**JPCHA**x

# THE JOURNAL OF PHYSICAL CHEMISTRY

PUBLISHED BIWEEKLY BY THE AMERICAN CHEMICAL SOCIETY

# THE JOURNAL OF PHYSICAL CHEMISTRY

# BRYCE CRAWFORD, Jr., Editor STEPHEN PRAGER, A ssociate Editor ROBERT W. CARR, Jr., FREDERIC A. VAN-CATLEDGE, Assistant Editors

**EDITORIAL BOARD :** A. O. ALLEN (1970–1974), J. R. BOLTON (1971–1975), F. S. DAINTON (1972–1976), M. FIXMAN (1970–1974),

H. S. FRANK (1970–197 $\leq$ ), R. R. HENTZ (1972–1976), J. R. HUIZENGA (1969–1973), W. J. KAUZMANN (1969–1973), R. L. KAY (1972–1976), W. R. KRIGBAUM (1969–1973), R. A. MARCUS (1968–1972), W. J. MOORE (1969–1973), J. A. POPLE (1971–1975), B. S. RABINOVITCH (1971–1975), H. REISS (1970–1974), S. A. RICE (1969–1975), F. S. ROWLAND (1968–1972), R. L. SCOTT (1968–1972), R. SEIFERT (1968–1972), W. A. ZISMAN (1972–1976)

CHARLES R. BERTSCH, Manager, Editorial Production

AMERICAN CHEMICAL SOCIETY, 1155 Sixteenth St., N.W., Washington, D. C. 20036 FREDERICK T. WALL, Executive Director

Books and Journals Division JOHN K CRUM, Director JOSEPH H. KUNEY, Head, Business Operations Department RUTH REYNARD, Assistant to the Director

©Copyright, 1972, by the American Chemical Society. Published biweekly by the American Chemical Society at 20th and Northampton Sts., Easton, Pa. 18042. Second-class postage paid at Washington, D. C., and at additional mailing offices.

All manuscripts should be sent to *The Journal of Physical Chemistry*, Department of Chemistry, University of Minnesota, Minneapolis, Minn. 55455.

Additions and Corrections are published once yearly in the final issue. See Volume 75, Number 26 for the proper form.

Extensive or unusual alterations in an article after it has been set in type are made at the author's expense, and it is understood that by requesting such alterations the author agrees to defray the cost thereof.

The American Chemical Society and the Editor of *The Journal* of *Physical Chemistry* assume no responsibility for the statements and opinions advanced by contributors.

Correspondence regarding accepted copy, proofs, and reprints should be directed to Editorial Production Office, American Chemical Society, 20th and Northampton Sts., Easton, Pa. 18042. Manager: CHARLES R. BERTSCH. Assistant Editor: EDWARD A. BORGER.

Advertising Office: Century Communications Corporation, 142 East Avenue, Norwalk, Conn. 06851.

#### Business and Subscription Information

Remittances and orders for subscriptions and for single copies,

notices of changes of address and new professional connections, and claims for missing numbers should be sent to the Subscription Service Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Allow 4 weeks for changes of address. Please include an old address label with the notification.

Claims for missing numbers will not be allowed (1) if received more than sixty days from date of issue, (2) if loss was due to failure of notice of change of address to be received before the date specified in the preceding paragraph, or (3) if the reason for the claim is "missing from files."

Subscription rates (1972): members of the American Chemical Society, \$20.00 for 1 year; to nonmembers, \$60.00 for 1 year. Those interested in becoming members should write to the Admissions Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Postage to Canada and countries in the Pan-American Union, \$5.00; all other countries, \$6.00. Single copies for current year: \$3.00. Rates for back issues from Volume 56 to date are available from the Special Issues Sales Department, 1155 Sixteenth St., N.W., Washington, D. C. 20036.

This publication and the other ACS periodical publications are now available on microfilm. For information write to: MICROFILM, Special Issues Sales Department, 1155 Sixteenth St., N.W., Washington, D. C. 20036.

Notice to Authors last printed in the issue of December 23, 1971

# THE JOURNAL OF PHYSICAL CHEMISTRY

Volume 76, Number 8 April 13, 1972

JPCHAx 76(8) 1089-1230 (1972)

Cyclization and Decomposition of 4-Penten-1-yl Radicals in the Gas Phase	1089
Radiative and Nonradiative Pathways in Solution: Excited States of the Europium (III) Ion Yehuda Haas and Gabriel Stein*	1093
Photosensitized Decomposition of Hexaamminecobalt(III) by Biacetyl and by Quinoline Harry D. Gafney and Arthur W. Adamson*	1105
Vacuum-Ultraviolet Photolysis of the C <sub>4</sub> H <sub>6</sub> Isomers. IV. 1-Butyne Kevin L. Hill and Richard D. Doepker*	1112
Pulse Radiolysis Study of Dimer Cation Formation of Aromatic Hydrocarbons in Benzonitrile Solution Akira Kira, Shigeyoshi Arai,* and Masashi Imamura	1119
Reactions of Energetic Positronium Atoms in Solutions Lawrence J. Bartal, J. Blair Nicholas, and Hans J. Ache*	1124
An Investigation of the Low Energy Singlet-Triplet and Singlet-Singlet Transitions in Ethylene Derivatives by Ion Impact John H. Moore, Jr.	1130
Primary Processes in Excited Charge-Transfer Systems N. Orbach, R. Potashnik, and M. Ottolenghi*	1133
Infrared Spectra and Dielectric Properties of Crystalline Hydrogen Cyanide P. F. Krause and H. B. Friedrich*	1140
Raman Spectra and an Assignment of the Vibrational Stretching Region of Water W. F. Murphy and H. J. Bernstein*	1147
Measurement of Longitudinal Relaxation Times for Spin-Decoupled Protons Michael J. Gerace and Karl F. Kuhlmann*	1152
New Electrochemical Measurements of the Liquidus in the LiF-BeF2 System. Congruency of Li2BeF4 K. A. Romberger, J. Braunstein,* and R. E. Thoma	1154
Theory for a Homogeneous Reaction following a Quasireversible Electrode Reaction	1160
Multicomponent Diffusion in a System Consisting of a Strong Electrolyte Solute at Low Concentrations in an Ionizing Solvent	1166
Catalytic Polarographic Current of a Metal Complex. VIII. Effect of Weakly Complexing Supporting Electrolytes Josip Čaja, Hubert C. MacDonald, Jr., E. Kirowa-Eisner, Lowell R. McCoy, and Harry B. Mark, Jr.*	1170
Oxidation Pathways of 2,2'-Benzothiazolinone Azines. I. Electrochemistry Jiři Janata* and Michael B. Williams	1178
Viscosity Effects on Ion-Recombination Kinetics. Bromocresol Green in Water–Glycerol Mixtures P. Warrick, Jr., J. J. Auborn, and Edward M. Eyring*	1184
The Viscosity Dependence of a Putative Diffusion-Limited Reaction Charles Cerjan and Ronald E. Barnett*	1192
Solubility and Partial Molar Properties of Helium in Water and Aqueous Sodium Chloride from 25 to 100° and 100 to 600 Atmospheres	1195
Use of F Centers for the Investigation of Alloy Thermodynamics. The Potassium-Lead System J. S. Bookless and J. J. Egan*	1202

Pressure Effects in Polymer Solution Phase Equilibria. I. The Lower Critical Solution Temperature of Polyisobutylene and Polydimethylsiloxane in Lower Alkanes L. Zeman, J. Biros, G. Delmas, and D. Patterson\* 1206

Pressure Effects in Polymer Solution Phase Equilibria. II. Systems Showing Upper and Lower Critical Solution Temperatures L. Zeman and D. Patterson\* 1214

#### **COMMUNICATIONS TO THE EDITOR**

#### **AUTHOR INDEX**

ź

Ache, H. J., 1124 Adamson, A. W., 1105 Arai, S., 1119 Auborn, J. J., 1184 Barnett, R. E., 1192 Bartal, L. J., 1124 Bernstein, H. J., 1147 Biros, J., 1206 Bonner, O. D., 1228 Bookless, J. S., 1202 Braunstein, J., 1154 Čaja, J., 1170	Delmas, G., 1206 Doepker, R. D., 1112 Egan, J. J., 1202 Evans, D. H., 1160 Eyring, E. M., 1184 Friedman, H. L., 1229 Friedrich, H. B., 1140 Fripiat, J. J., 1220 Gafney, H. D., 1105 Gardiner, G. E., 1195 Gerace, M. J., 1152	Hamlet, P., 1226 Hill, K. L., 1112 Imamura, M., 1119 Janata, J., 1178 Kevan, L., 1226 Kira, A., 1119 Kirowa-Eisner, E., 1170 Krause, P. F., 1140 Kuhlmann, K. F., 1152 Lin, D. G., 1226 MacDonald, H. C., Jr.,	Mark, H. B., Jr., 1170 McCoy, L. R., 1170 Mestdagh, M. M., 1220 Moore, J. H., Jr., 1130 Murphy, W. F., 1147 Nicholas, J. B., 1124 Olsen, D. K., 1089 Orbach, N., 1133 Ottolenghi, M., 1133 Patterson, D., 1206, 1214	Romberger, K. A., 1154 Smith, N. O., 1195 Stein, G., 1093 Stone, W. E., 1220 Thoma, R. E., 1154 Warrick, P., Jr., 1184 Watkins, K. W., 1089 Williams, M. B., 1178 Woclf, L. A., 1166
Cerjan, C., 1192	Haas, Y., 1093	1170	Potashnik, R., 1133	Zeman, L., 1206, 1214

In papers with more than one author the name of the author to whom inquiries about the paper should be addressed is marked with an asterisk in the by-line.

# THE JOURNAL OF PHYSICAL CHEMISTRY

Registered in U.S. Patent Office © Copyright, 1972, by the American Chemical Society

# VOLUME 76, NUMBER 8 APRIL 13, 1972

# Cyclization and Decomposition of 4-Penten-1-yl Radicals in the Gas Phase

by K. W. Watkins\* and D. K. Olsen

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521 (Received October 8, 1971) Publication costs borne completely by The Journal of Physical Chemistry

Azo-*n*-propane vapor was irradiated in the presence of acetylene in the temperature range 46–132°. Products were identified and measured quantitatively by gas chromatography. The significant products were interpreted as arising from the 4-penten-1-yl radical, rather than the expected 1-penten-1-yl radical. The 4-penten-1-yl radicals when formed had an average excess vibrational energy of 46 kcal mol<sup>-1</sup>. Two unimolecular reactions of the excited radicals were observed. These were intramolecular addition to form cyclopentyl radicals and decomposition into ethylene and allyl radicals. At 46°, the average unimolecular rate constants for intramolecular addition and decomposition were 2.4  $\times$  10<sup>8</sup> and 2.2  $\times$  10<sup>9</sup> sec<sup>-1</sup>, respectively. Other kinetic data reported are: the rate constant for addition of *n*-propyl to acetylene,  $k_1 = 10^{12.06} \exp(-9.0 \times 10^3/RT) \mod^{-1} \operatorname{cm}^3 \operatorname{sec}^{-1}$ ;  $\Delta(c-\operatorname{Pe}, n-\operatorname{Pr}) = 0.21$ ; and  $\Delta(n-\operatorname{Pr}, c-\operatorname{Pe}) = 0.35$ .

The isomerization of chemically activated *n*-pentyl and 3-methyl-1-butenyl radicals has been studied recently.<sup>1,2</sup> These isomerizations involved 1,4 hydrogen atom transfers. Our purpose in the present study was to generate vibrationally excited 1-penten-1-yl radicals to observe the effect of a six-membered-ring activated complex, since this radical would isomerize by a 1,5 hydrogen atom transfer. This isomerization will generate 4-penten-1-yl radicals which have the interesting ability to undergo cyclization by an internal addition reaction. Intramolecular addition reactions were first observed in the gas phase in the early 1960's.<sup>3</sup> Since 1963 these reactions have become of great interest to organic chemists who have studied them generally in solution.<sup>4</sup>

The first reported cyclization was that of 5-hexen-1yl radical. An interesting observation was that 5hexenyl preferentially cyclized to a five-membered ring, while the five-carbon system, 4-pentenyl, failed to cyclize.<sup>4b</sup> To our knowledge, 4-pentenyl has not been observed to cyclize.<sup>5</sup> In this note we present kinetic data on the cyclization and decomposition of vibrationally excited 4-pentenyl radicals.

