule would be almost of the same magnitude as that of N,N'-dimethylaniline.

Table IV, however, shows that ΔF_{ϵ} , the free energy of activation for the relaxation process, is always less than ΔF_{η} , the free energy of activation for viscous flow, as is always expected. The values of ΔS_{η} for all the molecules are negative whereas ΔS_{ϵ} values have been found to be positive. It is therefore apparent that there must be a considerable difference between the molecular processes involved and that of any concept of "internal viscosity." Furthermore, when the values of this entropy are as large as they often are here (especially in case of aniline), we know that activation must involve more than merely a single molecule. In order to explain the large positive values of ΔS_{ϵ} , especially in cases of dimethyl and diethyl anilines, the author would like to state the following.

Suppose we attempt to go from one stable arrangement of a small region in a dielectric to another in the most rapid manner possible, utilizing only the thermal motions of molecules. Therefore, the surrounding of a given molecule must move simultaneously with the molecule. This might occur in two ways, *i.e.*, (a) the various molecules involved may cooperate in their movements and rotate together in much the

Table V:	: Dipo	le Moment	(in Debye	units)	at 30°
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Substance	۳Onsager (pure liquid)	#Higasi (soln, in benzene)
Diphenyl ether	1.11	1.19
Dibutyl ether	1.29	1.18
N,N'-Dimethylaniline	1.48	1.62
N,N'-Diethylaniline	1.67	1.79

(19) S. K. Garg and C. P. Smyth, unpublished work; this value has been quoted in the Chemical Society Publication, "Molecular Relaxation Processes," No. 20, Academic Press, London, 1966, p.8.

(22) K. Chitoku and K. Higasi, Bull. Chem. Soc., Jap. 39, 2160 (1966).

⁽²⁰⁾ E. L. Grubb and C. P. Smyth, J. Amer. Chem. Soc., 83, 4879 (1961).

⁽²¹⁾ W. H. Surber, Jr., J. Appl. Phys., 19, 514 (1948).

⁽²³⁾ K. Chitoku and K. Higasi, ibid., 39, 2166 (1966).

same manner as a set of interlocked gears or (b) the molecules may momentarily completely disengage one another and resume their stable configuration with their net dipole moment oriented in a new direction. Process (a) will presumably require little energy, while (b) will require considerable energy. The possibility of process (a) seems to be less probable if one looks at Table V which gives the values of dipole monents for pure liquids, calculated by Onsager's equation

$$\mu^2 = \frac{9kT}{4\pi N} \frac{M}{d} \frac{(2\epsilon_0 + \epsilon_\infty)(\epsilon_0 + 2)}{3\epsilon_0(\epsilon_\infty + 2)} \left[\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right]$$

and the dipole moments of these substances in benzene as solvent, calculated by Higasi's equation²⁴

$$\mu = B(a_0 - a_D)^{1/2}$$

Since these values do not show any appreciable difference, the possibility of mechanism (a) is less probable as other wise $\mu_{(Onsager)}$ would be different than $\mu_{(Higasi)}$ because the latter case deals with the solutions in a very low concentration range where the interlocking effect is absent, while with mechanism (b), on the other hand, there will be a great increase of freedom in the activated complex, so giving a positive entropy of activation whose magnitude will be a measure of the extent of the momentary violation of the requirements for stability. Incidently, the hydrogen bonding of aniline has already been reported.^{25,26} Maybe therefore, this is the reason for very large observed relaxation times in the cases of dimethyl- and diethylanilines.

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(24) K. Higasi, Oyo Denki Kenkyusho Iho, 4, 231 (1952).

(25) J. C. Dearden and W. F. Forbes, Can. J. Chem., 38, 896 (1960).

(26) B. N. Rao, et al., ibid., 40, 963 (1962).

Semiempirical Calculation of $3.7RT_m$ Term in the Heat of Activation

for Viscous Flow of Ionic Liquid

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The heat of activation in transport in ionic liquids is rededuced in terms of the work of hole formation in the liquid. Theoretical values calculated for the simple molten salts for which data are available agree reasonably with those determined experimentally.

1. Previous Position

It has been found experimentally¹ that the Arrhenius type activation energies for viscous flow, E_{η} , self-diffusion of cations, $E_{D_{\star}}$, and anions, $E_{D_{-}}$, all reveal practically the same value in a molten salt, namely as

$$E_{\eta} \cong E_{D_{+}} \cong E_{D_{-}} \cong 3.7RT_{m} \tag{1}$$

where R is the gas constant and T_m is the melting point of the molten salt. Equation 1 is also applicable to simple organic liquids and to some liquid metals (Figure 1).

Several attempts have been made in our laboratory to interpret the above relationship by extending the arguments of the theory of holes proposed by Fürth,² who considered the liquid state to be a mixture of holes and the matter outside them. The matter is a continuum with the normal surface tension, σ , of the liquid. The distribution of hole sizes is given by the formula

$$W(r) = \int \cdots \int C e^{-E/kt} dp_r dp_z dp_y dp_z$$
(2)

where C, the normalizing factor, is obtained by integrating W(r) from zero to infinity with respect to r; p_x , p_y , p_z are the momenta corresponding to the coordinates x, y, and z, and p_r is the momentum corre-

L. Nanis and J. O'M. Bockris, J. Phys. Chem., 67, 2865 (1963);
 J. O'M. Bockris and S. R. Richards, *ibid.*, 69, 671 (1965).

⁽²⁾ R. Furth. Proc. Cambridge Phil. Soc., 37, 252 (1941); F. H. Stillinger in "Molten Salt Chemistry," Ed., M. Blander, Interscience Publishers, New York, N. Y., 1964, p 1.



Figure 1. Energies of activation for viscous flow and self-diffusion (inset) vs. melting temperature.

sponding to the variable r. The total energy of hole, E, is given by

$$E = \frac{4}{3} \pi r^{3} (P - P_{0}) - 4\pi r^{2} \sigma + (p_{x}^{2} + p_{y}^{2} + p_{z}^{2})/2m_{1} + p_{r}^{2}/2m_{2} \quad (3)$$

where P is the external pressure, P_0 is the pressure of the saturated vapor, and the apparent mass of the hole for a translation, m_1 , and that for expansion, m_2 , are taken to be equal to the values derived by classical hydrodynamics, *i.e.*, $2/_3\pi r^3\rho$ and $4\pi r^3\rho$ (ρ is the density of the liquid), respectively. It is shown that the distribution of size among the holes is narrow. Then, by assuming that the irregular Brownian motion of the holes produces a transfer of momentum between adjacent layers in a moving liquid, an expression was given for viscosity as³

$$\eta = N_{\rm h} k T \tau \tag{4}$$

where $N_{\rm h}$ is the number of the holes per unit volume of the liquid, τ is the mean lifetime of a hole which is given by^{3,4}

$$\tau = \frac{2}{3} r \left(\frac{2\pi m}{kT}\right)^{1/2} \exp\left(\frac{A}{RT}\right)$$
(5)

in which m is the mass of a molecule and A is the energy required to release one mole of molecules from the hole surfaces of the liquid into the holes.

Bockris and Hooper⁵ considered that the number of particles per unit volume of the liquid is equal to that of holes per unit volume of the liquid, and that the value of A is a sum of the heat of activation for jumping, ΔH_J^{\pm} , and the work of hole formation per mole of holes, ΔH_h . It was assumed that (cf. ref 5, p 231) ΔH_J^{\pm} is much smaller than ΔH_h . Then A becomes approximately

$$A \cong \Delta H_{\rm h} = 4\pi \langle r^2 \rangle \sigma N_0 \tag{6}$$

where N_0 is the Avogadro number, and the average surface area of a hole is given by

$$4\pi \langle r^2 \rangle = 4\pi \int_0^\infty r^2 W(r) dr = 3.5 kT/\sigma$$
 (7)

From eq 6 and 7

$$A = 3.5RT \tag{8}$$

(3) R. Furth, Proc. Cambridge Phil. Soc., 37, 281 (1941).

(4) J. Frenkel, "Kinetic Theory of Liquids," Oxford Univ. Press, Oxford, 1946.

(5) J. O'M. Bockris and G. W. Hooper, Discussions Faraday Soc., 32, 218 (1961).

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In order to achieve consistency with experimental facts shown by plot of molecular area vs. surface tension (cf. Ramsay-Shields equation), Bockris and Hooper modified eq 8 to the form

$$A(T) = A(T_m) - BT = 3.5RT_m - BT$$
 (9)

and argued that the constant B could be calculated

$$B = -dA/(T)/dT = \frac{12}{11} [(x_e/x)^2 - (x_e/x)^{13}]3.5RT_m \quad (10)$$

where x is the distance between cation and anion, and x_e is the equilibrium value of this distance.

Later, Bockris, Richards, and Nanis⁶ took the term $4\pi \langle r^2 \rangle \sigma$ in eq 6 as a free energy. Then, with $\sigma = \sigma_m - B'T(\sigma_m; \sigma \text{ at } T_m, B'; \text{ constant})$

$$\Delta F_{\rm h} = 4\pi r^2 N_0 \sigma = 4\pi r^2 N_0 (\sigma_{\rm m} - B'T) \quad (11)$$

 $\Delta H_{\rm h}$ was identified with $4\pi r^2 N_0 \sigma_{\rm m}$ and r replaced r_0 which was given by

$$r_{0} \cong \langle r_{\mathrm{m}}^{3} \rangle^{1/2} = \left[\int_{0}^{\infty} r^{3} W(r) \mathrm{d}r \right]_{T=T_{\mathrm{m}}}^{1/2} = 0.546 \left(\frac{kT_{\mathrm{m}}}{\sigma_{\mathrm{m}}} \right)^{1/2}$$
(12)

Hence

$$\Delta H_{\rm h} = 4\pi N_0 \left[0.546 \left(\frac{kT_{\rm m}}{\sigma_{\rm m}} \right)^{1/2} \right]^2 \sigma_{\rm m} \simeq 3.7RT_{\rm m} \quad (13)$$

Equation 4 was converted into the diffusion equation by making use of the Stokes-Einstein equation. Differentiating the diffusion equation by temperature, the Arrhenius type activation energy for diffusion follows as

$$E_{\rm D} = \Delta H_{\rm h} - \frac{1}{2} RT + RT^2 \left(\alpha + \frac{1}{\sigma} \frac{{\rm d}\sigma}{{\rm d}T} \right) \quad (14)$$

where α is the expansivity of the liquid. The final terms in eq 14 largely compensate each other, leaving $E_{\rm D} \simeq 3.7 RT_{\rm m}$, in agreement with experiment.

As has been criticized elsewhere,^{7.8} however, eq 13 does not stand because of the fact that the substitution of eq 7 into eq 11 gives, whatever the expression for σ (cf. eq 11) is, $\Delta F_{\rm h}$ equal to 3.5RT. This means $\Delta H_{\rm h}$ is zero since $\Delta H_{\rm h} = \Delta F_{\rm h} - T(\partial \Delta F_{\rm h}/\partial T)$. Then, eq 14 gives results inconsistent with the observations cited.¹

2. Rededuction in Terms of the Heat of Formation of Holes

The physical meaning of the term A/N_0 in eq 5 is the work necessary to release an ion from the surface of a hole into a hole. Evaluation of A from first principles by taking into account the various kinds of interactions among ions and holes would be difficult. It is possible, however, to derive approximately the value of A in terms of the work of hole formation as follows. The average redius of a hole in a liquid is

$$\langle r \rangle = \int_0^\infty r W(r) \mathrm{d}r = 0.51 \langle kT/\sigma \rangle^{1/2}$$
(15)

As shown in eq 16, the ratio of the average surface area of a hole [eq 7] to the average radius of the hole agrees with the value of $\pm \pi$ within 10%.

$$\frac{4\pi \langle r^2 \rangle}{\langle r \rangle^2} = \left(3.5 \frac{kT}{\sigma}\right) / \left(0.51\right)^2 \frac{kT}{\sigma} \cong 13.5 \cong 4\pi \ (\cong 12.6)$$
(16)

This means that the statistical distribution of the value r is so crowded at $\langle r \rangle$ that small error arises if every hole may be considered to have the same radius as $\langle r \rangle$. This is convenient because in eq 4 it is assumed that all the holes are of average size.

The average hole radius, $\langle r_m \rangle$, at the melting point is calculated by eq 15 for some simple molten salts and is listed in Table I together with the radii of the cation and anion in the corresponding salt.

It can be seen from the table that the size of a hole at $T_{\rm m}$ is roughly that of lons in the corresponding salt. Thus, it is reasonable to assume that, at the melting point, the work (per particle in the liquid), $A(T_{\rm m})/N_0$, done to fill a hole is numerically equal to the work expended to form a surface of $4\pi \langle r_{\rm m}^2 \rangle$. Let it be assumed that this filling is done on average by one ion at $T_{\rm m}$. Now at a temperature T above $T_{\rm m}$, the volume of the hole $v_{\rm T}$ is larger than that at $T_{\rm m}$. Hence, compared with the number at the melting point (one), a larger number of ions (n) will be needed to fill a hole. Then, the expressions for A/N_0 (work per particle) at T and $T_{\rm m}$ become

$$A(T_{\rm m})/N_0 = 4\pi \langle r_{\rm m}^2 \rangle \sigma_{\rm m}$$
 (18)

(17)

Now *n* is given by the ratio of the number of ions per hole, n_T , at *T* to that, n_m , at T_m . By considering the fact that the difference between the volume of the liquid salt and that of the corresponding solid (ΔV) is due only to holes, the number of holes per mole of salt becomes

 $A(T)/N_0 = 4\pi \langle r_T^2 \rangle \sigma_T/n$

$$N_{\rm h} = \Delta V_T / v_T \tag{19}$$

where $v_{\rm T}$ is now given by $4/{}_3\pi \langle r_T^2 \rangle^{3/2}$. Then, for a 1-1 salt

(6) J. O'M. Bockris, S. R. Richards, and L. Nanis, J. Phys. Chem., 69, 1627 (1965).

⁽⁷⁾ M. Blander, private communication which is cited in reference 8, and H. T. Davis, invited lecture at the University of Pennsylvania, March 22, 1968.

⁽⁸⁾ S. J. Yosim and H. Reiss, Ann. Rev. Phys. Chem., 19, 59 (1968).

Salt	T _m , °K	$\langle r_{\rm m} \rangle^a$	r+ a	r - ^a	Съ	$E_{\eta}{}^{a}$	E_{D}^{a}	$(E_{\eta}/RT_{\rm m})$	$(E_{\rm D}/RT_{\rm m})$
LiCl	883	1.52	0.60	1.81	0.92	7.1	7.5	4.06	4.29
NaCl	1074	1.82	0.95	1.81	0.89	8.8	8.8	4.14	4.14
KCl	1049	1.94	1.33	1.81	0.99	7.8	7.9	3.76	3.80
RbCl	988	1.90	1.48	1.81	1.02	6.9	8.9	3.53	4.55
CsCl	919	1.89	1.69	1.81	0.86	8.0	7.9	4.40	4.34
AgCl	728	1.21	1.26	1.81	1.02	5.0	5.5	3.46	3.82
BaCl ₂	1235	1.64	1.35	1.81	1.00	8.5	9.0	3.48	3.68
NaBr	1020	1.92	0.95	1.95	0.96	7.8	8.1	3.86	4.01
KBr	1007	2.01	1.33	1.95	0.98	7.1	7.0	3.56	3.51
AgBr	707	1.29	1.26	1.95	1.03	4.9	5.6	3.50	4.00
NaI	933	1.95	0.95	2.16	0.83	8.2	8.0	4.44	4.33
KI	954	2.08	1.33	2.16	0.88	7.8	7.8	4.13	4.13
NaNO3	580	1.34	0.95	2.31°	0.98	4.3	4.9	3.75	4.27
KNO3	607	1.41	1.33	2.31	1.40	2.7	3.1	2.25	2.58
AgNO3	485	1.08	1.21	2.31	0.96	3.6	4.0	3.75	4.17
Average					1.01			3.84	4.07

Table I: Theoretical Activation Energies for Viscous Flow and Self-Diffusion in Some Simple Molten Salts

^a $\langle r_m \rangle$, r_+ , r_- in Å, and E_η , E_D in kcal/mol. ^b $C = (T_m/T)^{3/2} (\sigma_T/\sigma_m)^{1/2} (\Delta V_T/\Delta V_m)$. ^c Radius of free rotation sphere reported by G. J. Janz and D. W. James, *Electrochim. Acta*, 7, 427 (1962). ^d Average values exclude corresponding values of KNO₃.

$$n_T' = 2N_0 / \left(\frac{\Delta V_T}{v_T}\right) \tag{20}$$

Hence

$$n_T'/n_m' = (\Delta V_m/\Delta V_T)(v_T/v_m)$$
(21)

where $\Delta V_{\rm m}$ and $v_{\rm m}$ are the values of ΔV and v at $T_{\rm m}$. From eq 7, 17, 18, and 21, one has

$$A(T) = (T_{\rm m}/T)^{1/2} (\sigma_T/\sigma_{\rm m})^{3/2} (\Delta V_T/\Delta V_{\rm m}) A(T_{\rm m})$$
 (22)

If one restricts the range of experiment to about 200° above the melting point, then, for simple molten salts, using experimental values, one calculates (cf. Table I)

$$(T_{\rm m}/T)^{1/2} (\sigma_T/\sigma_{\rm m})^{3/2} (\Delta V_T/\Delta V_{\rm m}) \cong 1 \qquad (23)$$

Thus, one has, from eq 18, 22, 23, and 7

$$A(T) \cong A(T_{\rm m}) = 4\pi \langle r_{\rm m}^2 \rangle \sigma_{\rm m} N_0 = 3.5 R T_{\rm m}/\text{g-ion} \quad (24)$$

Now, the expression for the viscosity of molten salts becomes, from eq 4 and 5

$$\eta = 0.6 \frac{\Delta V_{\rm T} \sigma_{\rm T}}{V_{\rm T}} \left[\frac{2\pi m}{kT} \right]^{1/2} \exp(3.5RT_{\rm m}/RT) \quad (25)$$

where V_{T} is the molar volume of the molten salt. By using the Stokes-Einstein relation, this turns into

$$D = \frac{0.17 V_T kT}{\Delta V_T \sigma_T^{1/2} (2\pi m)^{1/2}} \exp(-3.5 RT_m/RT) \quad (26)$$

The applicability of the Stokes-Einstein relation has been discussed by Bloom and Bockris.⁹ The theoretical expressions for the Arrhenius type activation energies for viscous flow and diffusion can be immediately derived as

$$E_{\eta}(\text{theo.}) = 3.5RT_{\text{m}} + \frac{1}{2}RT - RT^{2} \left(\frac{1}{\Delta V_{T}} \frac{\mathrm{d}\Delta V_{T}}{\mathrm{d}T} + \frac{1}{\sigma_{T}} \frac{\mathrm{d}\sigma_{T}}{\mathrm{d}T} - \frac{1}{V_{T}} \frac{\mathrm{d}V_{T}}{\mathrm{d}T} \right) \quad (27)$$

and

 $E_{\rm D}$ (theo.) = $3.5RT_{\rm m} + RT -$

$$RT^{2}\left(\frac{1}{\Delta V_{T}}\frac{\mathrm{d}\Delta V_{T}}{\mathrm{d}T} + \frac{1}{2\sigma_{T}}\frac{\mathrm{d}\sigma_{T}}{\mathrm{d}T} - \frac{1}{V_{T}}\frac{\mathrm{d}V_{T}}{\mathrm{d}T}\right) \quad (28)$$

3. Comparison with Experiment

The values of E_{η} (theo.) and $E_{\rm D}$ (theo.) for some simple molten salts have been calculated from eq 27 and 28 and are listed in Table I. Although the two equations include temperature-dependent terms, these terms compensate each other within the temperature range examined, and practically temperature independent values are obtained for E_{η} (theo.) and $E_{\rm D}$ (theo.). Both values are, of course, nearly identical. These values are compared in Figures 2 and 3 with E_{η} (obs.) and $E_{\rm D}$ (obs.) determined experimentally.^{6,10} The comparison of theory and experiment has been made here for molten salts. However (see Figure 1), the experimental relation $E_{\rm D} \simeq E_{\eta} \simeq 3.7 RT_{\rm m}$ has a much larger range of validity which seems to extend from the rare gas liquids to molten metals.

As indicated by vertical lines in Figure 2, considerable scatter exists still in E_{η} (obs.), and, at the same time, a rather limited number of results is available to $E_{\rm D}$ (obs.) for molten salts. Excluding the case of KNO₃ which

⁽⁹⁾ H. Bloom and J. O'M. Bockris in "Fused Salts," B. R. Simlhein, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 15.

⁽¹⁰⁾ G. J. Janz, "Molten Salt Handbook," Academic Press, New York, N. Y., 1967; A. V. Grosse, *Rev. Int. Hautes Temp. Refract.*, 4, 171 (1967).



Figure 2. Comparison between theoretical and experimental energies of activation for viscous flow.

indicates marked deviation from the approximation made (eq 23), there is an adequate agreement between the calculated values and observed values. Further, the average values of E_{η} (theo.)/ $RT_{\rm m}$ and $E_{\rm D}$ (theo.)/ $RT_{\rm m}$ are about 3.9, which agrees reasonably with the demonstrated relationship, *i.e.*, eq 1.

The model of holes in liquids is thus able to give a fair numerical account of the heat of activation for transport at constant pressure in simple liquids. No interpretation of this fact has as yet been given in terms of models other than that of thermally distributed holes.

Two major assumptions have been made in the above treatment. One is that an ion in a hole behaves like an ideal gas (the basis of eq 5). Another is that the functional dependence of σ on r does not meaningfully affect the integration (eq 2), where it is tacitly assumed



Figure 3. Comparison between theoretical and experimental energies of activation for self diffusion.

that σ does not depend on r. The former assumption may be more plausible than the latter. However, if the dependence of the surface energy on the radius of a hole is such that the phase integral of the radius-dependent term and the normalizing integral of the radiusdependent term cancel each other in eq 7, then the dependence does not formally change the average calculation. In this case, the work required to create a surface of $4\pi \langle r_m^2 \rangle$ is indeed $3.5kT_m$ (eq 24). This cancellation may underlie the adequate agreement obtained here between the calculated values and observed values.

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Osmotic and Activity Coefficients of Ammonium Heteropolymolybdates

by Eugene Meyer, Jr., and Rick Huckfeldt

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The osmotic coefficients of ammonium 6-molybdochromate(III) and ammonium 6-molybdoaluminate(III) have been measured at 37° in aqueous solutions of concentration ranging from 0.002 to 0.02 m. Activity coefficients derived therefrom have been compared to those of the simple 3:1 salt, LaCl₃. The interionic distances calculated from the Debye-Hückel extended equation have been determined as 2.9 and 4.3 Å for the molybdo-chromate and -aluminate salts, respectively.

Introduction

Activity coefficients of complex ion electrolytes are of theoretical interest in connection with factors responsible for the stabilization of complex ions in solution, *e.g.*, polarization, dispersion factors, *etc.* However, there is a notable paucity of such data in the literature which limits the interpretation of solution behavior of complex ions.

Robinson¹ first reported significant measurements of activity coefficients of the complex ion electrolyte $K_4Fe(CN)_6$, a 1:4 salt. This study was extended by Brubaker² to include K₄Mo(CN)₈ and the 4:1 electrolyte $Pt(en)_{3}Cl_{4}$. The activity coefficients were notably larger in value for the two 1:4 salts. A further study³ was reported for the 3:1 electrolytes $Co(en)_3(NO_3)_3$, $Co(pn)_3(ClO_4)_3$, and $Co(en)_3(ClO_4)_3$; a 1:3 electrolyte $K_3Co(CN)_6$, and the 3:2 electrolyte $[Co(en)_3]_2(SO_4)_3$. Agreeable comparison of the experimental activity coefficients with those calculated from the Debye-Hückel extended equation was observed only for the choice of relatively low values of \hat{a} , the mean distance of closest approach for the ions in solution. Additional studies⁴ on Pt(pn)₃Cl₄, $[N(CH_3)_4]_4M_0(CN)_8$, $K_4W(CN)_8$ and $K_2Pt(CN)_4$ similarly required low values of a to fit the data.

In studying the activity coefficients of acidopentaamminecobalt(III) complexes of the type $[Co(NH_3)_5-A]X_2$ where A is acetate, propionate, or isobutyrate and X is NO₃-, I⁻, Br⁻ or Cl⁻, Berka and Masterton⁵ noted activity coefficients were independent of the organic ligand in the complex but varied somwhat with the anion. Earlier measurements by Masterton and Scola⁶ had demonstrated that activity coefficients of 2:1 electrolytes compared more favorably with those of simple 1:2 electrolytes and were considerably lower than known values of simple 2:1 salts. Similar comparisons of such measurements applied to other valence types are unavailable.

As a continuation in studying variations of activity coefficients of complex electrolytes, a series of ammonium 6-molybdometallates of general formula $(NH_4)_3$ - $[MeMo_6O_{24}H_6] \cdot H_2O$ was originally selected where Me represents one of the metal ions Cr, Co, Fe, or Al. Aside from the point that thermodynamic data are completely lacking on solutions of these compounds, their choice presented a similar investigation as mentioned above where the general nature of the electrolyte is changed to 1:3. The main disadvantage in their selection with reference to this point is a limited solubility in water, averaging around 3 g/100 ml at 25°. Unfortunately, only one simple salt having the same valence index has been studied in the range of concentrations accessible up to the saturated solution.

Recently, Hallada, et al.,⁷ proposed activity coefficient effects to explain pH measurements of the molybdovanadophosphoric acids, $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}-V_2O_{40}]$, in solutions of low ionic strength. Further investigation of the solution properties of heteropolymolybdate anions was thus prompted.

In order that activity coefficient measurements be thermodynamically meaningful, it is necessary that the complex salts be stable to aquation. Solutions of the 6-molybdoferrate salt decompose near 40° which prevented valid measurements at the temperature chosen for this study. Similarly, unreproducible results were obtained for the -cobaltate. Consequently, activity coefficients of only the 6-molybdoaluminate and -chromate salts are reported here.

Experimental Section

Samples of the ammonium heteropolymolybdates were obtained as gifts from the Climax Molybdenum Co., New York, N. Y. The samples were purified as described by Baker.⁸ Aqueous solutions of known

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- (2) C. H. Brubaker, *ibid.*, 78, 5762 (1956).

(3) R. A. Wynveen, J. L. Dye, and C. H. Brubaker, *ibid.*, 82, 4441 (1960).

(4) K. O. Groves, J. D. Dye, and C. Brubaker, *ibid.*, 82, 4445 (1960).

(5) L. H. Berka and W. L. Masterton, J. Phys. Chem., 70, 1641 (1966).

(6) W. L. Masterton and J. A. Scola, ibid., 68, 14 (1964).

(7) C. J. Hallada, G. A. Tsigdinos, and B. S. Hudson, *ibid.*, 72, 4304 (1968).

⁽⁸⁾ L. C. W. Baker, B. Loew, and T. P. McCutcheon, J. Amer. Chem. Soc., 72, 2374 (1950).

molality were prepared gravimetrically using doubly distilled and deionized water.

The classic methods of experimentally determining activity coefficients (isopiestic, emf, etc.) are inconvenient when studying complex electrolytes, since long periods of time may be involved before equilibrium is established and a measurement can be made. Consequently, a method^{5,6,9} employing a vapor pressure osmometer [Model No. 301A, Mechrolab, Inc., Mountain View, Calif.] was employed for determining osmotic coefficients from which the activity coefficients were derived. The principles and practices of vapor pressure osmometry have been reviewed by Brady¹⁰ and Burge.¹¹ Although earlier work using a vapor pressure osmometer was limited to solutions of concentration greater than 0.01 m, the measurements reported here were extended to as low as 0.002 m. All measurements were made at 37°.

Values of the osmotic coefficient (ϕ) at various molalities are readily measured from osmometric resistance readings ΔR using the equation

$$\phi = k \Delta R / \nu m \tag{1}$$

where ν is the total number of ions per mole of electrolyte. The value of the constant k is determined in an alternate experiment using solutions of KCl whose osmotic coefficients are known accurately from isopiestic measurements.¹² The experimental values of the osmotic coefficient were adjusted to the empirical equation

$$1 - \phi = am^{1/2} + bm + cm^{3/2} + dm^2 \qquad (2)$$

by a least-squares method, so that new activity coefficients could be calculated at rounded molalities, allowing eventual comparison between the two 1:3 heteropoly salts at the same concentration. The mean ionic activity coefficients were then obtained through the classic expression

$$\int d \ln \gamma_{\pm} = \int d\phi + \int (\phi - 1) d \ln m \qquad (3)$$

where the lower limit of integration refers to the reference state. Substituting (2) and integrating gives

$$\ln \gamma_{\pm}/\gamma_{\pm (ref)} = -[3am^{1/2} + 2bm + 5/3cm^{3/2} + 3/2dm^2]^m_{m (ref)}$$
(4)

Since it was found impossible to extrapolate to m = 0, the reference molality was chosen as 0.003 m, one of the lower concentrations.

Finally, the Debye-Hückel expression for a 1:3 electrolyte is

$$-\log \gamma_{\pm} = \frac{3A\sqrt{6m}}{1+Ba\sqrt{6m}} \tag{5}$$

where A = 0.5193 and B = 0.3300 at 37° from which the interionic distance could be evaluated.

The actual computations were programmed¹³ for the Lewis College Honeywell 200 Computer.

Results and Discussion

The osmotic and activity coefficient data obtained on $(NH_4)_3CrMo_6O_{24}H_6$ and $(NH_4)_3AlMo_6O_{24}H_6$ are given in Tables I and II, respectively. Deviations between the experimentally observed osmotic coefficient and that calculated on the basis of eq 2 are listed for each independent value together with the deviation of the activity coefficient from the Debye-Hückel value.

Interionic distances are calculated as d = 2.9 and 4.3 Å for the ammonium 6-molybdochromate and -aluminate, respectively. From conductivity measurements and the Fuoss-Onsager equation, 4.0 and 3.3 Å have been established as the interionic distances in the two molybdovanadophosphoric acids⁷ mentioned earlier. The values of the four heteropolymolybdate species are consistent with each other but smaller than radii reported from X-ray studies^{14,15} on similar heteropoly anions.

Insofar as we have been able to determine, this represents the first reported measurement of activity coefficients of electrolytes of the 1:3 valence type in solutions of concentration less than 0.1 m. The activity coefficients are similar for the two salts, a fact expected from their apparent structural similarities, and decrease considerably within the small range of concentration. This large lowering of the magnitude of the activity coefficient in solutions of low ionic strength is a commonly observed feature for polyvalent salts but not for 1:1 electrolytes.

Similar measurements have been made on several 3:1 electrolytes, although results are only available in sufficiently dilute solutions for lanthanum chloride¹⁶ where γ_{\pm} varies from 0.788 at 0.001 *m* to 0.484 at 0.02 *m*. The data on the 1:3 polyatomic salts are somewhat comparable to this simple salt having the same valence index. Exact duplication is not expected due to the different choice of reference states. The trend of the activity coefficient to decrease extensively in value at such low concentrations appears to be even more prominent in LaCl₃ than in the complex salts.