Reactions of Excited 1-Penten-1-yl Radicals. The 1pentenyl radicals were generated by the photolysis of azo-n-propane vapor in the presence of acetylene at 46°. The procedure was the same as described previously.<sup>1,2</sup> At high pressure (450–480 Torr), the main products besides those from  $n-C_3H_7$  disproportionation and combination were 1-pentene, trans-4-octene, and 1-octene. The ratio of trans-4-octene to 1-octene was  $\sim 1:10$ . Minor products were 1-pentyne, 1-hexene, benzene, and ethylene. At pressures in the range of 90–250 Torr, the most important products were ethylene, cyclopentane, cyclopentene, 1-pentene, 1-hexene, and 1-octene. 4-Methyl-1-heptene, butadiene, and benzene were minor products.<sup>6</sup>

The average energy of the 1-pentenyl radicals,  $\langle E \rangle$ , when formed was calculated from the equation

$$\langle E \rangle = \Delta E_0 + E_{C_3H_7} + E_{C_2H_2}^{vib} + E_{C_3H_7}^{vib} + 3RT$$
 (I)

(1) K. W. Watkins and D. R. Lawson, J. Phys. Chem., 75, 1632 (1971).

(2) K. W. Watkins and L. A. O'Deen, ibid., 75, 2665 (1971).

(4) (a) R. C. Lamb, P. W. Ayers, and M. K. Toney, J. Amer. Chem. Soc., 85, 3483 (1963); (b) C. Walling and M. S. Pearson, *ibid.*, 86, 2262 (1964).

(5) (a) A. L. J. Beckwith, Chem. Soc., Spec. Publ., No. 24, 239 (1970);
 (b) M. Julia, Pure Appl. Chem., 15, 167 (1967).

<sup>(3) (</sup>a) S. Arai, S. Sato, and S. Shida, J. Chem. Phys., 33, 1277 (1960);
(b) A. S. Gordon and S. R. Smith, J. Phys. Chem., 66, 521 (1962).

 $C_3H_6$ 

 $C_3H_8$ 

Scheme I

n-C.H. C<sub>2</sub>H<sub>2</sub> cis- and trans- CH3CH2CH2CH=CH. trans-4-C.H.  $(n \cdot C_3 H_7)$ (<u>M</u>) trans-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH<sup>+</sup> trans-CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH· 1-C<sub>5</sub>H<sub>10</sub> + C<sub>3</sub>H<sub>6</sub> 1-C<sub>5</sub>H<sub>8</sub> +  $C_3H_8$ ·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub> cas-CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH· (M) ·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub> CH<sub>3</sub>CHCH<sub>2</sub>CH=CH<sub>2</sub> (n-C<sub>3</sub>H<sub>7</sub>) (M) 1-C<sub>8</sub>H<sub>16</sub> CH<sub>3</sub>CHCH<sub>2</sub>CH=CH<sub>2</sub> (n-C<sub>3</sub>H<sub>7</sub>)  $1 - C_5 H_{10} + C_3 H_6$ propylcyclopentane  $(n-C_3H_7)$  $1, 4 - C_5 H_8 + C_3 H_8$ 4-methyl-1-heptene

where  $\Delta E_0$  is the energy change for the addition reaction at absolute zero,  $E_{C_3H_7}$  is the activation energy for the addition of n-C<sub>3</sub>H<sub>7</sub> to acetylene,  $E_{C_2H_2}$ <sup>vib</sup> and  $E_{C_3H_7}$ <sup>vib</sup> are the vibrational energies of acetylene and propyl radical at temperature *T*, and 3*RT* accounts for the conversion of three degrees of translational and three degrees of rotational freedom into vibrational degrees of freedom. Available thermochemical data give  $\Delta E_0 = 24.0 \text{ kcal mol}^{-1}$ , and in the next section we find  $E_{C_3H_7} = 9.0 \text{ kcal mol}^{-1}$ . Thus, at 46°,  $\langle E \rangle = 36.3 \text{ kcal mol}^{-1}$ . The heats of formation of all the free radicals observed in this work are given in Table I.

Table I: Enthalpies of Formation and Bond Energies at  $0^{\circ}K$  (kcal mol<sup>-1</sup>)

$\Delta H_{\rm f}^{\rm o}(n-{\rm C_3H_7}) \ 25.1^{\rm o}$	$D_0^{\circ}(n-C_3H_7-H)$ 96.2 <sup>b</sup>
$\Delta H_{f}^{\circ}(1\text{-penten-1-yl}) 55.4$	$D_0^{\circ}(C_3H_7CH=C-H) = 106^{\circ}$
$\Delta H_{\rm f}^{\circ}$ (4-penten-1-yl) 45.7	$D_0^{\circ}(\mathrm{H-C_3H_6CH=CH}) 96.2^{b}$
$\Delta H_{\rm f}^{\rm o}({\rm cyclopentyl}) 30.7$	$D_0^{\circ}(c-C_3H_9-H) 93^d$
$\Delta H_{\rm f}^{\rm o}({\rm allyl}) 37.8$	$D_0^{\circ}(C_3H_5-H) 81^d$

<sup>a</sup>  $\Delta H_f^{\circ}$  values of radicals were calculated by the procedure in ref 1. <sup>b</sup> C. W. Larson and B. S. Rabinovitch, J. Chem. Phys., 52, 5181 (1970). <sup>c</sup> S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; value corrected to 0°K. <sup>d</sup> S. Furuyama, D. M. Golden, and S. W. Benson, Int. J. Chem. Kinet., 2, 83 (1970); value corrected to 0°K.

In view of the fact that 1-pentenyl radicals when first formed are vibrationally excited, the mechanism given in Scheme I is adequate to explain the main features of this system. A reaction coordinate diagram is shown in Figure 1.

From a model it is apparent that while *cis*-1-pentenyl can isomerize by 1,5 H atom migration, the *trans*-1-pentenyl radical cannot. From the products, we found

no evidence of stabilized *cis*-1-pentenyl even at the highest pressure of 480 Torr. Evidently, all of the excited *cis*-1-pentenyl isomerized. Thus, we could not study the pressure dependence of 1-pentenyl isomerization as planned. Since the rate constant for stabilization at 480 Torr is about  $0.7 \times 10^{10} \text{ sec}^{-1}$ , the rate constant for isomerization must be greater than  $10^{11} \text{ sec}^{-1}$ .

Rate Constant for Addition of n-Propyl to Acetylene. From runs carried out over the temperature range 70–132°, the rate constant for addition of n-propyl to acetylene,  $k_1$ , was estimated from the expression

$$\frac{k_1}{k_2^{1/2}} = \frac{R(1-\text{pentenyl})}{R^{1/2}(n-C_6H_{14}) [C_2H_2]_0}$$
(II)

where  $k_2$  is the rate constant for the combination of *n*propyl radicals,  $[C_2H_2]_0$  is the initial acetylene concentration, and R(1-pentenyl) is the total rate of formation of products resulting from 1-pentenyl radicals (see ref 6). The activation energy difference,  $E_1 - \frac{1}{2}E_2$ , was found to be 9.0 kcal mol<sup>-1</sup> from a least-squares treatment of a plot of log  $k_1/k_2^{1/2}$  vs. 1/T. The intercept was log  $A_1/A_2^{1/2} = 5.39$ . Assuming log  $A_2 = 13.34$ and  $E_2 = 0$  gives the rate constant  $k_1 = 10^{12.06} \exp(-9.0 \times 10^3/RT) \mod^{-1} \text{ cm}^3 \sec^{-1}$ .

Reactions of Excited 4-Penten-1-yl Radicals. Reactions of excited 4-pentenyl radicals were studied at 46° over the pressure range of 90–480 Torr. At these pressures essentially all excited *cis*-1-pentenyl radicals isomerize to 4-pentenyl. Thus, the 4-pentenyl radicals are formed with an average energy  $\langle E' \rangle$  given by

<sup>(6)</sup> Actual yield data used for the calculations to follow will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JPC-72-1089. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

# $\langle E' \rangle = \langle E \rangle + \Delta E_0'$

where  $\Delta E_0' = 9.7$  kcal mol<sup>-1</sup>, which is the difference in the enthalpies of formation of 4-pentenyl and 1-pentenyl radicals. Therefore,  $\langle E' \rangle = 46.0$  kcal mol<sup>-1</sup>. If the threshold energies for cyclization and decomposition are less than 46.0 kcal mol<sup>-1</sup>, then these reactions can occur. The products containing the C<sub>5</sub> ring arise reasonably from cyclization of 4-pentenyl, while the products ethylene and allyl radical presumably result from its decomposition. Stabilized 4-pentenyl radicals react with *n*-propyl to yield 1-octene. Methylcyclobutane was never observed in any of the runs. This suggests that no cyclization occurred to form cyclobutylcarbinyl radicals.



Figure 1. Schematic reaction coordinate diagram.

In chemical activation systems the average rate constant  $k_{a}^{i}$  for a unimolecular reaction *i* is given by  $k_{a}^{i} =$  $\omega(D_i/S)$ , where  $\omega$  is the effective stabilization rate constant which is usually the specific collision frequency of the excited radical,  $D_i$  is the rate of formation of products from reaction i, and S is the rate of formation of products from stabilization. Thus, for the cyclization reaction,  $k_{a}^{c} = \omega(C/S)$ , and for the decomposition reaction  $k_{a^{d}} = \omega(D/S)$ , where C = R(cyclopentane) +R(cyclopentene) + R(propylcyclopentane), D = $R(C_2H_4)$ , and S = 1.12R(1-octene). The constant 1.12 accounts for 4-pentenyl radicals which undergo disproportionation. The collision diameters used to calculate the collision frequency of  $C_5H_9^*$  were  $\sigma(C_2H_2)$ = 4.22 Å,  $\sigma(azo) = 7.60$  Å, and  $\sigma(C_5H_9) = 5.80$  Å. Plots of the functions C/S and D/S vs.  $1/\omega$  are shown in Figure 2. Least-squares treatments give  $k_{a}^{c} = 2.4 \times$  $10^8 \text{ sec}^{-1}$ , and  $k_{a^d} = 2.2 \times 10^9 \text{ sec}^{-1}$ .

Because the threshold energies for these reactions are unknown, we have tried to estimate them from our re-



Figure 2. Plot of the functions C/S and D/S vs.  $1/\omega$  at 46°.

sults. The deduction of useful thermochemical data from measured chemical activation rate constants, when combined with RRKM calculations using reliable models for a complex and radical has been demonstrated.<sup>7</sup> For simplicity, the measured rate constants were matched to the  $k_E$  that corresponds to the average energy of the 4-pentenyl radicals, rather than matching to a  $k_a$  obtained by averaging the  $k_E$ 's over the distribution function. The difference in this case amounts to about 5%. This technique for finding the critical energies is quite sensitive, since a change in the critical energy for decomposition,  $E_0^d$ , by 2.0 kcal mol<sup>-1</sup> causes  $k_E$  to change by a factor of 3.2.

Radical decomposition reactions have been studied extensively. The models used for the activated complexes have been well tested and have been applied to a large number of reactions.<sup>7,8</sup> We have followed the procedure of Pearson and Rabinovitch<sup>8</sup> to assign frequencies to the radical and dissociation complex (see Table II). The best agreement between  $k_E$  and the experimental  $k_a$  was found for  $E_0^d = 22$  kcal mol<sup>-1</sup>. The activated-complex model corresponds to log  $A_d$ (sec<sup>-1</sup>) = 13.59 and  $E_{expt1} - E_0^d = 0.73$  kcal mol<sup>-1.9</sup> The thermal rate constant would be log k = 13.59 $-(23 \pm 2)/\theta$ . These rate parameters differ somewhat from estimates made by Walsh.<sup>10</sup>

The above technique will now be applied to estimate  $E_0^{\circ}$ , the threshold energy for 4-pentenyl cyclization. However, the results will depend, to some extent, on

(8) M. J. Pearson and B. S. Rabinovitch, ibid., 42, 1642 (1965).

(9) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., p 195.

(10) R. Walsh, Int. J. Chem. Kinet., 2, 71 (1970).

<sup>(7) (</sup>a) C. W. Larson, B. S. Rabinovitch, and D. C. Tardy, J. Chem. Phys., 47, 4570 (1967); 49, 299 (1968); (b) C. W. Larson and B. S. Rabinovitch, *ibid.*, 52, 5181 (1970); (c) H. W. Chang and D. W. Setser, J. Amer. Chem. Soc., 91, 7648 (1969); (d) R. L. Johnson, W. L. Hase, and J. W. Simons, J. Chem. Phys., 52, 3911 (1970).

		(A) 4-Pentenyl Dec	omposition		
C—C stretch	Skeletal bend for C==C==C	$\begin{array}{c} C {\longleftarrow} C \\ \texttt{stretch} \rightarrow C \\ \texttt{stretch} \end{array}$	Libration	Frequency lowerings	Torsion for forming double bond
870 <b>→</b> 0	382 <b>→</b> 191	1046 <b>→</b> 1350	$102 \rightarrow 51$	$1445 \rightarrow 722$ $1342 \rightarrow 671$ $188 \rightarrow 94$	$102 \rightarrow 500$
		(B) Cyclopentyl Ris	ng Opening	CH	
C-C stretch	C==CC bend	stretch $\rightarrow$ C=C stretch	Ring pucker	frequency lowerings	Skeletal bend
1013 → 0	<b>870 → 4</b> 35	1013 → 1360	$290 \rightarrow 145$	$1290 \rightarrow 990$ $1290 \rightarrow 990$	<b>870 → 435</b>

#### Table II: Frequency Changes for Radical - Activated Complex

the model used for the activated complex, because this is the first attempt to describe a model for intramolecular addition (cyclization). It was conceptually easier to assign frequencies to this complex by starting with the cyclopentyl radical frequencies which could be obtained from those for cyclopentane,<sup>11</sup> and then consider changes as ring opening occurs. Frequency changes from the cyclopentyl radical are shown in Table II. The best agreement between the calculated  $k_E$  and experimental  $k_{\rm a}$  occurred when  $E_0^{\circ}$  was 18 kcal mol<sup>-1</sup>. At best, it is safe to estimate that the threshold energy for intramolecular addition is in the range 15-20 kcal mol<sup>-1</sup>. The frequency changes used to construct the activatedcomplex model correspond to log  $A_c = 11.34$  and  $E_{\text{exptl}} - E_0^{\circ} = -0.5 \text{ kcal mol}^{-1}$ . Thus, a reasonable thermal rate constant for cyclization is  $\log k = 11.34$ -  $(18 \pm 3)/\theta$ . The rate parameters for cyclization allow an estimate to be made of the rate constant for ring opening of the cyclopentyl radical of  $\log k = 13.85$  $-(33 \pm 3)/\theta$ .

The relatively high activation energy and low A factor for cyclization are presumably the reason for not observing intramolecular addition of 4-pentenyl in solution, since bimolecular H atom abstraction from other molecules present is a much faster reaction.

Cross-Disproportionation to Combination of n-Propyl and Cyclopentyl Radicals. Under conditions where H atom abstraction by cyclopentyl is negligible (low temperature, low pressure) the cross-disproportionation to combination ratio,  $\Delta$ (c-Pe, n-Pr), is given by the ratio R(cyclopentane)/R(propylcyclopentane). And under conditions where cyclopentyl\* does not significantly decompose to cyclopentene + H (high pressure), the ratio R(cyclopentene)/R(propylcyclopentane) gives the value of  $\Delta$ (n-Pr, c-Pe). From 14 runs at low pressure,  $\Delta$ (c-Pe, n-Pr) = 0.21  $\pm$  0.05, and from 11 runs at high pressure,  $\Delta$ (n-Pr, c-Pe) = 0.35  $\pm$  0.05.

(11) V. Schettino, M. P. Marzocchi, and S. Califaro, J. Chem. Phys., 51, 5264 (1969).

# Radiative and Nonradiative Pathways in Solution: Excited

# States of the Europium(III) Ion

## by Yehuda Haas and Gabriel Stein\*

Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel (Received October 29, 1971) Publication costs assisted by the Israel Academy of Sciences

The role of the solvent in determining radiative and radiationless pathways of electronic excited states in solution is the subject of this paper, with special emphasis on the differences between solid and liquid media. Excited states of solute ions are taken as examples, Eu<sup>3+</sup> being a specific case. Two nonradiative pathways are analyzed in detail: the quenching by intramolecular high energy vibrations of solvent molecules, and transitions induced by the free motion of the solvent molecule as a whole. This is done by looking on the ion and its solvation shell as a "large molecule." The Hamiltonian of this molecule is written as the sum of three contributions: the Hamiltonian of the free ion, static interactions with neighbor molecules, and dynamic interactions. Transitions between electronic levels of the ion are induced by rotational, vibrational, and translational (such as displacement reactions) motions of the molecules forming the "large molecule." In this case transitions take place to the quasicontinuum formed by the dense vibrational levels pertaining to lower electronic states. Analysis of the role of high energy vibrations is facilitated by considering only one vibrational mode (e.g., theO-H stretching mode). Experimental evidence, namely the independent quenching action of each water molecule, is the basis for this "small molecule" approach. In this case transitions take place to a restricted continuum in the neighborhood of an electronic or discrete vibrational level formed by collisional broadening. A kinetic scheme for the decay of the  ${}^{5}D_{0}$  and  ${}^{5}D_{1}$  levels of Eu<sup>3+</sup> is given and analyzed in detail. It is shown that in systems consisting of two emitting levels lying close to each other the lifetime and quantum yield of their fluorescence need not be affected to the same extent by deuteration.

# I. Introduction

In the past few years, considerable effort has been applied to elucidate the nature of radiationless transitions in molecules. Several reviews<sup>1-3</sup> have covered the literature and dealt extensively with possible mechanisms. Most experimental and theoretical work applies to aromatic molecules. It has been found that many radiationless processes occur even in dilute gases and so must be perceived as intramolecular processes. The nonradiative pathway is essentially conversion of electronic energy into kinetic energy of the nuclei which is ultimately released as infrared radiation or lost by collisions. The procedure consists of a calculation of the probability of transfer from a discrete state to a quasicontinuum formed by the dense vibrational levels of a lower electronic state. Irreversibility is introduced by the large number of states degenerate with the discrete state.4

Calculations start with a zero-order Hamiltonian, usually using the Born-Oppenheimer approximation. It is assumed the system is prepared in a nonstationary Born-Oppenheimer state, and the time evolution of this state is followed by considering coupling of the initial state with other nonstationary states through interactions neglected in the zeroth approximation. These are mainly spin-orbit coupling between states of different multiplicities and vibronic or electrostatic  $(1/r_{ij})$ coupling<sup>5</sup> between states of the same multiplicities.

Next to the aromatic molecules, the most extensively

studied systems are the rare earth ions in various environments. A considerable amount of experimental data has been accumulated, and several pathways of radiationless transitions have been studied in detail.

In this paper we wish to survey some of the radiative and radiationless pathways for excited rare earth ions and to try to classify them according to different mechanisms. The rare earth ions have several features that makes them most promising systems for the study of radiationless transitions.

(1) The isolated ion is a comparatively simple system, and its energy levels have been calculated to considerable accuracy.

(2) The separation between energy levels as computed for the gaseous ion do not change much upon embedding it in a crystal or even in solution. This is due to the fact that the lowest energy levels belong to a  $f^n$ configuration, and the f electrons are sufficiently close to the nucleus and move with sufficiently high kinetic energy, that interaction with environment can be treated as a small perturbation to the electrostatic and mag-

(1) B. R. Henry and M. Kasha, Ann. Rev. Phys. Chem., 19, 161 (1968).

(3) (a) W. Siebrand, J. Luminescence, 1, 2, 122 (1970). (b) R. S. Berry, Rec. Chem. Progr., 31, 9 (1970).

(4) G. W. Robinson and R. P. Frosch, J. Chem. Phys., 38, 1187 (1963).

(5) B. Sharf, Chem. Phys. Lett., 4, 364 (1970).

<sup>(2)</sup> J. Jortner, S. A. Rice, and R. M. Hochstrasser, Advan. Photochem., 7, 151 (1969).

netic coupling among these electrons and between them and the nucleus.<sup>6</sup> The effect of solvation on the energy levels will be discussed later.

(3) The interaction with the environment manifests itself mainly in two respects. (a) Radiative and non-radiative transitions within the  $f^n$  manifold become partially allowed. (b) New energy levels are formed, usually higher than the lowest  $f^n$  levels. These levels, due for example to charge-transfer states, are of considerable importance in the study of the energetics of the system.

(4) The rare earth ion, when in solution or in a solid matrix, cannot be looked upon as an isolated system. Rather, it is useful to regard it, together with its immediate neighbors (ions or molecules), as a loose molecular system. Thus the energy of the various f levels will depend to some extent on the relative distance between the ion and these neighbors. This distance can be looked upon as an additional degree of freedom which may provide, under favorable conditions, new pathways for nonradiative decay of the excited levels of the ion.

As will be discussed further on, this feature leads to fundamental differences in the behavior of the excited states in solids and in solution.

(5) The energy levels of the ions, at least at equilibrium position of the neighboring molecules, are usually well separated from each other. This enables one to excite the ions selectively to willfully chosen levels. Furthermore, in many cases, notably in solid media, it is possible to observe directly the decay of several levels.

In the gas phase, only radiative coupling is allowed between the various levels of the rare earth ions. These are forbidden transitions as long as the levels belong strictly to the  $f^n$  configuration and electric dipole transitions are considered. Although the transitions become partially allowed in dense media, they are still weak and lead to long lifetimes, so that comparatively slow quenching mechanisms can be studied. Furthermore, in many systems, the "shielded" f electrons undergo such weak interactions with the environment that usual quenching mechanisms in dense media such as collisional deactivation, are inefficient, so that other mechanisms reveal themselves much more clearly than in other systems. This makes the rare earth ions of unique interest to the study of radiationless transitions.

The  $Eu^{3+}$  ion is perhaps the most extensively studied rare earth ion in this respect. In the following we shall briefly summarize previous work and our own results concerning this ion. To define better particular mechanisms we shall compare it to other rare earth ions.

A schematic partial energy level diagram is given in Figure 1. It applies to the ion in aqueous solution.<sup>6</sup> We focus our attention on the lower part and particularly on the <sup>7</sup>F ground state manifold and the <sup>5</sup>D manifold which is the lowest excited one. We note that  $F_1$ is sufficiently close to the ground  $F_0$  state, so that at room temperature it is copopulated to a significant



Figure 1. Partial energy level diagram of  $Eu^{3+}$  in solution.

degree. The emitting levels are the  ${}^{5}D_{0}$ ,  ${}^{5}D_{1}$ ,  ${}^{5}D_{2}$ , and  ${}^{5}D_{3}$ . Emission from all these levels has been observed in crystal lattice,<sup>7,8</sup> while in solution only the  $D_{0}$  and  $D_{1}$  levels are observed.

# II. Summary of Experimental Results in Solid and Liquid Media

As noted above, in a crystalline lattice, many excited states of  $Eu^{3+}$  have sufficiently long lifetime that emission of radiation is observed. The main pathways for radiationless decay in the crystalline state have been found.

(a) Concentration quenching, supposedly via an ion-pair resonance mechanism. This applies only to levels higher than  $D_0$ .<sup>7</sup> Similar quenching has been found with other rare earth ions.<sup>9,10</sup> A related mechanism is quenching by other rare earth ions (e.g., ref 11 and references therein).

(11) G. E. Peterson, Trans. Metal Chem., 3, 202 (1966).

<sup>(6)</sup> B. G. Wybourne, "Spectroscopic Properties of Rare Earths," Interscience, New York, N. Y., 1965; W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys., 49, 4450 (1968).

<sup>(7)</sup> M. J. Weber, Phys. Rev., 171, 283 (1968).

<sup>(8)</sup> G. E. Barrasch and G. H. Dieke, J. Chem. Phys., 43, 988 (1965).

<sup>(9)</sup> G. E. Peterson and P. M. Bridenbaugh, J. Opt. Soc. Amer., 53, 1199 (1963).

<sup>(10)</sup> L. G. Van Uitert, E. F. Dearborn, and J. J. Rubin, J. Chem. Phys., 46, 420 (1967).

(b) Quenching via a charge-transfer state. It has been found that when the charge-transfer state, due to a transition from nearby oxygen to the  $Eu^{3+}$  ion, has energy levels close to the  $D_2$  or  $D_1$  levels, these are quenched.<sup>12</sup> This mechanism seems to be specific for easily reducible ions such as  $Eu^{3+}$ .

Temperature dependence of the emission is usually determined by mechanisms a or b. Thus the  $D_0$  emission is not temperature dependent at low temperatures. At high temperatures it may be depopulated *via* higher levels such as  $D_1$ , or CT levels.

These two mechanisms are operative in all crystalline matrices. In hydrated crystals we find an additional, sometimes more effective mechanism (c).