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Molality	Фехр	ϕ_{calcd}	Deviation	Molality	γ_{\pm}	γDH	Deviation
0.0021	0.857	0.860	0.003				
0.0032	0.886	0.865	-0.021	0.0030	0.787	0.787	0.000
0.0043	0.867	0.868	0.001	0.0040	0.760	0.761	-0.001
0.0053	0.858	0.868	0.010	0.0050	0.738	0.740	-0.001
0.0070	0.855	0.863	0.008	0.0060	0.720	0.722	-0.002
0.0074	0.864	0.861	-0.003	0.0070	0.703	0.705	-0.002
0.0084	0.841	0.856	0.015	0.0080	0.686	0.691	-0.005
0.0097	0.844	0.848	0.004	0.0090	0.671	0.678	-0.007
0.0104	0.852	0.844	-0.008	0.0100	0.656	0.666	-0.010
0.0123	0.849	0.833	-0.016	0.0110	0.643	0.655	-0.012
0.0147	0.851	0.825	-0.026	0.0120	0.630	0.645	-0.015
0.0169	0.841	0.826	-0.015	0.0130	0.619	0.635	-0.016
0.0191	0.853	0.839	-0.014	0.0140	0.609	0.626	-0.017
0.0210	0.842	0.862	0.020	0.0150	0.600	0.618	-0.018
				0.0160	0.593	0.610	-0.017
				0.0170	0.588	0.602	-0.014
				0.0180	0.585	0.595	-0.010
				0.0190	0.584	0.589	-0.005
				0.0200	0.586	0.582	0.004

Table I: Osmotic and Activity Coefficients of Ammonium 6-Molybdochromate(III)

Molality	Фехр	\$calcd	Deviation	Molality	γ_{\pm}	γDH	Deviation
0.0023	0.861	0.885	0.024				
0.0030	0.930	0.878	-0.052	0.0030	0.798	0.798	0.000
0.0044	0.839	0.869	0.030	0.0040	0.765	0.775	-0.010
0.0053	0.866	0.867	0.001	0.0050	0.740	0.756	-0.016
0.0073	0.882	0.867	-0.015	0.0060	0.722	0.739	-0.017
0.0085	0.847	0.868	0.021	0.0070	0.707	0.725	-0.018
0.0097	0.858	0.860	0.002	0.0080	0.695	0.713	-0.018
0.0102	0.882	0.870	-0.012	0.0090	0.685	0.701	-0.016
0.0125	0.886	0.872	-0.014	0.0100	0.677	0.691	-0.014
0.0146	0.872	0.871	-0.001	0.0110	0.669	0.682	-0.013
0.0166	0.865	0.867	0.002	0.0120	0.662	0.673	-0.011
0.0187	0.866	0.860	-0.006	0.0130	0.655	0.665	-0.010
0.0212	0.838	0.845	0.007	0.0140	0.649	0.657	-0.008
				0.0150	0.643	0.650	-0.007
				0.0160	0.636	0.644	-0.008
				0.0170	0.630	0.637	-0.007
				0.0180	0.623	0.632	-0.009
				0.0190	0.615	0.626	-0.011
				0.0200	0.607	0.621	-0.014

Poirier¹⁷ has made calculations based on Mayer's adaptation¹⁸ of the cluster-sum theory of imperfect gases to electrolytic solutions. Agreement with experiment was found to be good for LaCl₃ up to a concentration of 0.02 *m*. According to this theory the only variable quantity in determining an activity coefficient value at a given molality for compounds of the same valence index is the interionic distance. Therefore, it is to be expected that favorable agreement of the heteropolymolybdate data with this theory would similarly occur. Principally, the same large decrease in γ_{\pm} would be obvious. The remarkable feature of this theory is that the trend in activity coefficient is essentially predictable without regard to such factors

as hydration, change in dielectric constant, volume, etc This tends to support a prominent role to electrostatic factors only in determining activity coefficients in solutions of low ionic strength and minor roles to other factors which, however, become increasingly important as the concentration of the solution increases. With large spherical ions, solvation effects are minimized³ owing to the lower charge densities on the surfaces, which would lead to higher mobilities. Further, formation of ion pairs and higher ion clusters would be expected to be very important in solutions where the

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(18) J. E. Mayer, ibid., 18, 1426 (1950).

species charge is high. Such ionic association would cause the calculated d values to be smaller than in the solid state. Apparently, the forces of interionic attraction are even further reduced in the complex salt solutions than in LaCl₃. Of course, one cannot overlook the possibility that numerous effects are contributing to the activity coefficient and are being absorbed by the single d parameter. However, Poirier's calculations serve to emphasize that this single variable is the most significant one in solutions of low ionic strength. Many additional data are required in order to substantiate this point and to determine the effect of size and structure upon the activity coefficients of polyvalent electrolytes.

Acknowledgment. The authors wish to thank Mr. L. R. Wolf for his assistance in the computer calculations.

Thermodynamics of Aqueous Mixtures of Electrolytes and Nonelectrolytes.

IX. Nitromethane in Pure Water and in 1 m Potassium

Chloride from 15 to 35°

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Calorimetric enthalpies of solution of liquid nitromethane to low concentrations (0.01-0.02 m) in pure water and in 1 m potassium chloride, respectively, are reported from 15 to 35°. The enthalpies are positive, with the former giving rise to a third-order dependence on temperature illustrating the complicated nature of interactions in the purely aqueous environment over a 20° span. The latter appears to be linear with temperature and is lower, showing the striking change in the solution as a result of the added water-structure-breaking electrolyte. The temperature derivatives of the enthalpies yield the appropriate heat capacity differences between the dissolved and pure liquid nitromethane. While the heat capacity difference to pure water changes rapidly and ranges from 73 to 115 cal/deg mol between 15 and 35° with a minimum of ca. 10 cal/deg mole near 24°, that to 1 m KCl remains constant at 25 cal/deg mol. The positive heat capacity differences, especially when their values are high, may be assumed to be due to net structure making by nitromethane. In pure water near 25°, complicated changes in nitromethane-water interaction caused by water-structure shifts may be taking place, while in KCl, specific ion-nitromethane and ion-water interactions may predominate over the entire temperature range. Heat capacities of transfer of dissolved nonpolar gases from water to electrolyte solutions, calculated from solubility measurements, are briefly discussed.

Introduction

This contribution reports on the calorimetric enthalpy of solution of liquid nitromethane in pure water, ΔH_3° , and in 1 *m* KCl, ΔH_3 , at 2 to 5° intervals between 15 and 35°. These data also yield the enthalpy of transfer, $\overline{\Delta H_3}$, for CH₃NO₂(H₂O) = CH₃NO₂(1 *m* KCl), where $\overline{\Delta H_3} = \Delta H_3 - \Delta H_3^{\circ}$, and the heat capacity differences for nitromethane between the following final and initial states: aqueous and pure liquid, $\Delta C_{p_1}^{\circ}$, in 1 *m* KCl and pure liquid, ΔC_{p_2} , and the heat capacity cf transfer, $\overline{\Delta C}_{p_3}$, where $\overline{\Delta C}_{p_2} = \Delta C_{p_1} - \Delta C_{p_1}^{\circ}$. Heat capacity differences have proved to be valuable in the complicated problem of water structure by showing the part of the solute in local structure changes. For example, large positive heat capacity differences observed for nonelectrolytes containing nonpolar groups have been attributed to their net structure-making.¹ No other calorimetric study of this type, in the presence and absence of an electrolyte at temperatures other than 25°, appears to have been reported to date.

Many nonelectrolytes are not suitable since their low solubility precludes calorimetric measurements. Heat capacities may also be calculated from the second derivatives of analytical equations of the solubility with

^{(1) (}a) J. H. Stern and A. Hermann, J. Phys. Chem., 72, 364 (1968);
(b) G. C. Kresheck and L. Benjamin, *ibid.*, 68, 2476 (1964); (c) L. A. D'Orazio and R. H. Wood, *ibid.*, 67, 1435 (1963); (d) H. S. Frank and W. Wen, Discussions Faraday Soc., 24, 133 (1957).

temperature. Such data may, however, be among the most uncertain of thermodynamic properties since repeated differentiation of smoothed equations causes losses in precision. For example, studies in the field of aqueous weak electrolyte ionization indicate that calorimetric ΔC_p for ionization is frequently a complicated function of temperature. Such results would not be attainable from the second derivative of the ionization constant with temperature.²

Nitromethane was chosen for two main reasons. The low enthalpies of solution in water and in 1 m KCl have in a previous study³ at 25° yielded accurate enthalpies of transfer ($\overline{\Delta H_3} = -150 \text{ cal/mol}, \Delta H_3^\circ = 630 \text{ cal/mol}$). The transfer was later experimentally shown to take place in the limiting region of ion-nonelectrolyte interaction;⁴ that is, enthalpies of transfer consist of additive contributions from the cation and anion and that nitromethane solute-solute or self interaction effects⁵ are negligible at the experimentally low nitromethane concentrations (ca. 0.01-0.02 m). Vaporization of nitromethane at these low concentrations is negligible. The electronic absorption spectrum in water shows large solvent shifts relative to the spectrum in n-heptane⁶ which are of the order of magnitude of hydrogen bond enthalpies. Since both equilibria $CH_3NO_2 \rightleftharpoons H^+ +$ OH

$$CH_2NO_2^{-}(K \cong 10^{-11})$$
 and $CH_3NO_2 \rightleftharpoons CH_2 = N$

lie very far on the left side,^{7,8} the principal form of liquid and aqueous nitromethane appears to be the

resonance hybrid CH₃—N +

Experimental Section

Measurements and Materials. The calorimeter has been described previously.⁹ Measurements were carried out within ca. 0.1° of the reported temperatures and were initiated at balanced Wheatstone bridge decade settings corresponding to these temperatures, checked by a calibrated mercury-in-glass thermometer accurate to 0.01° . The experimental procedure and materials were described elsewhere.³

Results and Discussion

All enthalpies of solution are summarized in Tables I and II with uncertainty intervals equal to the standard deviations $(\bar{\sigma})$ of the tabulated values. The over-all concentration of nitromethane in all solutions ranged from 0.01 to 0.02 m.

Both ΔH_3° and ΔH_3 increase rapidly with temperature, and the former doubles in magnitude approximately with each 10° rise in temperature. The ΔH_3° curve in

Table I :	Enthalpies of	Solution of	of Nitroi	nethane
in Pure W	ater			

T, °K	No. of runs	ΔH_3^{o} , cal/mol
288	5	350 ± 10
291	4	550 ± 20
293	3	590 ± 10
295	4	600 ± 20
298	4	630 ± 10^{a}
303	7	790 ± 10
308	4	$1150~\pm~10$
^a Data from ref 3	3.	

Table II: Enthalpies of Solution of Nitromethane in 1 m KCl

T, °K	No. of runs	ΔH_3 , cal/mol
288	3	240 ± 10
293	4	360 ± 10
298	7	480 ± 10^{a}
303	4	570 ± 20
308	4	750 ± 10
^a Data from ref 3.		

Figure 1 represents the least-square fit of enthalpies in Table I with their weighting factors of $1/\sigma^{-2}$ to a power series with temperature

$$\Delta H_3^{\circ} = 650 + 13.3(T - 298) + 1.05(T - 298)^2 + 0.269(T - 298)^3 \quad (1)$$

while that for ΔH_3 is based similarly on the least-squares equation

$$\Delta H_3 = 488 + 25.4(T - 298) \tag{2}$$

The experimental data from Tables I and II are shown in Figure 1 by circles and triangles for ΔH_3° and ΔH_3 , respectively. The estimated uncertainty of enthalpies calculated from eq 1 and 2 is ± 30 cal/mol.

Values of ΔC_{p} ° and ΔC_{p_1} are obtained directly from the temperature derivatives of eq 1 and 2, with an estimated error of ± 3 cal/deg mol, and are shown in Figure 2 plotted against temperature. There are great differences in ΔC_{p_1} ° and ΔC_{p_1} reflecting changes of interaction in both media. The former has remarkably

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(3) J. H. Stern and A. Hermann, J. Phys. Chem., 71, 309 (1967).

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Figure 1. Enthalpies of solution of nitromethane.



Figure 2. Heat capacity differences of nitromethane.

high values on both sides of a minimum near 24°. The rapidly changing values of $\Delta C_{p_{0}}^{\circ}$ ° also show that great caution must be used in comparisons and interpretations of heat capacity differences as well as other thermodynamic and transport properties of nonelectrolytes in aqueous solution determined at a single temperature (usually 25°). The minimum in the present study could be evidence for a structural transition in water^{10,11} or for a change in the nitromethane-water interaction, both of which are indistinguishable by the present macroscopic thermodynamic measurements. The value of $\Delta C_{p_{0}}$ remains constant with temperature and except for the region between *ca.* 20 and 28° is

lower than $\Delta C_{p_a}^{\circ}$. Since potassium chloride is a known structure breaker,¹² the aqueous electrolyte solution is less ordered than pure water, with possibly less structure making by nitromethane and consequently a lowered heat capacity change than in pure water. The added KCl also appears to "smooth out" water structure changes and their effect on specific water-nitromethane interactions by substitution of much stronger and regularly varying specific ion-nitromethane and structure-breaking ion-water effects, with temperature apparently playing a smaller part than in pure water. Thus, the net behavior of the ternary nitromethanewater-KCl system appears to be deceptively simpler than the binary nitromethane-water system. Measurements at lower KCl concentrations may show the limit of its structure-breaking effects.

Values of the absolute partial molal heat capacities in pure water, $C_{p_i}^{\circ}$, or in 1 m KCl, C_{p_i} may easily be obtained by adding the constant heat capacity of liquid nitromethane (25 cal/deg mol¹³) to $\Delta C_{p_s}^{\circ}$ and $\Delta \hat{C}_{p_{ij}}$ respectively. In contrast to $C_{p_{ij}}^{\circ}$, the variation of the partial molal heat capacity of aqueous strong 1-1 electrolytes, $C_{p_{0}}^{\circ}$, with temperature appears to be much smaller. For example $C_{p_1}^{\circ}$ of NaCl increases from -28to -19 between 10 and 40° .¹⁴ The heat capacity of transfer, $\overline{\Delta C}_{p_{i}}$, is negative (except near room temperature), and there are very few other aqueous systems for comparison. That for argon, based on solubilities in water and in 1-1 electrolytes is also negative, and with few exceptions this is generally true for alkanes from methane through butane.¹⁵ Thus, the transferred solutes appear to make less structure in the electrolyte solutions than in pure water. However, most of the ΔC_{p_1} decrease with temperature are monotonic and nearly linear. This may be due to the difference between polar nitromethane and nonpolar solutes, and due to the inaccuracy of the solubility method. A calorimetric study with undissociated acetic acid¹⁶ between 18 and 35° has been initiated.

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Thermodynamics of Hydrocarbon Gases in Aqueous

Tetraalkylammonium Salt Solutions¹

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Solubilities of methane, ethane, propane, and butane in water and in aqueous solutions of 0.1 to 1 m NH₄Br' (HOC₂H₄)₄NBr, and R₄NBr (where R = CH₃, C₂H₅, n-C₃H₇, and n-C₄H₉) have been measured at 5, 15, 25 and 35°. The hydrocarbons were found to be salted in by Et₄NBr, Pr₄NBr, and Bu₄NBr, but salted out by NH₄Br. They were either salted in or out by Me₄NBr and (HOC₂H₄)₄NBr depending upon the hydrocarbon size and temperature. The dependence of the gas solubility on the salt concentration was linear for NH₄Br and (HOC₂H₄)₄NBr but was distinctly nonlinear for large R₄NBr salts, particularly at lower temperatures. The standard molal free energies, ΔF_{tr}° , entropies ΔS_{tr}° , and enthalpies, ΔH_{tr}° , of transfer of hydrocarbons from water to 0.1 m salt solutions have been calculated. The Setchénow constants defined as $k = 1/m \log s^{\circ}/s$ for m = 0.1 were also calculated for these systems. The values of ΔF_{tr}° and k for the four hydrocarbons in Me₄NBr, Et₄NBr, Pr₄NBr, and Bu₄NBr solutions were found to be all negative, except methane in Me₄NBr solution at 5°. At 25 and 35°, the observed order of the ΔF_{tr}° values for each gas was $\Delta F_{tr}^{\circ}(H_2O \rightarrow Et_4NBr) > \Delta F_{tr}^{\circ}(H_2O \rightarrow Bu_4NBr)$, but at 5°, a striking change in the order of the salt effect was noticed

$$\Delta F_{tr}^{\circ}(\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{Bu}_{4}\mathrm{NBr}) > \Delta F_{tr}^{\circ}(\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{Pr}_{4}\mathrm{NBr}) > \Delta F_{tr}^{\circ}(\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{Et}_{4}\mathrm{NBr})$$

These observations were explained in terms of the important role played by the structure modifications of water and the hydrophobic bonds between the cations and hydrocarbon molecules.

Introduction

Since 1928, many interesting physical properties of symmetrical tetraalkylammonium salts in water have been reported.²⁻⁴⁰ These studies seem to indicate the uniqueness of the interaction between these salts and water and point out the importance of understanding the water structural changes induced by the presence of the large hydrophobic cations. Effects of these salts on the solubilities of organic compounds such as urea, benzene, and naphthalene in aqueous solutions

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have also been investigated in recent years.^{41–45} They found the solubilities of these organic compounds to increase considerably in the presence of these salts. The salting-in effects of the tetraalkylammonium salts are in contrast to the salting-out effects of the small inorganic salts. Since the tetraalkylammonium cations modify the structure of water around them in a similar way as some simple aliphatic hydrocarbons do, it would be of considerable interest to see how this structural interaction affects the solubilities of hydrocarbon gases. There have been some scattered studies on the solubilities of gases in the aqueous solutions containing these salts, but the results appear to be rather inconclusive.^{46,47} From these considerations, we have undertaken a systematic study of the solubilities of methane, ethane, propane, and butane in pure water and in aqueous solutions of 0.1 to 1m NH₄Br, (CH₃)₄NBr, (C₂H₅)₄NBr, (n-C₃H₇)₄NBr, (n-C₄H₉)₄NBr, and (HOC₂H₄)₄NBr at 5, 15, 25, and 35°.

Experimental Section

Materials. The laboratory distilled water was redistilled in an all-Pyrex glass apparatus. This water gave a specific conductivity of about 1.5 \times 10⁻⁶ mho-cm⁻¹. Tetraalkylammonium salts were obtained from Eastman Kodak Co., and recrystallized twice or more from the suitable solvents⁴⁸ and dried at proper temperatures⁴⁹ before use. The gravimetric analysis of the cations as tetraphenylborides and the anions as silver salts showed their purities to be higher than 99.9%. Tetraethanolammonium bromide was prepared by the method of Evans, et al.⁵⁰ After several recrystallizations, the bromide content determined gravimetrically as the silver salt was 99.9 $\pm 0.1\%$ $(mp \ 102^{\circ}).$ Baker Analyzed ammonium bromide was found to be 99.9% or better in purity and was used without further purification. Four hydrocarbon gases (methane, ethane, propane, and butane) used were obtained from the Matheson Co. and stated to be of at least 99.9 mol % purity.

Apparatus. The apparatus used was similar to that described by Ben-Naim and Baer⁵¹ except that all the stopcocks were replaced by Teflon needle valves. These valves were employed to avoid the use of grease which might absorb gases or hydrophobic solutes. The apparatus was built in a water bath which was approximately 70×70 cm² in bottom area and 90 cm in height. Stainless steel plates were used for the inside walls of the bath and a glass plate was fitted in the front side to serve as a window. For the purpose of good insulation, the outside surface of the stainless steel plates was wrapped with polyurethane sheets. The solubility apparatus consisted of three main parts: a dissolution cell, a gas volume measuring column, and a manometer. We used gas dissolution cells (see Figure 1) with capacities of 300 to 600 ml. In



Figure 1. The gas dissolution cell. A, Teflon needle valve; B, magnetic stirring bar.

order to stir the liquid in the dissolution cell, a magnetic stirrer was sealed in a box of Perspex glass and placed under the cell in the water. The temperature of the bath was controlled to within $\pm 0.005^{\circ}$ by using a mercury thermoregulator and a transistorized electronic relay. For other details of the apparatus and experimental procedure, consult the Ph.D. thesis of Hung.¹

Results

The solubilities of methane, ethane, propane, and butane in water at 5, 15, 25, and 35° were measured and compared with those of other workers⁵²⁻⁵⁴ in Table I. The solubility is expressed by the volume of gas at standard condition (1 atm and 0°) dissolved in 1000 g of water. The data obtained in this work fall between those of Claussen and Polglase⁵² and of Winkler.⁵³ The reproducibility of the solubility in this work is to within $\pm 0.3\%$.

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Gas	T, °C	Claussen and Polglase ⁵³	This work	Winkler ⁶³ or Morrison ⁵⁴
Methane	5	49.42	49.48 ± 0.08	47.72
	15	38.57	38.49 ± 0.11	37.02
	25	31.80	31.35 ± 0.10	30.14
	35	27.24	26.51 ± 0.08	25.70
Ethane	5	82.10	80.19 ± 0.23	80.33
	15	56.75	55.55 ± 0.15	55.24
	25	43.00	41.20 ± 0.12	41.18
	35	33.55	32.27 ± 0.10	32.34
Propane	5		69.57 ± 0.11	
	15		45.75 ± 0.06	46.12
	25	32.71	32.31 ± 0.08	33,30
	35		23.91 ± 0.07	26.00
Butane	5		62.00 ± 0.10	
	15		39.20 ± 0.05	38.28 (14°)
	25	32.8 (20°)	26.34 ± 0.06	25.88
	35	23.4 (30°)	19.27 ± 0.06	19.41

 Table I:
 Solubilities of Methane, Ethane, Propane, and Butane in Pure Water at Different Temperatures

 (Unit:
 ml of gas/1000 g of water)

Table II: Solubilities of Methane in Aqueous R4NBr Solutions at Different Salt Concentrations and Temperatures

	E9_		E0_		20		
ma	**************************************	m ³	<i>s^b</i>	ma	8 ^b	ma	85°
(0)	(49.48)	(0)	(38.49)	(0)	(31.35)	(0)	(26.51)
0.096	49.82	0.096	38.86	0.096	32.03	0.099	27.43
0.098	49.85	0.102	38.95	0.099	32.00	0.192	28.20
0.100	49.80	0.103	38.96	0.194	32.32	0.415	29.45
0.187	49.88	0.185	39.10	0.415	33.30	0.537	30.18
0.201	49.86	0.403	39.44	0.526	33.79	0.693	31.38
0.409	49.27	0.523	39.40	0.704	34.53	0.993	33.60
0.526	48.91	0.703	39.69	1.022	36.72		
0.785	46.67	1.0.8	40.10				
0.990	46.10						
			CH4 in Aqueous	Pr4NBr Solution	ns		
			15°		25°		35°
ma	s ^b	m^a	s ^b	m^a	s ^b	m^a	a ^b
(0)	(49.48)	(0)	(38.49)	(0)	(31.35)	(0)	(26.51)
0.099	50 .06	0.098	39.00	0.097	31.87	0.105	27.21
0.103	50.03	0.223	39.67	0.102	31.99	0.245	27.87
0.224	50.31	0.227	39.48	0.230	32.43	0.443	28.73
0.223	50 .46	0.415	39.60	0.235	32.58	0.706	30.17
0.431	49.60	0.620	39.97	0.410	33.14		
0.587	48.74			0.632	33.63		
		(CH4 in Aqueous (E	tOH) ₄ NBr Solut	tions		
	5°		15°		25°		85°
ma	8 ⁶	m^a	8 ^b	m^a	a ^b	ma	8 ^b
(0)	(49.48)	(0)	(38.49)	(0)	(31.35)	(0)	(26.51)
0.086	49.10	0.091	38.22	0.085	31.20	0.085	26.50
0.152	48.70	0.174	38.03	0.167	31.02	0.173	26.59
0.155	48.86	0.177	37.96	0.173	31.04	0.339	26.53
0.173	48.47	0.355	37.34	0.347	30.81	0.508	26.51
0.341	47.87	0.517	36.87	0.510	30.42		
	10.00						

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			C ₂ H ₆ in Aqueous	Pr.NBr Solutio	ons		
	-5°		15°		25°		350
ma	8 ⁶	ma	eb.	ma	ab	ma	8 ⁰
(0)	(80.19)	(0)	(55.55)	(0)	(41.20)	(0)	(32.27)
0.102	81.59	0.280	58.85	0.270	44.70	0.255	35.60
0.208	82.73	0.410	59 .97	0.270	44.79	0.462	37.66
0.267	82.96	0.451	60.74	0.410	46 .13	0.736	40.98
0.461	83.92	0.771	61.82	0.461	46.80		
0.470	83.70			0.749			
0.805	82.37						
		C	² H ₆ in Aqueous (1	EtOH) ₄ NBr Solu	tions		
	-5°	·15°		25°		35°	
ma	a ^b	ma	8 ^b	ma	s ^b	m^a	a ^b
(0)	(80.19)	(0)	(55.55)	(0)	(41.20)	(0)	(32.27)
0.092	79.93	0.103	55.43	0.099	41.44	0.096	32.41
0.184	79.67	0.202	55.53	0.198	41.46	0.154	32.74
0.355	79.27	0.401	55.62	0.386	41.76	0.193	32.96
0.526	78.86	0.577	55.73	0.565	42.16	0.380	33.56
						0.558	33.81
			C ₂ H ₆ in Aqueous	NH ₄ Br Solution	18		
	-5°		15°		25°		35°
m^a	s ^b	ma	8 ^b	ma	8 ^b	m^a	ə ^b
(0)	(80.19)	(0)	(55.55)	(0)	(41.20)	(0)	(32.27)
0.205	77.24	0.108	54.51	0.104	40.51	0.109	31.60
0.644	70.96	0.214	53.39	0.218	39.56	0.214	31.20
		0.409	51.78	0.486	38.81	0.415	29 .99
		0 662	40 40	0 676	37.53	0 672	29 47

Table III: Solubilities of Ethane in Aqueous Solutions at Different Salt Concentrations and Temperatures

Table IV: Solubilities of Propane in Aqueous Solutions at Different Salt Concentrations and Temperatures

$C_{2}H_{8}$ in Aqueous $Pr_{4}NBr$ Solutions

5°		15°		25°		35°	
ma	്ം	ma	a ^b	ma	e ^b	ma	eb.
(0)	(69.57)	(0)	(45.75)	(0)	(32.31)	(0)	(23.91)
0.103	70.99	0.110	47.24	0.102	33.77	0.107	25.61
0.210	72.73	0.210	48.58	0.267	35.65	0.271	27.72
0.271	73.35	0.267	49.51	0.420	37.38	0.457	30.66
0.410	74.41	0.415	51.54	0.609	39.96	0.656	32.73
0.436	74.61	0.465	51.78	1.050	43.80		
0.492	73,85	0.689	53.14				
0.784	73.82	1.070	54.78				
0.963	73.28						

C_3H_8 in Aqueous NH₄Br Solutions

			150		25°	35°	
ma	a ^b	ma	8 ^b	ma	8 ^b	ma	8 ^b
(0)	(69.57)	(0)	(45.75)	(0)	(32.31)	(0)	(23.91)
0 107	68.06	0.106	44.60	0.107	31.61	0.105	23.50
0 224	67.08	0.220	43.78	0.210	31.28	0.224	23.26
0 428	63.47	0.418	42.02	0.407	29.87	0.427	22.88
0.707	60 23	0.672	39.90	0.631	28.99	0.667	21.69
0.942	50.86	0.905	38.47	0.850	27.76	0.885	21.03
Malality	East kml/1000	a of water					

^a Molality of salt. ^b ml/1000 g of water.
			CH₄ i	in Aqueous Solu	itions					
				50		0.59	-21			
Solute	ma	s ^b	ma	s ^b	m ^a	8 ^b	ma	8 ^b		
	(0)	(49.48)	(0)	(38.49)	(0)	(31.35)	(0)	(26.51)		
Et.NBr	0.093	49.89	0.173	39.30	0.182	32.36	0.209	27.68		
	0.095	49.97			0.183	32.34				
MeaNBr	0.179	49.48	0.190	38.57	0.179	31.64	0.302	27.10		
	0.176	49.27	0.194	38.70	0.193	31.47				
NH₄Br	0.196	47.93	0.202	37.43	0.200	30.56	0.181	26.03		
			C_2H_6	in Aqueous Solu	itions					
		-5°		15°		250		350		
Solute	ma	8 ^b	ma	ab	ma	s ^b	ma	8 ⁶		
	(0)	(80.19)	(0)	(55.55)	(0)	(41.20)	(0)	(32.27)		
Bu ₄ NBr	0.099	81.15	0.193	58.18	0.165	43.75	0.103	34.05		
	0.193	82.03	0.304	59.30	0.290	45.45	0.205	35.90		
Et ₄ NBr	0.116	81.90	0.152	56.96	0.161	42.98	0.098	33.41		
	0.436	85.56	0.436	60.05	0.428	45.86	0.423	36.62		
Me ₄ NBr	0.169	80.65	0.170	55.84	0.165	41.73	0.184	33.02		
-			0.310	56.39	0.325	42.46				
NH₄Br	0.205	77.24	0.214	53.39	0.104	40.51	0.109	31.60		
					0.218	39.56				
Urea	0.495	78.89	0.495	55.55	0.495	41.60	0.495	32.72		
			C_3H_8	in Aqueous Solu	utions					
		5°		15°		250		5°		
Solute	ma	8 ^b	ma	80	ma	sb	ma	8 ^b		
	(0)	(69.57)	(0)	(45.75)	(0)	(32.31)	(0)	(23.91)		
Bu₄NBr	0.165	71.78	0.180	48.68	0.305	37.26	0.193	28.06		
	0.300	72.70	0.300	50.35	0.624	43.25	0.304	30.24		
Et ₄ NBr	0.161	72.50	0.158	47.95	0.154	33.65	0.174	25.94		
	0.425	76.60	0.425	51.82	0.425	36.75	0.425	28.50		
Me ₄ NBr	0.165	70.44	0.165	46.32	0.328	33.59	0.165	24.68		
	0.325	71.52	0.325	47.03	0.885	35 .84	0.325	25.46		
(EtOH) ₄ NBr	0.153	69 . 92	0.160	46.13	0.159	32.64	0.154	24.78		
					0.508	33.93				
Urea	0.495	69.10	0.495	46.08	0.495	32.66	0.495	24.72		
			C4H10	in Aqueous Solu	utions					
				15°		250		50		
Solute	m ³	s ^b	ma	a ^b	ma	8 ⁶	ma	8 ^b		
	(0)	(62.00)	(0)	(39.20)	(0)	(26.34)	(0)	(19.27)		
Bu ₄ NBr	0.310	66.65	0.310	44.35	0.310	31.92	0.310	25.56		
Pr₄NBr	0.405	69 .09	0.405	45.36	0.405	32 ,09	0.405	25.02		
Et₄NBr	0.405	70.79	0.405	44.87	0.405	30.55	0.405	23.44		
Me₄NBr	0.850	69.23	0.850	44.13	0.850	30.25	0.850	23 . 10		
^a Molality of sol	lute. ° ml	of gas/1000 g of w	ater.							

Table V:	Solubilities of	Aliphatic	Hydrocarbon	Gases in	Aqueous	Solutions
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The solubilities of methane in aqueous solutions of Bu_4NBr , Pr_4NBr , and $(EtOH)_4NBr$ at different concentrations and temperatures are given in Table II; those of ethane in aqueous solutions of Pr_4NBr , (Et-OH)₄NBr, and NH₄Br are listed in Table III; those of propane in aqueous solutions of Pr_4NBr and NH₄Br are tabulated in Table IV. Table V gives solubilities of hydrocarbon gases in solutions of salts not included in Tables II, III, and IV. As examples, the data for ethane at 5 and 35° are plotted in Figures 2 and 3. The striking difference of the effects of different types

of salts on gas solubilities are clearly seen from these figures.

Generally speaking, large tetraalkylammonium salts such as Pr_4NBr and Bu_4NBr increase the solubility of hydrocarbon gas, while NH_4Br and $(EtOH)_4NBr$ decrease it. Moreover, the dependence of the gas solubility on the salt concentration is linear for NH_4Br and $(EtOH)_4NBr$ but is nonlinear and curved for large R_4NBr salts. This nonlinearity seems to be accentuated more at lower temperatures. As examples, the logarithm of the gas solubility ratio is plotted



Figure 2. Solubilities of ethane at 5° in aqueous solutions at different concentrations.



Figure 3. Solubilities of ethane at 35° in aqueous solutions at different concentrations.

against the salt molality in Figures 4, 5, and 6 for methane in solutions of Bu_4NBr , Pr_4NBr , and $(EtOH)_4$ -NBr, respectively. In the particular case of methane in aqueous solutions of Bu_4NBr at 5°, the solubility increases very slightly as the salt concentration increases from 0 to 0.2 m, but then decreases to a value which is much lower than that in pure water with the further increase of the concentration as shown



Figure 4. Plot of log (s°/s) vs. m for methane in aqueous Bu₄NBr solutions at different temperatures.



Figure 5. Plot of log (s°/s) vs. m for methane in aqueous solutions of Pr₄NBr at different temperatures.



Figure 6. Plot of $\log(s^{\circ}/s)$ vs. m for methane in aqueous (EtOH)₄NBr solutions at different temperatures.

Hydrocarbon	Solute	٥°	15°	25°	35°
Methane	NH₄Br	+0.068	+0.061	+0.054	+0.047
	(EtOH) ₄ NBr	+0.042	+0.033	+0.022	-0.001
	Me₄NBr	+0.007	-0.005	-0.017	-0.028
	Et₄NBr	-0.036	-0.049	-0.049	-0.094
	Pr₄NBr	-0.045	-0.061	-0.082	-0.110
	Bu₄NBr	-0.030	-0.053	-0.096	-0.152
Ethane	NH₄Br	+0.082	+0.073	+0.065	+0.056
	(EtOH) ₄ NBr	+0.014	+0.002	-0.013	-0.038
	Me₄NBr	-0.016	-0.028	-0.040	-0.052
	Et₄NBr	-0.082	-0.095	-0.117	-0.147
	Pr₄NBr	-0.075	-0.105	-0.141	-0.190
	Bu₄NBr	-0.063	-0.101	-0.155	-0.225
	Urea	+0.013	-0.002	-0.010	-0.012
Propane	NH₄Br	+0.095	+0.086	+0.076	+0.066
•	(EtOH) ₄ NBr	0.000	-0.025	-0.061	-0.113
	Me ₄ NBr	-0.029	-0.039	-0.059	-0.091
	Et ₄ NBr	-0.096	-0.125	-0.158	-0.207
	Pr₄NBr	-0.080	-0.130	-0.187	-0.273
	Bu₄NBr	-0.066	-0.146	-0.248	-0.386
	Urea	+0.005	-0.009	-0.020	-0.030
Butane	Me ₄ NBr	-0.049	-0.064	-0.074	-0.100
	Et₄NB r	-0.149	-0.152	-0.168	-0.226
	Pr₄NBr	-0.120	-0.165	-0.227	-0.307
	Bu,NBr	-0.104	-0.180	-0.286	-0.435

Table VI: Setchénow Constants of Salts and Urea toward Four Hydrocarbons at Different Temperatures (m = 0.1)

in Figure 4. In other words, as the concentration of the salt increases, the effect changes from saltingin to salting-out at 5° .

Hydrocarbon gases are salted in by $0.1-0.2 \ m R_4 NBr$ at all the temperatures studied except methane in Me₄NBr solution at 5°.⁶⁵ Since the slope of gas solubility curve decreases with the increase of salt concentration, we have chosen to compare Setchénow constants of R₄NBr at a concentration of 0.1 m using eq 1

$$k = (1/m)\log(s^{\circ}/s)$$
 (m = 0.1) (1)

where s° is the solubility of a hydrocarbon in pure water and s is the solubility of the same hydrocarbon in salt solution measured at the same temperature. The values of k of various salts and urea toward four hydrocarbons are given in Table VI.

At 25 and 35° the order of Setchénow constants for each hydrocarbon is found to be

$$|k(\mathrm{Bu}_{4}\mathrm{NBr})| > |k(\mathrm{Pr}_{4}\mathrm{NBr})| >$$

 $|k(\mathrm{Et}_{4}\mathrm{NBr})| > |k(\mathrm{Me}_{4}\mathrm{NBr})|$ (2)

At 5°, however, a striking change in the order of the salt effect is observed as shown by the following order of k values

$$|k(\text{Et}_{4}\text{NBr})| > |k(\text{Pr}_{4}\text{NBr})| > |k(\text{Bu}_{4}\text{NBr})| > |k(\text{Me}_{4}\text{NBr})| \quad (3)$$

On the other hand, NH_4Br salts out four gases at all the concentrations and temperatures studied. The



Temperature

Figure 7. Standard molal free energies of transfer of methane from pure water to 0.1 m aqueous solutions at different temperatures.

salting-out effect of NH₄Br toward one hydrocarbon decreases slightly with the increase of temperature, while the effect at one temperature seems to increase with the hydrocarbon size.

(55) Methane is also salted out by $0.5-1.0 \text{ m Bu}_4\text{NBr}$ at 5°.

Hydrocarbon	Solute	5°	15°	25°	35°
Methane	NH₄Br	+9.6	+8.5	+7.6	+7.0
	(EtOH) ₄ NBr	+5.0	+4.0	+2.8	-0.2
	Me ₄ NBr	+0.9	-0.7	-2.3	-4.0
	Et ₄ NBr	-4.5	-6.5	-9.5	-13.2
	Pr₄NBr	-5.6	-8.2	-11.0	-15.5
	Bu₄NBr	-3.8	-7.0	-13.1	-21.5
Ethane	NH₄Br	+10.4	+9.5	+8.7	+8.1
	(EtOH)₄NBr	+1.7	+0.3	-1.7	-5.4
	Me ₄ NBr	-2.0	-3.7	-5.4	-7.3
	Et ₄ NBr	-10.4	-12.5	-16.0	-20.7
	Pr₄NBr	-9.6	-13.8	-19.2	-26.8
	Bu₄NBr	-8.0	-13.3	-21.1	-31.7
	Urea	+1.6	-0.3	-1.3	— 1. 7
Propane	NH₄Br	+12.2	+11.5	+10.3	+9.1
-	(EtOH)₄NBr	0.0	-3.3	-8.4	-15.8
	Me ₄ NBr	-3.9	-5.2	-8.0	-12.7
	Et₄NBr	-12.8	-16.5	-21.5	-29.7
	Pr₄NBr	-9.6	-16.3	-25.5	-38.2
	Bu₄NBr	-8.8	-19.3	-33.5	- 53.0
	Urea	+1.2	-1.6	-3.4	-4.2
Butane	Me₄NBr	-6.2	-8.4	-10.1	-14.1
	Et ₄ NBr	-19.0	-20.0	-22.9	-31.9
	Pr₄NBr	-15.3	-21.8	-31.0	-43.3
	Bu₄NBr	-13.2	-23.7	-39.0	-61.3

Table VII: Standard Molal Free Energies of Transfer of Hydrocarbons from Pure Water to 0.1 *m*. Aqueous Solutions at Different Temperatures

The effect of 0.1 m urea on the hydrocarbon solubilities is very small. It is barely discernible that urea decreases the solubilities of ethane and propane at 5° but increases them at 15, 25, and 35°.

Table VIII:	Standard Molal Entropies of Transfer of
Hydrocarbon	s from Pure Water to 0.1 m Aqueous Solutions
at Different 1	C emperatures

Hydro- ΔS_{tr}° (cal/mol deg) 5° 15° 35° carbon Solute 25° NH₄Br 0.12 0.10 0.08 0.05Methane 0.210.39 (EtOH)₄NBr 0.09 0.110.16 0.17 Me₄NBr 0.16 0.16 Et₄NBr 0.25 0.33 0.40 0.15 Pr₄NBr 0.250.27 0.36 0.540.170.73 0.95 0.46 Bu₄NBr Ethane NH₄Br 0.10 0.09 0.07 0.05(EtOH)₄NBr 0.13 0.17 0.28 0.45 0.19 0.23Me₄NBr 0.17 0.17 Et₄NBr 0.28 0.41 0.53 0.14 0.65 Pr₄NBr 0.36 0.48 0.87Bu₄NBr 0.65 0.92 1.20 0.41 0.23 0.15 0.07 0.01Urea $\mathbf{0}$. $\mathbf{05}$ 0.120.12Propane NH₄Br 0.10(EtOH)₄NBr 0.240.420.62 0.85 Me₄NBr 0.06 0.200.37 0.57 0.98 0.31 0.43 0.66 Et₄NBr Pr₄NBr 0.55 0.79 1.09 1.44 Bu₄NBr 0.87 1.23 1.68 2.210.23 0 03 0.33 0.13 Urea Me₄NBr 0.20 0.23 0.27 0.32Butane Et₄NBr 0.23 0.330.530.73 1.380.79 1.07 Pr₄NBr 0.50 Bu₄NBr 0.71 1.29 1.882.58 The free energies of transfer of hydrocarbons from pure water to 0.1 *m* aqueous solutions (ΔF_{tr}°) are shown in Table VII and plotted in Figures 7-10. From these figures, we see that the temperature dependence of ΔF_{tr}° is the smallest for NH₄Br and the largest for Bu₄NBr, and for other salts it ranges between the two extremes.



Figure 8. Standard molal free energies of transfer of ethane from pure water to 0.1 m aqueous solutions at different temperatures.



Figure 9. Standard molal free energies of transfer of propane from pure water to 0.1 m aqueous solutions at different temperatures.



Figure 10. Standard molal free energies of transfer of butane from pure water to 0.1 m aqueous solutions at different temperatures.

By comparing these four figures we can see, for a given salt, that the temperature dependence of ΔF_{tr}° is larger for a larger hydrocarbon molecule. This tendency is also apparent from the entropy data given in Table VIII and Figures 11 and 12. The corresponding standard molal enthalpies of transfer are given in Table IX. The **Table IX:** Standard Molal Enthalpies of Transfer ofHydrocarbons from Pure Water to 0.1 m AqueousSolutions at Different Temperatures

			$-\Delta H_{\rm tr}^{\circ}$ (c	al/mole)-	
Hydrocarbon	Solute	5°	15°	25°	35°
Methane	NH₄Br	43	37	31	22
	(EtOH)₄NBr	30	36	65	120
	Me₄NBr	45	45	45	48
	Et,NBr	37	66	89	110
	Pr ₄ NBr	64	70	96	151
	Bu ₄ NBr	44	126	204	271
Ethane	NH₄Br	38	35	30	24
	(E⁺OH)₄NBr	38	49	82	133
	Me ₄ NBr	45	45	51	64
	Et, NBr	29	68	106	143
	Pr ₄ NBr	91	124	175	241
	Bu₄NBr	106	174	253	338
	Urea	66	43	20	1
Propane	NH₄Br	26	40	46	46
	(EtOH)₄NBr	67	118	176	246
	Me₄NBr	13	52	102	163
	Et ₄ NBr	73	107	175	272
	Pr ₄ NBr	143	211	299	405
	Bu ₄ NBr	233	335	467	628
	Urea	93	65	35	5
Butane	Me₄NBr	49	58	70	85
	Et.NBr	45	75	135	193
	Pr ₄ NBr	124	206	288	382
	Bu₄NBr	184	348	522	739

values of ΔH_{tr}° and ΔS_{tr}° were obtained from the temperature derivatives of ΔF_{tr}° and may contain much larger errors than (up to ten times) those in ΔF_{tr}° . However, the data listed in these tables should be good



Figure 11. Standard molal entropies of transfer of methane from pure water to 0.1 m aqueous solutions at different temperatures.



Figure 12. Standard molal entropies of transfer of propane from pure water to 0.1 m aqueous solutions at different temperatures.

enough to indicate the sign and the trend of these thermodynamic functions.

Discussion

According to Eley,⁵⁶ the greater the number of cavities existing in water, the higher is the gas solubility. Following this point of view, Ben-Naim⁵⁷ and Namiot⁵⁸ have used the two-structure model of liquid water to explain some of the properties of water and aqueous solutions.

The R_4N^+ ions affect the solubility of the hydrocarbon gas (RH) through two effects: (i) indirect interaction through changes in the structure of the medium, and (ii) direct interaction through hydrophobic contacts between R_4N^+ and RH. In discussing effect (i), it seems necessary to consider the following four factors, *i.e.*, (a) number of voids existing in the liquid water; (b) number of voids occupied by the hydrocarbon chains of R_4N^+ ions; (c) stability of water clusters or "cages" surrounding the R_4N^+ ions; and (d) size of R_4N^+ ion and RH molecule. These factors will be elaborated below.

(a) The number of voids in water is greater at lower temperatures than at higher temperatures. If the gas molecules are assumed to go mostly into the voids on dissolution, then one can explain why the solubilities of hydrocarbon gases in water decrease with the increase of temperature in the range of 5 to 35° .

(b) At low to moderate concentrations (0.1 to 1 m) the number of voids in water will decrease with the concentration increase because R_4N^+ ions will occupy available voids. In other words, water molecules will form

cage-like structure to "hide" the hydrocarbon chains of R_4N^+ ion inside and by so doing they will reduce the number of voids.²⁰ The "caging effect" seems to manifest clearly only at lower temperatures and for larger R_4N^+ ions and result in a decrease of hydrocarbon solubilities.

(c) When water clusters or cages surrounding $R_4 N^+$ ions are relatively stable, it will be that much harder for RH molecules to get into the solution because of the resistance which the system will exert toward the rearrangement of water molecules and ions to accommodate RH molecules. Since the clusters or cages surrounding Bu_4N^+ ions are particularly stable at low temperatures, one would expect the solubilities of hydrocarbons to be small in the presence of Bu_4NBr when compared with those in the presence of $smaller R_4NBr$ salts at 5°. This expectation is in agreement with the experimental results in which the order of the solubilities of hydrocarbons in Bu_4NBr , Pr_4NBr , and Et_4NBr is reversed to that at 25 or 35°.

(d) If we visualize the gas dissolution process in terms of the hydrocarbon molecule entering into one of the available voids in solution, it is obvious that the size of RH as well as R_4N^+ must play an important role. We have already discussed the effect of the size of R_4N^+ ions in factors (b) and (c) above. It will also be mentioned in effect (ii) below. The size of RH molecule in relation to the size of void will have a direct bearing on the solubility of hydrocarbon in water. From the solubility data it is not difficult to rationalize why the order of decreasing solubility in pure water is ethane > propane > methane, since the size of water "cage" is probably most suitable to accommodate ethane while it is slightly too small for propane and too large for methane.

Effect (ii) is the so-called hydrophobic interaction. When hydrocarbon molecules are allowed to make direct contacts with R_4N^+ ions, "hydrophobic bonds"⁵⁹⁻⁶¹ are formed. It is expected that the greater the extent of "hydrophobic bonds," the greater will be the solubility of a gas. The "hydrophobic bonding" should, of course, depend on the size of RH molecule and the size of R_4N^+ ions as well as on the temperature. For a given hydrocarbon gas at constant temperature (say, 25 or 35°) its solubility is expected to increase with the increase of the cationic size of R_4NBr salts in agreement with experimental results. At lower temperatures, "hydrophobic bonds" will decrease due to the "hydration" of R_4N^+ ions which will hinder the direct contacts

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between RH molecule and the ions. For larger R_4N^+ ions at lower temperatures (5°, for example), the factors discussed in (b) and (c) above will tend to dominate and, as a result, diminish the solubilities of hydrocarbons.

In conclusion, for the systems investigated, the "hydrophobic bonds" between RH molecules and R_4N^+ ions seem to be important at higher temperatures (say, above 25°), while the "caging effect" of water and the related void occupancy of R_4N^+ ions become important at lower temperatures (say, below 15°). The two opposite trends with temperature change are particularly obvious with large R_4N^+ ions such as Bu_4N^+ ion.

So far our discussion has mainly concerned with the solubilities, but the basic factors mentioned above are consistent with the observed enthalpies and entropies of transfer of hydrocarbons from pure water to aqueous R_1NBr solutions. According to the two-structure model for liquid water, the standard entropy and enthalpy of solution of the gas is written in the form⁵⁷

$$\overline{\Delta S}^{\circ} = \Delta S^* + \Delta S^{\mathrm{r}} \tag{4}$$

$$\overline{\Delta H}^{\circ} = \Delta H^* + \Delta H^{\mathrm{r}} \tag{5}$$

where ΔS^* and ΔH^* refer to a solution where the equilibrium between the two forms is "frozen in," while the relaxation term ΔS^r and ΔH^r take into account the change in the distribution of water molecules between the two forms. As can be seen from Tables VIII and IX, the values of ΔH_{tr}° and ΔS_{tr}° are all positive for our systems. In terms of the two-structure model, the major effect is the relaxation part of enthalpy ΔH^r which is positive due to the decrease of the number of cavities caused by the addition of the solute. The relaxation part of entropy ΔS^r is also positive since the number of cavities decreases as T increases.

The greater number of voids in solution at lower temperatures is expected to result in negative contributions to ΔH_{tr}° and ΔS_{tr}° . The observed values at 5° are indeed smaller positive than those at higher temperatures. Even at lower temperatures, however, these negative contributions are still not great enough to change the positive sign of ΔH_{tr}° and ΔS_{tr}° . However, we notice a reversal or near reversal in the order of these values with respect to the size of R_4N^+ ions. For example, for methane at 5°, both ΔH_{tr}° and ΔS_{tr}° seem to be smaller for Bu₄NBr than for Pr₄NBr as shown in Tables VIII and IX.

The hydrophobic contacts between RH molecules and R_4N^+ ions would increase the values of both ΔH_{tr}° and ΔS_{tr}° as a result of the overlap of the hydration cospheres. This trend becomes greater for larger RH and R_4N^+ , at higher salt concentrations, and at higher temperatures in agreement with our experimental observations.

The heat capacities of transfer of hydrocarbons $(\Delta C_{p(tr)}^{\circ})$ appear to be positive in the presence of R₄NBr

in contrast to near zero or negative values observed in the presence of inorganic salts by Ben-Naim and Egel-Thal for argon.⁶² This is deduced from the observation that, in the presence of inorganic salts, ΔF_{tr}° vs. Tcurves are nearly straight or slightly concave upward, while in the presence of R₄NBr salts, ΔF_{tr}° vs. T curves are slightly concave downward as can be seen in Figure 9. This difference can be attributed to the different water structure around different types of ions. In the presence of R₄N⁺ ions the water structures are enhanced and they would partially "melt" with the increase of the temperature. In contrast, in the presence of inorganic salts, the hydrated water would not "melt" with the increase of temperature.

The range and the magnitude of the salt effect of $(EtOH)_4NBr$ is very similar to that of Me₄NBr in spite of the fact that the size of (EtOH)₄NBr is closer to that of Pr_4NBr . This is to be expected since the terminal hydroxyl groups of the cation can fit well into the structure of water and, consequently, interfere with the hydrophobic interaction of the neighboring CH₂ groups with the surrounding water molecules. Studies of the partial molal volumes²² and heat capacities⁶³ of $(EtOH)_4NBr$ have also indicated that $(EtOH)_4N^+$ ion hardly changes the structure of water at 25°. In the present study we observed, however, a salting-in effect of (EtOH)₄NBr toward propane at higher temperatures as shown in Figure 9. The effect of this salt is a sensitive function of the hydrocarbon size as well as temperature. It salts out methane at 25° but salts in propane at 25°. The effects on propane at 5° or on ethane at 15° are very near to zero. The transition from salting-out to salting-in for (EtOH)₄NBr is similar to that for Me₄NBr. By changing the hydrocarbon size and temperature we conclude that, though the hydrophobic effect of $(EtOH)_{4}N^{+}$ is certainly smaller than that of Pr_4N^+ or Bu_4N^+ and can be even "hydrophilic" at lower temperatures, it shows a hydrophobic effect at higher temperatures toward larger hydrocarbon molecules.

As a concluding remark, it should be recognized that the nature of structure promotion by hydrocarbons or tetraalkylammonium salts is not well defined and that the detailed mechanism is still the subject of considerable debate.⁶⁴

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Internuclear Potential Energy Functions for Alkali Halide Molecules¹

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Hafemeister and Zahrt have obtained values for ρ for twenty diatomic alkali halide molecules by fitting the equation $A \exp(-r/\rho) = K\Sigma S^2/r$, where S is the overlap of the outer shell free ion wave functions. It is shown that these ρ values reproduce the spectroscopic data very well when used in an overlap potential energy function of the form $V_r = A_1 \exp(-r/\rho) + A_2 \exp(-r/2\rho) + A_3 \exp(-r/3\rho)$. The coefficients, A_i , correlate simply with effective charge and effective distance parameters that are independent of the data. The correlation requires four parameters for the twenty molecules and returns sixty spectroscopic constants with approximately the following average errors: $r_e (2\%)$, $D_e (3\%)$, $\omega_e (6\%)$. The overlap potential function suggests that the simple Born-Mayer expression holds best with ions of similar size and atomic number, *e.g.*, NaF or KCl, but is poor for dissimilar ions, *e.g.*, LiI or CsF.

Introduction

An approximate internuclear potential energy function for ionic, diatomic molecules is

$$V = Ae^{-\tau/\rho} - e^2 \left[\frac{1}{r} + \frac{\alpha_1 + \alpha_2}{2r^4} + \frac{2\alpha_1 \alpha_2}{r^7} \right] - \frac{C}{r^6} \quad (1)$$

This function is due to Rittner,^{1b} although it has been studied in detail by several others.² It contains two parameters for each kind of diatomic molecule, namely, ρ and A, which are generally determined from experimental data. However, it is known that the repulsive potential energy used above (the Born-Mayer potential) arises in approximate quantum mechanical considerations of overlapping closed-shell systems.^{3,4} In the case of the twenty alkali halide diatomic molecules, Hafemeister and Zahrt⁴ have listed values of ρ obtained by fitting the equation

$$Ae^{-\tau/\rho} = K\Sigma S^2/r \tag{2}$$

where the S are overlaps of the outer electrons calculated using SCF free ion wavefunctions. Reliable values of A were not determined from the constant This equation demonstrates an accurate func-*K*. tional relationship between the quantum mechanical free ion overlap and r but yields only a rough approximation for the interaction potential energy due to the overlap of the ionic charge clouds. The values of ρ are near those reported empirically from the data for the Born-Mayer potential function; however, they are inadequate to accurately reproduce experimental results. In the present work ρ is retained as a basic constant for each ion pair; however, more extensive overlap potential functions incorporating these quantum mechanical ρ values are appraised. Since ρ is independent of experimental data, this means other parameters are released for study by means of data fitting.

V_r , the Overlap Potential Function

The Rittner potential function, eq 1, contains electrostatic and van der Waals attractive terms and the Born-Mayer repulsive potential. In this section various empirical terms are added to the Born-Mayer expression in order to determine the best form for V_r , the overlap potential. The new terms turn out to be attractive or repulsive, depending upon the specific molecule. In addition to providing the basic repulsion, V_r is considered to account for the perturbations induced by overlap on the multipole moment expansion, free ion polarizabilities, covalent tendencies, and similar concepts used to describe the system. The Hafemeister-Zahrt (H-Z) ρ values are used throughout.

The potential energy curves are determined by forcefitting two or three of the spectroscopic constants $k_{\rm e}$, $r_{\rm e}$, and $D_{\rm e}$ and are judged by comparing the calculated and observed $\alpha_{\rm e}$ and $\omega_{\rm e} X_{\rm e}$ values.

The equations for α_e and $\omega_e X_e$ are

$$\alpha_{e} = -\left[\frac{X_{3}r_{e}}{3} + 1\right]\frac{6B_{e}^{2}}{\omega_{e}}$$

$$\omega_{e}X_{e} = \left[\frac{5}{3}X_{3}^{2} - X_{4}\right]\frac{hN}{64\pi^{2}C\mu_{A}}$$

$$X_{n} = (\partial^{n}V/\partial r^{n})_{r_{e}}/(\partial^{2}V/\partial r^{2})_{r_{e}}$$
(3)

The experimental values of α_{\circ} and $\omega_{\circ}X_{\circ}$ are accurately known from electric resonance-molecular beam mea-

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	$V_t = F_1 A_1 \exp(-\tau/\rho)$	$+ F_2 A_2 \exp(-\tau/2\rho) + b$	$F_3A_3 \exp(-\tau/3\rho)$	~		e errors				
No.	Fı	F_2	F_{3}	D_{e}	k _e	ae	ω_{e}/X_{e}			
1 ^{<i>a</i>}	1			2.7%	12.6%	7.6%	12.5%			
2^b	$\exp(-\rho/r_{\rm Ritt})$			2.0		5.5	5.2			
3-5°	1	$1, r, r^2$		2.3 - 4.0		4.9-8.2	7.5 - 13.8			
6-8	1		$1, r, r^2$	3.3-13.4	• • • •	6.6 - 12.5	10.6 - 24.8			
9-17 ^{d,e}	1	$1, r, r^2$	$1, r, r^2$			3.6-5.3	6.5-8.0			
18	1 + br)			2.0		7.7	5.2			
19	$(1 + b_1 r + b_2 r^2)$					16.2	14.8			
20	$(1 + b_1 r + b_2/r)$					23.7	15.0			
21 - 35	1	$(0, 1, r, r^2)x$	$(0, 1, r, r^2)x$	2.1-2.3,		17.0-113	5.4 - 92			
		$\exp(-3r/2\rho)$	$\exp(-5r/2\rho)$	cf. Nos. 3-8						
36-38	1	$(1, r) + b (1, r^2)$				4.5-3.7	7.7-7.2			
39 ⁷	1	$(2-r/\rho)$	$(27-18r/\rho + 2r^2/\rho^2)$			5.8	8.6			
40 ^{<i>g</i>}	1	$(5-r/\rho)$	$(4-r/\rho)$			6.8	10.6			
41 ^h	1	$\exp(-2\rho/\mathrm{s})$			• • •	16.6	36			

Table I: Empirical Overlap Potentials, Vr, Used in the Rittner Function

^a Standard Rittner function using H-Z_ρ values; r_e is force-fit. ^b Standard Rittner function from ref 2 using solid-state polarizabilities; r_e and k_e are force-fit. ^c Three different V_r functions. Potential 3 is: $V_r = A_1 \exp(-r/\rho) + A_2 \exp(-r/2\rho)$. ^d The first of these functions is given in eq 4 and is considered to be the best overall V_r . ^e The force fit on no. 16 ($F_1 = r^2, F_2 = r$) yields peculiar A_i values for several molecules. The average errors are α_e , -28.5%; $\omega_e X_e$, -42.4%. ^f Expansion with orthogonal functions. ^e This function has critical points near the experimental r_e values. ^h This function force-fit the data using a constant in the exponential correction term. It yielded inferior results in addition to departing the objective of testing the H-Z_ρ values.

surements. The values used below are taken from the tabulation of Varshni and Shukla,^{5a} with the exception of the fluoride molecules.^{5b} Free-ion values for the polarizabilities^{6a} and van der Waals constants² are used in the calculations since the ultimate objective is a potential energy function determined completely independently of experimental data for the diatomic molecules.

The results are summarized in Table I. Potential 1 is the Rittner function using the H-Z ρ and the

Table II:	Potential Const	tants Used	in Eq 4	
	p, Å ^a	$A_1 \times 10^8 \text{ ergs}$	$A_2 imes 10^{10}$ ergs	$A_3 imes 10^{10}$ ergs
LiF	0.252	0.168	0.0557	0.0704
LiCl	0.299	0.221	0.523	-0.0566
LiBr	0.311	0.231	0.947	-0.182
LiI	0.335	0.243	0.118	-0.257
NaF	0.264	0.316	-0.0843	0.0970
NaCl	0.305	0.391	0.435	-0.0228
NaBr	0.316	0.399	0.896	-0.136
NaI	0.340	0.400	1.029	-0.176
KF	0.299	0.343	-0.484	0.158
KCl	0.333	0.514	-0.129	0.815
KBr	0.344	0.535	0.275	-0.0196
KI	0.365	0.572	0.330	-0.0263
\mathbf{RbF}	0.314	0.368	-0.793	0.228
RbCl	0.346	0.570	-0.414	0.132
RbBr	0.357	0.601	-0.0558	-0.0389
RbI	0.377	0.651	0.0196	0.0257
\mathbf{CsF}	0.336	0.355	-1.122	0.303
CsCl	0.364	0.570	-0.344	0.0696
CsBr	0.375	0.596	0.125	-0.0570
CsI	0.394	0.666	0.155	-0.0563
^a Refere	nce 4.			

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Figure 1. Observed values for A_1 using eq 4.

observed r_{\circ} values. This single-parameter function is not very accurate, as expected. It can be compared with potential 2, the standard Rittner function as evaluated by Varshni and Shukla.² They determined A and ρ using the observed r_{\circ} and k_{\circ} values (with solid state polarizabilities^{6b}) and calculated D_{\circ} with an average error of 2%; the errors for α_{\circ} and $\omega_{\circ}X_{\circ}$ were 5.5% and 5.2%, respectively. Potential 9

$$V_{r} = A_{1}e^{-r/\rho} + A_{2}e^{-r/2\rho} + A_{3}e^{-r/3\rho}$$
(4)

using H-Z ρ values, is forced to fit the experimental

^{(5) (}a) Reference 2, Table II; (b) S. E. Veazey and W. Gordy, Phys. Rev., 138A, 1303 (1965).

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		Å		Md/Å	De, ke	cal/m	weXe,	cm -1		e cm -1
	Exptl	Cor ^b	Exptl	Cor ^b	Exptl	Cor ^b	Exptl	Eq 4 ^c	Exptl	Eq 4 ^c
LiF	1.564	1.584	2.502	2.996	178.3	174.1	8.895	8.917	240.9	204.6
Cl	2.021	1.941	1.415	1.875	148.0	148.8	4.200	4.665	80.12	75.90
Br	2.170	2.160	1.205	1.396	142.9	137.8	3.88	3.629	56.40	53.65
Ι	2.392	2.382	0.972	1.102	134.3	127.9	3.39	2.941	40.90	39.39
NaF	1.926	1.876	1.761	2.099	149.0	151.7	3.83	3.598	45 .59	42.18
Cl	2.361	2.271	1.086	1.389	127.8	131.1	1.755	1.898	16.25	16.26
Br	2.502	2.492	0.935	1.083	123.6	123.2	1.16	1.280	9.410	9.437
Ι	2.711	2.731	0.770	0.870	116.6	114.4	0.964	1.002	6.478	6.622
KF	2.172	2.202	1.366	1.408	134.2	129.6	2.43	2.462	23.35	22.39
Cl	2.667	2.577	0.851	0.983	113.2	114.9	1.167	1.299	7.899	8.140
Br	2.821	2.831	0.738	0.771	109.4	107.5	0.758	0.812	4.048	4.142
Ι	3.048	3.048	0.611	0.642	102.3	101.6	0.574	0.630	2.678	2.812
RbF	2.270	2.290	1.274	1.362	128.9	124.3	1.80	1.942	15.22	14.79
Cl	2.787	2.677	0.795	0.945	108.8	109.5	0.856	0.940	4.536	4.690
Br	2.945	2.965	0.692	0.716	105.1	101.2	0.463	0.508	1.860	1.911
Ι	3.177	3.177	0.575	0.597	98.4	95.9	0.335	0.364	1.095	1.149
\mathbf{CsF}	2.345	2.455	1.217	1.173	125.9	116.2	1.62	1.680	11.051	11.595
Cl	2.906	2.816	0.748	0.828	107.8	103.9	0.74	0.761	3.375	3.393
Br	3.072	3.122	0.652	0.624	104.7	95.7	0.360	0.376	1.241	1.218
Ι	3.315	3.325	0.543	0.529	97.6	91.1	0.254	0.260	0.683	0.684

Table III: Spectroscopic Constants^a

^a Experimental values (rounded off) from Table II of ref 2, except the alkali fluorides from ref 5b. ^b Calculated from correlated A_1 values (eq 7); $C_1 = 1.00 \times 10^{-9}$; $C_2 = 3.00 \times 10^{-12}$; $C_3 = 7.00 \times 10^{-13}$; $C_4 = 6.00 \times 10^{-12}$. The listed r_e (cor) are within about ± 0.005 Å of the true $r_e = r_{\min}$ for each potential function. ^c Calculated using eq 4; r_e , k_e , and D_e are force-fit.

 $r_{\rm e}$, $D_{\rm e}$, and $k_{\rm e}$ values and matches the standard Rittner function in its $\alpha_{\rm e}$ and $\omega_{\rm e}X_{\rm e}$ errors. None of the potential functions is significantly better than this, particularly when correlations of the three sets of twenty A_i values are attempted. This potential function is used in the following discussion; it is displayed in detail in Tables II and III and in Figures 1–3.

Potential functions which depend upon quantum mechanically determined ρ values hold special promise.



Figure 2. Observed values for A_2 using eq 4.



Figure 3. Observed values for A_3 using eq 4.

They may be valid over an extended range of internuclear distance and can, in principle, specifically include many-body interactions for polyionic species, *e.g.*, following lines rationalized with the exchangecharge model.⁴ As discussed in the next section, the number of empirically determined parameters can be greatly reduced if they can be accurately correlated or independently calculated, as were the H–Z ρ values.

Correlation of V_r for Alkali Halide Molecules

The systematic variation of the A_i values seen in Figures 1-3 resembles that found for other properties

of these compounds. A number of correlations of the A_i values were made, with particular emphasis on relating to calculated and/or free-ion properties. The best correlation that was discovered relates the A_i values through the following parameters.

1. An effective charge given very simply by

$$N_{+} = N + 1$$

$$N_{-} = N - 1$$
(5)

for the cation and anion, respectively. N is the total number of electrons in the outer two shells, except for Li⁺ and F⁻, which possess only one shell.

2. An effective radius given by

$$R_{+} = \frac{1}{2} (r_{e} - (S_{+} - S_{-}))$$

$$R_{-} = \frac{1}{2} (r_{e} + (S_{+} - S_{-}))$$
(6)

for the cation and anion, where S_+ and S_- are the orbital maxima for the outer electrons calculated by Waberand Cromer.⁷ These radii locate a point halfway between the ions as measured from "hard" radii, S_+ and S_- , determined by the outer electron shell of each. The radii are given at the observed equilibrium internuclear distances in Table IV.