(c) Quenching via high energy vibrations of molecules also embedded in the crystal. This accounts for the fact that most hydrated rare earth ions do not show fluorescence. In  $Eu^{3+}$  it has been found that the  $D_0$ and  $D_1$  levels are affected to about the same extent upon substituting  $H_2O$  and  $D_2O$  in the hydration sphere.<sup>13</sup> Another work<sup>14</sup> reports by far smaller effects of  $D_2O$  on both  $D_0$  and  $D_1$ . However the author claims that inasmuch as the  $H_2O$  content was not known, the values for  $D_2O$  are only lower limits.

Work on the fluorescence of rare earth ions in solution can be divided into two main topics: solutions of chelates and complexes and solutions of simple salts.

Some chelates fluoresce very strongly in solution, a property used to obtain liquid lasers. This led to very intense work in this field, continuing to this day. Many parameters have been found to influence the efficiency of fluorescence, such as the nature of the ligands and solvents, etc. We shall be interested in chelates only as a sort of intermediate case between solids and solutions of salts. Accordingly, we highlight only a few properties, relevant also to the study of simple solutions.

(a) A transfer of energy has been observed from the rare earth ion levels to the energy levels of the ligands (singlets or triplets).<sup>15,16</sup> Similarly, energy was found to pass from ligand electronic levels to the ion, a property used to pump light energy to the weakly absorbing ions *via* the strongly absorbing ligands. Both transfers are usually downwards. In some cases upward temperature-dependent energy transfer has been observed, when the ligands' levels lie close enough to those of the ions.

(b) The quantum efficiency of f-f emission is determined mainly by the intimate environment of the ion. Thus, eight coordination is preferred to six coordination.<sup>17</sup> Moreover, effective shielding of the ion from the solvent by an "insulating sheath" enhances fluorescence.<sup>18</sup> These observations show that, although weak, coupling to solvent molecules takes place when contact is possible.

We turn now to the luminescent behavior of the  ${}^{5}D_{1}$ and  ${}^{5}D_{0}$  levels of nonchelated Eu<sup>3+</sup> in solution. (a) In anhydrous crystals,<sup>8</sup> the lifetime of the  $D_1$  level is comparable to that of  $D_0$  level, in hydrated crystals it reduces to about one-tenth,<sup>13</sup> and in solution it decreases further to  $10^{-2}$  to  $10^{-4}$  of the lifetime of  $D_0^{19,20a}$  which is in general not appreciably shortened. (However, see below for specific OH effect on  $D_0$ .)

(b) The quantum yield from the  $D_0$  level is a sensitive function of the solvent (for a given anion). It is low in hydroxylic solvents (2–10%), about 50% in CH<sub>3</sub>CN and (CH<sub>3</sub>)<sub>2</sub>SO and over 70% in some deuterated solvents such as CD<sub>3</sub>CN, D<sub>2</sub>O, and (CD<sub>3</sub>)<sub>2</sub>SO.<sup>20a</sup>

(c) Deuteration affects the D<sub>0</sub> level most strongly in water. Reported values for the ratio of fluorescence intensity in D<sub>2</sub>O to the intensity in H<sub>2</sub>O are in the range 20-50.<sup>20a-23</sup> We found recently that this ratio, as well as the quantum yield, is anion dependent. In perchlorate solution (where anion complexing is lowest and the main species is  $[Eu(H_2O)_n]^{3+}$ ;  $n \simeq 9$ ) it turns out to be 40.<sup>20a</sup>

(d) Values for rate constants governing the behavior of the excited states of Eu<sup>3+</sup> are scarce. We have recently published some such rate constants.<sup>20</sup> As shown briefly in ref 20a and discussed more extensively in section IV, these, and not the intensity ratios, are the important physical parameters.

(e) Anions affect strongly the fluorescence of the  $D_0$  level in several solvents.<sup>20a,21</sup> A similar effect has been found in crystals<sup>14</sup> though quantum yields were not cited. In solution, such ions as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and especially CNS<sup>-</sup>, are shown to be better quenchers than  $D_2O$ , though less efficient than  $H_2O$ . A value for the rate constant of quenching by CNS<sup>-</sup> was proposed.<sup>20a</sup>

(f) The quenching of  $D_0$  by  $H_2O$  has been shown to occur by a transfer of energy to a single water molecule vibration and not to a collective mode.<sup>20a</sup> A rate constant of  $\sim 1000 \text{ sec}^{-1}$  was calculated for this process.<sup>24</sup>

(g) The  $D_0$  emission is temperature dependent, especially in nonhydroxylic solvents.<sup>19</sup> The activation energy was found to be somewhat higher than but close

- (14) J. Heber, Phys. Kondens. Mater., 6, 381 (1967).
- (15) R. E. Whan and G. A. Crosby, J. Mol. Spectrosc., 8, 315 (1962).
- (16) M. Kleinerman. J. Chem. Phys., 51, 2370 (1969).
- (17) D. L. Ross and J. Blanc, Advan. Chem. Ser., No. 71, 155 (1967).
- (18) F. Halverson, J. S. Brinen, and J. R. Leto, J. Chem. Phys., 41, 157 (1964).
- (19) J. L. Kropp and W. R. Dawson, *ibid.*, 45, 2419 (1966).
- (20) (a) Y. Haas and G. Stein, J. Phys. Chem., 75, 3668 (1971); (b) R. A. Vellapordi, R. Reisfeld, and L. Boehm, 9th Rare Earth Conference, Washington, D. C., 1971.
- (21) J. L. Kropp and M. W. Windsor, J. Chem. Phys., 42, 1599 (1965).
- (22) P. K. Gallagher, ibid., 43, 1742 (1965).
- (23) A. Heller, J. Amer. Chem. Soc., 88, 2058 (1966).
- (24) Y. Haas and G. Stein, J. Phys. Chem., 75, 3677 (1971).

<sup>(12)</sup> C. W. Struck and W. H. Fonger, J. Luminescence, 1, 2, 456 (1970).

<sup>(13)</sup> J. P. Freeman, G. A. Crosby, and K. E. Lawson, J. Mol. Spectrosc., 13, 399 (1964).

to 1700 cm<sup>-1</sup>, the energy gap between the  $D_0$  and  $D_1$  levels. A similar effect was found in chelates.<sup>25,26</sup> Whenever there is another stationary level directly above the emitting level, such as a triplet of a chelate, it is through this level that the depopulation occurs.

(h) Recently we found a direct proof of the proposed mechanism of thermal bleeding of the  $D_0$  level via the  $D_1$  level.<sup>27</sup> It is found that the  $D_1$  luminescence is present when only the  $D_0$  is excited by monochromatic light. Furthermore, this luminescence is enhanced when temperature is increased with an energy of activation somewhat higher than but close to the energetic gap between the levels.

(i) The probability of transfer of the ion from the  $D_1$  level to the  $D_0$  level is approximately constant for many solvents and is in the range of  $0.4-0.6.^{20a}$  In several anhydrous glasses this probability reaches  $0.9.^{20b}$  Similar data for other rare earth ions are available only in the case of Tb<sup>3+</sup> for the H<sub>2</sub>O-D<sub>2</sub>O system<sup>25</sup> where the probability for transition from the D<sub>3</sub> to the D<sub>4</sub> level is 80% compared to 50% for the D<sub>1</sub>  $\rightarrow$  D<sub>0</sub> transition in Eu<sup>3+</sup>.

(j) The isotopic enhancement of fluorescence from the  $D_1$  level is much smaller than from  $D_0$ . As total fluorescence from this level is weak compared to  $D_0$ , it is difficult to obtain reliable data. The enhancement of fluorescence does not exceed two- to threefold and is possibly smaller.<sup>20a</sup>

(k) A charge-transfer band appears in solutions of  $Eu^{3+}$ . The maximum absorption occurs at different wavelengths depending on anion and solvent.<sup>28-30</sup> It has been shown that light absorption in this band can lead to either fluorescence or dissociation of water molecules.<sup>29</sup>

(1) Concentration quenching and quenching by other ions are usually unimportant in  $Eu^{3+}$  solutions. In special cases when such quenching has been found<sup>31,32</sup> it is due to some mechanism that brings the ions together to close steric proximity and denies free motion of the ions.

(m) In some crystals<sup>11,14</sup> chelates<sup>33,34</sup> and certain solutions,<sup>20</sup> the population of the  $D_0$  level from higher levels is slow enough to be observed directly. Since the rate of this process has been found to be equal or similar to the rate of depopulation of the  $D_1$  level, this is a direct proof for the so-called "cascade" mechanism of depopulation of excited states of rare earth ions.

We shall now attempt to construct a theoretical framework to account for the experimental facts.

# III. The Hamiltonian of the Ion in Solution

The Hamiltonian of a rare earth ion in solution can be written as the sum of three contributions

$$H = H^{\circ} + H^{\circ} + H^{\circ}$$
(3-1)

 $H^{\circ}$  is the Hamiltonian of the free ion,  $H^{\circ}$  the static interactions with the crystal field, and  $H^{\circ} = H_{s}^{\circ} +$   $H_{L^{D}}$ , the dynamic interactions in solid and liquid phase, respectively.

The origin of  $H^c$  is in the reduction of the spherical symmetry which the free ion sees in the gas phase. The neighboring ions and molecules, assumed to be fixed, induce an electrostatic potential in the vicinity of the rare earth ion, causing a change in the energy levels. The interactions with this potential are small compared to the internal interactions between the f electrons, and so can be regarded as a perturbation on  $H^\circ$ . (The splittings due to  $H^\circ$  are of the order of 1000 cm<sup>-1</sup>, while those due to the crystal field are in the range of 10–100 cm<sup>-1</sup>.<sup>35</sup>)

It is convenient to regard  $H^c$  as composed of two components: a holohedric, or even, component which can cause mixing between functions of the same symmetry, and its main contribution is lowering of the baricenter of all the levels. In solution this is the main contribution to the solvation energy. The hemihedric part of the potential can cause mixing of configuration with different symmetry, thus allowing electric dipole transition between levels belonging to the lowest  $f^n$  configuration. Calculations of the oscillator strength of electric dipole transition, carried out by considering the effect of configuration interaction due to the lowering of symmetry were carried out successfully.<sup>6,36</sup>

The dynamic part of the Hamiltonian,  $H^{D}$ , represents the interaction of the RE ion with the motion of the neighboring molecules or ions. This part is time dependent and can also cause transitions between different levels belonging to the same configuration. Motions that were considered in this context were<sup>35,37</sup> phonons in lattices, motion of the RE ion relative to its neighbors, and internal vibrations of neighboring molecules. In solution one can generalize the second motion to collisions between solvent molecules and the ion and add rotational motion of neighboring molecules.

This part of the Hamiltonian leads to broadening or splitting of absorption and emission bands into vibronic transitions and to radiationless transitions. Recently

- (25) W. R. Dawson, J. L. Kropp, and M. W. Windsor, J. Chem. Phys., 45, 2410 (1966).
- (26) J. J. Mikula and R. E. Salomon, *ibid.*, 48, 1977 (1968).
- (27) Y. Haas and G. Stein, Chem. Phys. Lett., 8, 636 (1971).
- (28) Y. Haas and G. Stein, ibid., 3, 313 (1969).
- (29) Y. Haas, G. Stein, and M. Tomkiewicz, J. Phys. Chem., 74, 2558 (1970).
- (30) J. C. Barnes, J. Chem. Soc., 3886 (1964).
- (31) F.S. Quiring, J. Chem. Phys., 49, 2448 (1968).

(32) B. M. Antipenko and V. L. Ermolaev, Opt. Spektrosk., 37, 504 (1970).

- (33) M. L. Bhaumik and L. J. Nujent, J. Chem. Phys., 43, 1680 (1965).
- (34) E. Nardi and S. Yatsiv, ibid., 37, 2333 (1962).

- 1953, Translation Series of the U.S. Atomic Energy Commission.
- (36) B. R. Judd, Phys. Rev., 127, 750 (1962).
- (37) K. Hellwege, Ann. Phys., 40, 529 (1942).

<sup>(35)</sup> M. A. Elyashevick, "Spectra of the Rare Earths," Moscow,

we gave direct evidence of such coupling in solutions<sup>38</sup> of  $Gd^{3+}$  in  $H_2O$  and  $D_2O$ .

These phenomena in crystals have been described many years ago,<sup>35</sup> and a correlation has been established between them. Thus it was found that line broadening and vibronic transitions are most prominent for the first elements in the rare earth series ( $Pr^{3+}$ ,  $Nd^{3+}$ ), the effect is weaker in the middle ones and becomes stronger again in the heaviest ( $Ho^{3+}$ ,  $Tm^{3+}$ ). Fluorescence in crystals and solutions is strongest with the ions in the middle of the series, mostly with  $Gd^{3+}$ , and weakens as one passes to other ions, heavier or lighter. This trend has been explained by the more effective radiationless transitions in the lightest and heaviest elements.