Using these parameters, the values for A_1 , A_2 , and A_3 for each alkali halide are given by

$$A_{1} = C_{1} \sqrt{\frac{N_{+}N_{-}}{N_{+} + N_{-}}} r_{e}$$
(7a)

$$A_2 = C_2 \left(N_+ R_- - N_+ R_+ \right) \tag{7b}$$

$$A_3 = C_3 (N_+R_+ - N_-R_-) + C_4$$
 (7c)

where C_1 , C_2 , C_3 , and C_4 are constants for the twenty molecules.

These functions are plotted in Figures 4-6 against the A_i values from Table I. The experimental r_0 values



Figure 4. Correlation of observed A_1 values with $(Nr_e)^{1/2}$, where $N = N_+ N_- / (N_+ + N_-)$.

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Table IV:	Effective	Charge and	Effective	Distance	Parameters
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	N_+^a	8+, Å ^b	<i>R</i> +, Å [¢]	N_	<i>s</i> _, Å	<i>R</i> -, Å
\mathbf{LiF}	3	0.189	0.677	9	0.400	0.887
LiCl			0.734	15	0.742	1.287
LiBr			0.745	25	0.896	1.425
LiI			0.758	25	1.065	1.634
NaF	11	0.278	0.902			1.024
NaCl			0.949			1.412
NaBr			0.956			1.546
NaI			0.962			1.749
KF	17	0.592	1.182			0.990
KCl			1.259			1.408
KBr			1.272			1.549
KI			1.288			1.760
RbF	27	0.734	1.302			0.968
RbCl			1.390			1.39 7
RbBr			1.405			1.540
RΙ			1.423			1.754
\mathbf{CsF}	27	0.921	1.433			0.912
CsCl			1.543			1.363
CsBr			1.562			1.510
CsI			1.586			1.729

^a From eq 5. ^b Outer shell orbital maxima from ref 7. ^c From eq 6, using experimental r_o values.



Figure 5. Correlation of observed A_2 values with $(N-R_- - N_+R_+) = \Delta$.

are used in these figures. The constants for the lines drawn into the figures are $C_1 = 1.00 \times 10^{-9}$, $C_2 = 3.00 \times 10^{-12}$, $C_3 = 7.00 \times 10^{-13}$, and $C_4 = 6.00 \times 10^{-12}$, yielding A_i in ergs/molecule, R_+ and R_- in angstroms, and integer values for N_+ and N_- . Using these constants and the r_e values determined from the minimum of each potential energy curve to recalculate the A_i , the spectroscopic constants for the twenty alkali halide molecules were calculated with the following average errors: r_e (1.7%), D_e (3.1%) and ω_e (5.6%). This calculation is summarized in Table III and Figure 7.

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Figure 6. Correlation of observed A_3 values with $(N_-R_- - N_+R_+) = \Delta$.



Figure 7. Display of per cent errors found using A_i correlation of Figures 4-6. Open circles signify an error in the calculated r_{\bullet} of less than 2%, closed circles greater than 2%. The maximum error is +4.7% for CsF.

The sensitivity of the calculation of spectroscopic constants is indicated using the following C_i values which were chosen as more-or-less limiting values compatable with the data points. C_1 (.96 \times 10⁻⁹), C_2 (2.70 \times 10⁻¹²), C_3 (4.00 × 10⁻¹³), C_4 (-6.70 × 10⁻¹²) gave r_e $(3.2\%), D_{e} (3.0\%), \omega_{e} (9.9\%)$ while $C_{1} (1.04 \times 10^{-10}),$ C_2 (3.30 × 10⁻¹²), C_3 (8.00 × 10⁻¹³), C_4 (-7.30 × 10⁻¹²) gave r_{e} (2.5%), D_{e} (5.4%), and ω_{e} (3.1%). It appears that the spectroscopic constants are returned to approximately r_{\bullet} (2%), D_{\bullet} (3%), and ω_{\bullet} (6%).

Discussion and Conclusions

The alkali halide spectroscopic properties are very sensitive to the choice of ρ and it is possible that a different form of potential function and/or different correlation of A_i values would ensue if a different set was used. Hafemeister and Zahrt⁴ chose the "best available" free-ion SCF wave functions and found eq 2 to hold to about 0.2% in a neighborhood extending through diatomic and crystal radii. They found little contribution to ρ from the inner shell electrons and ignored this. It seems likely that their ρ values constitute a meaningful property of the interacting alkali halide ions and that they are not subject to a gross change in future calculations.⁸ On this basis, discussion of several points concerning the overlap potential functions is justified.

The effective ρ value calculated from the quan-(1)tum mechanical overlap can be used successfully in the Rittner potential when the Born-Mayer repulsive term is extended as illustrated in eq 4. Other forms tested were not as generally successful in both matching the α_{e} and $\omega_{e}X_{e}$ values and in yielding correlatable A_{i} values.

(2) The preexponential terms in the chosen overlap potential correlate in a simple manner with effective charge (N_+, N_-) and effective distance (R_+, R_-) parameters (eq 5 and 6). The A_2 and A_3 terms are observed to be smallest for the most like ions and, according to the correlation, vanish when $N_+R_+ = N_-R_-$. The Born-Mayer potential is seen to be poor for many alkali halides, since the potential given in eq 4 cannot be fit well with a single term, *i.e.*, $B \exp(-R/b)$, when more than one A_i coefficient is large. The data indicate (Figures 5 and 6) the largest deviations of the Born-Mayer equation occur for LiI and CsF-the most dissimilar ion pairs.

(3) A correlation of the A_i values with effective charge times distance parameters is anticipated by quantum mechanical approximations that express the true interaction integrals in terms of overlap integrals. The nature of the overlap integrals and their superficial resemblance to eq 7 is illustrated by $S_{1S_A,1S_B}$, the simplest example (which does not occur for alkali halides). It is written in confocal elliptical coordinates λ, μ , and ϕ as

$$S_{1S_{A},1S_{B}}, = \frac{1}{\pi} \zeta_{A}^{3/2} \zeta_{B}^{3/2} \left(\frac{r}{2}\right)^{3} (A_{2}B_{0} - A_{0}B_{2}) \int_{0}^{2\pi} d\phi$$

$$A_{2} = \int_{1}^{\infty} \lambda^{2} \exp\left(-\frac{r}{2} (\zeta_{A} + \zeta_{B})\right) d\lambda \qquad (8)$$

$$B_{0} = \int_{-1}^{+1} \mu^{0} \exp\left(-\frac{r}{2} (\zeta_{A} - \zeta_{B})\right) d\mu$$

where r is the internuclear separation and ζ_A and ζ_B are the effective nuclear charges and the subscript on A_{i} , B_i is the exponent on λ^i , μ^j .

(8) Relativistic corrections for the wave functions can reduce the overlap integrals between the heavy ions by up to 10%. Reference 4 and D. W. Hafemeister, J. Chem. Phys., 46, 1929 (1967).

Other easily obtained effective nuclear charge parameters were tried, the most successful based on the tables of Clementi and colleagues;⁹ however, they did not quite match the effectiveness or simplicity of N_+ and N_- . The effective nuclear charges were never calculated at specific distances, *e.g.*, R_+ or R_- , using SCF wave functions directly.

The use of effective numbers of outer shell electrons has occurred previously in discussions of dispersion forces,¹⁰ and Pauling even brought forth their possible use for closed shell systems in his classic paper on alkali halide crystals.¹¹

The Waber-Cromer orbital maxima are known to bear a close relationship to atomic sizes, as demonstrated by Slater,¹² and (despite being alkali and halide ions) they provided the best distance parameters, giving both the best correlation and being independent of the data. The rules (eq. 6) are arbitrary, but work well and yield virtually constant radii for all of the ions except Li⁺ and F⁻, as seen in Table IV.

The correlation for A_1 seems best using eq 7a; however, nearly equivalent results are obtained for most molecules using

$$A_{1} = \left(\frac{1}{N_{+}R_{+}} + \frac{1}{N_{-}R_{-}}\right)^{-1/2} = \left(\frac{N_{+}R_{+}N_{-}R_{-}}{N_{+}R_{+} + N_{-}R_{-}}\right)^{1/2}$$
(9a)

or

$$A_{1} = \left(\frac{1}{\sqrt{N_{+}R_{+}}} + \frac{1}{\sqrt{N_{-}R_{-}}}\right)^{-1}$$
(9b)

Equation 9a is identical with 7a when $R_+ = R_-$. Perhaps these formulas can be more easily derived from approximating the quantum mechanical interaction integrals than can eq 7a.

It is not easy to justify the exact form of eq 7 in view of the many terms that are effectively averaged into these equations.³ McLean¹³ and Matcha¹⁴ have performed detailed *ab initio* quantum mechanical calculations of LiF¹³ and LiCl, NaF, NaCl, and KF¹⁴ that reproduce the spectroscopic constants to a few per cent. The A_i values were determined for these potential curves in an attempt to determine the C_i values independently of any data. The C_1 values were about 20% too high; C_2 and C_3 were scattered. (4) At least two interesting correlation schemes for A_1 seem to be less effective than that given above (that is using the H-Z ρ values and A_1 only, not an effective, single term Born-Mayer potential). These are the expression derived by Hafemeister and Zahrt using the exchange-charge model⁴

$$A_{1} = 4 eK \left[(R_{+}^{i} + R_{-}^{i}) \left(\frac{Q_{+}}{R_{+}^{i}} + \frac{Q_{-}}{R_{-}^{i}} \right) \right] \quad (10)$$

and the Born-Mayer force equation with an equal force, f, for all molecules¹⁵

$$A_1 = f \rho \exp\left(+\frac{r_o}{\rho}\right)$$
(11)

The four-parameter, correlated potential energy (5)function returns reasonable spectroscopic constants, comparing well, for example, with the calculations performed by Hofer and Ferreira¹⁶ on twelve alkali halide molecules. It is hoped that, ultimately, improved potential functions can be evolved, particularly those suitable for higher alkali halide molecules and for estimation of the intermolecular interactions between alkali halides molecules and rare gas atoms. The future seems bright for any effective overlap potential function between nonbonded systems (including, perhaps, core electrons in covalent bonded systems) that can be refined to the point that reliable parameters, based on computation and/or free particle properties. follow with minimal labor.

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Dipole Polarizabilities of Ions in Alkali Halide Crystals^{1,2}

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A compressible conducting sphere is proposed as a model to describe the polarizability of halide ions and the changes these polarizabilities undergo in ionic crystals. On the basis of this model, two empiricial correlation schemes are developed, both of which provide an accurate representation of the polarizabilities of the alkali halide crystals with the sodium chloride structure. The second scheme (Model II) provides for variable cation polarizabilities that are larger than the free-ion values; it leads to reasonable estimates for the polarizabilities of the free anions. These values (1.56, 4.41, 5.84, and 8.91 Å³ for F^- , Cl^- , Br^- , and I^- , respectively) are larger than those commonly accepted. Curiously, the cube roots of these quantities are equal or nearly so to values recently proposed for the corresponding ionic radii. The model also accounts approximately for the effect of compression on crystal polarizabilities. Implications of the model for the calculation of London energies are discussed.

Introduction

The polarizability of an ion is sensitive to its environment. For example, the best spectroscopic value³ for the polarizability of the free lithium ion is 0.0283 Å³ and the most recent theoretical estimates^{4,5} for the polarizability of the free fluoride ion are 1.56 and 1.40 Å³. The sum of these lies between 1.59 and 1.43 Å³ whereas the experimental polarizability per ion pair in crystalline LiF (Table I) is 0.915 Å³. An even more striking example⁶ is afforded by NaH (*ca.* 30 vs. 1.75 Å³).

The existence of such effects was demonstrated in principle over 40 years ago by Spangenberg,⁷ who showed that the polarizabilities per ion-pair in the crystalline alkali halides cannot be accurately described as sums of constant polarizabilities for the component ions. This is illustrated by the fact (Table I) that the difference in polarizability between NaF and NaBr is 3.24 Å³ whereas the corresponding difference in the rubidium salts is 3.43 Å³.

A qualitative explanation for the observed lack of additivity was advanced very soon thereafter by Fajans and Joos.⁸ The purpose of the present paper is to present a model which accounts quantitatively for the observed lack of additivity and leads to a new set of estimates for the polarizabilities of the free halide ions. In view of the long and not widely appreciated history of research in this field, it seems appropriate to precede the presentation of our model with a summary of some earlier developments.

Fajans and Joos⁸ proposed on the basis of quite general arguments that the polarizability of a positive ion is increased in the coulomb field of an anion, while the polarizability of a negative ion should be decreased in the coulomb field of a cation. In an extensive review of the information available at that time, they applied these ideas to correlate not only the polarizabilities of ionic compounds in crystals and in solution but also those of molecules composed of groups differing substantially in electronegativity. The application of these concepts to a great variety of substances has been pursued subsequently by Fajans and his collaborators in a long series of publications.^{9,10}

Fajans and Joos⁸ also proposed a formalism for estimating the polarizabilities of the free ions, both positive and negative, on the basis of two qualitative rules: (1) $\alpha^+/\alpha^\circ > \alpha^\circ/\alpha^-$ where the superscripts +, 0, - refer to monatomic cation, noble gas, and anion in an isoelectronic series, and (2) $(\alpha^+/\alpha^\circ)_n < (\alpha^+/\alpha^\circ)_{n+1}$ where n is the principal quantum number of the valence shell in an isoelectronic pair. These rules, together with experimental values for the polarizabilities α_n° , independent estimates of α^+ for the lighter cations, and plausible assumptions about the trends in the inequalities in rules (1) and (2), led to estimates for the polarizabilities of the free ions. These estimates were influenced also by the estimated polarizabilities⁸ of the heavier anions in aqueous solution; with minor modifications, they are current today.¹¹ They appear to have had a significant influence on the selection of parameters for Pauling's semiempirical calculation¹² of the polarizabilities of the free alkali and halide ions.

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- (6) K. Fajans, Chimia, 13, 354 (1959).
- (7) K. Spangenberg, Z. Krist., 57, 494 (1923).
- (8) K. Fajans and G. Joos, Z. Physik, 23, 1 (1924).

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⁽⁴⁾ H. D. Cohen, J. Chem. Phys., 43, 3558; 45, 10 (1966).

⁽⁹⁾ K. Fajans, "Chemical Forces," McGraw-Hill, New York, N. Y., 1931.

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⁽¹¹⁾ K. Fajans, "Encyclopedia of Chemistry," Clark and Hawley,

Ed., Reinhold, Publ. Co., New York, N. Y., 1957, p 764.

⁽¹²⁾ L. Pauling, Proc. Roy. Soc., 114, 181 (1927).

						5.0			
Salt	τ_{e} , ^a Å	۵D, ^b Å ⁸	$\overline{\mathbf{F} - \mathbf{BF}}$	WC – BF	TKS	—α _∞ , A ^{sc} — ΡΚ	Corr	wc	Accept
LiF	2.013	0.9276(2)	0.916	0.916	0.909		0.915	0.915	0.915
NaF	2.317	1.196(2)	1.178	1.177	1.163	1.167	1.178	1.177	1.178
KF	2.673	2.023(5)	2.014	1.991	2.008		2.015	1.992	1.992
\mathbf{RbF}	2.820	2.634(11)			2.572	2.528	2.582	2.582	2.582
CsF	3.007	3.686(5)				3.603	3.624	3.624	3.624
LiCl	2.570	2.992(3)			2.903		2.911	2.90	2.905
NaCl	2.820	3.380(1)	3.283	3.285	3.263	3.262	3.282	3.282	3.283
KCl	3.146	4.301(1)	4.183	4.182	4.173	4.146	4.175	4.175	4.178
RbCl	3.291	4.956(1)	4.833	4.813	4.712	4.712	4.808	4.808	4.81
LiBr	2.750	4.172 (8)			4.138		4.151	4.02	4.02
NaBr	2.986	4.613 (11)	4.437	4.447	4.388	4.388	4.417	4.417	4.42
KBr	3.300	5.546(2)	4.337	5.340	5.293	5.298	5.332	5.332	5.33
RbBr	3.445	6.237(10)	6.022	6.011	5.920	5.919	6.012	6.012	6.01
LiI	3.005	6.255(13)			6.226		6.232	5.90	5.90
NaI	3.237	6.754 (6)			6.264		6.299	6.40	6.35
KI	3.533	7.831 (4)	7.454	7.454	7.388	7.387	7.429	7.44	7.44
RbI	3.670	8.546 (20)	8.188	8.126	8.093	8.091	8.117	8.12	8.13
			Cesiu	ım Chloride S	tructure				
CsCl	3.570	6.038 (8)	5.866	5.876	5.829	5.828	5.885	5.88	5.88
CsBr	3.719	7.292(4)	7.058	7.029	7.020	7.020	7.053	7.053	7.05
CsI	3.955	9.611 (2)			9.119	9.119	9.157	9.17	9.17

Table I: Structural and Polarizability Data for Alkali Halide Crystals

^a Nearest-neighbor anion-cation distance; basis recent data for unit cell dimensions at room temperature. ^b Polarizability per ion pair calculated from the refractive index at the wavelength of the Na D line and the density calculated from the unit cell dimensions. The number in parentheses is our best estimate of the uncertainty in the last significant figure, or the last two figures given. ^c Estimates by various authors for the polarizability per ion pair extrapolated to infinite wavelength: F - BF, recent estimates of α_D by Fajans (private communication) minus the values given for $(\alpha_D - \alpha_m)$ by Bauer and Fajans;¹⁰ WC - BF. Our estimates of α_D minus the values of $(\alpha_D - \alpha_m)$ given by Bauer and Fajans,¹⁰ TKS, values given by Tessman, Kahn, and Shockley;¹³ PK, revision of TKS values, basis more recent polarizability data assembled by Pirenne and Kartheuser;²² WC, estimates by the present authors, basis a review of dispersion data and correlations of dispersion data; Corr, revision of estimates by TKS or PK, whichever is based on better dispersion data, on basis of modern values for lattice parameters; Accept, accepted values of α_m basis conservative estimates of the uncertainties involved in extrapolation to infinite wavelength, and an examination of trends in the differences in polarizability between adjacent pairs of salts in the alkali and halide series.

Despite the evidence summarized above that ionic polarizabilities vary with environment, many authors have based their estimates of polarization energies and London energies in ionic systems on the "constant" or additive ionic polarizabilities assigned by Tessman, Kahn, and Shockley.¹³ These values were chosen to minimize the mean-square deviations from additivity in the polarizabilities of ionic crystals, but with due consideration of independent estimates of the polarizabilities of the lighter free alkali ions, especially Li+. Clearly, the use of these additive polarizabilities must be regarded as only a first approximation; more realistic estimates of the secondary interactions in ionic systems could be made if reliable values were available for ionic polarizabilities in different environments. Indeed, the values deduced by TKS¹³ by difference for the polarizability of the oxide ion, O^{2-} , in a number of crystals ranged from 0.9 to 3.2 Å³, illustrating again the existence of a substantial environmental effect.

At the level of approximation represented by the highly successful Born-Mayer model¹⁴ of ionic crystals, it is natural to represent the polarizability of an ionic crystal as the sum of anionic and cationic component polarizabilities. From the point of view of a quantum mechanical description of the system, however, this procedure cannot be strictly justified. The nature and validity of the quantum-mechanical approximations involved in this additivity concept have been discussed by Ruffa.¹⁵ Making use of a well-established description of the polarizability of an atom or ion as proportional to the number of its electrons and inversely proportional to a weighted mean-square excitation energy, Ruffa extended his analysis to carry out what amounts to a semiquantitative treatment of the hypothesis of Fajans and Joos.⁸ On the basis of a somewhat intuitive estimate of the effects of the lattice interactions on the mean-square excitation energy, he confirmed their contention that the polarizability of a cation is increased by the lattice interactions, whereas the polarizability of an anion is decreased even more. As Ruffa

- (14) M. Born and J. E. Mayer, Z. Physik, 75, 1 (1932).
- (15) A. R. Ruffa, Phys. Rev., 130, 1412 (1963).

⁽¹³⁾ J. K. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev., 92, 890 (1953).

himself admits, however, some of the parameters that entered his theory could be estimated only roughly and his estimates of the magnitude of the changes in polarizability may have been too large. In addition, he based his estimates of the mean-square excitation energies of the unperturbed ions on Pauling's estimates¹² of the free-ion polarizabilities. As will be shown below, subsequent work has made available more reliable estimates for the polarizabilities of the lighter ions in the free state and has raised doubts about the accuracy of Pauling's estimates for the polarizabilities of the heavier ones.

The effect of lattice interactions on the polarizabilities of the component ions in the chlorides and fluorides of lithium, sodium, and potassium has also been analyzed by Mitskevich¹⁶ on the basis of variation theory. His treatment leads to the same qualitative conclusions: the polarizability of the positive ions is increased in the crystal and that of the negative ions is decreased. relative to the values that characterize the free ions. His estimates of the changes involved, however, are considerably smaller than those made by Ruffa.¹⁵

An alternative approach to this problem was made earlier by Burns and Wikner,¹⁷ who calculated the polarizability of the fluoride ion from the approximate wave functions proposed by Yamashita¹⁸ for the free ion and for the fluoride ion in the crystal of LiF. They obtained a polarizability of 1.31 Å³ for the free ion but a smaller polarizability of 1.11 Å³ for the contracted wave function of the fluoride ion in the crystal. The model which we present below is related conceptually to the results of these calculations.

A Model for the Polarizability of Anions in Crystals. Our model can be based on the following arguments.¹⁶ The major contribution to the polarizability of a closedshell atom or ion is made by the electrons of its highest occupied subshell (see ref 20b). In the halide ions, these electrons are relatively weakly bound and might therefore be expected to respond to a polarizing field rather as if they were the electrons of a conducting sphere. Classically, the polarizability of a conducting sphere is the cube of its radius. In applying this concept to a halid ion, it is not clear how the radius should be chosen. We shall defer consideration of that question until a later section; for the moment, we simply assume that the polarizability of an anion responds to its environment as if it were proportional to a radius cubed, *i.e.*, to a volume.

We would not expect this model to apply as well to the polarizabilities of cations or of the noble gases since the ionization potentials of these systems are much higher than those of the halide ions. That one should not expect a proportionality between polarizability and volume in general is shown by the form of one of the well known quantum theory expressions for one-electron polarizabilities (see ref 20c, eq 116, 121, and 124) as the square of a sum of terms of the form $\langle \mu_i r^2 \mu_i \rangle$ and $|\langle \mu_i r_i \mu_j \rangle|^2$ where r_i is the radius from the nucleus to the *i*th electron and μ_i is the corresponding one-electron wave function. Our basic assumption is that for the halide ions the proportionality will be close enough to be useful. It is an assumption based on a qualitative idea and to be justified, if it all, by its consequences.

In a condensed phase the electron distribution of the anion will be subjected to a symmetrically distributed compressive force F by repulsive interactions with the electron distributions of its neighbors. We assume that an increment dF of the compressive force results in a proportionate decrease of the polarizability, similar to the decrease in effective volume. Thus we write for the ith ion

$$\mathrm{d}\alpha_i = -k_i \alpha_i F_i \tag{1}$$

where k_i is a constant analogous to a compressibility. Integration yields

$$\ln \alpha_i = \ln \alpha_i^0 - k_i F_i \tag{2}$$

where α_i^{0} is the polarizability of the free ion.

Let us approximate the lattice free energy U of a crystal as a sum of the coulomb term and a repulsive potential R; we ignore for the moment the kinetic energy and entropy terms and the London potentials. The use of a more elaborate model will be discussed in a later section. Thus we write

$$U = -\frac{\mu e^2}{r} + R(r) \tag{3}$$

where μ is the Madelung constant. At the equilibrium nearest-neighbor distance, r_{e}

$$\left(\frac{\mathrm{d}U}{\mathrm{d}r}\right) = \mu e^2/r_\mathrm{e}^2 + R'(r_\mathrm{e}) = 0$$

Here the attractive and repulsive forces acting on the ions are in balance and we may write for the compressive force $F(r_{\rm e})$

$$F(r_{\rm e}) = - R'(r_{\rm e}) = \mu e^2/r_{\rm e}^2$$
 (4)

Then eq 2 for correlating ionic polarizabilities between

- (16) V. V. Mitskevich, Soviet Phys.-Solid State, 6, 557 (1964).
- (17) G. Burns and C. G. Wikner, Phys. Rev., 121, 155 (1961).
- (18) J. Yamashita, J. Phys. Soc. Jap., 7, 284 (1952).

(19) The model was originally developed as an intuitive extension of an earlier, moderately successful, empirical model proposed by one of us in which the polarizabilities of "individual" ions in a crystal were represented by equations of the form $\alpha_i = \alpha_i^{\circ} (1 - k_i \alpha_i^{0} / r_e^{3})$ where k_i is an empirical constant, α_i° is the free-ion polarizability and r_e is the shortest anion-cation distance in the equilibrium crystal (see ref 20a). The arguments given above were developed in response to the critical comments of a referee whose identity is not known to us but for whose stimulus we are grateful.

(20) (a) Quarterly Progress Reports, ARPA Contract No. DA-31-124-ARO(D)-54, Shell Development Co., 1965–1966, administered by the U.S. Army Research Office, Durham, N. C.; (b) J. N. Wilson, J. Chem. Phys., 43, 2564 (1965); (c) See review of methods by A. Dalgarno, Advan. Phys., 79, 281 (1962).

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$$\ln \alpha_i = \ln \alpha_i^0 - k_i \mu e^2 / r_e^2 \qquad (5)$$

or

$$\log \alpha_i = \log \alpha_i^0 - b/r_e^2 \qquad (6)$$

We have ignored the difference between the compressive forces acting on ions of differing "size."

Application to Alkali Halides with the Sodium Chloride Structure. To test eq 6 we have used the available data for the polarizabilities per ion pair in the crystalline alkali halides, extrapolated to infinite wavelength. The values that we have chosen are listed in Table I where they are compared with the values assigned by previous authors.

Our polarizabilities were calculated from selected refractive index data from the literature by means of the Clausius-Mosotti equation, based on the Lorentz-Lorenz internal field. We did not apply the corrections for overlap suggested by Theimer and Paul;²¹ these corrections are difficult to estimate accurately and in any case are appreciable only for salts composed of a small cation and a large, highly polarizable anion. The molar volumes V_m used in our calculations were based on recent determinations of the unit cell dimensions. In several cases where adequate dispersion data were available, we obtained α_{∞} by the conventional extrapolation against $1/\lambda^2$. These values of α_{∞} agreed within ± 0.002 with those given by Pirenne and Kartheuser²² (PK) provided their values are corrected to the same $V_{\rm m}$ used by us. In their revision of the earlier compilation by Tessman, et al.,13 PK made use of more recent dispersion data but retained Wyckoff's^{23a} earlier X-ray values for V_m which differ significantly from his more recent selections. Both the corrected and uncorrected values from PK are given in Table I. In choosing an acceptable value of α_{∞} we have made use also of the values given for $\alpha_D - \alpha_\infty$ by Bauer and Fajans.¹⁰ In some cases where dispersion data of adequate reliability appeared to be missing, we estimated $\alpha_{\rm D} - \alpha_{\infty}$ by interpolation or extrapolation on empirical plots of $\alpha_{\rm D} - \alpha_{\infty}$ for series of salts with a common anion against suitable parameters such as the estimated polarizability of the free cation. Some of the values of α_{∞} in Table I are given to three decimals. This should be regarded as a measure of internal consistency only, since we found that the use of more elaborate dispersion relations^{23b} leads to variations as large as ± 0.02 Å³. We have not been able to find reliable data²⁴ for the refractive indices of the unstable NaCl structures of CsCl, CsBr, or CsI.

Model I. Constant Cation Polarizability. As a first approximation, it was assumed that the polarizabilities of Li⁺ and of Na⁺ remain constant at their well-known vacuum values³ of 0.0283 and 0.148 Å³, respectively. Equation 6 was then applied to the data of Table I in the following way: in each of the lithium and sodium salts the polarizability of the halide ion was obtained by subtracting the polarizability of the cation, assumed to be constant, from the polarizability per ion pair of the salt. These anion polarizabilities were extrapolated by means of eq 6 to the values of r_e^{-2} for the corresponding potassium salts, and the polarizability of the potassium ion was obtained for each salt by difference. The values obtained for $\alpha(K^+)$ ranged from 0.75 to 0.84 Å³ with no obvious trend with r_e^{-2} ; it was therefore assumed that $\alpha(K^+)$ was approximately independent of r_e^{-2} . The average value was 0.787 Å³ with an average deviation of 0.024 Å³; this value was used to obtain $\alpha(X^{-})$ at the values of r_e^{-2} obtaining in the potassium salts. These values were used together with those obtained from the lithium and sodium salts to extrapolate to r_e^{-2} for the rubidium salts. The values of $\alpha(Rb^+)$ obtained as before ranged from 1.31 to 1.36, and again showed no systematic trend with r_e^{-2} ; the values obtained from the fluoride and iodide salts were almost identical. The average value for $\alpha(Rb^+)$, 1.328 Å³ with an average deviation of 0.015 Å³, was then used as before to obtain $\alpha(Cs^+)$ in CsF. Here the value obtained was 2.31 Å³. The logarithmic slopes and intercepts were calculated from the mean of the points derived for the Li⁺ and Na⁺ salts and the mean of those for K^+ and Rb^+ . The results obtained are presented in Table II together with those from a variant of this treatment (Model II). The precision with which the parameters are given is not physically significant but is required in order to interpolate the data for the crystals in a consistent way. The fit of the values obtained for the halide ions to eq 6 is shown graphically in Figure 1 and compared there with the approximate theoretical values calculated by Ruffa.¹⁵

The simple model is remarkably successful. As shown later, it correlates the experimental values for the polarizabilities of the alkali halide crystals extremely well. In addition, as shown in Table III, it leads to freeion values for the polarizabilities of K⁺, Rb⁺, and Cs⁺ which are in quite respectable agreement with the most reliable independent estimates for these quantities by the Meyers,²⁵ Risberg,²⁶ and Street.²⁷

- (21) O. Theimer and R. Paul, J. Appl. Phys., 36, 3678 (1965).
- (22) J. Pirenne and E. Kartheuser, *Physics*, **30**, 2005 (1964); **31**, 284 (1965).
- (23) (a) R. W. G. Wyckoff, "Crystal Structures," Interscience, New York, N. Y., 1948. (b) Landolt-Börnstein Tables, 6th ed, Vol. II, part 8, Springer-Verlag, Berlin, 1962, pp 2–415.
- (24) The literature values of α for the NaCl structures of CsCl, CsBr, and CsI all appear to be based on a correlation with density suggested by Spangenberg⁷ on the basis of his belief that the sample of CsF studied by him (n = 1.578) had the CsCl structure and that the lower value reported by Merwin (J. Wash. Acad. Sci., 12, 248 (1922)) of $n_{\rm D} = 1.478$ must have been for the NaCl structure. On the other hand, Weir and Pirami (J. Res. NBS 68A, 105 (1964)) claim the first observation of the CsCl phase of CsF.
- (25) J. E. Meyers and M. Goeppert-Mayer, *Phys. Rev.*, 43, 605 (1933). Their method, based on an analysis of the deviations of the higher spectral term values of the alkali metal atoms from agreement with a hydrogenic model, is the basis for more recent estimates by Edlén and his associates.
- (26) P. Risberg, Arkiv Fysik, 10, 583 (1956).
- (27) K. Street, private communication.

Ion	Model I	Model II	Model I	-Slope, 0"	Buffab	Ion	Model I	A ^a	Madel J	e, Ca
101	Model 1	Model II	Model 1	Model II	Runa	101	Model I	Model 11	Model 1	Model II
						Li +	(0.0283)°	(0.0283) ^c	(0)	(0.160)
F-	1.830	1.556	1.306	0.999	0.88	Na ⁺	(0.148)	(0.148)	(0)	0.116
Cl-	4.670	4.407	1.378	1.209	1.18	\mathbf{K}^+	0.787	(0.0811)	0	0.082
Br-	6.126	5.842	1.404	1.225	0.95	Rb+	1.328	1.37(0)	0	0.047
I-	9.160	8.910	1.743	1.645	0.80	Cs+	2.31	2.45ª	(0)	(0.02)

Table II: Parameters for Polarizabilities of Alkali Halide Ions

It is also reassuring (Figure 1) that the approximate theoretical values derived by Ruffa¹⁵ for the polarizabilities of the anions conform reasonably well to eq 6 and the slopes of the relation between his values of log α and r_e^{-2} are not grossly different (Figure 1) from those obtained in our empirical fit to the present model. This implies that eq 6 is a reasonable empirical description of the interactions invoked by Ruffa to account for the decrease in the polarizabilities of the halide ions in crystals. To be sure, the intercepts of the lines representing Ruffa's theoretical points fall considerably lower than ours, but this is a consequence of the fact that Ruffa¹⁵ assumed Pauling's values¹² for the polarizabili-



Figure 1. Anion polarizability, dependence on interionic distance in equilibrium alkali halide crystal.

ties of the isolated halide ions in his perturbation theory kind of calculation. However, the intercepts from Ruffa's points come reasonably close to the Pauling estimates only for F^- and Cl^- , as shown in Figure 1.