To study the effect of motions of the solvent on radiationless transitions between the energy levels, we shall assume that the solution to the static Hamiltonian is known. In this Hamiltonian we include  $H^{\circ} + H^{\circ}$  and the Hamiltonian of the neighboring molecules participating in the radiationless process, without the interaction between them.  $H^{D}$  will be the interaction Hamiltonian. Generally it is a function of the internal coordinates of the molecules, and the distances between them and the ion. Denoting these coordinates  $Q_i$ , and the coordinates of the electrons of the RE ion by  $q_i$ , the eigenfunctions of the static Hamiltonian will be  $\psi_{n\alpha}$  =  $\phi_n(q,Q)\chi_\alpha(Q)$  where  $\phi_n$  is a function of q and Q, and  $\chi_\alpha$ is a function of Q only. We may express two dynamic factors in this way: internal vibrations of molecules or ions adjacent to the RE ion and the motion of such molecules or ions relative to the RE ion. Taking Q to be an internal vibration coordinate,  $\chi$  can be represented by a product of harmonic oscillator functions. Taking it to be the distance between the ion and the molecule,  $\chi$  could be represented at large enough distances by a translatory function such as  $e^{ik \cdot Q}$  where k is the linear momentum of motion along the coordinate Q.

One can write  $H^{\rm D}$  as an infinite power series in the coordinates  $Q_{\rm i}$ 

$$H^{\rm D} = V_0 + \sum_{i} V_i Q_i + \sum_{ij} V_{ij} Q_i Q_j + \dots \quad (3-2)$$

where the  $V_i$ 's are functions of the electronic coordinates only.  $V_0$  is not really a dynamic component and may be included in  $H^c$ .

The transition probability  $W_{n\beta\to m\alpha}$  between eigenfunctions of the static Hamiltonian is proportional to the square of the following matrix element

$$\langle \psi_{m\alpha} | H^{\mathrm{D}} | \psi_{n\beta} \rangle = \langle \chi_{\alpha} | \chi_{\beta} \rangle \langle \phi_m | V_0 | \phi_n \rangle +$$

$$\sum_i \langle \chi_{\alpha} | Q_i | \chi_{\beta} \rangle \langle \phi_m | V_i | \phi_n \rangle + \dots \quad (3-3)$$

In eq 3-3 we assume that the electronic integrals, e.g.,  $\langle \phi_m | V_0 | \phi_m \rangle$ , are independent of Q. Practically one can often assume that only one, or few, coordinates are active in inducing transitions (promoting modes). Furthermore, the contribution of different terms in the infinite series (even in the case of one coordinate) is not

the same. In fact, usually the first nonvanishing term is the dominant one. Accordingly we omit terms due to  $\sum V_{ij}Q_iQ_j$  and higher terms.

The foregoing theoretical considerations may be applied both to the case of radiationless transitions induced by coupling to high energy vibrations<sup>24</sup> and those induced by coupling to motions of solvent molecules.<sup>20a</sup>

In the next section we shall make use of eq 3-3 in calculating the isotopic effect on the quantum yield of the  $D_0$  level due to coupling to high energy vibrations.

## **IV.** Role of High Energy Vibrations

Most calculations done so far (e.g., ref 14 and 39) on the problem of quenching by high energy vibrations have tried to relate the high effectiveness of the O-H vibrations to the electrostatic interaction between the ion and the water dipole. The difference between light and heavy water was accounted for mainly by the different vibrational levels that have to be excited in order to conserve energy. Calculations made use of high order perturbation theory and of parameters known from optical spectra. However, these theoretical calculations were based on incomplete experimental results and were aimed at parameters which turn out to be of no central kinetic significance, such as intensity ratios. In what follows we present a theory of the isotopic effect, based on the recently developed methods in radiationless transitions. Before we outline the theory we wish to re-define the problem in order to underline some relevant experimental results which were unknown to, or overlooked by previous workers.

The complete kinetic scheme will be dealt with in the next section. For the present purposes we wish only to define accurately what we mean by isotopic effect. The observed parameters are the lifetime  $\tau$  and the quantum yield  $\phi$ . Assuming we can divide all the rate constants relevant to a given level into three classes, namely radiative, nonradiative depending on high energy vibrations and other nonradiative, we have<sup>21</sup>

$$\tau = \frac{1}{k_t + k_H + k_x} \tag{4-1}$$

$$\phi = \frac{k_{\rm f}}{k_{\rm f} + k_{\rm H} + k_{\rm x}} \tag{4-2}$$

where  $k_{\rm f}$  is the radiative rate constant,  $k_{\rm H}$  (or  $k_{\rm D}$ ) the radiationless rate constant of quenching by H<sub>2</sub>O (or D<sub>2</sub>O), and  $k_{\rm x}$  all other radiationless rate constants put together.

We thus have

$$\frac{\phi_{\rm D}}{\phi_{\rm E}} = \frac{\tau_{\rm D}}{\tau_{\rm H}} = \frac{k_{\rm f} + k_{\rm H} + k_{\rm x}}{k_{\rm f} + k_{\rm D} + k_{\rm x}}$$
(4-3)

It is assumed that neither  $k_f$  nor  $k_x$  are affected by isotopic substitution. Previous workers<sup>39,40</sup> have assumed

(38) Y. Haas and G. Stein, Chem. Phys. Lett., 11, 143 (1971).

that the parameter  $\tau_{\rm D}/\tau_{\rm H}$  is the one to be calculated from theory. This is true only in the limiting case where  $k_{\rm H}$  and  $k_{\rm D}$  are much greater than the sum of  $k_{\rm f}$ and  $k_x$ . In the case of D<sub>2</sub>O this is certainly not the case. Furthermore, it has been shown<sup>20a</sup> that anions such as  $Cl^{-}$  and  $NO_{3}^{-}$  quench the fluorescence in the presence of D<sub>2</sub>O. This is a direct proof that  $k_x > k_D$  in this case. Much of the previous work was based on work with the chlorides and the nitrates which complex Eu<sup>3+</sup> to some extent. The relevant ratio to be calculated is  $k_{\rm H}/k_{\rm D}$ which unfortunately cannot be obtained directly from experiment. We obtained a value of 200 as a lower limit for solutions of Eu(ClO<sub>4</sub>)<sub>3</sub>.<sup>20a</sup> The perchlorate ion was shown to complex  $Eu^{3+}$  to the smallest extent. However, as the quantum yield in D<sub>2</sub>O depends on temperature, data obtained at room temperature are only rough estimates to the real value. Our data suggest that quenching by  $D_2O$  is very ineffective indeed.

At this point, we wish to refer to the work of Heber,<sup>14</sup> who calculated the isotopic enhancement of fluorescence from the  $D_1$  level by assuming that the dominant mode of depopulating it is to the  $D_0$  level via O-H or O-D vibrations. Heber showed that by considering electrostatic interaction (in the crystalline state) between the  $Eu^{3+}$  ion and surrounding  $H_2O$  molecules, one can obtain the value of  $10^5 \text{ sec}^{-1}$  for the radiationless transition  $D_1 \rightarrow D_0$ . He did not carry out calculations for  $D_2O$  molecules. Neither did he calculate explicitly the effect on the transition  $D_0 \rightarrow F$ .

Our model is an attempt to account for the high ratio of rate constants  $k_{\rm H}/k_{\rm D}$ , for which we derived a lower limit of 200.<sup>20a</sup> It has been accepted that the ultimate reason for the higher quenching constant of H<sub>2</sub>O is due to the difference in the vibrational frequencies. Thus it was argued<sup>23,39</sup> that the effect arises from the fact that a different number of vibrational quanta have to be excited in order to match the energy gap between the excited D<sub>0</sub> state and the ground multiplet. It is 4-5 with H<sub>2</sub>O and 5-7 with D<sub>2</sub>O.

We shall now apply eq 3-3 to the problem of dynamic quenching by high energy internal vibrations of water molecules in crystals and in solution. The first term on the right-hand side of eq 3-3 is the static crystal field contribution. The dynamic effect of vibrations is expressed in the second term.

Isotopic substitution affects the electronic part of this integral to a much lesser extent than the nuclear part. In calculating the ratio of rate constant between deuterated and protonated solvent, one can safely assume that the electronic part will largely cancel out, and the only essential difference will arise from the change in the overlap integrals associated with the nuclear functions. It has been pointed out by Robinson and Frosch<sup>4</sup> that many of the features of radiationless transitions can be explained by considering such overlap integrals. The problem is closely related to calculation of intensities in the absorption or emission spectrum of molecules in connection with the Franck-Condon principle. Much effort has been applied to calculation of these integrals for the case of large molecules. The solution of the problem is hampered by the large number of vibrational degrees of freedom that have to be taken into account, and various methods, mostly utilizing data from emission spectra, have been suggested.<sup>41-43</sup> Within the assumptions of our models of the "large molecule" consisting of the central RE ion and all the molecules in the solvation shell, we can simplify the treatment of quenching by high energy vibrations by a model of "small molecule." The small molecule consists of the RE ion coupled to one O-H oscillator. This approximation greatly simplifies the calculation and is justified by the experimental observation<sup>24</sup> that each O-H vibration appears to act independently in the quenching process. As the exact wave functions are not known, we suggest two procedures which give at least semiquantitative results.

First we note that the integral  $Q_{\alpha\beta} = \langle \chi_{\alpha} | Q | \chi_{\beta} \rangle$  is exactly the same as that describing the vibrational spectrum of the OH molecule. As an approximation we shall use the exact data obtained by Heaps and Herzberg<sup>44</sup> for the O-H molecule in the atmosphere. They obtained the following relative values for the matrix elements  $|Q_{\alpha\beta}|^2$ , and hence for  $W_{\alpha \rightarrow \beta}$  (Table I).

**Table I:** Relative Transition Probabilities for the Transition  $(0 \rightarrow n)$  Calculated by Heaps and Herzberg for the O-H Molecule

n	Value without quadratic correction	Value with quadratic correction
1	100	100
2	9.381	3.102
3	1.113	0.1338
4	0.1528	0.007140
5	0.02517	0.000267
6	0.004893	0.000023
7	0.001105	0.0000022

The values calculated with quadratic correction were considered by the authors as more realistic. We see that the values are such that only the transitions leading to the lowest possible energy level are important. Thus we need consider for  $H_2O$  only the 0-4 transition and for  $D_2O$  the 0-5 transition. To obtain the ratio between the O-H and O-D oscillator, we have to take into account the effect of isotopic substitution on these

(39) D. N. Terpilovski, Opt. Spektrosk. (Engl. Trans.), 24, 313 (1968).

- (40) R. E. Ballard, Spectrochim. Acta, Part A, 24, 65 (1968).
- (41) J. P. Byrne, E. F. McCoy, and I. G. Ross, Aust. J. Chem., 18, 1588 (1965).
- (42) W. Siebrand, J. Chem. Phys., 44, 4055 (1965).
- (43) R. Englman and J. Jortner, Mol. Phys., 18, 145 (1970).
- (44) H.S. Heaps and G. Herzberg, Z. Phys., 133, 48 (1952).

matrix elements. We make use of the equation derived by Penner<sup>45</sup> on the basis of Heaps and Herzberg's work

$$\langle s|Q|0\rangle^2 = \mu_1^2 \left(\frac{r_e^2 B_e}{\omega_e} x_e^{s-1} \frac{s!}{s^2}\right)$$
 (4-4)

where  $r_e$  is the equilibrium distance of the oscillator,  $B_e$  the rotational constant,  $\omega_e$  the vibrational constant,  $x_e$  the anharmonicity constant, and  $\mu_1$  the first correction in the expansion of the dipole moment of the oscillator  $\mu = \mu_0 + \mu_1 (r - r_e)$ . Isotopic substitution affects mostly  $B_e$ ,  $\omega_e$ , and  $x_e$ . For the pair O-H and O-D we get

$$\langle s|Q|0\rangle_{\rm OH}^2/\langle s|Q|0\rangle_{\rm OD}^2 = 2^{s/2} \tag{4-5}$$

We finally obtain, using the values in Table I

$$W_{\rm OH}(0 \rightarrow 4)/W_{\rm OD}(0 \rightarrow 5) \simeq 200 \qquad (4-6)$$

In eq 4-6 we use the fact that the transition probability W is proportional to the square of the matrix element appearing in eq 3-3. It is customary to use Fermi's golden rule, thus introducing a density of states. In our model, as outlined above, a density of states is not yet defined, as it pertains to energy transfer between two discrete levels. This is, however, an unrealistic situation, since energy matching is usually impossible under such conditions. In reality, the vibrational energy levels in solution are not discrete. In particular, we have recently shown that vibronic transitions due to water molecules in the hydration sphere of Gd<sup>3+ 38</sup> are remarkably broad ( $\sim 100 \text{ cm}^{-1}$ ). This was interpreted as collisional broadening of the vibronic levels involved in the transition. Each vibrational level is thus appreciably broadened in liquid solution, enabling good energy matching, and also providing the high density of states needed for efficient energy transfer. One can therefore write the radiationless transition probability for our limit of "small molecule" interaction with the liquid as

$$W_{n\beta \to m\alpha} = F_{nm} \langle \beta | Q | \alpha \rangle^2 \cdot \rho(E)$$
(4-7)

where  $F_{nm}$  is the electronic part, and  $\rho(E)$  the density of states. Both are not expected to change much upon isotopic substitution. This is in contradistinction to the case of large aromatic molecules where the density of states changes appreciably with isotopic substitution. In our case the density is due to broadening of the discrete electronic levels of the ion and vibrational levels of the neighbor molecule by collisions with solvent molecules. The correlation time for such collisions, and thus the broadening, is only slightly affected by isotopic substitution.