The values obtained for the free-ion polarizabilities of the anions by our admittedly long extrapolation (Figure 1) to infinite separation are considerably higher than the widely accepted values proposed many years ago by Pauling.¹² These high values gain some support from the suggestions by several authors^{28,29} that the dipoledipole van der Waals coefficients for the cesium salts should be considerably higher than those evaluated from the usually accepted polarizabilities. More significantly, our extrapolated values are in reasonable agreement (except for F⁻) with those recommended on quite independent grounds by Street.²⁷ The polarizabilities α_0 obtained for the free ions from our model are compared in Table III with those proposed by a number of previous authors.

It should be mentioned that polarizabilities calculated for the fluoride ion by Hajj³⁰ from optical absorption coefficients in the crystalline alkali salts are not in agreement with those proposed here. The analysis used by Hajj follows one proposed earlier by Mayer.³¹ This analysis, however, encounters several difficulties of which the major one is that as excitation energy increases, the excited states of alkali halide crystals become to an increasing extent communal properties of the constituents of the unit cell; in qualitative terms, the excitation energy of the halide ion is increasingly perturbed by the possibility of electron transfer to the cation. When plotted after the manner of Figure 1. log $\alpha(F^{-})$ from the calculations of Hajj increases very steeply with decreasing values of r_e^{-2} and extrapolates to an unreasonably high value of α_0 ; for the heavier halide ions, his calculated polarizabilities vary in ar. irregular way with the atomic number of the cation.

In spite of the encouraging aspects of the results ob-

- (28) A. May, Phys. Rev., 52, 339 (1937); 54, 629 (1938).
- (29) M. Chandra and B. Sharan, Proc. Phys. Soc., 91, 257 (1967).
- (30) F. Hajj, J. Chem. Phys., 44, 4618 (1966).
- (31) J. E. Mayer, *ibid.*, 1, 270 (1933).

Ion	Model I	is work ^a Model II	Ref 3, 26	Ref 27	Ref 11	Ref 12	Ref 25	Ref 16	Theory ^b
Li+	(0.0283)	(0.0283)	0.0283		0.032		0.025	0.03	$0.0280,^{\circ}$ $0.0281-0.0286^{\circ}$
Na ⁺	(0.148)	(0.148)	0.148		0.195	0.181	0.17	0.17	$0.140;^{c,d}$ $0.145-0.152^{g}$
K+ Rb+ Cs+	$0.79 \\ 1.33 \\ 2.31$	(0.811) 1.37 2.45-2.42	0.811	1.35	$0.89 \\ 1.48 \\ 2.54$	0.840 1.413 2.44	$0.80 \\ 1.5 \pm 0.3 \\ 2.35$	0.9	0. 7 89 ^e
F-	1.83	1.56		1.62	0.95	1.05	1.00	1.4	$1.31;^{f}$ 1.56; ^{σ} 1.40; ^{d} 1.2-1.8 ^{g}
Cl- Br- I-	4.67 6.13 9.16	4.41 5.84 8.91		5.1 6.4–6.9 10.0–10.5	3.48 4.82 7.22	3.69 4.81 7.16		4.6	$3.76;^{e}5.0-6.2^{g}$

Table III: Comparison of Free-Ion Polarizabilities from Various Sources

^a Assumed values in parentheses. ^b Recent quantum mechanical calculations by indicated authors. ^c H. D. Cohen, ref 4. ^d J. Lahiri and A. Mukherji, *Phys. Rev.*, 155, 24 (1967). ['] G. Burns and C. G. Wikner, ref 17. ^eA. Dalgarno, *Advan. Phys.*, 11, 281 (1962); a review of the theory and of results of earlier calculations.

tained with Model I, there are at least two respects in which these results are inadequate. First, the extrapolated value of α° for the fluoride ion is appreciably higher than the most recent theoretical estimates.^{4,6} Second, as will be shown later, the dependence of the polarizability on compression of the crystals, as predicted by Model I, is considerably higher than that given by experiment. Both of these discrepancies are probably consequent to the assumption that the polarizabilities of Li⁺ and Na⁺ remain unchanged when the ions enter the crystal from free space.

Model II. Variable Cation Polarizability. In view of the considerations summarized in the Introduction to this paper, it is very likely that the polarizabilities of the alkali cations are larger in ionic crystals than in free space. The magnitude of the increase is far from certain, however, since the increase resulting from electrostatic effects is opposed by the repulsive interactions with neighboring ions.

The approximation proposed by Ruffa¹⁵ for the polarizability α_c^+ of a cation in a crystal can be written in the form

$$\alpha_0^{+}/\alpha_c^{+} = (1 - 2.434 \alpha_0^{1/2}/n^{1/2}r_e)^2$$
(7)

where α_0^+ is the free-ion polarizability, *n* is the total number of electrons in the ion, and r_e is the near-neighbor anion-cation distance. We have used this expression to calculate cation polarizabilities in the alkali halides on the basis of the spectroscopic estimates^{3,26,27} of the free-ion polarizabilities rather than the Pauling estimates¹² used by Ruffa. The resulting values for K⁺, Rb⁺, and Cs⁺, though smaller than Ruffa's, appeared still to be much too large on the basis of the values obtained by difference for the polarizabilities of the anions in the crystals. Thus, for example in the fluorides, the resulting value of $\alpha(F^-)$ increased as expected from LiF to NaF but then declined through the salts of K⁺ and $\mathrm{Rb^{+}}$ to the unreasonably low value of 0.23 Å³ in CsF. It therefore appeared likely that eq 7 overestimates also the polarizabilities of Li⁺ and Na⁺ in their salts.

In the "bootstrap" procedure described below, we have assumed that the functional form of eq 7 provides a reasonable approximation for interpolation or extrapolation with respect to $r_{\rm e}$, but have used it for this purpose in the following empirical form, in which C_i is a constant characteristic of the *i*th cation

$$(\alpha_0/\alpha_c)_{+}^{1/2} = 1 - C_i/r_e \tag{8}$$

For the range of values of C_i which we found useful to describe the experimental data, eq 8 is very closely approximated by

$$\alpha_{\rm c}^{+} = \alpha_{\rm 0}^{+} \exp(2C/r_{\rm e}) \tag{9}$$

which is somewhat analogous to eq 5 and 6. We then took as a starting point the revised Ruffa estimates from eq 7 for the polarizabilities of Li⁺ and Na⁺ in the chlorides (0.036 and 0.184 Å³, respectively). This choice was made because the accuracy of Ruffa's approximation should be highest for these small ions and errors in their relatively small polarizabilities should cause relatively small errors in the anion polarizabilities obtained by difference. The alkali chlorides, moreover, have moderately large values of α_{∞} whose magnitudes have been estimated (Table I) with relatively high precision.

From this starting point, values of $\alpha(\text{Cl}^-)$ were obtained by difference and extrapolated by means of eq 6 to r_e^{-2} for KCl. Then $\alpha(\text{K}^+)$ was obtained by difference and extrapolated by means of eq 8 to r_e^{-1} for KF. The resulting value, 0.844 Å³, though appreciably higher than the value 0.811 taken for α_0 , is much lower than has been estimated by either Ruffa¹⁵ or Mitskevich.¹⁶ Values of $\alpha(\text{F}^-)$ were then obtained in KF using this value of $\alpha(\text{K}^+)$ and in LiF using the revised Ruffa value

for Li⁺. These values were interpolated by means of eq 6 to obtain $\alpha(F^{-})$ in NaF. The value then obtained for $\alpha(Na^+)$ by difference was larger than the free-ion value but again smaller than estimated by Ruffa or by Mitskevich. This value for Na⁺ was then interpolated by means of eq 8 to a lower value than the starting one for $\alpha(Na^+)$ in NaCl and the entire process was recycled. After several cycles, the constant C in eq 8 appeared to be converging for K^+ and Na^+ to values that were smaller than the theoretical (Ruffa) values by factors of about 0.2 and 0.4, respectively; the final cycle was then made setting the constant C for Li⁺ arbitrarily to 0.6 times its calculated value. This change, which had an appreciable influence on the final result only for the fluorides, was made on the basis that even the lithium ion experiences appreciable overlap with the electron distributions of neighboring anions, especially in the fluoride and chloride.

The parameters thus obtained for Li⁺, Na⁺, and K⁺ were found to lead to an excellent representation of the bromide and iodide ions in conformity with eq 6. Polarizabilities for all the halide ions were then extrapolated to obtain $\alpha(Rb^+)$ by difference; within experimental error the result was consistent with eq 8, though the proper choice of α_0 was somewhat uncertain. Estimation of α_0 for the halide ions by means of eq 6 was then carried out with the use of all of the parameters assigned to the cations. The final result of this process is displayed in Table II for comparison with the results from Model I and in Table III for comparison with other estimates of α_0 . The values obtained for Rb⁺ and Cs⁺ are still in reasonable agreement with the recent estimates by Street²⁷ and the early ones by the Meyers,²⁵ but the values obtained for the halide ions are appreciably lower than before, especially in the case of fluoride. The latter value is only slightly lower than the isoelectronic extrapolation value estimated by Street.²⁷ The *a priori* calculation of atomic or ionic polarizabilities by quantum mechanical methods is notoriously difficult,^{20c} especially for systems bearing one or more loosely bound electrons. Most of the methods used by earlier workers gave results that were systematically too high. The methods used recently by Cohen⁴ and by Lahiri and Mukherji⁵ (LM), on the other hand, give results that tend to be systematically low. The values calculated by these two sets of authors are in excellent agreement with each other for Mg^{2+} , Na⁺, and Ne. In comparison with the values estimated from spectroscopic data for the cations and the experimental value for Ne, their calculated values are low by 0.6% for Mg²⁺, 5.6% for Na⁺, and 12.6% for Ne. It is therefore conceivable that even Cohen's calculated value for $\alpha(F^{-})$, which agrees precisely with our extrapolated value (Model II) is too low. Similarly, the polarizabilities calculated⁵ by LM are low by 2.7%for K^+ and by 8.5% for Ar; their value for Cl^- is lower than our extrapolated value (Model II) by 15%.

It is interesting to compare (Table II) the logarithmic slopes b, obtained by fitting the polarizabilities calculated by Ruffa¹⁵ to our eq 6, with those obtained from Model II. The Ruffa slope is in fair agreement with our empirical one for the chloride ion, but for all other anions it is appreciably lower. This is especially marked in the case of the relatively large iodide ion. It may be possible to use the empirical slopes to reevaluate some of the parameters that enter Ruffa's theory.

The slopes C, defined by eq 8 of Model II, are observed to decrease systematically as the atomic number of the cation increases (Table II). According to eq 7, however, these slopes should be nearly equal for Li⁺ and Na⁺, and those for K⁺, Rb⁺, and Cs⁺ should be comparable to each other but about 65% larger. The observed behavior can be rationalized on the basis of Model II as the result of a competition between the electrostatic enhancement of α^+ , as represented by eq 7, and the compressive reduction of α^+ which increases as α_0^+ increases.

Relation between Polarizabilities and Radii. A comparison is shown in Table IV between our values of α_0 for the anions and the cube of the ionic radii recently proposed by Morris³² on the basis of the electron density distribution in sodium chloride and by Ladd³³ on the basis that anion contact determines the lattice spacing in lithium iodide. The almost precise agreement for the three lightest halide ions with the cube of the Morris radii is astonishing, especially in view of the fact that the radii apply to the packing in a crystal whereas α_0 is obtained from an extrapolation to infinite separation. Nevertheless, the results shown in Table IV are gratifingly consistent with our model. As is shown in Figure 2, the polarizabilities of the cations and of the noble gases show a different behavior in accordance with expectation. Even so, the departures from linearity in the relation between $\alpha_0^{1/2}$ and r are surprisingly small. The curve for the noble gases is shifted to a position between the two ionic curves if high-temperature collision radii are used instead of crystal radii.

Table IV: Comparison of Free-Anion Polarizabilities and Ionic Radii Cubed $(\hat{\mathbb{A}}^s)$

Anion	αι, This work, Model II	Morris ³²	Ladd ³³
\mathbf{F}^{-}	1.56	1.56	1.68
Cl-	4.41	4.41	4.91
Br-	5.84	5.83	6.54
I -	8.91	8.49	9.53

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Comparison with Experiment. (a) Correlation of Experimental Crystal Polarizabilities. A comparison is shown in Table V between the experimental polarizabilities of the alkali halide crystals and those predicted by means of the present Models I and II. Both models correlate the data reasonably well. Despite its larger number of empirical parameters (13 vs. 10), Model II does not provide an appreciably better fit than Model I except for the fluorices, where its success is dramatic. The standard deviation obtained from Model II, basis $\Delta \alpha / \alpha$, is 0.37% and the maximum deviation is 0.91%; this can be compared with similar values of 2.8 and 4.8% for the correlation of TKS¹³ (for values of α_D) as revised by Pirenne and Kartheuser²² (lithium salts excluded) and with 1.2 and 1.6% for the empirical correlation proposed by the latter authors²² for all but the lithium salts; their model assigns an empirical additive polarizability to each ion and uses one additional "interaction" parameter to account for environmental effects.

 Table V:
 Comparison of Experimental and Calculated

 Polarizabilities of Alkali Halide Crystals

	Po	olarizabilitie	s, Å ³ of Sa	.lts,
Cation	F -	Cl-	Br -	I -
Li ⁺ , Exptl	0.915	2.905	4.02	5.90
Model I	0.900	2.917	4.023	5.901
Model II	0.915	2.924	4.057	5.890
Na+, Exptl	1.178	3.283	4.42	6.35
Model I	1.193	3.282	4.411	6.393
Model II	1.178	3.267	4.419	6.368
K÷, Exptl	1.992	4.173	5.33	7.44
Model I	1.988	4.177	5.339	7.428
Model II	1.990	4.182	5.363	7.429
Rb ⁺ , Exptl	2.582	4.81	6.01	8.12
Model I	2.585	4.812	5.993	8.128
Model II	2.582	4.818	6.015	8.132

(b) Change in Polarizability on Compression. The volume dependence $d\alpha/dV$ of the polarizability of a cubic crystal can be derived from the change in refractive index on uniform compression; correction must be made for the simultaneous change in density. Less accurate values can be derived from the photoelastic constants which describe the birefringence resulting from mechanical distortion; the interpretation of these measurements is subject to some uncertainty because the departure of the distorted crystal from cubic symmetry may require a different expression for the internal field than that implied by the Clausius-Mosotti equation. To start with, it may be noted that the basic assumption underlying our model (comparability between ionic volume and polarizability) implies that $(V/\alpha)(d\alpha/dV)$ should be of order of magnitude unity, as indeed it is. We have attempted to derive values of $(V/\alpha)(d\alpha/dV)$ from the simple



Figure 2. Relation between free-ion or atom polarizability and the Morris ionic radii³² or the noble gas crystal radii.

model described by eq 1 to 5. It is not proper to differentiate eq 6 directly, since that equation is valid only for the unstressed equilibrium crystal. Instead we write, from eq 2

$$d \ln \alpha_i^{-}/dr = - k dF/dr = kR^{\prime\prime}(r)$$
(10)

Thermodynamically, to the same approximation as before (neglect of thermal components of the lattice free energy)

$$18 r_{\rm e}/\beta_0 = U^{\prime\prime}(r_{\rm e}) = -2\mu e^2/r_{\rm e}^3 + R^{\prime\prime}(r_{\rm e}) \quad (11)$$

where β_0 is the compressibility of the uncompressed crystal and μ , as before, is the Madelung constant. Thus

$$(d \ln \alpha/dr)r_{\rm e} = k(18 r_{\rm e}/\beta_0 + 2 \mu e^2/r_{\rm e}^3) \qquad (12)$$

For the crystal as a whole we may write

$$\frac{V}{\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}V} = \frac{r_{\mathrm{e}}}{3\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}r_{\mathrm{e}}} = \frac{r_{\mathrm{e}}}{3\alpha}\left[\alpha_{-}\left(\frac{\mathrm{d}\ln\alpha_{-}}{\mathrm{d}r}\right)_{r_{\mathrm{e}}} + \left(\frac{\mathrm{d}\alpha_{+}}{\mathrm{d}r}\right)_{r_{\mathrm{e}}}\right]$$
(13)

and we can obtain a value for $d\alpha^+/dr_e$ from eq 8

$$\frac{\mathrm{d}\alpha_{+}}{\mathrm{d}r_{\mathrm{e}}} = -\frac{2C\alpha_{+}}{r_{\mathrm{e}}^{2}} \left(\frac{\alpha_{\mathrm{e}}}{\alpha_{0}}\right)_{+}^{1/2} \tag{14}$$

Thus we obtain

$$(V/\alpha)(\mathrm{d}\alpha/\mathrm{d}V) = [(2.303 \, b\alpha_{-})/3\alpha](18 \, r_{\mathrm{e}}^2/\mu_{\mathrm{e}}^2\beta_0 + 2/r_{\mathrm{e}}^2) - (2 \, C\alpha^{+})/3 \, r_{\mathrm{e}}\alpha(1 - Cr_{\mathrm{e}}^{-1})^3$$
(15)

where α is the polarizability per ion pair of the crystal and the coefficients *b* and *C* are given in Table II. The predictions of eq 15 are compared with experimental data³⁴⁻³⁷ in Table VI.

Salt	LiF	NaCl	KCI	KBr	KI	RbCl	RbBr	RbI
β_0 , cm ² /dyn $\times 10^{12^{a}}$	1.529	4.260	5.744	6.844	8.62	6.55	7.72	9.52
α [–] , ų, Model I	0.872	3.134	3.390	4.552	6.641	3.48	4.66	6.80
Model II	0.882	3.091	3.319	4.491	6.575	3.409	4.608	6.727
$18 \ r_{\rm e}^2/\mu e^2 \beta$, A ⁻²	1.172	0.834	0.771	0.711	0.646	0.720	0.688	0.635
$2/r_{e}^{2}$, Å ⁻²	0.495	0.252	0.202	0.184	0.160	0.185	0.169	0.149
$(V/\alpha) d\alpha/dV$, calcd I	1.59	1.09	0.834	0.825	1.253	0.689	0.713	0.959
Model II	1.22	0.949	0.688	0.677	0.878	0.588	0.610	0.889
Exptl (Na D line)	0.99^{b}	0.558	0.58°	0.44 ⁶	0.41°	0.43^{d}	0.40^{d}	0.47^{d}
	0.71 ^e	0.62°	0.49 ^e	0.49 ^e				
Ratio theory (Model II)/exptl	1.23	1.61	1.25	1.54	2.14	1.37	1.53	1.89

Table VI: Test of Predicted Dependence of Polarizability on Volume

^a Taken from an unpublished critical compilation by one of us (RMC).^{20a} ^b Calculated from the data of Waxler and Weir³⁴ but using the Clausius-Mosotti equation to convert refractive index to polarizability. ^c Calculated from photoelastic constants tabulated by Krishnan.³⁵ ^d Calculated from data of Bansigir.³⁷ ^c Calculated from data of Iyengar.³⁶

Though it is gratifying that the calculated value of d ln α /d ln V agrees in order of magnitude with experiment and that the trends in the data are reproduced fairly well, the quantitative agreement is disappointing. Nevertheless, we are aware of no alternative theory that fits the data better. Model II comes closer to agreement than Model I. Among the possible sources of error, neglect of the thermal components of the lattice free energy cannot be important since these depend only slightly on volume. From the data given by Iyengar³⁶ we estimate that extrapolation of d ln α /d ln V from the wavelength of the sodium D line to infinite wavelength will increase the disagreement slightly, rather than decrease it. It seems plausible that the major source of error is neglect of the London terms in the lattice energy U. Though these make only a minor contribution to U, they contribute appreciably to U' and even more strongly to U''. Indeed, it will be noticed that the disagreement for the potassium and rubidium salts tends to increase systematically with increasing polarizability of the anion. An attempt was made to modify the treatment to take account cf the influence of the first London term in an approximate way, but the result obtained for KCl was worse rather than better. The modified treatment will not be given here since it is tedious and approximate, though straightforward. One conclusion from this treatment that may be of general interest, however, is that the significance of the empirical constant b in eq 6 is more complicated than eq 1-5 imply. In the modified treatment, the original definition of $b = k\mu e^2/2.303$ is multiplied by the average value of a complicated expression of the form

$$1 + 6C_6/\mu_e^2 r_e^5 - \text{higher terms}$$
(16)

where C_6 , the first London coefficient, is defined later and the average is taken over all of the alkali salts formed by a given halide ion. The higher terms involve not only the polarizabilities but also derivatives of them and of C_6 with respect to r.

Discussion

Despite its flimsy theoretical foundation, the correlation scheme proposed here has a number of attractive features. It leads to a simple empirical representation of the results of Ruffa's calculations for anions; it provides in both of its versions an accurate correlation of the polarizabilities of the alkali halide crystals; and, in one of its versions (Model II), it leads to new estimates that appear to be quite reasonable for the polarizabilities of the free anions. It also provides at least an approximate representation for the effect of compression on the polarizability of alkali halide crystals. Curiously, we find that values of $\alpha(x^{-})$ calculated by means of the Rittner³⁸ electrostatic model from the equilibrium interatomic distance and the dissociation energy of the alkali halide gas-phase molecules fit accurately on our empirical curves for the Li⁺ salts. The agreement is fair for the Na⁺ and K⁺ salts but poor for the Rb⁺ and Cs⁺ salts.

The present model has interesting implications for calculating the contribution of the London terms to the lattice energy of the alkali halides. For the alkali halides, the coefficient C_6 of the first London term, $-C_6/r_e^6$, may be written³⁹

$$C_6 = 6.595a_{12} + 0.9034(a_{11} + a_{22}) \tag{17}$$

where a_{12} is the London coefficient for the interaction of an anion-cation pair. This expression takes no account of three-body and higher interactions, which are now believed to be significant. For our present purposes, however, we shall neglect them. It has been shown by

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one of us^{20b} that for the London interactions among rare gas atoms the coefficient a_{12} is very well approximated by the Slater-Kirkwood equation

$$a_{12} = 2.517 \times 10^{-23} \alpha_1 \alpha_2 / [(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}] \text{ erg cm}^6 \quad (18)$$

provided empirical values are used for N_1 and N_2 , the effective number of electrons on each atom. These numbers are 1.5, 3.8, 5.7, 6.5, and 6.5 for He, Ne, Ar, Kr, and Xe, respectively. We shall assume that the same numbers apply to the isoelectronic ions.

The principal difficulty in applying eq 18 is that the polarizabilities α depend on the interionic distance. Thus we must write for the first London pairwise interaction L_{ii} between like ions *i*, at interion distance *r*

$$L_{ii} = 2.517 \times 10^{-23} N_i^{1/2} \times 3 \int_r^\infty \alpha_i^{3/2}(r) r^{-7} dr \quad (19)$$

In order to evaluate expressions of the form of eq 19 we must know the dependence of the polarizabilities of the interacting ions on distance at all separations. Our representation of this dependence in eq 6, 8, or 9 is valid only in the vicinity of $r_{\rm e}$.

If we were to take our model at face value, we would apply eq 2 and use for the repulsive potential R_{ii} an expression of the form $A_{ij} \exp(-r_{ij}/\rho)$. It was shown by Born and Mayer¹⁴ that a reasonable approximation to R_{ii} in the alkali halides can be obtained by setting the parameter $\rho = 0.345$ Å in all cases. Though it is now reasonably certain that a better approximation can be achieved with variable ρ , we shall accept this approximation for our present purposes. This approach leads to the approximation

$$\alpha_{t} = \alpha_{0t} \left[1 - B_{ij} \exp(-r_{ij}/\rho) + 0.5 B_{ij}^{2} \exp(-2r_{ij}/\rho) - \text{etc.} \right] \quad (20)$$

where the parameter $B_{ij} = k_i A_{ij} / \rho$ can be determined from the value of α/α_0 in the equilibrium crystal. Thus in KCl, $B \simeq 2.5 \times 10^3$ whereas in RbBr, $B \simeq 5.2 \times 10^3$. In both cases the term in B^2 is small compared to the term in B. As might be expected from the steep dependence of eq 20 on r in the vicinity of $r_{\rm e}$, exploratory calculations of the coefficients a_{ij} with this expression lead to values only slightly lower (order of magnitude, 10%) than those that are obtained by substituting the free-ion polarizabilities α_0 in eq 18.

The difficulty with this treatment, however, is that it takes no account of the long-range electrostatic effects on α as treated by Ruffa.¹⁵ These must certainly dominate at values of r much larger than $r_{\rm e}$. The analog of eq 7, when applied to the anions, overestimates the decrease of the anion polarizabilities between vacuum and crystal. Indeed, as Ruffa has pointed out,¹⁵ the anions require a different treatment than the cations. Unfortunately, his equation for the polarizability of the anions in a crystal (eq 4.6 of his paper) cannot be extrapolated to large ionic separations. The development of a more general treatment poses a significant challenge to the theoreticians.⁴⁰

Finally, a comment should be made about the longestablished fact that the polarizability per ion pair of the alkali halides in aqueous solution is not very different from the corresponding quantity in the crystal. This implies that the halide ions and the heavier alkali ions are subject to a compression in aqueous solution that is comparable to that which they experience in the crystal. Indeed, this notion is consistent with the fact that the enthalpy of solution of an ionic crystal is small in comparison with its lattice energy. To be sure, the comparison is complicated by the decrease in the polarizability of the water molecules in the first coordination sphere of the ions, and especially in that of the small cations.⁹ A more meaningful comparison may be that the difference in polarizability between the chlorides and iodides in aqueous solution^{9,41} is 3.7 Å³, whereas in the alkali halides with the sodium chloride structure (Table I) it ranges from 3.0 to 3.3 Å³. The difference in our estimated values of α_0 (Model II) is 4.5 Å³.

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(40) We have noticed that an expression of the form

$$\alpha_0/\alpha_c = [(\mu - 1)e^2/r + E_1]^2/E_1^2$$

accounts for a large fraction of the apparent decrease in anion polarizability between the free ion and the crystal in NaF and NaCl, but only a relatively small fraction in the case of NaBr or NaI. This expression is similar in form to that proposed by Ruffa¹⁶ for anions, though it differs in detail. Its advantage is that it behaves properly at infinite separation. E_1 is the effective excitation energy of the free anion as defined by Ruffa¹⁶ in terms of its polarizability and the number of electrons. We suggest that an approximate calculation of the first London energy may be based on an expression for α - which is the product of two terms, one based on the expression given above and the other in the form of eq 20, again with B_{ij} chosen to fit the anion polarizability in the crystal.

A similar expression is suggested for α_+ , in which one term is based on eq 7 and the other has the form of eq 20.

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Interaction of Pyronine-G with Poly(styrenesulfonic acid)¹

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A spectrophotometric study of the interaction of poly(styrenesulfonic acid) and pyronine-G has allowed the identification of three different species for the bound dye which have been recognized as monomer, dimer, and aggregate dye molecules. The experimental distribution among the three species is in agreement with the distribution computed by a statistical method including first- and second-neighbor interactions.

The interaction between cationic dyes and biological polymers has been the subject of a very extended literature in the recent years. The binding of acridine dyes to DNA and polyribonucleotides has been particularly studied using several techniques which include dialysis equilibrium,² viscosity,^{3,4} optical spectrometry,^{2,5-9} induced optical rotation,¹⁰⁻¹² circular dichroism,^{13,14} fluorescence,^{4,15} X-ray on fibers,^{3,9} and low angle X-ray scattering.^{16,17} The great interest in the acridine dyes binding to polynucleotides is mainly due to the remarkable mutagenicity of acridines which can interfere in the replication of DNA by causing deletions or insertions of base pairs.¹⁸ As Bradley and Lifson recently pointed out,¹⁹ the accumulation of so much experimental knowledge has not yet allowed a unified picture of the binding process. On the other hand, the binding of dyes to synthetic polyelectrolytes has been generally neglected. Synthetic polyelectrolyte molecules are simpler systems and, to our opinion, the study of their interaction with dyes should give interesting information to help in approaching problems connected with biological polymers.

The main feature of the binding of a lot of cationic dyes to biopolymers is the so-called "methachromasia;"^{20,21} this effect was recognized as due to different binding modes of the dye molecules which can exhibit different absorption spectra in the visible region. The absorption bands show that the dye molecules bind as monomer, or they interact with each other on the polyelectrolyte molecule to form dimers or aggregates similar to those existing in concentrated aqueous solutions.^{22–25} Bradley and Wolf⁵ proposed a simple model which accounts for this behavior in terms of dilution of the dye molecules along the polymer chain.

The interaction of synthetic polyelectrolytes with methachromatic dyes is similar to that of biological polymers.^{26,27} The tendency of dye molecules to stack each other is much higher,^{26–29} and generally it is difficult to observe the spectrum of monomer bound dye. The Bradley and Wolf model does not apply satisfactorily in this case. The behavior of synthetic polyelectrolytes can be attributed to the higher flexibility of their chains^{5,26,28} with respect to

those of biopolymers. In this respect the poly(styrenesulfonic acid) has found more resemblance to DNA and to polyribonucleotides than to the synthetic electrolytes with a polyvinyl chain.^{26,28,25} The

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aim of this paper is to show the behavior of poly(styrenesulfonic acid) with a methachromatic dye very similar to the acridine orange.



Experimental Section

The pyronine-G (PG) hydrochloride, Fluka, was purified by dissolving the dye in methyl alcohol and precipitating with ether. The molar extinction coefficient of the monomer dye was found to be 46,500 at λ 550 m μ (ϵ 45,900 at $c = 10^{-5}$ mol/l., ϵ 45,600 at $c = 1.5 \times 10^{-5}$ mol/l.) and did not change by further purification. This value is higher than the value reported by Koizumi and Mataga.³⁰ Poly(styrenesulfonic acid) (PSSA) was obtained by sulfonation of polystyrene (Bios product, $\overline{M_v} = 160,000$), as already reported.³¹

Spectrophotometric measurements have been taken at room temperature with a Beckman DK-2 spectrophotometer. The measurements on PG at varying concentration (see Figure 1) have been taken in aqueous HCl solutions (0.001 mol/l.) to standardize the pH and the ionic strength; however, the dye spectra have been found not to vary in acid and neutral solutions. The stock solutions of the PG were found to be stable for weeks. The measurements with PSSA have been taken at constant dye concentration ($\sim 1.5 \times$



Figure 1. Molar extinction coefficients of pyronine-G in aqueous HCl solutions $(0.001 \ m)$: 1, extrapolated extinction coefficients of monomer dye; 2, dye concentration $1.486 \times 10^{-4} \text{ mol/l.}$; 3, dye concentration $4.406 \times 10^{-4} \text{ mol/l.}$; 4, dye concentration $9.18 \times 10^{-4} \text{ mol/l.}$; 5, dye concentration $18.36 \times 10^{-4} \text{ mol/l.}$; 6, dye concentration $25.9 \times 10^{-4} \text{ mol/l.}$; 7, limiting extinction coefficients of dimer dye.

 10^{-5} mol/l.) by mixing a concentrated PSSA solution containing the dye and a dye solution in distilled water. A dilution cell was used which allowed volume changes from 3 to 50 ml.

Results

Free Dye in Aqueous HCl Solutions. The behavior of PG in water is very similar to that of other methachromatic dyes well described in literature.²²⁻²⁵ Increasing the dye concentration, the optical extinction coefficients curves change, clearly showing an equilibrium between two species (Figure 1, curves 2, 3, and 4) with two well-defined isosbestic points and maxima at about 550 and 512 m μ . In agreement with the previously studied dyes an equilibrium between a monomeric (550-mu maximum) and a dimeric species $(512-m\mu \text{ maximum})$ may be assumed. At higher concentrations a shift appears in the maximum of the dimer (Figure 1, curves 5 and 6) toward lower wavelengths, and the isosbestic points disappear. This is due to the aggregation of the dye molecules. By extrapolating the data of several runs the spectrum of the monomer (Figure 1, curve 1) and the limiting spectrum of the dimer (Figure 1, curve 7) were drawn.

The equilibrium constant was estimated to be

$$K = \frac{2\alpha^2 c}{1 - \alpha} = 0.0012$$
 (1)

The agreement between experimental and calculated values of the extinction coefficients is good up to a concentration of about 5×10^{-4} mol/l. (see Figure 2). The value of the equilibrium constant is higher than



Figure 2. Comparison of experimental extinction coefficients of pyronine-G in aqueous HCl (0.001 m) solutions with the values computed through eq 1.

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Table I:	Optical Density Data of the Mixtures of Pyronine-G-Poly(styrenesulfonic acid) at Three
Significant	Wavelengths (Dye Concentration 1.45×10^{-5} mol/l.)

No.ª	P/D^b	$(P/D)_{c}^{c}$	$A_{exptl^{550}}d$	$A_{exptl^{560^6}}$	Acort	$A_{\mathrm{exptl}^{\delta 179}}$	A corr ^{617h}
1	0		0.660	0.	496	0.2	95
2	0.	.031	0.642	0.	480	0.2	91
3	0.	.062	0.615	0.	467	0.2	86
4	0.	. 093	0.581	0.	433	0.2	80
5	0.	.124	0.550	0.	415	0.2	74
6	0.	.155	0.508	0.	380	0.2	65
7	0.	.186	0.469	0.	353	0.2	56
8	0.	.217	0.432	0.	328	0.2	47
9	0.	.242	0.393	0.	305	0.2	38
10	0.	.278	0.359	0.	278	0.2	30
11	0.	.311	0.332	0.	247	0.2	21
12	0.	.340	0.294	0.	230	0.2	13
13	0.	.371	0.265	0.	204	0.2	07
14	0.	.402	0.244	0.	187	0.2	01
15	0.	432	0.220	0.	172	0.1	94
16	0.	496	0.190	0.	150	0.1	89
17	0.	555	0.169	0.	133	0.1	88
18	0.	616	0.155	0.	127	0.1	86
19	0.	739	0.137	0.	116	0.1	84
<i>i</i> 20	U.	1 075	0.127	0.115	107	0.100	
20	1,042	1.075	0.127	0.115	0.103	0.193	0.190
21	1.169	1,221	0.132	0.121	0.111	0.200	0.198
ι 00	1.340	1.372	0.140	0.124	0.115	0.017	0.205
22	1.492	1.020	0.142	0.137	0.129	0.217	0.210
20	2.09	9.11		0.152	0.140	0.230	0.200
24	2.08	2.11		0.170	0.109	0.2	-00 -62
26	2.40	2.40		0.100	0.104	0.2	79
20	2.58	3 74		0.211	0.209	0.2	77
28	4 46	4 40		0.221	0.220	0.2	78
29	5 20	5 23		0.272	0.202	0.2	78
30	5.94	5.97		0.286	0.285	0.2	77
31	7 41	7 44		0.310	0.309	0.2	74
32	8.88	8.90		0.330	0.329	0.2	70
33	11	1.80		0.	358	0.2	64
34	14	1.70		0.	380	0.2	59
35	19	9.00		0.	405	0.2	53
36	24	1.6		0.	429	0.248 0.245 0.243	48
37	31	1.5		0.	450		45
38	38	3.3		0.	468		43
39	47	7.6		0.	480	0.2	38
40	64	Ł.1		0.	502	0.2	31
j	15	5.2		0.	389	0.2	259
j	58	3.2		0.	492		• 1
j	120)		0.	518		
j	252	2		0.	536	0.2	18
j	14,100)		0.	548	0.2	15

^a Number corresponding to the graphs for Figure 3. ^b Ratio of polyelectrolyte to dye concentration (in the text the reverse D/P of this ratio has been used). ^c Corrected values of the ratios P/D including only the bound dye. ^d Experimental optical densities at the wavelength of the maximum absorption of monomeric free dye ($\lambda \sim 550 \text{ m}\mu$). ^e Experimental optical densities at the wavelength of the maximum absorption of monomeric free dye ($\lambda \sim 550 \text{ m}\mu$). ^e Corrected optical densities (see text) at $\lambda \sim 560 \text{ m}\mu$. ^e Experimental optical densities (see text) at $\lambda \sim 517 \text{ m}\mu$. ⁱ Spectral graphs not registered in Figure 1. ^j Data of a run not reported in Figure 3.

those of the similar dyes: acridine orange^{23,25,32} ($K = 1.08 \times 10^{-4}$) and methylene blue²⁴ ($K = 2.2 \times 10^{-4}$). The aggregation of dye in aqueous solution is a typical case of hydrophobic interactions;³³ the presence of oxygen in the PG molecule and its possibility to build

up specific interactions with the water molecules

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through hydrogen bonds should weaken these interactions and an increase of the K constant must be expected.

Polyelectrolyte-Pyronine Interaction. The methachromatic behavior of PG with polyelectrolytes has already been shown in the past.³⁰ The interaction with poly(styrenesulfonic acid) can be seen in Figure 3 where the absorption spectra of PG solution (1.45 \times 10⁻⁵ mol/l.) have been reported as a function of wavelength for various amounts of added PSSA; the concentration data are given in Table I.



Figure 3. Optical absorption spectra of PG $1.45 \times 10^{-5} M$ in presence of different amounts of poly(styrenesulfonic acid): A, excess of dye; D/P > 1; B, excess of PSSA, D/P < 1. The PSSA concentration data are given in Table I.

Increasing the polyelectrolyte concentration the graphs of Figure 3A show the gradual binding of the dye to the PSSA; the equilibrium between only two species (free and bound dye) is supported by the existence of isosbestic points. When the polyelectrolyte exceeds the dye amount (D/P < 1) the absorption spectra exhibit again the band of a monomer (Figure 3B) with a red shift of the maximum ($\lambda \sim 560$ m μ) as found for other dyes.^{5,26,27}

It is possible to titrate the ionized groups of PSSA using PG with an accuracy higher than 1% as it can be done with acridine orange and DNA.^{6,34} The appearance of the monomer dye has been attributed to the dilution of the dye over the polyelectrolyte molecule owing to the increased number of available binding sites. This effect has been very well discussed by Bradley and Wolf⁶ who studied the binding of acridine orange to a number of biological polymers including DNA. The Bradley and Wolf model, however, can be applied only to rigid polymers, and it was not found satisfactory for synthetic polyelectrolytes.³⁵

In this respect the behavior of PSSA is peculiar; the absorption band of the monomer bound dye ap-



Figure 4. Dialysis equilibrium experiments for mixtures of PG and PSSA; concentration of free dye outside the dialysis bags as a function of the D/P ratio inside the dialysis bags.

pears immediately under the D/P = 1 ratio and for D/P values of 0.05 to ~0.04 the dye exists mainly as monomer. The PSSA behaves very similarly to the DNA; and as in the case of DNA and acridine orange⁵ we may talk of a strong binding for the monomeric dye and a weak binding for the aggregate dye³⁶ (see Figure 4).

We suggest that the high stability of the monomeric bound dye can be due to the benzene side rings in the PSSA molecules which might promote some kind of dye intercalation similar to that proposed for acridine orange and DNA.³

Spectra B of Figure 3 show very clearly the dilution of the dye along the PSSA molecule: decreasing the D/P ratio we see the contemporary appearance of the monomer band at λ 560 m μ , and the shift of the maximum from \sim 505 to \sim 517 m μ ; no isosbestic points are present. In agreement with the behavior of PG in aqueous solutions (Figure 1) these spectra may be attributed to the gradual disappearance of aggregate dye in favor of the dimer and monomer forms. For D/P ratios lower than 0.25 to \sim 0.20 the probability of finding aggregates of more than two molecules becomes very small, and we see again an equilibrium between only two species: the monomer and the dimer with two quite well-defined isosbestic points at $\lambda \sim$ 527 m μ and $\lambda \sim$ 580 m μ .

The clear interpretation of the absorption spectra of Figure 3 B suggested trying to apply them a statistical treatment similar to that used by Bradley and Wolf.⁵ Recently, Lifson³⁷ published a very simple statistical mechanical method for computing the partition function of linear chain molecules easily applicable to the binding of dyes to linear chains.¹⁹ According to Lifson's treatment the partition function for such a

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⁽³⁵⁾ L. Costantino, V. Crescenzi, and V. Vitagliano, paper presented at the Tenth Meeting of the Italian Chemical Society, Padova, 1968.

⁽³⁶⁾ Some experiments of dialysis equilibrium have shown that for D/P ratios lower than 0.04–0.02, a negligible amount of dye can be detected outside the dialysis bags (see Figure 4).

system is obtained as the highest root of the equation

$$U(x)V(x) - 1 = 0$$
 (2)³⁵

where

$$U(x) = \sum_{i=1}^{\infty} q_0^{i} x^{-i} = q_0 / (x - q_0)$$
(3)

$$V(x) = q_{\mathbf{a}}\lambda_{\mathbf{a}}x^{-1} + q_{\mathbf{1}}q_{\mathbf{a}}^{2}\lambda_{\mathbf{a}}^{2}x^{-2} + \dots +$$

$$q_{m-1}\ldots q_1^{m-1}(q_{\mathbf{a}}\lambda_{\mathbf{a}})^m x^{-m} \sum_{j=m} (q_m q_{m-1}\ldots q_1 q_{\mathbf{a}}\lambda_{\mathbf{a}} x^{-1})^{j-m} \quad (4)$$

By assuming only first- and second-neighbor interactions, eq 4 reduces to

$$V(x) = \left[1 + \frac{q_{\mathbf{a}}\lambda_{\mathbf{a}}q_{1}}{x - q_{\mathbf{a}}\lambda_{\mathbf{a}}q_{1}q_{2}}\right]q_{\mathbf{a}}\lambda_{\mathbf{a}}x^{-1}$$
(5)

saying $v = q_a \lambda_a x^{-1}$, one obtains the following expression

$$v = \frac{q_2 + F_1(1 - q_2) - \sqrt{F_1^2(1 - q_2) + q_2F_1}}{q_1q_2^2 + q_1q_2F_1(1 - q_2)}$$
(6)

where $F_1 = X_1$ is the fraction of monomer dye bound to the polyelectrolyte chain

$$P/D = 1 + \frac{(1 - q_1q_2v)[1 + v(1 - q_1q_2) + v^2(q_1 - q_1q_2)]}{v[1 + 2(q_1 - q_1q_2)v - q_1q_2(q_1 - q_1q_2)v^2]}$$
(7)

For $q_2 = 1$, eq 7 reduces to eq 13 of ref 19, where $q_1 = k$ is the so-called staking coefficient.

The fractions of monomer and dimer dye are

$$X_{1} = F_{1} = (1 - q_{1}q_{2}v)^{2} / [1 + 2(q_{1} - q_{1}q_{2})v - q_{1}q_{2}(q_{1} - q_{1}q_{2})v^{2}]$$
(8a)

$$X_2 = 2F_2 = 2F_1 q_1 v \tag{8b}$$



Figure 5. Fraction of dimer as a function of the fraction of monomer for different values of the second-neighbor interaction parameter q_2 , computed through eq 6, 7, and 8.

The fraction of the dye molecules in the *m*th aggregate state³⁹ is (Figure 5)

$$X_m = mF_m = mF_1q_2^{m-2}(q_1v)^{m-1}$$
(9)

where, of course

$$\sum_{m=1}^{\infty} X_m = \sum_{m=1}^{\infty} m F_m = 1$$
 (10)

To apply Lifson's treatment to our data we had to make some simplifying assumptions. First, we corrected the experimental values of optical density for the presumed amount of free dye.⁴⁰ From the graphs of Figure 3A we assumed the following value for the optical density of aggregate bound dye at 550 m μ

$$E_3 = 0.110$$

This corresponds to a concentration of free dye at D/P = 1 of 0.046 $\times 10^{-5}$ mol/l. Assuming a linear dependence of $c_{\rm free}$ on D/P the optical densities of all graphs of Figure 3B have been corrected by subtracting the absorption of the free dye, and the data have been normalized to a dye concentration of 1.45 mol/l. The true D/P ratios have also been computed using only the concentration of the bound dye. All results for two significant wavelengths are given in Table I.

The optical densities of monomer bound dye at 560 and 517 m μ have been found by graphical extrapolation at D/P = 0 of the experimental data $E_1 = 0.552$ at λ 560 m μ and $E_1 = 0.214$ at λ 517 m μ . The optical densities of the aggregate bound dye at the same wavelengths were $E_3 = 0.095$ at λ 560 m μ and $E_3 = 0.180$ at λ 517 m μ . A more drastic but reasonable assumption was to take the same optical density for dimer and aggregate at λ 560 m μ : $E_2 = E_3 = 0.095$ at $\lambda = 560$ m μ . Based on these assumptions, it was possible to calculate a set of values for the fraction of monomer bound dye

$$X_1 = F_1 = \frac{A_{560} - 0.095}{0.552 - 0.095} \tag{11}$$

 A_{560} being the corrected optical densities at 560 m μ given in Table I. At 517 m μ a value for the dimer optical density has been taken giving the best agreement between the F_1 computed at this wavelength and those computed at 560 m μ in the range of D/P values where the

(39) It can be easily seen that the fractions X_m are functions only of F_1 and q_2 and that they do depend on q_1 only through the dependence of F_1 on q_1 (Figure 5).

(40) The dialysis data (Figure 4) cannot be used for this purpose because we are dealing with a complicated Donnan equilibrium and the concentration of free dye inside the dialysis bags is certainly less than that outside.

⁽³⁸⁾ The same expressions have been used here as in Lifson's paper: q_0 is the partition function of a desorbed state site; q_a is the partition function of a site in an absorbed state; λ_a is the absolute activity of the the dye in the solution. Furthermore, it is assumed that neighboring adsorbed molecules interact each other such that a pair of first neighbors has a partition function of pairwise interaction q_1 , a pair of second neighbors has a partition function q_2 , and so on up to the *m*th order of neighborhood.



Figure 6. Comparison of experimental monomer and dimer fractions with the values computed through eq 6, 7, and 8 for $q_1 = 5.5$ and $q_2 = 0.26$.

amount of aggregates higher than dimers is negligible: $E_2 = 0.355$ at 517 m μ . Using these data and eq 11 the distribution of the different species was computed through the equation

$$A_{517} = 0.214X_1 + 0.355X_2 + 0.180(1 - X_1 - X_2) \quad (12)$$

The experimental data of X_1 and X_2 have been compared with the values given by eq 6-8. The best agreement has been obtained for the following values of the q constants: $q_1 = 5.5$ and $q_2 = 0.26$. The graph of Figure 6 shows that the agreement between experimental and statistical data is very good for the X_1 and reasonably good for the X_2 values.

A low value of q_2 indicates a particular stability of dimers with respect to higher order aggregates; the fraction of dimer molecules is in fact much higher than that expected in the absence of second-neighbor interactions ($q_2 = 1$) (see Figure 5). The agreement of the experimental results with the statistical model seems to us of some interest because generally statistical treatments do not apply easily to the binding of small molecules because of the too many factors implied in the phenomenon. The good agreement obtained in our case, even with the limitation of several simplifying assumptions, by using only two binding parameters should be a good point in favor of the actual possibilities for a statistical treatment of the binding of dyes to polymers.

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NOTES

Rates of Mercapto Proton Exchange of

Mercaptoacetic Acid in Acetic Acid¹

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Recently there has been a great interest in the utilization of high-resolution and pulse nuclear magnetic resonance for the study of protolysis kinetics. For the great part this work has concentrated upon the exchange of amines and carboxylic acids in a variety of solvents.³⁻⁷ An interesting and important acidic functional group which has received less study is the mercapto group.^{8,9} The importance of this functional group in compounds of chemical and biological interest

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led us to investigate the nature of the protolysis kinetics of a representative compound. Because of its own importance and the similarity between some other important compounds, mercaptoacetic acid was chosen.

Other mercapto compounds which have been studied include 2-mercaptoethanol in aqueous solution⁸ and

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thiophenol-methanol proton exchange in carbon tetrachloride.⁹ The mercapto proton exchange of 2-mercaptoethanol was reported to be base catalyzed but not acid catalyzed up to 11 M perchloric acid. This is contrary to the well known exchange behavior of alcoholic protons which undergo fast exchange in both acidic and basic media.¹⁰ The proposed rate expression for 2-mercaptoethanol was given as

$$1/\tau = \frac{\text{rate}}{[RSH]} = k_1 + k_B[B] \tag{1}$$

where k_1 is a pseudo-first-order rate constant and k_B is a second-order rate constant of a reaction catalyzed by a base B. Rate constants for proton exchange at room temperature of $k_1 = 32 \text{ sec}^{-1}$ and $k_{OAc} = 2 \times 10^3 \text{ l}$. mol⁻¹ sec⁻¹ for the acetate ion catalyzed exchange were reported. Both acid and base catalysis of the mercapto proton exchange have been observed in liquid 2-mercaptoethanol.¹¹ However, quantitative data are not available.

The proton exchange between thiophenol and methanol in CCl₄ was found to be catalyzed by HCl or sodium methoxide. The second-order rate constants at 27° are $k_{\rm B} = (1.4 \pm 0.3) \times 10^4$ l. mol⁻¹sec⁻¹for the basecatalyzed exchange and $k_{\rm A} = (2.8 \pm 0.5) \times 10^2$ l. mol⁻¹ sec⁻¹ for the acid-catalyzed reaction. Corresponding activation energies are 7.5 ± 0.5 and 11.0 ± 0.5 kcal/ mol, respectively. In the absence of a catalyst the exchange is too slow to be measured by nmr.

Experimental Section

Mercaptoacetic acid (Eastman grade, Distillation Products Industries) was distilled under vacuum before use. The methyl ester of mercaptoacetic acid was obtained by fractional distillation of a mixture of mercaptoacetic acid and methanol. Glacial acetic acid (J. T. Baker, AR) was further purified by the addition of acetic anhydride followed by fractional crystallization.¹² The solvent was stored in a sealed container prior to use. The acetate salts used were all reagent grade anhydrous materials and were used without further purification.

The nmr spectra were recorded using a Hitachi-Perkin-Elmer R-20 high resolution spectrometer equipped with a variable-temperature probe. The spectrometer settings varied but were checked to ascertain that saturation was not encountered. All temperatures reported with the nmr data were calibrated and are accurate to $\pm 1^{\circ}$. A low-temperature limit of 30° was used because viscosity broadening became significant below this temperature. All data are at 40° unless stated otherwise. Limitations upon the precision of activation energy data were determined by the inaccuracies given for temperature calibration and the narrow temperature range of approximately thirty degrees. This range was established by viscosity broadening at the low temperature side and coalescence on the high-temperature limit. Viscosity broadening can be distinguished from kinetic broadening quite easily before the spectrum has coalesced. An increase in temperature will sharpen the multiplet broadened as a result of viscosity but will normally lead to increased kinetic broadening as a result of the relationship between rate and temperature. The precision of the activation data is given with the results as the standard deviation of the data.

The natural line width of the sample was determined several times during each run. These line widths were approximately 0.5 Hz and assumed to be determined by magnetic field homogeneity. The ¹³C side band of the acetic acid methyl resonance was found to be a convenient monitor of the field homogeneity and was used for that purpose. Variation of the concentration of mercaptoacetic acid had no effect on the line width.

Results and Discussion

The nmr spectrum of mercaptoacetic acid in glacial acetic acid is simple. There is at riplet at τ 7.77-(SH), a doublet at τ 6.69(CH₂), and the merged spectrum of the solvent and sample carboxyl protons at lower field. The mercapto proton is hidden by the methyl proton resonance of the solvent unless d_3 -acetic acid is used. In principle, either the SH or methylene proton resonance may be used for the exchange study. The spin-spin coupling between these protons will collapse as the exchange rate is increased. The shape of the methylene proton signal is therefore determined by the rate of exchange. Because the coupling constant (7.88 cps) is much smaller than the chemical shift difference between the SH and solvent carboxyl proton resonance, the coupling will collapse at a slower exchange rate than the coalescence of the SH and solvent peaks. In practice it is advantageous to use the methylene doublet to determine the exchange rate to avoid interference of the solvent methyl resonance or the alternative use of d_3 -acetic acid. Therefore, the observed phenomenon of direct interest is a broadening and eventual coalesence of the methylene proton resonance. The rate of exchange is computed from individual spectra using a computer program prepared utilizing the general approach as given by Arnold.13 Several relative intensities at various points in the methylene resonance spectrum are used as data and the program computes the rate of exchange by minimizing the differences between the relative intensities of the experimental and simulated spectra. As in most applications, it is necessary to assume that the spectral parameters of the compound are not dependent upon

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Figure 1. Rate of mercapto proton exchange of mercaptoacetic acid vs. salt concentration: \times , potassium acetate; O, sodium acetate; Δ , barium acetate.

the conditions which are varied in order to vary the rate of exchange.

A plot of the rate of mercapto proton exchange vs. the concentration of potassium, sodium, and barium acetate gave linear plots as shown in Figure 1. These results indicate that the species which catalyzes the proton exchange is the ion pair of the added salt rather than the acetate ion. If the acetate ion were the catalytic agent, consideration of the ion pair dissociation equilibrium shows that the rate of exchange would be proportional to the square root of the added salt concentration. The fact that the exchange rate is dependent upon the cation is further evidence that the ion pair is involved in the reaction. The pK_d values for the ion-pair dissociation of potassium, sodium, and barium acetates in acetic acid have been given as 6.1, 6.56, and 6.48, respectively.¹⁴

Therefore, if the reaction were catalyzed by acetateion, at a given concentration of the three salts the decreasing order of rates would be potassium, barium, and sodium. This is not the case. A plot of the exchange rate $\imath s$. the concentration of mercaptoacetic acid showed no dependence upon the concentration of the acid.

A study of the exchange of the methyl ester of mercaptoacetic acid was performed. Figure 2 shows a plot of the rate of mercapto proton exchange for the methyl ester of mercaptoacetic acid vs. the concentration of added potassium, sodium, and barium acetate. Like the acid, there was no dependence of the exchange rate upon the concentration of the ester.

Because there is no dependence of the exchange rate of the mercapto protons upon the acid or ester concentration, any mechanism involving the transfer of the protons between these molecules is not an important contributor to the observed rate. It would be expected that the extraction of a mercapto proton by acetate ion is a more effective process than extraction by the ion



Figure 2. Rate of mercapto proton exchange of mercaptoacetic acid methyl ester vs. salt concentration: \times , potassium acetate; O, sodium acetate; Δ , barium acetate.

pair. However, the ion-pair concentration in all experiments reported here is approximately one hundred times the concentration of acetate ion. Therefore, an exchange reaction catalyzed by the latter would be required to be better than ten times faster than that of the ion-pair catalyzed reaction to be detected. Evidently, this is not the case.

Therefore, a reasonable proposed mechanism is the transfer of the thiol proton to the acetate ion of an ion pair acetate. This newly formed solvent molecule could then diffuse into the bulk solvent to permit the reprotonation of the thiolate ion by the solvent. This cycle would accomplish the observed proton exchange at the sulfhydryl site. The observation that barium acetate is the most effective catalyst of the three investigated is at least partially explained by the fact that there are two acetate groups in the ion pair to accept the thiol proton.

The exchange of the mercapto acetic acid is measurably faster than that of the ester. This observation indicates that the carboxyl group may lead to an intramolecular exchange route of some significance. Although the carboxyl protons are undergoing rapid exchange with the solvent, these reactions occur by a route which involves the exchange of protons with solvent molecules hydrogen bonded to the carboxyl site.⁵ However, base catalysis is an important reaction which is generally too fast to measure by nmr. Under base catalysis, for example, by acetate ions or an ion pair, a low concentration of carboxylate ions is formed which will be protonated at a very rapid rate. An intramolecular transfer of protons from the mercapto site to the carboxylate ion may occur. This provides an exchange route for the acid which is not available to the ester.

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The rate expressions for the mercapto proton exchange may be written as

$$1/\tau = (k_1 + k_2)$$
[MOAc]

for the acid and

 $Na(C_2H_3O_2)$

 $Ba(C_2H_3O_2)_2$

$$1/\tau = k_3[MOAc]$$

for the ester where k_1 and k_3 represent the second-order rate constants for the direct exchange of the proton from the mercapto site in the acid and ester, respectively. If k_1 and k_3 are assumed to be equal, k_2 which represents the transfer of a proton from the mercapto site to the carboxylate ion is obtained from the difference between the observed exchange rates for the acid and ester. Values of the second-order rate constants are given in Table I.

Table I:	Rate Cons	tant for Mercapto Proto	on Exchange ^a
	Salt	$(k_1 = k_3) \times 10^{-3}$ l. mol ⁻¹ sec ⁻¹	$k_2 \times 10^{-3}$ l. mol ⁻¹ sec ⁻¹
K(C	C ₂ H ₃ O ₂)	0.68 ± 0.1	2.1 ± 0.1

^a Mercaptoacetic acid solutions were 0.72 M and the mercaptoacetic acid methyl ester solutions were 0.46 M.

 0.71 ± 0.1

 2.1 ± 0.1

 1.3 ± 0.1

 1.4 ± 0.1

The values for k_2 are in the expected order if the transfer of the proton from the mercapto group involves the dissociation of the ion pair formed between the carboxylate group of mercaptoacetic acid and the cation present. However, the direct exchange rate of the mercapto proton, k_1 , is mostly influenced by the number of acetate ions available in the ion pair. Because there are two such groups in the barium salt, the exchange in the presence of barium acetate is the most rapid.

The thiol proton exchange was investigated as a function of temperature in acetic acid. The activation parameters obtained were $E_a = 12.4 \pm 0.9$ kcal/mol; log $A = 8.5 \pm 0.6$ and $E_a = 11.4 \pm 1.0$ kcal/mol; log $A = 9.4 \pm 0.7$ for mercaptoacetic acid and the methyl ester respectively. The activation parameters in trifluoroacetic acid were obtained for mercaptoacetic acid and found to be $E_a = 14.9 \pm 0.9$ kcal/mol; log $A = 10.8 \pm 0.6$. An exchange of approximately 2 sec⁻¹ was measured at 40° in this solvent with no added salts.

The results of this investigation support the previous conclusions^{8,9} that base-catalyzed exchange of mercapto protons is significantly faster than acid catalyzed exchange. In special cases such as the one presented here, the base may be part of the molecule under study. In solvents of low dielectric constant, the base may be

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Solvated Radius of Ions in Nonaqueous Solvents

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an ion-pair species.

If in the conduction processes of electrolyte solutions the ions are regarded as spheres moving in a continuous medium, then the radius of an ion is given by the relationship

$$r_{\rm s} = \frac{0.82|z|}{\lambda^{\circ}_{+}\eta} \tag{1}$$

where λ_{\pm}° is the limiting equivalent conductance of the ion, |z| is its absolute charge, and η is the viscosity of pure solvent. The r_{s} values obtained from eq 1 in aqueous and nonaqueous solvents are always too small.

In order to obtain the correct radius of ions in nonaqueous solvents we have reported, for the tetraalkylammonium ions, a plot of the crystallographic radius (r_c) against the Stokes radius (r_s) , using Nightingale's suggestion for aqueous solutions.¹ In each solvent the r_{s} values of the tetraalkylammonium ions, except the methyl, are a linear function of r_c . This fact suggests the hypothesis that the tetramethylammonium ion is partly solvated in solution.^{1,2} A further support to the idea of a partial solvation of the Me_4N^+ ion in all the solvents considered is given by the results of Figure 1 and Table I. From this figure it appears that while $\lambda^{\circ} + \eta$ products of Et₄N⁺, Pr₄N⁺, and Bu₄N⁺ ions increase linearly increasing η , the $\lambda^{\circ} + \eta$ product of Me_4N + is not a definite function of the medium viscosity. (We are currently engaged in this problem and we will give more definite conclusions in a further note.)

Returning to the main problem with which we are concerned, a calibration curve has been prepared by plotting the Stokes radius against the crystallographic radius for all the tetraalkylammonium ions except the tetramethylammonium ion in all the solvents considered. Figure 2 shows the results in methanol; in the same figure, the Stokes radius values are also shown plotted against the crystallographic radii for a number of cations and anions. The Stokes radius of the anions and the cations of a given charge type is a linear function of the crystallographic radius. (This is also true in the other solvents considered.)

(1) E. R. Nightingale, Jr., J. Phys. Chem., 63, 1381 (1959).

⁽²⁾ E. G. Taylor and C. A. Kraus, J. Amer. Chem. Soc., 69, 1731 (1947).

Table I:	Limiting Equivalent	Conductivities	and Walden	Products of	$Tetraalkyl {\bf a} mmonium$	Ions in
Various Se	lvents ()°, in ohm-	$1 \text{ cm}^2 \cdot \text{ m in } \mathbf{P}$				

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Solvent	Viscosity	M	84N +	Et	4N +	Pr	4N +	Bu	4N +
Acetonitrile ^a	0.00346	94.2	0.384	83.7	0.288	69.6	0.240	61.3	0.211
$Methanol^b$	0.00547	66.7	0.365	58.2	0.318	43.9	0.230	36.9	0.202
Dimethyl- ^c									
formamide	0.00796	38.9	0.311	35.4	0.283	29.1	0.233	26.2	0.210
Formamide ^d	0.0330	12.5	0.413	10.0	0.330			6.8	0.224
Dimethylacetamide ^e	0.00919			32.7	0.301	26.2	0.241	22.8	0.210
Nitrobenzene	0.01811	17.1	0.310	16.2	0.293	13.3	0.241	11.7	0.212
$Sulfolane^{g}$	0.0987	4.31	0.425	3.95	0.390	3.23	0.319	2.80	0.276

^a A. H. Harkness and H. M. Daggett, Can. J. Chem., **43**, 1215 (1965). ^b E. C. Evers and A. G. Knox, J. Amer. Chem. Soc., **73**, 1739 (1951). ^c P. G. Sears, E. D. Wilhoit, and L. R. Dawson, J. Phys. Chem., **59**, 373 (1955). ^d J. M. Notley and M. Spiro, *ibid.*, **70**, 1502 (1966). ^e G. R. Lester, T. A. Gover, and P. G. Sears, *ibid.*, **60**, 1076 (1956). ^f E. G. Taylor and C. A. Kraus, J. Amer. Chem. Soc., **69**, 1731 (1947). ^g M. Della Monica, U. Lamanna, J. Phys. Chem., **72**, 4329 (1968).

Table II :	Stokes Radii a	and Solv	ated Ra	dii of Io	ns in Sol	ution $(r_s$	and r_{cor}	in Å)						
Ion	Me	он	HCO	DNH₂	HCON	(CH ₈) ₂	CH₃CO	N(CH ₃) ₂	C ₆ H	δNO2	СН	I₃CN	C₄H	SO ₂
	r_8	r_{cor}	r_8^a	$r_{\rm cor}$	$r_{\rm B}$	$r_{\rm cor}$	τ_8^a	$\tau_{\rm cor}$	τ_{s}	r_{cor}	r_8^a	$r_{\rm cor}$	τ_8	$\tau_{\rm cor}$
\mathbf{Li}	3.77^{b}	4.74	2.92	4.36	4.12°	5.10					2.98	4.13	1.92^h	3.74
Na	3.32^b	4.46	2.46	3.99	3.45°	4.46	3.49	4.60	2.78'	3.99	3.10	4.24	2.30^{h}	4.23
к	2.86^{b}	4.16	1.96	3.58	3.34°	4.36	3.54	4.65	2.54^{f}	3.77	2.86	4.04	2.05^{h}	3.92
\mathbf{Rb}	2.62°	4.02	1.94	3.57	3.18	4.22							2.00^{h}	3.85
\mathbf{Cs}	2.40°	3.88	1.84	3.48	2.99^{e}	4.04					2.44	3.68	1.95^{h}	3.78
NH4	2.59°	3.99	1.59	3.30	2.66^{e}	3.70			2.46^{f}	3.70			1.67^{h}	3.36
Ag	2.75	4.25			2.90^{e}	3.95					2.36	3.59		
Ca	2.51^{d}	3.94												
Mg	2.57^{d}	3.99												
$\mathbf{C}\mathbf{d}$	2.60^{d}	4.01												
Zn	2.55^{d}	3.97												
\mathbf{Sr}	2.54^{d}	3.97												
Ba	2.50^d	3.93												
Cl	2.86^{b}	4.16	1.45	3.14	1.87^{e}	3.00			2.04^{g}	3.32	2.54	3.76	0.89^{h}	1.98
\mathbf{Br}	2.65^{b}	4.08	1.44	3.14	1.92^{e}	3.08	2.06	3.51	2.10^{g}	3.39	2.35	3.60	0.93^{h}	2.06
Ι	2.39^{b}	3.88	1.50	3.21	1.97°	3.09	2.13	3.56	2.22	3.49	2.38	3.56	1.15^{h}	2.47
ClO	2.11°	3.70	1.45	3.14	1.97°	3.08	2.08	3.54	2.17^{o}	3.46	2.31	3.55	1.24^{h}	2.64
NO_3	2.80°	4.14	1.44	3.14	1.80°	2.92	1.92	3.40	2.00^{g}	3.30	2.24	3.48		

^a The references for the three solvents are the same as those reported in Table I. ^b R. E. Jervis, D. R. Muir, J. P. Butler, and A. R. Gordon, J. Amer. Chem. Soc., 75, 2855 (1953). ^c M. Barak and H. Hartley, Z. Phys. Chem., 165, 272 (1933). ^d H. Hartley and H. R. Raikes, Trans. Faraday Soc., 23, 393 (1927). ^e J. E. Prue and P. J. Sherrington, *ibid.*, 57, 1795 (1961). ^f C. R. Witschonke and C. A. Kraus, J. Amer. Chem. Soc., 69, 2472 (1947). ^e E. G. Taylor and C. A. Kraus, *ibid.*, 69, 1731 (1947). ^h M. Della Monica, U. Lamanna, and L. Senatore, J. Phys. Chem., 72, 2124 (1968).