The calculation was made by taking into account only the changes in the matrix element  $\langle \beta | Q | \alpha \rangle$ , and these in turn were assumed to arise only because of anharmonicity. As can be seen from eq 4-4, the result is critically dependent on the value of the anharmonicity constant  $x_{e}$ . For a better approximation equally exact data on the ir or Raman spectrum of OH in water molecules close to Eu<sup>3+</sup> are required. Our results on the infrared spectra of hydrated Eu<sup>3+</sup> show that in the vicinity of the ion anharmonicity increases.<sup>46</sup> The value obtained can thus be looked upon as a lower value.

A different approach, which is less direct for the case in hand, but may prove more useful in other systems, will be also outlined. Following McCoy and Ross<sup>47</sup> we assume that the overlap integral is due mainly not to anharmonicity, but to different displacement of the oscillator with respect to the ion, when the latter is in the excited or ground states. A similar approach was used recently by Levine.<sup>53</sup> Using the harmonic approximation, one can carry out exact calculations of transition probabilities. Hutchisson<sup>48</sup> derived a formula for the overlap integrals of such oscillators. This formula gives for the case of  $0 \rightarrow n$  transitions, the following approximate value<sup>47</sup>

$$\langle n | \mathbf{0} \rangle^2 = Q^{2n} \exp(-Q^2) / n!$$
 (4-8)

where  $Q = (2\pi^2 m \nu/h)^{1/2} \Delta R$  and  $\Delta R$  is the relative displacement of the oscillators. Using eq 4-8 we obtain the ratio  $w_{\rm H} (0 \rightarrow 4)/W_{\rm D} (0 \rightarrow 5)$  as a function of  $\Delta R$ . This is shown in Figure 2. It is seen that the ratio rises very steeply as  $\Delta R$  is decreasing. A realistic value of R will be between  $10^{-2}$  and  $10^{-3}$ Å. The ratio rises from about 200 to  $2 \times 10^4$  in this interval. It should be realized that the absolute values of the integrals involved become very small. The overlap integral decreases about  $10^8$ -fold as  $\Delta R$  is decreased from  $10^{-2}$  to  $10^{-3}$ Å. Thus we would not expect this model to be of physical value for small  $\Delta R$ , as other mechanisms would be much more effective. When  $\Delta R$  is small, the anharmonicity allows a better approximation to the calculation of rate constants.

An accurate calculation will have to take into account both anharmonicity and displacement of the equilibrium position.

# V. The Role of the Solvent in Inducing Radiationless Transitions

In this section we discuss the role of the solvent in inducing the most prominent difference between the solid and liquid state, *i.e.*, the lack of change in the behavior of the  $D_0$  level vs. the fundamental change in the behavior of the  $D_1$  level. We shall attribute this to differences in coupling to motions of solvent molecules.

Solvation of an ion is an exothermic reaction. In general, the decrease of free energy in different electronic states by solvation needs not be the same. It

(46) Y. Haas and G. Stein, to be published.

(48) G. E. Hutchisson, Phys. Rev., 36, 410 (1930).

<sup>(45)</sup> S. S. Penner, "Quantitative Molecular Spectroscopy and Gas Emissivities," Addison-Wesley, Reading, Mass., 1959.

<sup>(47)</sup> E. F. McCoy and I. G. Ross, Aust. J. Chem., 15, 573 (1962).



Figure 2. Relative transition probabilities for OH and OD oscillators as a function of  $\Delta R$  (see text).

has been found experimentally that the spacings between the energy levels of the trivalent rare earth ions do not change much upon transfer of the ion from the gas phase to the solution, in spite of the considerable solvation energy. To account for the radiationless transitions we must take into account also the energy levels of the surrounding molecules. Looking on the ion with its first hydration sphere as a large molecule. we can conceive its energy level diagram as being composed of electronic levels of the ion with superimposed vibrational levels due to neighboring molecules as shown experimentally by the broadening of the lines and by the appearance of vibrational satellites.<sup>35,38</sup> When translational motion of the neighbor molecules is prohibited, one obtains the dotted curves in Figure 3, pertaining to the solid state (see also ref 12). The scheme must be different when considering fluid solution. Here we must take into account the dependence of the energy levels on such motions as rotations and translations. One can schematically modify the energy level diagram by introducing a "dissociative" coordinate along which the energy reaches an asymptotic value which is a measure of the hydration energy by one molecule (solid curves in Figure 3). Although this presentation displays clearly the great difference between solid and fluid solution, it has a severe drawback

Each of the stationary states of the  $Eu^{3+}$  ion finds itself in solution in a potential well of equal depth. Now it is important to note that this holds only for one "coordinate," the one that describes the approach of solvent molecules, in the proper orientation, from



SOLVATION COORDINATE

Figure 3. Energy level diagram for the  $\operatorname{Eu}^{s+}$  ion in dense media as a function of the distance between it and its nearest neighbors. Dotted curves: in the solid state.

infinity to the ion. To be more specific let us look at the currently accepted model of hydration of the rare earth ions. It is believed that nine water molecules are nearest neighbors to the ion, forming a kind of triangular parallelepiped.<sup>49</sup> The oxygen atoms are pointed toward the ion. It is clear that for any different spatial configuration, the energy of the system must rise. Such a configuration might be formed by a rotation of one of the solvent molecules or by collision of the complex with another molecule, etc. It is clear that the energetics of the system cannot be fully described by use of just one coordinate. In fact a multidimensional energy level diagram should be provided in order to fully explain the behavior of each energy level as a function of the configuration of the ion's nearest neighbors. The case of the ground state is simplest-whenever the ion is somehow disturbed from equilibrium-it has to return back to the energetically favorable configuration, i.e., to the initial state. The situation is drastically changed when we pass to any excited state. It is true that the stationary states lie in a potential well as deep as the ground state. However, this well is better described as a multidimensional gutter.<sup>50</sup> Infinitesimal perturbations would inevitably result in return to the bottom of the

<sup>(49)</sup> J. A. A. Ketelaar, *Physica*, 4, 619 (1937); D. R. Fitzwater and R. E. Rundle, *Z. Krist.*, 112, 000 (1970).

<sup>(50)</sup> H. F. Hameka, "Advanced Quantum Chemistry," Addison-Wesley, Reading, Mass., 1965, p 80.

well. Finite perturbations may, under certain conditions, promote the system to an energy higher than the rim of the gutter in a critical dimension. In such a case the ion will find its way to the ground state. releasing the excess energy to the solvent. The nature of such a perturbation may be a rotation of a molecule in the solvation layer, or translational displacement in which a solvent molecule leaves the solvation sheath or enters it from the bulk, exchange of molecules, etc. Let us look, for example, at the substitution reaction in which one solvent molecule leaves the solvation shell, and another enters. This reaction is known to be very fast  $(k \simeq 10^7 \text{ sec}^{-1})$  for the ground state of the ion<sup>51,52</sup> and there is no reason to believe that it is slower in excited electronic states. Physically it is most improbable for a molecule to leave the ion without being replaced by another, *i.e.*, to have the need for the total activation energy in Figure 3 instead of a path necessitating only a small fraction of it. Thus one could perhaps better approximate the situation by looking on the substitution reaction as a reactive collision of the type  $A + BA \rightarrow AB + A$ .

It is evident that the energy of activation needed for such a process can be much less than the strength of the A-B bond.

Such reactions can either increase or decrease the internal (vibrational) energy of the resultant molecule AB. In our case this can correspond to either change in vibrational energy of the bond between the ion and the molecule, or in the internal (electronic) energy of the ion. The latter is probable when the gap between the two electronic levels is small enough, as is the case with the  $D_0-D_1$  pair in  $Eu^{3+}$ . This is probably the mechanism leading to the anti-Stokes emission observed by  $us^{27}$  in which  $D_0$  is promoted thermally to  $D_1$ , utilizing the energy of the solvent medium.

One can now account for the difference in the behavior of the  $D_0$  and  $D_1$  levels in the following way. Utilizing Figure 4, we see that the  $D_1$  level is degenerate with a dense quasicontinuum of F states and a much less dense manifold of states belonging to the  $D_0$  level. In liquid solution the transitions between the  $D_0$  and  $D_1$  levels are quite frequent. Moreover, the vibrational levels are broadened by collisions, enhancing transition rates between the three manifolds. The transition probability from the origin of the  $D_0$  level is small because of the relatively large spacings between vibrational levels. Since the density of states of the accepting level, F, is not changed much with increasing energy, one would expect an exponential rise in transition probability as one ascends in the vibronic levels of  $D_{0.43,53}$  The process of decay into F states must compete with the efficient vibrational relaxation. This transfer to F states will be more efficient, if somehow the higher vibronic levels of  $D_0$  become more stable. We suggest that the longer-lived low vibrational levels of the D<sub>1</sub> electronic state provide a reservoir to short-



Figure 4. Vibrational energy levels in the vicinity of the electronic  ${}^{\delta}D_{1}$  state.

lived higher vibrational energy levels isoenergetic with it belonging to the  $D_0$  electronic state. This is achieved by maintaining a steady-state population with a lifetime similar to that of the  $D_1$  level (1 µsec) by efficient interconversion due to solvent molecules colliding with the ion. The same mechanism shortens the lifetime of the  $D_1$  level compared to that observed in solid matrices.

The fact that one observes thermal quenching of  $D_0$ fluorescence with an energy of activation slightly higher than the spectroscopic gap between the  $D_0$  and  $D_1$  levels may be due to vibrational overlapping factors favoring population of somewhat excited  $D_1$  states. These in turn decay quickly to the ground  $D_1$  state which couples effectively to both  $D_0$  and F.

# VI. Analysis of the Evolution of the $D_0$ and $D_1$ States in Aqueous Solutions (H<sub>2</sub>O and D<sub>2</sub>O)

We now proceed to describe in detail the time evolution of these two levels. Let us take the case of the  $D_0$  level first. Experimental results show that we need consider the processes

$$\mathbf{F} + h\nu \xrightarrow{k_1} \mathbf{D}_0 \tag{6-1}$$

$$D_0 \xrightarrow{k_2 = k_{H^0}} F \tag{6-2}$$

$$D_0 \xrightarrow{\kappa_3} D_1 \tag{6-3}$$

$$D_0 \xrightarrow{k_4} F$$
 (6-4)

$$D_1 \xrightarrow{k_5} D_0$$
 (6-5)

$$D_0 \xrightarrow{k_{\theta}} F + h\nu \tag{6-6}$$

Equation 6-1 describes the preparation of the  $D_0$  level by light absorption; equation 6-2 the quenching of the state by high energy vibrations. It has been shown that this quenching process proceeds independently for each molecule in the hydration shell.<sup>24</sup> Since we shall hereafter consider only fully hydrated species, we

- (51) G. Geier, Ber. Bunsenges. Phys. Chem., 69, 617 (1965).
- (52) Y. Haas and G. Navon, submitted for publication.
- (53) R. D. Levine, Chem. Phys. Lett., in press.

shall describe this process by a unimolecular rate constant  $k_{\rm H_0}$ , corresponding to maximum hydration. The rate constant governing the transition of D<sub>0</sub> upwards to D<sub>1</sub> is temperature dependent.<sup>19,27</sup> We presume it arises from such perturbations as described above and write it as  $k_3 = k_3^0 \exp(-\Delta E_3/RT)$ . According to the same model it, is clear that  $k_4$  is also temperature dependent, and we denote it by  $k_4 = k_4^0 \exp[-\Delta E_4/RT]$ .