Figure 1. Walden products $\lambda^{\circ}\eta$ against viscosity for tetraalkylammonium ions in various solvents. \bullet , values of ionic conductance in these solvents obtained from transference number measurements; O, values of ionic conductance in these solvents not accurately known. Figure 2 shows also that the monovalent cations are more solvated than the bivalent cations of comparable crystallographic radius and the difference decreases from Li^+ to K^+ . For brevity the calibration curves for the correction to the Stokes radius in the other solvents considered have not been reported.

Table II compares the Stokes radius and the solvated radius for a number of ions in the various solvents. From the data of Table II it appears that monovalent anions, oxygenated or not, have a solvated radius decreasing from Cl^- to ClO_4^- in methanol and in acetonitrile; in formamide, dimethylformamide, and dimethylacetamide the solvated radius is almost constant, while in sulfolane the solvated radius increases from Cl^- to ClO_4^- .³ The NO_3^- anion has a solvated radius greater than that expected only in methanol; in

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Notes



Figure 2. Calibration curve for the correction to Stokes law radius of some ions in methanol.

the other solvents it is on the straight-line plot with the other anions.

The radii of the monovalent cations in solution are decreasing from Li^+ to Cs^+ in almost all the solvents; the behavior of the Li^+ ion in acetonitrile⁴ and in sulfolane⁵ is exceptional in the sense that it has a value smaller than that of the Na⁺ ion.

Acknowledgement. We are grateful to Dr. Joseph Steigman, Polytechnic Institute of Brooklyn, for a helpful comment.

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Molecular Structures and Enthalpies of

Formation of Gaseous Alkali Metal Hydroxides

by D. E. Jensen

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Reliable values for the zero-point standard enthalpy changes ΔH°_{0} of the reactions

$$A(g) + OH(g) \rightleftharpoons AOH(g)$$
 (1)

(where A is an alkali metal atom) are frequently needed in thermochemical calculations on high-temperature systems. Values of ΔH°_{0} available in the literature (e.g., ref 1-3) stem largely from third-law calculations based on experimentally determined equilibrium constants and consequently require knowledge of the rotational and vibrational contributions to the total partition functions of AOH. Both linear and bent configurations for AOH have been proposed; the most recent work, however, indicates a linear or nearly linear configuration.⁴⁻⁹ The purpose of this note is to reinterpret the results of ref 3 (where it was assumed that each AOH molecule was bent) in terms of a linear model and to compare values of ΔH°_{0} obtained with those given previously.³

Table I shows measured⁴⁻⁹ and estimated² vibration frequencies and molecular moments of inertia for AOH (linear). Corresponding quantities for AOH (bent) are tabulated in ref 3. Application of elementary statistical thermodynamics to the equilibrium of reaction (1) at 2475° K (the temperature of the thirdlaw calculations of ref 3) provides

$$K_{1} = 7.8 \times 10^{-31} (m_{AOH}/m_{A})^{3/2} \times (f_{vib_{J}rot})_{AOH} \exp(-\Delta H^{\circ}_{0}/RT)$$
(2)

In eq 2, *m* represents a molecular mass and $f_{vib}f_{rot}$ the product of vibrational and rotational partition functions. K_1 is in units of ml molecule⁻¹. The constant in (2) is independent of the configuration of AOH and comes directly from JANAF data.¹

Table II shows calculated zero-point standard enthalpy changes for reaction 1 for both linear (data of Table I) and bent (data of ref 3) models. The equilibrium constants used stem from the flame experiments on all five metals.³

For all metals except lithium, ΔH°_{0} (linear) and ΔH°_{0} (bent) are closely similar: increases in $f_{\rm vib}$ and decreases in $f_{\rm rot}$ which take place as the configuration is changed from bent to linear (cf. values in Table I and in ref 3) approximately compensate for one another. Recommended values of ΔH°_{0} for these metals are: $\Delta H^{\circ}_{0,\rm Na} = -325 \pm 16 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$; $\Delta H^{\circ}_{0,\rm K} = -339 \pm 9 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$; $\Delta H^{\circ}_{0,\rm Rb} = -347 \pm 9 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$, and $\Delta H^{\circ}_{0,\rm Cs} = -380 \pm 12 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$. The dispersions in these values are due largely to the experimental uncertainties in values of $K_{1.3}^{\circ}$

For lithium, ΔH°_{0} (bent) exceeds ΔH°_{0} (linear) by 14 kJ mol⁻¹. However, the estimated vibration frequencies for LiOH (linear) may well be too high note that measured frequencies⁹ are considerably lower than estimated frequencies² for NaOH (linear)—and it would seem premature to recommend decreasing the value of ΔH°_{0} for lithium to this extent at present. A flame value of ΔH°_{0} for lithium of -430 ± 12 kJ

(1) "JANAF Thermochemical Tables," Dow Chemical Company, Midland, Mich., June 1968.

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⁽⁷⁾ C. Matsumura and D. R. Lide, *ibid.*, 50, 71 (1969).

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⁽⁹⁾ N. Acquista and S. Abramovitz, to be published.

Table I: Molecular Parameters of the Alkali Metal Hydroxides^a

Partition functions at 2475°K		ee,	Vibration frequenci				
10 ^{-s} frot	fvib	10381	$10^8 \tau_{A-O}$	43	¥2	ν1	Molecule
1.36	68	0.22	(1.52)	(3800)	(410)	(800)	LiOH
4.1	161	0.66	(1.94)	(3650)	337	431	NaOH
6.7	17 1	1.09	(2.27)	(3610)	(340)	(400)	KOH
8.2	226	1.34	2.31	(3610)	309	354	RbOH
9.5	238	1.55	2.40	(3610)	310	336	CsOH

^a Vibration frequencies are in cm⁻¹, internuclear distances r_{A-0} in cm and molecular moments of inertia I in g cm². Vibration frequencies and moments of inertia in parentheses are estimates;² those not in parentheses stem from recent experiments.⁴⁻⁹

Table II :	Calculated	Zero-Point	Standard	Enthalpy	Changes
	Curcuratou	BOLO X OILLO		1 monte pj	C. angos

Metal	$K_{1,247b}$, ml molecule ⁻¹	ΔR°₀ (bent), kJ mol ⁻¹	∆H° ₀ (linear) kJ mol ⁻¹
\mathbf{Li}	$7.7 imes 10^{-16}$	-423	-437
Na	8.3×10^{-18}	-322	-325
K	2.2×10^{-17}	-338	-339
Rb	4.0×10^{-17}	-348	-347
Cs	2.2×10^{-16}	-382	-380

^a K₁ is calculated from equilibrium constants for the reaction $A + H_2O \rightleftharpoons AOH + H$ given in ref 3, the equilibrium constant for the reaction $H_2O \rightleftharpoons OH + H$ being taken to be 3.0×10^{14} molecule ml⁻¹ at 2475°K (JANAF¹ data).

mol⁻¹ (dispersion due approximately equally to uncertainties in K_1 and in $f_{vib}f_{rot}$) appears to be the best compromise until reliable experimental values for the molecular parameters of LiOH become available.

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$n-\pi^*$ Transition in the Dimethylthioacetamide-

Iodine and Thioacetamide-Iodine Complexes

by Arthur F. Grand and Milton Tamres

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Donor-acceptor interactions can be investigated by measuring either a property of the complex or a perturbed property of one of the components. In the specific case of the iodine interaction with thioacetamide, $CH_3C(S)NH_2$, thermodynamic data for the complex in dichloromethane¹ have been obtained from a study of the charge-transfer (CT) band at 286 m μ . In addition, on the low wavelength side of the CT band, the $\pi \rightarrow \pi^*$ band for thioacetamide was found shifted from 269 to 248 m μ . It was located in the spectrum of the complex because of its high intensity which was comparable to that of the unperturbed transition.

The iodine complex of dimethylthioacetamide, CH₃C-

(S)N(CH₃)₂, in carbon tetrachloride has been investigated utilizing the blue-shifted iodine band in the visible region.² The same complex has also been characterized by studying the charge-transfer band in the ultraviolet region.³ Unlike other thione-iodine complexes, however, a pronounced shoulder was observed on the high wavelength side of the CT band. This shoulder is attributed to a blue-shifted $n \rightarrow \pi^*$ transition in the donor, with an intensity greatly enhanced over that in the free donor. A similar band is also found to exist in the thioacetamide-iodine system that was not recognized previously.

Experimental Section

The purification of carbon tetrachloride, iodine, and dimethylthioacetamide have been described previously.³ Thioacetamide was obtained from Eastman Organic Chemicals and was recrystallized from anhydrous ethyl ether. Its ultraviolet spectrum agreed with that in the literature.¹ Reagent grade dichloromethane was dried and distilled prior to use.

The procedure to obtain spectrophotometric data and the mathematical treatment to determine spectral and thermodynamic properties also have been described.³

Results and Discussion

The composite band of the dimethylthioacetamideiodine complex in carbon tetrachloride is shown in Figure 1 (curve A). It was obtained by subtracting the absorbances of the equilibrium concentrations of free donor and of free acceptor from the total absorbance of the mixture. The band has a maximum at $\sim 310 \text{ m}\mu$ and a distinct shoulder at $\sim 340 \text{ m}\mu$. In addition, the curvature at the low wavelength indicates a contribution from the tail of another band, possibly the perturbed $\pi \rightarrow \pi^*$ band of the donor.

One way to test for the presence of more than one species in a complex band is to use the Liptay method.⁴ When this was done for dimethylthioacetamide-iodine

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Figure 1. Resolution of dimethylthioacetamide-iodine ultraviolet spectrum in carbon tetrachloride. (A) absorption of complex (corrected for free donor and acceptor), (B) extrapolation of major band (symmetrical with high-energy side), (C) curve A minus curve B; concentrations in 1-cm cell at 20°. Initial donor = $6.70 \times 10^{-6} M$, initial iodine = $1.44 \times 10^{-4} M$, complex at equilibrium = $1.37 \times 10^{-6} M$.

over the wavelength range 300-360 m μ no systematic variation in the Liptay matrix as a function of wavelength was found. In accord with this, calculations of the thermodynamic functions from the absorbances at 340 m μ matched those at 310 m μ^3 (in parentheses): $-\Delta H^\circ = 9.29 \pm 0.14 (9.77 \pm 0.37) \text{ kcal mol}^{-1}$; $-\Delta G^\circ_{298}$ = 4.34 (4.32) kcal mol}⁻¹, $-\Delta S^\circ = 16.6 \pm 0.5$ (18.3 \pm 1.3) eu, which are in reasonably good agreement with those obtained from a study of the blue-shifted iodine band.² These observations suggest that the peak at \sim 310 m μ and the shoulder at \sim 340 m μ must both be attributed to a single complex.

The overlapping bands were resolved qualitatively by making two assumptions; (1) the absorbance of the minor band is negligible below 310 m μ , and (2) the major band is symmetrical with respect to frequency. Subtracting the major band (curve B, Figure 1) from the total absorbance (curve A) produced the minor band (curve C).

The second assumption is an oversimplification because CT bands are generally asymmetric,⁵ but the presence of the unresolved tail on the high-frequency side partially compensates for the neglect of asymmetry. In spite of the approximations, the evidence is good that two bands exist, a more intense one at $\sim 306-308$ m μ and a minor one at $\sim 340-350$ m μ .

Six dimethylthioacetamide-iodine solutions were resolved in a similar manner, and the equilibrium constants and extinction coefficients were determined for the resolved bands at the wavelengths 307 and 340 $m\mu$. The data and results are shown in Table I. The equilibrium constants for the two bands are in reasonable agreement with one another and with those obtained prior to resolution.⁶

The earlier report on thioacetamide-iodine in dichloromethane did not indicate any complexity of the

 Table I:
 Data and Results for the Resolution of the

 Dimethylthioacetamide-Iodine Ultraviolet Absorption in

 Carbon Tetrachloride at 20°

$D_0^a \times 10^5$, mol/l.	$Z_0^b imes 10^4$, mol/l.	<i>A^c</i> , 307 mμ	A ^c , 340 mμ
6.70	1.44	0.505	0.130
7.81	6.95	1.640	0.389
6.70	2.88	0.864	0.207
5.70	4.63	0.987	0.233
5.70	2.32	0.636	0.162
2.01	8.63	0.470	0.105
		.	

^a Initial concentration of donor. ^b Initial concentration of acceptor. ^c Absorbance of the resolved band. For 307 mµ, $K = 1960 \pm 140 \text{ l./mol}$; ϵ 37,500 l./mol-cm. For 340 mµ, $K = 2760 \pm 580 \text{ l./mol}$; ϵ 7570 l./mol-cm.

CT band.¹ That study was repeated to see if the same resolution procedure would show a second band. The method was applied to four solutions at 20°. Figure 2 and Table II show the results. A small but apparent absorption band was located with a maximum at \sim 320-325 mµ, in addition to the main band at \sim 295-296 m μ . The equilibrium constants are in good agreement with each other and with the data of Lang¹ ($K_{20^{\circ}}$ calculated from his data is 11,100 l. mol⁻¹). The extinction coefficient of the 295-m μ band also is in reasonable agreement with that of Lang¹ (\sim 48,000 $mol^{-1} cm^{-1}$). The extinction coefficient of the second band at the higher wavelength is of similar general magnitude as that found for dimethylthioacetamideiodine.

Table II: Data and Results for the Resolution of theThioacetamide-Iodine Ultraviolet Absorption inDichloromethane at 20°

$D_0^a \times 10^5$, mol/l.	$Z_0^b \times 10^6$, mol/l.	A ^c , 295 mµ	A ^c , 325 mμ
6.47	6.92	1.035	0.130
6.47	9.69	1.295	0.145
6.47	13.8	1.590	0.200
6.47	27.7	0.479	0.059

^a Initial concentration of donor. ^b Initial concentration of acceptor. ^c Absorbance of the resolved band. For 295 mµ, $K = 11,500 \pm 1600 \text{ l./mol}$; $\epsilon 45,500 \text{ l./mol-cm}$. For 325 mµ, $K = 12,300 \pm 7380 \text{ l./mol}$; $\epsilon 5340 \text{ l./mol-cm}$.

 λ_{\max} and ϵ_{\max} for the $n \rightarrow \pi^*$ transition of dimethylthioacetamide in carbon tetrachloride are $\sim 360 \text{ m}\mu$ and $\sim 70 \text{ l. mol}^{-1} \text{ cm}^{-1}$, respectively, and of thioacetamide in dichloromethane¹ are $\sim 356 \text{ m}\mu$ and $\sim 40 \text{ l. mol}^{-1} \text{ cm}^{-1}$, respectively. The minor bands in Figures 1 and 2 are most likely blue-shifted $n \rightarrow \pi^*$ transitions of greatly enhanced intensity. The factor of ~ 100 -fold increase

⁽⁵⁾ G. Briegleb, "Elektronen Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, p 46.

⁽⁶⁾ The complex in dichloromethane as solvent had the same general absorption pattern as in carbon tetrachloride, with a slight blue shift of the two bands (to ~ 304 and $\sim 335 \text{ m}\mu$).


Figure 2. Resolution of thioacetamide-iodine ultraviolet spectrum in dichloromethane. (A) absorption of complex (corrected for free donor and acceptor), (B) extrapolation of major band (symmetrical with high energy side), (C) curve A minus curve B; concentrations in 1-cm cell at 20°. Initial donor = $6.47 \times 10^{-6} M$, initial iodine = $1.38 \times 10^{-4} M$, complex at equilibrium = $3.41 \times 10^{-5} M$.

in ϵ for the shifted band may be off appreciably, considering the possible errors in the resolution. There is no question, however, that the intensity must be greatly increased because, for the concentration of donor used, the absorbance of the unperturbed $n \rightarrow \pi^*$ transition would not be observable. The enhancement may be due to the transition being more allowed for the perturbed case, or intensity might be acquired from the mixing of states, particularly those of the weak intramolecular $n \rightarrow \pi^*$ band and the highly intense intermolecular CT band.7

It should be pointed out that since both the CT and perturbed $n \rightarrow \pi^*$ bands are the result of the same complexation, calculations of thermodynamic values rereported in the literature from ultraviolet studies on related complexes still are valid. However, in those cases where the two bands overlap too closely, the ϵ_{\max} calculated for the CT band may be high.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation, GP-6429. We wish to acknowledge helpful discussions with Dr. H. Hosoya and Professor S. Nagakura.

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Nuclear Magnetic Resonance Spectral Correlation of Symmetrically Substituted 1,2-Diols and 1,3-Dioxalanes

by M. Gianni, J. Saavedra, R. Myhalyk, and K. Wursthorn

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In a previous communication,¹ a method for an nmr structural correlation of symmetrically substituted

epoxides and olefins was presented. The method depends on the observation of the chemical shift for the methine (C-H) hydrogen and requires that both cis and trans isomers be available for comparison.

In the course of work on another problem, it became necessary to assign structures to a series of symmetrically substituted 1,2-glycols. Since only one isomer was available for some of these glycols, the previous method was not applicable. We now wish to report a method of unequivocal assignment of structure for disubstituted 1,2-glycols and 1,3-dioxalanes which obviates the necessity of observing the nmr spectra of both isomers. The synthetic sequence is illustrated below.



Previously, the best method of unequivocal structural assignment for the 1,2-glycols was optical resolution. The method is tedious and often difficult with tertiary alcohols. Dioxalane formation is easily accomplished and avoids difficulty with tertiary alcohols.^{2,3} The glycols are treated in benzene solvent with paraformaldehyde and catalytic amounts of *p*-toluenesulfonic acid employing a Dean–Stark apparatus for separation of the water from the reaction mixture.⁴ The nmr spectra of the dioxalanes are then used to scrutinize the methylene hydrogens. Dioxalanes of type 1 give an AB nmr spectrum due to the diastereotopic relationship⁵ of the methylene hydrogens. Dioxalanes of type 2 give an A_2 spectrum as a consequence of the enantiotopic relationship of the methylene hydrogens. Table I lists a series of such nmr values⁶ and the type of spectra observed.

The nmr values for the methine hydrogens in the 1,3-dioxalanes are consistent with the previous correlation rule: the methine hydrogen for the meso (cis) isomer absorbs at lower field than for the d_l racemate

- (4) The method of synthesis for all compounds reported is that of K. C. Branncock and G. Lappin, J. Org. Chem., 1366 (1956). All compounds gave satisfactory analytical data including ir and nmr.

⁽¹⁾ M. H. Gianni, E. L. Stogryn, and C. M. Orlando, J. Phys. Chem. 67, 1385 (1965). Summarized in this work were the cis and trans-2,3-butanediol carbonates of F. A. Anet, J. Amer. Chem. Soc., 84, 747 (1962), and the cis and trans isomers of symmetrically substituted cyclic hydrocarbons of D. Curtin, Chem. Ind. (London) 1205 (1958).

⁽²⁾ This is a consequence of the mechanism of acetal formation; M. Kreevoy and R. W. Taft, J. Amer. Chem. Soc., 77, 5590 (1955).

⁽³⁾ E. L. Eliel, ibid., 84, 2377 (1962).

⁽⁵⁾ For the terminology *diastereotopic* and *enantiotopic* as applied to these systems, see K. Mislow, "Topics in Stereochemistry," Vol. I, John Wiley and Sons, New York, N. Y., 1967.

⁽⁶⁾ Caution must be exercised in extending the method to conformationally mobile systems since a rapid inversion may cause the methylene hydrogens to give an A₂ spectrum due to averaging.

 Table I:
 Hydrogen Chemical Shifts of Some Symmetrically

 Substituted 1,3-Dioxalanes

	τ_{CH_2}	Type
meso-4,5-Dimethyl dioxalane	5.3, 5.01	AB
d,l-4,5-Dimethyl dioxalane	5.15	A_2
meso-4,5-Dipropenyl dioxalane	4.94, 5.20	AB
d,l-4,5-Dipropenyl dioxalane	5.08	A_2
meso-4,5-Divinyl dioxalane	4.85, 5.17	AB
d,l-4,5-Divinyl dioxalane	5.01	A_2

(trans). The nmr values of the 1,2-glycols also indicate that the methine hydrogens for the *meso* isomer absorbs at lower field than for the d,l racemate. This is in accordance with the findings of Wieman,⁷ who, however, notes that the tartaric acids are exceptions to the rule. The chemical shifts for the methine hydrogens for some 1,2-glycols and 1,3-dioxalanes are indicated in Table II.

Table II:Chemical Shifts of the Methine Hydrogen ofSome Symmetrically Substituted 1,3-Glycols and1,3-Dioxalanes

	$ au({ m CH})$
meso-Butane-3,4-diol	6.30
d,l-Butane-3,4-diol	6.50
meso-3,4-Dihydroxy-1,5-hexadiene	5.94
d,l-3,4-Dihydroxy-1,5-hexadiene	6.20
meso-4,5-Dihydroxy-2,6-octadiene	6.00
d,l-4,5-Dihydroxy-2,6-octadiene	6.20
meso-4,5-Dimethyl dioxalane	6.01
d,l-4,5-Dimethyl dioxalane	6.60
meso-4,5-Dipropenyl dioxalane	5.75
d,l-4,5-Dipropenyl dioxalane	6.18
meso-4,5-Divinyl dioxalane	5.60
d,l-4,5-Divinyl dioxalane	6.08

It is important to note here that the concentration of each of the isomers in the diol mixture was reflected in the isomer ratio of the dioxalanes. For example, a $60/40 \ meso/d,l$ isomer mixture of the 3,4-dihydroxy-1,5-hexadiene gave the corresponding $60/40 \ meso/d,l$ isomer ratio of the dioxalanes.⁸ Thus the mechanism as described by Kreevoy is valid for this reaction and no isomer scrambling occurred.

The correlations for the methine hydrogens in the 1,2glycols and for the methine and methylene hydrogens in the 1,3-dioxalanes are internally consistant. One may therefore proceed with confidence when confronted with the problem of configuration when only one isomer of a 1,2-glycol or 1,3-dioxalane is available.^{9,10}

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(7) J. Wieman and G. Dana, Comp. Rend., 258, 3724 (1964).

(8) Values determined from gc and integration of the appropriate nmr peaks. Since the *meso* and d, l dioxalanes most probably form at different rates, care must be taken to ensure complete reaction for both isomers.

(9) Observation of an AB spectrum reliably proves a *meso* form, but its absence cannot preclude a *meso* form due to the changes of accidental isochronicity. If accidental isochronicity is suspect, an aromatic solvent will usually serve to reveal the AB spectrum.

(10) All spectra were run as 23% solution in CCl₄ on a Varian A-60 spectrometer.

The Cobalt-60 γ -Ray Radiolysis of Aqueous Solutions of H₂ + O₂. Determination of $G_{e_{aq}}$ + G_{H} at pH 0.46-6.5¹

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Recent determinations of the primary yields in aqueous solutions indicate that the previously reported value of $G(H_2O_2) = 3.2^{2a,b}$ in γ -irradiated neutral solutions of $H_2 + O_2$ is too low. A similar G (peroxide) of 3.2^3 for the $CH_3CH_2OH + O_2$ system was recently explained by Bielski and Allen⁴ as due to an inhibitory effect of the reaction product CH_3CHO . The present work shows that when the $H_2 + O_2$ system is irradiated under conditions scavenging all the free radicals, $G(H_2O_2)$ equals 3.66. Because of the simple nature of the reactions involved, this system would be expected to provide a reliable means of determining the yield of the reducing radicals.

When OH in the irradiated $H_2 + O_2$ system reacts only with H_2 , and e_{aq}^- and H only with O_2 , the mechanism for the formation of H_2O_2 is

$$OH + H_2 \longrightarrow H_2O + H$$
 (1)

$$e_{aa}^{-} + O_2 \longrightarrow O_2^{-} \tag{2}$$

$$H + O_2 \longrightarrow HO_2$$
 (3)

$$"HO_2" + "HO_2" \longrightarrow H_2O_2 + O_2$$
(4)

" HO_2 " denotes the HO_2 radical without regard to its state of ionization.

(3) A. Hummel and A. O. Allen, Radiation Res., 17, 302 (1962).

⁽¹⁾ Work performed in part under the auspices of the U. S. Atomic Energy Commission.

^{(2) (}a) C. J. Hochanadel, J. Phys. Chem., 56, 587 (1952): (b) N. F. Barr and A. O. Allen, *ibid.*, 63, 928 (1959).

⁽⁴⁾ B. H. J. Bielski and A. O. Allen, Int. J. Radiat. Phys. Chem., 1, 153 (1969).

From reactions 1–4 $G(H_2O_2) = {}^1/_2(G_{e_{aq}} + G_H + G_{OH}) + G_{H_2O_2}$. Using the mass balance equation

$$G_{\rm OH} + 2G_{\rm H_2O_2} = G_{\rm e_{aq}^-} + G_{\rm H} + 2G_{\rm H_2}$$

we obtain

$$G(H_2O_2) = G_{e_{aq}} + G_H + G_{H_2}$$
 (a)

In order to avoid deviations from this mechanism, the conditions under which H_2O_2 is formed must be properly chosen.

(1) The rate constant $k(e_{aq}^{-} + H_2O_2) = 1.2 \times 10^{10} M^{-1} \sec^{-1.5}$ is nearly as large as $k(e_{aq}^{-} + O_2) = 2 \times 10^{10} M^{-1} \sec^{-1.5}$ It is necessary, therefore, to measure H_2O_2 at concentrations not exceeding a few per cent of the concentration of O_2 in order to avoid errors from the competition of

$$e_{aq}^{-} + H_2 O_2 \longrightarrow OH^{-} + OH$$
 (5)

with reaction 2 for e_{aq}^{-} . Moreover, in order to make an accurate correction for the reaction of O_2 with the reducing radicals in the spur, the concentration of O_2 should not exceed $\sim 100 \,\mu M.^6$ From these considerations it follows that the concentration of H_2O_2 in the irradiated solution must not exceed a few μM .

(2) Since the rate constant $k(\text{``HO}_2\text{''} + \text{``HO}_2\text{''})$ is low, ⁷⁻⁹ the steady-state concentration of '`HO₂'' in the irradiated solution is relatively high. Moreover, the rate constant $k(\text{OH} + \text{``HO}_2\text{''})$ (1.01 × 10¹⁰ M^{-1} sec⁻¹)¹⁰ is 200 times $k(\text{OH} + \text{H}_2)$ (5 × 10⁷ M^{-1} sec⁻¹).⁵ Hence the reaction

$$OH + "HO_2" \longrightarrow H_2O_3 \longrightarrow H_2O + O_2 \quad (6)$$

may lower $G(H_2O_2)$. A calculation based on $k("HO_2")$ + "HO₂") = 1.5 × 10⁷ M^{-1} sec⁻¹ (at pH 6.5)⁷ shows that with 750 $\mu M H_2$ the dose rate must be below 1 rad/sec in order to reduce the error in $G(H_2O_2)$ resulting from this reaction below 0.25%.

 H_2O_2 was determined by reaction with Fe^{II} in 0.40 M H_2SO_4 . The Fe^{III} was measured with a Cary 16 spectrophotometer, using ϵ (Fe^{III}) – ϵ (Fe^{II}) = 2201 M^{-1} cm⁻¹ at 304 m μ , 25°.¹¹ The determination of dose was based on G(Fe^{III}) = 15.60 for the standard FeSO₄ dosimeter.¹² The technique for removing impurities from the irradiated solutions has been described.¹¹

Figure 1 shows the dependence of H_2O_2 on dose in a solution of $150 \ \mu M O_2 + 750 \ \mu M H_2$ irradiated with Co^{60} γ rays, at 0.8 and 0.09 rad/sec, pH 6.5. The linear form of the dose curve shows that the effect of reaction 5 is negligible up to $3 \ \mu M H_2O_2$. The independence of H_2O_2 on dose rate shows that the effect of reaction 6 is also negligible. From the slope of the dose curve we obtain $G(H_2O_2) = 3.70$. The effect of the reactions of O_2 in the spur is appreciable at $150 \ \mu M O_2$,⁶ but reliable measurements cannot be made at lower concentrations of O_2 at neutral pH. Since $k(H + H_2O_2)$ is relatively low, we can, however, use lower concentrations of O_2 at acid pH. Such measurements indicate that $G(H_2O_2)$ is



Figure 1. Formation of H_2O_2 in a ⁶⁰Co γ -irradiated solution of 150 $\mu M O_2 + 750 \ \mu M H_2$. Dose rates 0.8 (O) and 0.09 (C) rad/sec, pH 6.5.

1.1% too high at 150 μM O₂. Making this correction, $G(H_2O_2) = 3.66$ in the absence of scavenging in the spur. Using $G_{H_2} = 0.45^{13}$ and $G_H = 0.55^{14}$ equation (a) gives $G_{e_{aq}-} = 2.66$. Earlier values obtained from other reactions are: Hochanadel and Casey (O₂ + CO) 2.58;¹⁵ Haissinsky (NO₃⁻ + HPO₃⁻), 2.65;¹⁶ Rabani, *et al.*, (C(NO₂)₄, pulse spectrophotometry), 2.60;¹⁷ Fielden and Hart (e_{aq}^- absorption), 2.65;¹⁸ Bielski and Allen (O₂ + C₂H₅OH), 2.71.⁴ The value reported by Bielski and Allen was corrected for the spur effect and to a $G(Fe^{III}) = 15.60$ for the FeSO₄ dosimeter.¹² Using the material balance equation and $G_{H_2O_2} = 0.71$,¹⁹ we obtain $G_{OH} = 2.69$.

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- (6) D. A. Flanders and H. Fricke, J. Chem. Phys., 28, 1126 (1958).
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(18) E. M. Fielden and E. J. Hart, Radiation Res., 32, 564 (1967).

(19) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., New York, N. Y., 1961, p 36. Similar measurements were made at lower pH's (Table I). Acidity was adjusted with H_2SO_4 , except at

Table I: $G_{e_{a_q}} + G_H$ Calculated from $G(H_2O_2)$ in Solutions of $O_2 + H_2$ and from $G(Fe^{III})$ in Air-Free Solutions of FeSO₄, Both Irradiated with Co⁶⁰ γ Rays. The pH's Were Adjusted with H₂SO₄ and Also with HClO₄ at pH 0.46

pН	$G(\mathrm{H_2O_2})$	$G_{_{eag}} - + G_{\mathrm{H}}^{a}$	$G(\mathrm{Fe^{III}})$	$G_{eag}^{-} + G_{\mathrm{H}}^{b}$
6.50	3.66	3.21		
4.25	3.66	3.21		
2.74	3.69	3.25	7.40	3.26
2.05			7.55	3.34
1.51	3.88	3.46	7.77	3.47
1.00			7.96	3.57
0.46^{c}	4.07	3.67	8.14	3.67
0.46			8.14	3.67
^a From eq a.	^b From eq	b. ° HClO4.		

pH 0.46. At this pH, HClO₄ was used in order to avoid complications from the reaction of OH with H₂SO₄ ($k = 4 \times 10^5 M^{-1} \text{ sec}^{-1}$).⁵ The values of $G_{e_{aq}} + G_H$ in the third column were calculated from eq a, using reported values for G_{H_2} .¹³ Since G_{H_2} has not been measured in pH 0.46 HClO₄, we used the same value 0.40 as in pH 0.46 H₂SO₄.¹³

For comparison, $G(\text{Fe}^{\text{III}})$ was measured in γ -irradiated air-free 5 mM FeSO₄ and $G_{e_{aq}}$ + G_{H} calculated from¹⁹

$$G_{e_{aq}} + G_{H} = (G(Fe^{III}) - 2G_{H_2})/2$$
 (b)

The two sets of values for $G_{e_{aq}} + G_H$ agree to within 0.3%. The $G(Fe^{III})$'s are the same in pH 0.46 HClO₄ and H₂SO₄.