Process 6-5, re-population of the  $D_0$  level from the  $D_1$  state, should also be taken into account, for the sake of completeness. As we shall see, it consists mainly of two processes: radiative transition (temperature independent) and nonradiative transitions similar to processes 2, 3, and 4. For the time being, we shall consider these as a single process. The difference between them will be made clear later.  $k_6$  is the radiative rate constant for transition to ground state.

The equation governing the time evolution of the  $\mathbf{D}_0$  state is

$$dD_0/dt = k_1 I + k_5 D_1 - (k_{H_0} + k_3 + k_4 + k_6) D_0 \quad (6-7)$$

where I is the intensity of the exciting light and  $D_1$  and  $D_0$  denote concentration of the Eu<sup>3+</sup> in these states. Assuming  $k_5D_1 \ll k_1I$ , as is the case in most experimental conditions, we can solve eq 6-7 exactly to get

$$D_0 = k_1 I [1 - \exp(k_{H_0} + k_3 + k_4 + k_6)t] / (k_{H_0} + k_3 + k_4 + k_6)$$
 (6-8)

where it is assumed that at t = 0,  $D_0 = 0$ .

Equation 6-8 predicts an exponential decay of the  $D_0$  level. As  $k_3$  and  $k_4$  depend on temperature, the rate constant of this decay is temperature dependent. We can estimate the various rate constants appearing in the equation.  $k_{\rm H_0}$  was found to be 9800 sec<sup>-1</sup> and  $k_{\rm f}$  190  $\sec^{-1}$ .<sup>20a</sup> At room temperature  $k_3$  and  $k_4$  can be neglected compared to  $k_{\rm Ho}$  as is evident from the fact that in  $H_2O$  the decay is temperature independent. In  $D_2O$ the decay is temperature dependent, with an energy of activation of about 2000  $cm^{-1}$ .<sup>27</sup> Assuming that the rate observed, 50 sec<sup>-1</sup>,<sup>20</sup> is due mainly to  $k_4$ , we get  $k_{4^0} \sim 10^6 \, {
m sec}^{-1}$ , in agreement with Dawson and Kropp.<sup>19</sup> We can thus safely assume that  $k_{D_0}$  (replacing  $\hat{k}_{H_0}$  in eq 2, when the solvent is  $D_2O$  is negligible compared to  $(k_3 + k_4)$ . This is the reason for the assertion made in section III, that only a lower limit to the ratio  $k_{\rm H_0}/k_{\rm D_0}$ is known experimentally as  $k_{D_0}$  is too small to be measurable at ordinary temperatures. Our results indicate that at low enough temperatures the quantum yield of fluorescence from the  $D_0$  state should approach unity.

The rate equation for the  $D_1$  level is somewhat more complicated. The processes we consider are enumerated below, for excitation directly to this level

$$\mathbf{F} + h\nu \xrightarrow{k_0} \mathbf{D}_1 \tag{6-9}$$

$$D_1 \xrightarrow{k_{\mathbf{H}_1}} F$$
 (6-10)

$$D_1 \stackrel{\kappa_5}{\longleftrightarrow} D_0$$
 (6-11)

$$D_1 \xrightarrow{k_{12}} F$$
 (6-12)

$$D_1 \xrightarrow{k_1} F + h\nu \qquad (6-13)$$

We again refer explicitly to only three distinct mechanisms connecting the excited state with ground state: a temperature-independent process involving vibrational excitation (eq 6-10), a temperature-dependent "gutter" mechanism, (eq 6-12, where  $k_{12}$  is given by  $k_{12}^0 \exp[-\Delta E_{12}/kT]$ ), and the radiative process (eq 6-13). Radiative coupling to D<sub>0</sub> is neglected.  $k_5$  itself as mentioned consists of two components, one temperature independent.<sup>13,14</sup> the other thermally activated.

The rate equation for  $D_1$  is thus

$$dD_{1}/dt = k_{9}I + k_{4}D_{0} - (k_{H_{1}} + k_{5} + k_{12} + k_{13})D_{1} \quad (6-14)$$

The rate equation for D<sub>0</sub> under the same conditions is

$$dD_0/dt = k_5D_1 - (k_H + k_3 + k_4 + k_6)D_0$$
 (6-15)

We thus have two coupled equations for the  $D_0$  and  $D_1$  states. We shall solve these for two limiting cases.

(a) Under usual steady-state experimental conditions we obtain

$$\mathrm{d}\mathrm{D}_{1}/\mathrm{d}t = \mathrm{d}\mathrm{D}_{0}/\mathrm{d}t = 0$$

so that

$$D_0 = k_5 k_9 I / (k_{H_0} + k_3 + k_4 + k_6) \times (k_{H_1} + k_5 + k_{12} + k_{12}) - k_4 k_5 \quad (6-16)$$

 $D_1 =$ 

$$\frac{k_{9}I[k_{H_{0}}+k_{3}+k_{4}+k_{6}]}{(k_{H_{0}}+k_{3}+k_{4}+k_{6})(K_{H_{1}}+k_{5}+k_{12}+k_{13})-k_{4}k_{5}}$$
(6-17)

The quantum yield from  $D_1$  will be proportional to  $k_{13}D_1$ . The isotopic effect, probability of transition from  $D_1$  to  $D_0$  and other parameters determined at steady-state conditions can be calculated through eq 6-17 (see below).

(b) Lifetime measurements are typically performed by exciting the system instantaneously to the desired level and following its decay. The excitation duration should be very short compared to the decay time measured. We can treat these conditions mathematically by assuming that at t = 0, D<sub>1</sub> concentration is D<sub>1</sub><sup>0</sup>, and the rate equations are the same as eq 6-14 and 6-15, except that in eq 6-14 the term  $k_{9}I$  is missing. The solution in this case is<sup>54</sup>

$$D_{1} = C_{1} \exp^{-1/2} [\lambda_{0} + \lambda_{1} + \sqrt{(\lambda_{0} + \lambda_{1})^{2} + 4(k_{4}k_{5} - \lambda_{0}\lambda_{1})}]t + C_{2} \exp^{-1/2} [\lambda_{0}\lambda_{1} - \sqrt{(\lambda_{0} + \lambda_{1})^{2} + 4(k_{4}k_{5} - \lambda_{0}\lambda_{1})}]t \quad (6-18)$$

where

$$\lambda_0 = k_{H_0} + k_3 + k_4 + k_6 \text{ and } C_1 + C_2 = D_1^0$$
  
 $\lambda_1 = k_{H_1} + k_5 + k_{12} + k_{13}$ 

It is evident that  $D_1$  will not generally show simple exponential decay. Similarly, the time dependence of the  $D_0$  level is given by the sum of two exponentials.

We can now use eq 6-17 and 6-18 to predict the behavior of the  $D_1$  level under certain limiting conditions of physical interest.

Case 1.  $k_5 \simeq k_{12} \gg k_{13}$ . This is the usual case in solution. This case is further divided according to the relative importance of the constants appearing in  $\lambda_0$  and  $\lambda_1$ .

Case 1a.  $k_{\rm H_0} \gg k_3$ ,  $k_4$ ,  $k_6$ ;  $k_{\rm H_1} \simeq k_{12}$  as in protonated solvents. The quantum yield from D<sub>1</sub> will be in this case

$$\phi_{\mathrm{D}_{1}} \simeq \frac{k_{13}k_{\mathrm{H}_{0}}}{k_{\mathrm{H}_{0}}(k_{5} + k_{12} + k_{\mathrm{H}_{1}})} = \frac{k_{13}}{k_{5} + k_{12} + k_{\mathrm{H}_{1}}} \quad (6-19)$$

The decay will be exponential as only the first term in eq 6-18 is appreciably different from zero. The lifetime will be

$$\tau \simeq (k_{\rm H_0} + k_5 + k_{12} + k_{\rm H_1})^{-1}$$
 (6-20)

Case 1b.  $k_3 \sim k_4 \sim k_6 > k_{H_0}$ ,  $k_{12} > k_{H_1}$  as is in deuterated solvents.

The quantum yield from D<sub>1</sub> will be

$$\phi_{D_1} = \frac{k_{13}(k_3 + k_4 + k_6)}{(k_3 + k_4 + k_6)(k_5 + k_{12}) - k_4 k_6} \quad (6-21)$$

It is seen that it will be higher than in case 1a, the exact amount of the isotopic effect varying according the precise values of the constants appearing in eq 6-21.

The decay is seen to be here exponential, as in case 1a, with a lifetime of

$$\tau \simeq (k_3 + k_4 + k_6 + k_5 + k_{12})^{-1}$$
 (6-22)

Provided  $k_5 + k_{12}$  is much higher than  $k_{H_0}$  in case 1a and than  $k_3 + k_4 + k_6$  in case 1b, the lifetime is expected to be the same for the two cases. It is evident, therefore, that a situation might arise where deuteration leads to equal lifetimes and to different quantum yields.

We can summarize case 1 by noting that if  $k_5$  and  $k_{12}$  are the largest rate constants governing the depletion of the D<sub>1</sub> level, the isotopic effect on lifetime is expected to be negligible, but the effect may be considerable for quantum yields. The probability for

population of the  $D_0$  level is given in this case by the ratio  $k_5/k_5 + k_{12}$  and is thus independent of deuteration. Therefore we expect that the deuteration effect on  $D_0$  will be the same upon excitation to  $D_1$  as upon direct excitation to  $D_0$ .

Case 2.  $k_5 \simeq k_{12}$ ;  $k_5 \ll k_{\rm H_1}$ ,  $k_{13}$ . This is the usual case in solid matrix. Again we divide this case into two subcases.

Case 2a.  $k_{\rm H} \gg k_3$ ,  $k_4$ ,  $k_6$ . The quantum yield from D<sub>1</sub> will be

$$\phi_{\rm D_1} \simeq \frac{k_{13}k_{\rm H_0}}{k_{\rm H_0}(k_{\rm H_1} + k_{13})} = \frac{k_{13}}{k_{\rm H_1} + k_{13}} \qquad (6-23)$$

The decay will be exponential, provided  $k_{\rm H_0} \simeq k_{\rm H_1} + k_{13}$ . Otherwise more complicated decay laws hold. In the assumed case, the lifetime will be given by

$$\tau \simeq [k_{\rm H_0} + k_{\rm H_1} + k_{\rm I3}]^{-1} \tag{6-24}$$

Case 2b.  $k_5 \gg k_3$ ,  $k_4$ ,  $k_H$  as is the case in deuterated or anhydrous crystals. The quantum yield is now

$$\phi_{\rm D_{\star}} \simeq \frac{k_{13}k_6}{k_6(k_{\rm H_1} + k_{13})} = \frac{k_{13}}{k_{\rm H_1} + k_{13}}$$
 (6-25)

yielding the same result as eq 6-23. It should be remembered that  $k_{\rm H_1}$  is expected to behave approximately as  $k_{\rm H_0}$  upon deuteration, so that in eq 6-25 we really have a quantum efficiency approaching unity, provided  $k_{\rm 13} \gg k_{\rm H_1}$ .

The decay of level  $D_1$  is in this case expected to be composed of two exponentials

$$C_1 e^{-k_{13}t} + C_2 e^{-k_0 t} \tag{6-26}$$

in which the first term is expected to be dominant, as under the initial conditions of very short time excitation  $C_2 \simeq 0$ .

We see that in case 2, the  $D_1$  level behaves very much like the  $D_0$  level. The isotopic effect on quantum yield and lifetime is expected to be quite large.

It should be mentioned that our analysis neglected the temperature-independent process of radiative transition from  $D_1$  to  $D_0$ . We assumed throughout that it is negligible compared to  $k_{13}$ , the radiative rate constant for the transition  $D_1 \rightarrow$  ground state. If this is not the case, the quantum efficiency in deuterated or anhydrous crystals will approach a limiting value, smaller than 1, if only emission to the ground multiplet is monitored.

The scheme presented above can be used to explain all the results summarized in section II and also to obtain numerical estimates of the rate constants involved.

(1) Lifetimes and Quantum Yields of the  $D_0$  Level. In H<sub>2</sub>O the lifetime is governed by  $k_{\rm H_0}$ , and is thus

<sup>(54)</sup> I. S. Sokolnikoff and R. M. Redheffer, "Mathematics of Physics and Modern Engineering," McGraw-Hill, New York, N. Y., 1958, Chapter 1.

 $\sim 10^{-4}$  sec. In D<sub>2</sub>O it is governed mainly by the natural lifetime. As shown, the lifetime is proportional to the quantum yield in both solvents. The reason for not obtaining 100% quantum efficiency is not coupling to O-D vibrations but thermal deactivation through promotion to D<sub>1</sub>.