COMMUNICATIONS TO THE EDITOR

Electronic Absorption Spectra of

Cyclohexadienyl Radical in

 γ -Irradiated Solids at 77°K

Sir: γ -Irradiated benzene in methanol glass at 77°K yields an absorption band of λ_{max} 3.9 eV which has been assigned to cyclohexadienyl radical formed by the reactions¹

$$CH_{3}OH \xrightarrow{\gamma} CH_{3}OH^{+} + e^{-}$$

$$e^{-} + C_{6}H_{6} \longrightarrow C_{6}H_{6}^{-}$$

$$C_{6}H_{6}^{-} + CH_{3}OH \longrightarrow C_{6}H_{7} + CH_{3}O^{-}$$

Reinvestigation of the spectrum revealed another feeble band at about 2.2 eV ($\epsilon_{556 \text{ nm}}: \epsilon_{316 \text{ nm}} \cong 1:40$). By irradiating for longer periods the weak band was uniformly magnified as shown in Figure 1 (lower). Concomitant appearance of the two bands for samples of thoroughly purified materials² convinced us to associate the 2.2-eV band with the cyclohexadienyl radical. (Failure of the detection of this band in the previous work¹ is attributed to high noise levels due to bubbling of the coolant liquid. In the present work the bubbling was prevented by lowering the temperature slightly below 77°K.) The assignment was supported by a calculation for electronic states of the radical; the H₂ unit of CH₂ was regarded as a pseudo atom from which a pseudo- π and a pseudo- σ electron were extracted.³ The four sp³ electrons of the carbon of CH_2 were also transformed into a $p\pi$ and three $sp^2 \sigma$ electrons. The seven π -electron system, analogous to the isoelectronic benzyl radical,^{4,5} was then treated after Longuet-Higgins and Pople⁵ with the molecular integrals over the pseudo AO being reduced into those over the hydrogen 1s AO's.³ The calculation predicts two bands at 2.03 and 3.95 eV with the respective oscillator strengths of 4.07×10^{-4} and 1.35×10^{-1} in remarkable agreement with the observed values of 2.22 eV (4.3 \times 10⁻⁴) and 3.92 eV (1.27 \times 10⁻¹), respectively. The two bands correlate, respectively, to the B_{2u} and E_{1u} states of benzene both strongly affected with the charge transfer between the H_2 pseudo- π electron and the ring- π electrons.⁶

Cyclohexadienyl radical has been known for some time in γ -irradiated polycrystalline benzene at 77°K

⁽¹⁾ T. Shida and W. H. Hamill, J. Amer. Chem. Soc., 88, 3689 (1966).

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⁽⁴⁾ G. Porter and E. Strachan, Spectrochim. Acta, 12, 299 (1958).

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Figure 1. Absorption spectra of cyclohexadienyl radical: upper, pure benzene in a 2-mm optical cell; lower, 1 mol/l. of benzene in methanol in a 1.5-mm cell; both γ -irradiated to a dose of 2.1 \times 10²¹ eV/g and measured at 77°K. For the pure polycrystalline benzene the apparent background absorption due to scattering of light increased monotonously toward shorter wavelengths. The background absorption has been subtracted in the above spectrum.

by its characteristic esr absorption.7 Thus we attempted to detect the 2.2-eV band for the irradiated pure benzene at 77°K. Using a thin cell (2.0 mm) and a Cary spectrophotometer (Model 14 RI) with an intensified lamp, we observed the spectrum shown in Figure 1 (upper). Except a few shaded ones, the peaks correspond well with those found in the alcoholic solution. Regarding the structure as vibrational, we analyzed the band system and deduced the fundamentals listed in Table I. The overtones and combinations could be determined to the accuracy inherent to the monochromator employed. The fundamentals bear resemblance to those of benzene in its ground electronic state.⁸ This suggests that the radical is subject to little skeletal change in its first electronically excited state. Similar analysis for the visible band system of irradiated pure perdeuteriobenzene yielded the fundamentals below which apparently correspond to those of the ground state C_6D_6 indicated in parenthesis for comparison,⁸ 391 cm⁻¹(337), 563 (576.7), 849 (813), 937 (944.7), 1425 (1333).

Table I ·	The Vibrational	Analysis for	CeH2 in CeF	Ŧ۰
тяшет:			U6117 III U61	× 6

Wave number, cm ⁻¹	Differ- ence, cm ⁻¹	Assign- ment	Wave number, cm ⁻¹	Differ- ence, cm ⁻¹	Assignment
17904		0-0	20218	2314	$\nu_3 + \nu_6$
18350	446	<i>v</i> 1	20374	2470	$\nu_4 + \nu_6$
18442	538	ν_2	20522	2618	$\nu_5 + \nu_6$
18750	846	vz	20721	2817	$\nu_5 + 2\nu_3$
18890	986	24	20858	2954	$2\nu_{6}$
19033	1129	V 5	21361	3457	$\nu_3 + \nu_5 + \nu_6$
19331	1427	$\nu_1 + \nu_4$	21528	3624	Foreign
19386	1482	ν ₆	21652	3748	$\nu_6 + 2\nu_5$
19582	1678	$2\nu_{8}$	21868	3964	Foreign
19753	1849	$v_3 + v_4$	22003	4099	$\nu_5 + 2\nu_6$
19886	1982	$\nu_3 + \nu_5$	22346	4442	326
		or 214	22636	4732	Foreign
20018	2114	$\nu_4 + \nu_5$	22823	4919	$\nu_3 + \nu_5 + 2\nu_6$
20170	2266	$2\nu_5$			

(7) S. Ohnishi, T. Tanei, and I. Natta, J. Chem. Phys., 37, 2402 (1962).

(8) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1949. The fundamentals in Table I are corresponding to those of benzene in parenthesis, ν_1 (404 cm⁻¹, e_{2u} , C[⊥]), ν_2 (605.6, e_{2g} , C^{||}), ν_3 (848.9, e_{1g} , CH[⊥]), ν_4 (991.6, a_{1g} , C-C), ν_6 (1037, e_{1u} , CH^{||}), ν_6 (1485, e_{1u} , C-C)

THE INSTITUTE OF PHYSICAL AND CHEMICAL RESEARCH YAMATOMACHI, KITAADACHI-GUN SAITAMA PREF., JAPAN

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Effect of Solvent on Hydrogen Bond Formation Equilibria

Sir: Recently, the argument has been advanced that hydrogen bond equilibrium studies using CCl₄ as a solvent are seriously in error because CCl₄ functions as a proton acceptor and thereby reduces the tendency of alcohols and other hydroxylic compounds to form aggregates.¹ To circumvent this problem, Fletcher has treated infrared spectral data for the system 1-octanolcarbon tetrachloride by utilizing values of association constants for the alcohol in *n*-decane and introducing an additional equilibrium constant for the competitive reaction $alcohol + CCl_4 = alcohol \cdot CCl_4$. Although we do not deny the possibility that CCl₄ may form hydrogen bonds with alcohols, we should like to point out the difficulties which are inherent in methods employed to infer association constants for reactions between a solvent and a solute.

Fletcher's procedure for analyzing spectral data resembles the technique developed by Dolezalek and

(1) A. N. Fletcher, J. Phys. Chem., 73, 2217 (1969).

coworkers for fitting vapor pressure data for binary systems. Dolezalek attributed all deviations from Raoult's law to the formation of specific complexes or compounds, each of which was assumed to behave ideally. Equilibrium constants for compound formation reactions were used as fitting parameters and treated as constants over the entire concentration range. Virtually any collection of data could be correlated by including a sufficient number of formation constants, although at times some unlikely species had to be proposed.²

The major weakness of the Dolezalek approach has been that it ignores the contribution of nonspecific molecular interactions to deviations from the ideal solution laws. The van Laar-Hildebrand-Scatchard school has introduced methods for treating nonspecific or physical effects on the activity coefficients of dissolved species, while recognizing that complex formation can also play a major role in nonideal solution behavior.³ Prevailing solution theories predict that complex formation constants will not be constant in different solvents, even if the maximum-randomness criterion of regular solution theory is met by all the species involved in the formation reaction in each of the solvents.⁴ Thus, it is anticipated that the formation constant for a given alcohol aggregate will have one value in the vapor phase, another in perfluoro-n-decane, and yet another in n-decane, even if no specific complexes form between solvent and solute.

To illustrate the influence even a nearly inert solvent can exert on hydrogen-bonding equilibria, we report the following results (derived from vapor pressure and vapor density data) for the reaction between methanol (M) and diethylamine (DEA), in vapor and in *n*-hexadecane at $25^{\circ 5}$

vapor
$$M$$
 + $DEA \xrightarrow{-6.7} M \cdot DEA$
 $-2.9 \downarrow (-1.25)$ $-5.6 \downarrow (-3.16)$ $-6.3 \downarrow (-4.15)$
n-hexadecane M + $DEA \xrightarrow{-4.5} M \cdot DEA$

Numbers enclosed in parentheses represent ΔG° values (in kcal/mol) for conversions between 1 mol/l. ideal dilute solution standard states; the remaining numbers are ΔE° values (in kcal/mol). It is clear that the solvation energies and free energies of the individual solute species are not small compared to the energies and free energies of the formation reaction.⁶ The equivalence of ΔG° for the reaction in vapor and in *n*-hexadecane would require that the sum of the solvation free energies of donor and acceptor equal the solvation free energy of the complex; however, there appears to be no theoretical or experimental basis for predicting the equality of these terms.^{7,8}

We know of no rigorous way to deduce equilibrium constants for the formation of complexes between a solvent and a solute. The only reactions in condensed phases for which unambiguous thermodynamic results have been reported are of the type: reactants (solvated solutes, dilute solution) = complex (solvated solute, dilute solution). The individual reactant and complex molecules, at sufficient dilutions, will obey Henry's law, Beer's law, and other limiting laws. In favorable situations, formation constants can be inferred from deviations of spectral, vapor pressure, or other results from the concentration dependence predicted by the dilute solution laws. However, when an attempt is made to infer the formation constant for a solvent-solute complex, it is necessary to vary the concentrations of the reacting components over such wide ranges that the nature of the medium changes and the limiting laws no longer apply. Then it becomes impossible uniquely to determine the relative importance of specific and nonspecific effects in causing departure from ideality.⁵

To summarize, it is our view that formation constants inferred for an association reaction in *n*-decane are neither superior nor inferior to those obtained using CCl_4 as the solvent. All thermodynamic constants reported for association reactions in condensed phases pertain to the conversion of solvated donor and acceptor into solvated complex. Only by investigating formation reactions in the vapor phase can the complicating effects of solvation entirely be avoided.

(3) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962.

(4) See, for example (a) H. Buchowski, J. Devaure, P. V. Huong, and J. Lascombe, Bull. Soc. Chim. Fr., 2532 (1966); (b) P. V. Huong, N. Platzer, and M. L. Josien, J. Amer. Chem. Soc., 91, 3669 (1969).

(5) E. E. Tucker, Ph.D. Dissertation, The University of Oklahoma, 1969.

(6) J. Grundnes and S. D. Christian, J. Amer. Chem. Soc., 90, 2239 (1968), discuss the important effect of a hydrocarbon solvent on the formation of the trimethylamin \ge SO₂ complex.

(7) Apparently, the word solvation does not mean the same thing to everyone. As we employ the term, it includes all the specific and nonspecific factors contributing to the interaction of a dissolved solute with the solvent. We refer to changes in thermodynamic functions for the conversion

A (ideal gas, unit molarity) = A (dissolved solute, ideal dilute solution at unit molarity)

as solvation energies, solvation free energies, etc., of the solute A. Consequently, our definitions are incompatible with the view that regular solution theory applies only in the absence of solvation effects;⁸ we believe that the success of the regular solution theory owes in large measure to its ability to predict thermodynamic constants for the solvation of nonpolar solutes.

(8) A. N. Fletcher, J. Phys. Chem., 74, 214 (1970).

(9) As Fletcher correctly notes,⁸ numerous reports on molecular complex formation—including some from this laboratory—have treated data for relatively concentrated solutions. We suspect that many published values of formation constants are seriously in error because the laws of dilute solution have been invoked throughout excessive ranges of concentration. Nevertheless, we feel that it is more realistic to assume that dissolved acetone species individually follow Henry's law (at total solute concentrations up to 0.3 M in n-hexadecane) than to employ the unmodified Dolezalek approach and attribute all deviations from Raoult's law (throughout the entire

⁽²⁾ For a critical discussion of Dolezalek's specific interaction or chemical treatment of nonideality, as contrasted with the physical approach, see J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Dover Publications, New York, N. Y., 1964, pp 175-197.

concentration range for a binary system) to the formation of discrete complexes.

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Reply to "Effect of Solvent on Hydrogen Bond

Formation Equilibria"

Sir: Christian and Tucker¹ have made the assumption that nonspecific physical interactions between solute and solvent will always have such a significant effect upon concentration equilibrium quotients and limiting law relationships that a wide range of solute concentrations cannot be used to determine specific chemical interactions. This assumption, if true, would not only invalidate a recent study on hydrogen bonding by this writer,² but it would also place doubt upon studies from their own laboratory.^{3,4}

Christian and Tucker cite the work of Buchowski, et al.,⁵ and Huong, et al.,⁶ as evidence that equilibrium quotients must change with changing characteristics of the solvent, e.g., changing solubility parameters. Examination of the data of the cited articles reveals that a different interpretation can be made than was made by the authors. If the solvents are divided into two groups, those with and those without nonbonding electrons, no significant changes in the concentration equilibrium quotients are observed within each solvent group despite the wide range of solubility parameters. The change that is evident between the two classes of solvents is in the direction that would be predicted for a specific chemical interaction between the solute and the solvent.

Additional evidence for a negligible physical effect upon concentration equilibrium quotients for hydrogen bonding may be seen in the study of the self-association of 1-octanol in *n*-decane performed by Fletcher and Heller.⁷ At all concentrations, from dilute to pure alcohol, over a 95° temperature range, the equilibrium quotients derived by the ratio of the self-association polymer O-H absorption band to the fourth power of the monomer absorption band were essentially constant at a given temperature. Here, the composition and the dielectric constant of the solution changed markedly without any apparent change in the concentration equilibrium quotients for either the acyclic or the cyclic tetramer. Yet a change in solvent from *n*-decane to that of CCl₄, both solvents having almost identical dielectric constants, resulted in a 15-fold reduction in the equilibrium quotients of both tetramers.² In addition, it was found that only a single 1:1 complex between CCl_4 and the monomer of 1-octanol was needed to explain the 15-fold change in the equilibrium quotients over the complete range of possible concentrations. Since hydrogen bonding of alcohols to chloroaliphatics is known to occur,⁸ and since there is independent evidence for a specific interaction of alcohols with CCl₄ from studies involving dipole moments,⁹ reaction kinetics,¹⁰ vapor pressure,¹¹ heats of mixing,¹² and spectral shifts,¹³ a hydrogen bond between an alcohol and CCl₄ does not produce an unlikely species. Thus 1-octanol shows no significant specific nor nonspecific interactions with the solvent *n*-decane and shows only a single specific interaction with the solvent CCl₄.

Just as the above evidence indicates that equilibrium quotients are not always limited to dilute solutions, neither are the limiting laws always restricted to dilute solutions. This is best evidenced by the fact that Raoult's law does hold for some solutions at all concentrations.¹⁴ If Raoult's law is valid, then Henry's limiting law is valid over the same concentration range.¹⁴

Specific and nonspecific interactions of a functional group must be distinguished from those of the molecule as a whole. Thus the gross thermodynamics reported by Christian and Tucker for the reaction of methanol with diethylamine are not clear evidence for a specific interaction involving the hydrocarbon solvent (excess thermodynamic relationships using equivalent hydrocarbons as reference materials are needed here).

In conclusion, since a specific "solvation" was observed for 1-octanol in CCl_4 but not for 1-octanol in *n*-decane,^{2,7} hydrocarbon solvents are preferable to CCl_4 and other acceptor solvents for the study of the equilibrium quotients of hydrogen-bonded systems. Although

(1) S. D. Christian and E. E. Tucker, J. Phys. Chem., 74, 214 (1970).

- (2) A. N. Fletcher, *ibid.*, 73, 2217 (1969).
- (3) T. F. Lin, S. D. Christian, and H. E. Affsprung, *ibid.*, 71, 1133 (1967).

(4) E. E. Tucker, S. B. Farnham, and S. D. Christian, *ibid.*, 73, 3820 (1969).

(5) H. Buchowski, J. Devaure, P. V. Huong, and J. Lascombe, Bull. Soc. Chim. Fr., 2532 (1966).

(6) P. V. Huong, N. Platzer, and M. L. Josien, J. Amer. Chem. Soc., 91, 3669 (1969).

(7) A. N. Fletcher and C. A. Heller, J. Phys. Chem., 71, 3742 (1967).

(8) (a) P. J. Krueger and H. D. Mettee, Can. J. Chem., 42, 288 (1964);
(b) W. W. Brandt and J. Chojnowski, Spectrochim. Acta, 25A, 1639 (1969).

(9) P. Huyskens, R. Henry, and G. Gillerot, Bull. Soc. Chim. Fr., 720 (1962).

(10) J. Koskikallio and K. Koivula, Suomen Kemistilehti, B-40, 138 (1967).

(11) H. Wolff and H. E. Hoeppel, Ber, Bunsenges. Phys. Chem., 72, 1173 (1968).

(12) J.-E. A. Otterstedt and R. W. Missen, Trans. Faraday Soc., 58, 879 (1962).

(13) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen and Co. Ltd., London, 1968, Chapter 8 and references cited therein.

(14) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Dover Publications, New York, N. Y., 1964, Chapter II.

the broad ^{15,16} definition of "solvation" used by Christian and Tucker allows them to place a label of "solvated" on all molecules in solution, the label does not necessarily mean that "solvation" is *always* going to play a significant part in the chemistry of the molecules.

(15) A fundamental part of the theory of regular solutions is the absence of "solvation" of the molecules of a solution.¹⁶ Thus in a regular solution, specific chemical interactions are considered absent.¹⁶ Christian and Tucker have included both physical and chemical interactions under their definition of "solvation."

(16) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962, p 3.

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The Chemistry of Nuclear Recoil Fluorine-18

Atoms. III. The Average Energy and

Mechanism for F-for-F Substitution in CH₃CF₃

Sir: Energetic substitution (1) is one of the novel chemical reactions that are uniquely characteristic of high-energy chemical systems.^{1,2}

$$\mathbf{X}^* + \mathbf{R}_j \mathbf{Y} \xrightarrow{\mathbf{X}\text{-for-}\mathbf{Y}} (\mathbf{R}_j \mathbf{X}^\dagger) + \mathbf{Y}$$
(1)

An important fundamental question about such reactions has to do with the energy ranges in which they occur. Experimental studies of the levels of vibrational excitation for the $(R_j X^1)$ product species have provided the available information about reaction energy ranges for T-for-H (2) and F-for-F (3) reactions³

$$T^* + CH_3CF_3 \xrightarrow{\text{T-for-H}} (CH_2TCF_3^{\dagger}) + H \qquad (2)$$

$$^{18}\text{F} + \text{CH}_3\text{CF}_3 \xrightarrow{\text{F-for-F}} (\text{CH}_3\text{CF}_2{}^{18}\text{F}^{\dagger}) + {}^{19}\text{F}$$
(3)

Average residual $(R_j T^{\dagger})$ energies from (2) have generally been found to lie within the range $5 \pm 1 \text{ eV.}^4$

We have sought similar information for F-for-F reactions based upon experiments with nuclear recoil ¹⁸F atoms. The results from our first experiments, which involved pressure-dependence studies with perfluorocyclanes, indicated extensive unimolecular decomposition of the products from (3) in $c-C_3F_6$ and $c-C_4F_8$ arising from remarkably large $\bar{E}^{vib}(R_j^{18}F)$ values.^{2,5a,5b} In an attempt to provide support for these unusual results, further experiments have been carried out involving activation of a single chemical species by *both* reactions 2 and 3. The primary goal of this work was the direct comparison of experimental unimolecular rate constants for $CH_3CF_2^{18}F$ from (3) and CH_2TCF_3 from (2), with the aim of minimizing errors in the calculated $\bar{E}^{vib}(R_jX)$ values. Activated $\rm CH_3CF_3$ undergoes unimolecular decomposition via concerted HF elimination.⁶ To provide an independent check on the $\rm CH_3CF_3$ parameters used in our calculations, we have also carried out a parallel study of activated ¹⁴CH₃CF₃ produced via radical recombination.

The recoil experiments involved ¹⁹F(n, 2n)¹⁸F and ³He(n, p)³H nuclear activation.^{5a-5c} Scavengers including H₂S, O₂, fluorinated olefins, and mixtures of these substances assured the efficient removal of thermalized recoil atoms and organic radicals. Identical results were obtained with these scavengers, except that H₂S permitted experimental determination of ¹⁸F-labeled radicals.^{5b} The ¹⁴CH₃COF₃ experiments involved co-photolysis of ¹⁴CH₃COCH₃-CF₃COCF₃ mixtures with large excesses of CH₃CF₃ present as "bath" species. All the experiments involved radiogas chromatographic analysis.^{5a-5c}

The CH₃CF₃ results and other relevant data are given in Table I.⁷ The ratio of $\overline{k_a(E)}$ values for (CH₃-CF₂¹⁸F): (CH₂TCF₃) was found to be 2200 \pm 300, which indicates unambiguously that \overline{E}^{vib} (CH₃CF₂¹⁸F) $\gg \overline{E}^{vib}$ (CH₂TCF₃).^{2,5a,8} Calculated \overline{E}^{vib} (R₂X) values

(1) (a) A. P. Wolf, Advan. Phys. Org. Chem., 2, 201 (1964); (b) R. Wolfgang, Ann. Rev. Phys. Chem., 16, 15 (1965); (c) R. Wolfgang, Accounts Chem. Res., 2, 248 (1969).

(2) Symbols include (*) and (†), translational and vibrational excitation; $\overline{E}^{vib}(\mathbf{R}_{i}X)$, mean residual energy from (1); k_{a*} unimolecular rate constant; A, S, and E_{a} , Kassel parameters (ref 8b, 8c); Z_{AA} and n_{A} , the binary collision frequency and molecular density at pressure P; Z, the gas compressibility factor; and d = s refers to the fugacity at which half the energized $(\mathbf{R}_{i}X^{\dagger})$ species undergo collisional stabilization.

(3) Center-of-mass X-for-Y reaction energies are related through energy conservation to the sum of reaction enthalpy changes, product internal excitation energies, and displaced atom kinetic energies. Since the latter are unknown, the present results provide *minimum* estimates for the average F-for-F and T-for-H reaction energies.

(4) (a) Available $\overline{E}^{vib}(R_{f}T)$ results include: CH₃T, 3.5 ± 1.0 eV (ref 4b, 4c); c-C₃H₅T, c-C₄H₇T, and c-C₄D₇T, 5 ± 1 eV (ref 4d-4f); (b) D. Seewald and R. Wolfgang, J. Chem. Phys., 47, 143 (1967); (c) Y. N. Tang and F. S. Rowland, J. Phys. Chem., 72, 707 (1968); (d) J. K. Lee, B. Musgrave, and F. S. Rowland, J. Amer. Chem. Soc., 81, 3803 (1959); (e) E. K. C. Lee, and F. S. Rowland, *ibid.*, 85, 897 (1963); (f) C. T. Ting and F. S. Rowland, J. Phys. Chem., 72, 763 (1968).

(5) (a) N. J. Parks, C. F. McKnight, and J. W. Root, *Chem. Eng. News*, Sept 15, 42 (1969); (b) C. F. McKnight and J. W. Root, *J. Phys. Chem.*, 73, 4430 (1969); (c) J. W. Root, *ibid.*, 73, 3174 (1969); (d) R. R. Pettijohn, K. A. Kroin, N. J. Parks, C. F. McKnight, and J. W. Root, manuscripts in preparation.

(6) (a) S. W. Benson and G. Haugen, J. Phys. Chem., 69, 3898 (1965);
(b) R. D. Giles and Z. Whittle Trans. Faraday Soc., 61, 1425 (1965);
(c) A. Maccoll, Chem. Rev., 69, 33 (1969);
(d) M. J. Berry and G. C. Pimentel, J. Chem. Phys., 49, 5190 (1968);
(e) D. C. Phillips and A. F. Trotman-Dickenson, J. Chem Soc., A, 1144 (1968);
(f) S. H. Bauer, J. Amer. Chem. Soc., 91, 3688 (1969).

(7) Y. N. Tang, T. Smail, and F. S. Rowland, *ibid.*, 91, 2130 (1969).
(8) (a) The basic Kassel relation is not applicable to situations that involve wide "excitation spectra." We define an average k_a as^{2 · 8b · c}

$$\overline{k_{a}(E)} = A \left(\frac{\overline{E}^{vib}(R_{j}X) - E_{a}}{\overline{E}^{vib}(R_{j}X)} \right)^{s-1} = (Z_{AA}/n_{A})_{d=s} \quad (5)$$

in which $(Z_{AA}/n_A)_{d=s}$ is calculated directly from the experimental quantity $(P/Z)_{d=s}$ (note 2). (b) N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959, Chapter VIII, p 164 ff; (c) N. B. Slater, *Trans. Roy. Soc.* (London), 246, 57 (1953); (d) Fugacity and collision diameter calculations have already been described (ref 5b,8e). Diameters estimated for CH_3CF_3 and CH_2FCF_3 were 4.98 and 5.0 Å. (e) J. W. Root, Ph.D. Dissertation, University of Kansas, 1964.

Product species	Reaction	Exptl half-fugacity, atm	Exptl $\overline{k_{B}(E)}$, sec ⁻¹	Calcd $\overline{E}^{vib}(\mathbf{R}_{j}\mathbf{X})$, eV	Ref
¹⁴ CH ₂ CF ₂	$^{14}CH_{2} + CF_{3}$	0.038 ± 0.001	1.32×10^{8}	4.33 ± 0.09	This work
CH ₂ TCF ₃	T-for-H	0.13 ± 0.03	4.6×10^{8}	4.7 ± 1.0	This work
CH ₃ CF ₂ ¹⁸ F	F-for-F	280 ± 50	$1.0 imes 10^{12}$	11.5 ± 2.0	This work
CH ₂ ¹⁸ FCF ₃	F-for-H	7.3 ± 0.1	$2.3 imes10^{10}$	6.7 ± 1.0	This work
				(8.8 ± 2.0)	5b
$c - C_4 F_7{}^{18}F$	F-for-F	12.0 ± 0.5	3.6×10^{10}	{ to	
				$(10.5 \pm 2.0$	
$CF_{3}^{18}F$	F-for-F	4.44		$>9.3 \pm 0.1$	5b, 7

Table I: Experimental $\overline{k_{a}(E)}$ and Calculated $\overline{E}^{vib}(\mathbf{R}, \mathbf{X})$ Values for Energetic Substitution Reactions

were obtained via a modified Kassel treatment,^{8,9} for which several sources of error can be anticipated.^{5b,10} Facts which support these calculated values include: (i) the ¹⁴CH₃CF₃ results agree with available kinetic background data for CH₂CF₃,^{6,9} (ii) the $\bar{E}^{\rm vib}$ (CH₂TCF₃) value is consistent with earlier T-for-H results;⁴ (iii) the $\bar{E}^{\rm vib}$ (CH₃CF₂¹⁸F) value is consistent with our previous $\bar{E}^{\rm vib}$ (c-C₄F₇¹⁸F) value;^{5a,5b} and (iv) thermodynamic evidence favoring large $\bar{E}^{\rm vib}$ (R¹⁸F) values from (3) is provided by the observation of extensive stepwise decomposition of CF₃¹⁸F to :CF¹⁸F. The minimum endoergicity for this process is 9.3 eV.^{5a-5c,7} Unfortunately, no data are available for comparison with our $\bar{E}^{\rm vib}$ (CH₂¹⁸FCF₃) value from (4)

$$^{18}\mathrm{F}^* + \mathrm{CH}_3\mathrm{CF}_3 \xrightarrow{\mathrm{F-for-H}} (\mathrm{CH}_2{}^{18}\mathrm{FCF}_3^{\dagger}) + \mathrm{H}$$
 (4)

but our results are consistent with the earlier report of extensive decomposition associated with (4) in cyclanes.¹¹

A concerted mechanism for F-for-F substitution follows. On the basis of the present results, we therefore conclude that the $\bar{E}^{vib}(\mathbf{R}_{j}^{18}\mathbf{F})$ values from (3) in CH₃CF₃, c-C₄F₈, and CF₄—and also by implication the mean reaction energies—exceed 10 eV.³ Although "direct" microscopic mechanisms have often been favored for X-for-Y reactions,¹ Bunker has demonstrated through an extensive classical trajectory study that T-for-H reactions involve the concerted participation of several atoms in the reactant molecules.¹² In agreement with his findings, our results support a "concerted" mechanism for F-for-F reactions, since $\bar{E}^{vib}(\mathbf{R}_{j}^{18}\mathbf{F})$ values invariably exceed the various C-F bond dissociation energies by factors of 2 or more. F-for-F reactions simply could not deposit residual energies of this magnitude via any process involving only one C-F chemical bond. The concerted participation of neighboring bonds serves to effect at least partial intramolecular distribution of the excess energy.

Acknowledgment. The authors express appreciation to Dr. J. R. Martin and Dr. R. J. Mattson of DuPont for gifts of fluorine chemicals; to the Crocker Laboratory staff and the University of Calfornia, Berkeley, Nuclear Reactor staff for cooperation; to the U. S. Atomic Energy Commission for support;¹³ and to Professor D. L. Bunker, University of California, Irvine, for advance communication of his results.

(9) (a) Kassel S parameters within a fluorohydrocarbon series increase with fluorine substitution (ref 5b,9b). $c-C_2F_xH_{6-z}$ values range from 13.0 to 21.0 (x = 0 to x = 4), and $C_2F_xH_{6-z}$ values range from 9.0 to 18.0 (x = 0 to x = 4), and $C_2F_xH_{6-z}$ values range from 9.0 to 18.0 (x = 0 to x = 6), corresponding to active participation of all vibrational modes for both fully fluorinated species. For CH₃CF₃ and CH₂FCF₃ log (A) = 13.5, and S = 13.5 and 15.0, respectively (ref 6a-6c). Our ¹⁴CH₃CF₃ experiments support $E_a = 2.73 \pm 0.06$ eV based upon $D_3(CH_3-CF_3) = 4.33 \pm 0.09$ eV (ref 9c) in agreement with earlier work (ref 6a, 9b). This value was also assumed for CH₂FCF₃ (ref 6a-6c). (b) F. P. Herbert, J. A. Kerr, and A. F. Trotman-Dickenson, J. Chem. Soc., 5710 (1965); (c) J. W. Coomber and E. Whittle, Trans. Faraday Soc., 63, 1394 (1967).

(10) Several sources of error can be anticipated: (i) large error limits were cited for $(P/Z)_{d=s}$ for CH₃CF₂¹⁸F, because its determination required extrapolation over a 20-fold pressure range. Our measurements spanned a 500-fold pressure range from 0.025 to 12.5 atm; other experimental errors are negligible in comparison; (ii) errors in the Kassel parameters (note 9) including their possible energy dependence (ref 5b, 10b); (iii) errors in the strong collision assumption; (iv) errors in our implicit assumption of identically shaped excitation spectra from (2) and (3) in CH₃CF₃. In partial support of this assumption available excitation spectra from (2) have been symmetric about $\overline{E^{vib}}(R_3T)$ for both Kassel and Rice-Marcus kinetic models (ref 4c-4f, 10c). (b) D. W. Placzek, B. S. Rabinovitch, and G. Z. Whitten, J. Chem. Phys., 43, 4071 (1965); (c) E. K. C. Lee, Ph.D. Dissertation, University of Kansas, 1963.

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- (13) This research was supported under A.E.C. Contract AT-(11-1)-

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