We propose that quenching is due mainly to the process described by eq 6-4, with  $\Delta E_3 = 2000 \text{ cm}^{-1}$  and  $k_4^0 \simeq 10^6 \text{ sec}^{-1}$ .

(2) Behavior of the  $D_1$  level. We make the following estimates concerning the values of the different rate constants appearing in eq 9 through 13.  $k_{13}$  is expected to be of the same order of magnitude as in crystals, *i.e.*, 10<sup>2</sup> to 10<sup>3</sup> sec<sup>-1</sup>.  $k_{\rm H_1}$  is reasonably taken to be the same as  $k_{\rm H_0}$ , since the energetic difference between the  $D_0$  and  $D_1$  levels is small compared to a quantum of O-H vibration. We found  $k_{\rm H}$  to be 10<sup>4</sup> sec<sup>-1</sup>. A lower limit for  $k_{12}$  may be taken as  $k_{40}^{-0}$  exp- $(-\Delta E/kT)$  where  $\Delta E$  is 300 to 800 cm<sup>-1</sup>. This gives  $k_{12} \sim 10^5$  to 10<sup>6</sup> sec. The only unknown left is  $k^5$ .

Since we found that the probability of  $D_1$  to decay to  $D_0$  is about equal to the probability to decay to F, independent of solvent,<sup>20a</sup> we must put  $k_5 \approx k_{12}$ .

We thus have the following: (a) The probability of transition from  $D_1$  to  $D_0$  or F is independent of the solvent as  $k_{12}$  and  $k_5$  are independent of isotopic substitution, and are larger than  $k_{\rm H_1}$ , so that the conditions of case 1 above prevail. (b) Effect of isotopic substitution on  $D_1$ . The lifetime in  $H_2O$  is given by eq 6-20.  $\tau_{\rm H_2O} \simeq (k_{\rm H_0} + k_5 + k_{12} + k_{\rm H_1})^{-1}$  and in  $D_2O$  (eq 6-22) by  $\tau_{\rm D_2O} \simeq (k_3 + k_4 + k_6 + k_9 + k_{12})^{-1}$ . Since the effect on lifetime was not measured because of the short lifetimes, we shall use data concerning quantum yields for evaluation of the rate constants. The enhancement of  $D_1$  fluorescence in steady state should be (eq 6-19 and 6-21)

$$\frac{(k_3 + k_4 + k_6)(k_5 + k_{12} + k_{H_1})}{(k_3 + k_4 + k_6)(k_5 + k_{12} + k_{D_1}) - k_4k_5}$$

The ratio  $k_6/k_4$  is seen to influence this expression strongly. The value of 4, cited in ref 20a was obtained by using 0.8 as the quantum yield in D<sub>2</sub>O. This ratio is very sensitive to the value of the quantum yield, thus a value of 0.4 for the quantum efficiency would yield  $k_6/k_4 = 0.7$ .

Numerical estimates, consistent with the experimental result that the radiative transition probability  $D_1 \rightarrow D_0$  is independent of deuteration, yield values of  $k_5 \sim k_{12} \sim 5 \times 10^5 \text{ sec}^{-1}$ , and yield an isotopic enhancement factor of 1.2-1.5 depending on the relative importance of the temperature-dependent and -independent (high vibrational) components of  $k_5 \times k_{\rm H_1}$  is an order of magnitude smaller than  $k_5$  and thus does not significantly contribute to the isotopic effect. The isotopic factor is somewhat less than the value of 2-3 estimated from experiment. The determination of the ratio is not very accurate due to the very weak fluorescence. The rate constants are based on solutions of europium nitrate in methanol used as standards for quantum yield determination<sup>20a</sup> and are also subject to some error.

(3) Behavior in a Solid Matrix. Compared to Figure 3 liquids, rotations, and translations are frozen in so that the potential barrier is much higher. This makes little difference in the case of  $D_0$ , so that lifetimes and fluorescence yields are similar in solid matrix to those in solution, isotope effects included.

In the case of  $D_1$ , the heightening of potential barriers makes  $k_4$ ,  $k_5$ , and  $k_{12}$  much smaller, because of the exponential term. We thus arrive in the solid at a system very similar to  $D_0$ , so that quantum yields, lifetimes, and isotopic effects should be similar. This is indeed observed experimentally. The remaining slight differences may be due to the term  $k_5$  which may be equal to  $k_{\rm H_1}$  or higher.

(4) Role of the Anions. The anions influence the radiative rate constants, because of changes of symmetry near the ion. They allow also new pathways for dissipation of energy, by introducing new degrees of freedom along which the system can decay. This is marked mainly with  $D_0$  where overall rate constants are small. In the case of  $H_2O$  which is an efficient quencher, anions lead to stabilization of the  $D_0$  level by keeping the O-H bonds at greater distance from the ion.

(5) Concentration Quenching. This phenomenon appears in crystals for excited levels higher than  $D_0$  and scarcely in solution. This is due to the efficient decay mechanisms present in solution and absent in solids. However, experimental results indicate that in suitable solvents, *i.e.*,  $(CD_3)_2SO$  or  $(CD_3)_2CO$  concentration quenching of  $D_1$  level should be observable at high concentrations and low temperatures.

In the present paper the small and large molecule approximations applied to radiationless transition by high energy vibrations and by translationalrotational motion, respectively, of the solvent molecules were discussed in detail for the case of  $Eu^{3+}$  solutions in light and heavy water. Similar analysis can be applied to solutions of  $Eu^{3+}$  and other rare earth ions in a variety of solvents. We plan to discuss this separately in the future.

# Photosensitized Decomposition of Hexaamminecobalt(III)

# by Biacetyl and by Quinoline

## by Harry D. Gafney and Arthur W. Adamson\*

Department of Chemistry, University of Southern California, Los Angeles, California 90007 (Received October 14, 1971) Publication costs borne completely by The Journal of Physical Chemistry

Biacetyl and quinoline photosensitize the decomposition of  $Co(NH_3)_6^{3+}$  to give Co(II). In the case of biacetyl the yield,  $\phi$ , increases with increasing ethanol content of the medium. The yield also increases with increasing pH in 50% ethanol-water; also, it goes through a maximum with increasing complex concentration. These observations plus the observed phosphorescence quenching suggest that the decomposition occurs in part through a mechanism involving radicals generated by biacetyl and in part through excitation energy transfer, although the maximum yield for the latter process is only about 0.06. Sensitization by quinoline, Q, occurs without consumption of the sensitizer so that no chemical mechanism appears to be present. The yield again increases with increasing alcohol content of the medium. In 20% ethanol-water,  $\phi$  decreases from 0.055 to 0.003 as the pH is decreased from 6 to 1, and in a manner corresponding to the change in the ratio QH<sup>+</sup>/Q for ground state sensitizer. The dependence of  $\phi$  on the concentrations of complex and of oxygen indicates that the triplet states of QH<sup>+</sup> and of Q are responsible for the sensitization. The general situation with respect to photosensitized decompositions of Co(III) ammines is discussed.

# Introduction

Photosensitized reactions have been reported for a number of systems involving coordination compounds and either organic<sup>1-7</sup> or complex ion sensitizers.<sup>8</sup> The sensitized reactions of Co(III) ammines have so far consisted exclusively of redox decompositions, and a concern is that the mechanism may generally be a chemical one involving radicals produced by the sensitizer, rather than actual excitation energy transfer. The concern is a serious one in the case of donors such as benzophenone and biacetyl. Both are known for triplet-state hydrogen abstraction from solvent molecules having loosely bound hydrogen atoms, to form potentially reducing radicals.<sup>9-11</sup>

There is an additional concern in the case of the biacetyl-Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> system. Seemingly contradictory results have been reported,<sup>1,2</sup> and the effect is to leave it uncertain whether biacetyl sensitizes this complex at all. The present investigation was undertaken with the intention of clarifying the specific question of the behavior of biacetyl as a sensitizer for Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, and also of broadening our understanding of the role of sensitizers with Co(III) ammines.

# **Experimental Section**

Materials.  $[Co(NH_3)_6]Cl_3$  was prepared by a standard procedure,<sup>12</sup> and its absorption spectrum agreed well with that in the literature.<sup>1,3</sup>  $[Co(NH_3)_6](ClO_4)_3$ was obtained by recrystallization of the chloride salt from perchloric acid solution.

Reagent grade biacetyl was distilled and stored in the dark. It should be noted that the intensity of the first singlet-singlet absorption band decreases rapidly to one-half of the initial absorbance in less than 15 min in 50% ethanol-water solution in the dark, presumably due to the formation of a stable hydration product.<sup>13,14</sup> For this reason, sclutions to be photolyzed were allowed to stand in the dark for at least 15 min before use. The spectra of such aged biacetyl solutions are independent of pH and of ionic strength at least down to 350 nm, or through the first absorption band. However, the pH slowly decreases over a period of hours, suggesting that some slow decomposition occurs. Quinoline was purified by fractional distillation, taking a 235-236° cut, and then stored in the dark.

Procedures. The general photolysis procedures were

(1) A. W. Adamson and A. Vogler, J. Amer. Chem. Soc., 90, 5943 (1968).

- (2) F. Scandola and M. A. Scandola, ibid., 92, 7278 (1970).
- (3) M. A. Scandola, F. Scandola, and V. Carassiti, Mol. Photochem., 1, 403 (1969).
- (4) G. B. Porter, J. Amer. Chem. Soc., 91, 3980 (1969).
- (5) A. W. Adamson, J. E. Martin, and F. Diomedi Camessi, *ibid.*, 91, 7530 (1969).
- (6) J. E. Martin and A. W. Adamson, Theor. Chim. Acta, 20, 119 (1971).
- (7) V. Balzani, R. Ballardini, M. T. Gandolfi, and L. Moggi, J. Amer. Chem. Soc., 93, 339 (1971).
- (8) J. N. Demas and A. W. Adamson, J. Amer. Chem. Soc., 93, 1800 (1971).
- (9) H. L. J. Backstrom and K. Sandros, Acta Chem. Scand., 12, 823 (1958).
- (10) H. L. J. Backstrom and K. Sandros,  $\mathit{ibid.}$ , 12, 8 (1958), and references therein.
- (11) K. Takeda and Y. Iwakura, Bull. Chem. Soc. Jap., 41, 268 (1968).
- (12) J. Bjerrum and J. P. McReynolds, Inorg. Syn., 2, 217 (1946).
- (13) R. P. Bell and A. O. McDougall, Trans. Faraday Soc., 56, 1281 (1960).
- (14) L.S. Forster, J. Amer. Chem. Soc., 77, 1417 (1955).

those previously described.<sup>6</sup> Solutions were 0.15 M in biacetyl and were irradiated at 410 nm. The natural pH of such solutions is 4.6-4.8. In the case of quinoline, Q, as sensitizer, solutions were  $3.4 \times 10^{-3} M$  in Q and 0.005 M in complex and in 20% ethanol-water, unless otherwise specified. Irradiation was now at 305 nm, at which wavelength the extinction coefficients are  $8.48 \times 10^3$  and  $2.89 \times 10^3 M^{-1} \mathrm{cm}^{-1}$  for QH + and Q, respectively, in 20% ethanol-water medium. In virtually all cases, the concentrations used were such that over 99% of incident light was absorbed by the sensitizer. No correction for direct photolysis of the  $Co(NH_3)_{6^{3+}}$  ion either by the irradiating light or by that emitted by the sensitizer was needed, since at the wavelengths involved the quantum yield for the photodecomposition of the complex is negligibly small, both as previously reported<sup>2,15</sup> and as confirmed in the present study. Photolyses were carried out at 22-24°.

All solutions were deaerated by either  $N_2$  or Ar bubbling, to eliminate the effect of dissolved oxygen, except when the oxygen dependence was studied. For example, a 50% decrease in sensitization yield occurs with Q or QH<sup>+</sup> as sensitizer if air saturated solutions are used. Ferrioxalate actinometry was employed.<sup>16,17</sup>

Analyses for produced  $Co^{2+}$  were made by the thiocyanate method described earlier.<sup>1</sup> The reported pH values are simply those obtained with the use of a standard glass-calomel electrode and Beckman research pH meter, calibrated against a standard aqueous buffer. However, as noted further below, medium corrections were small in 20% ethanol-water. (Mixed-solvent solutions were prepared by taking a known volume of aqueous solution and diluting with ethanol to a desired final volume. The per cent ethanol is reported as 100[(final volume) - (volume of aqueous solution)]/(final volume).

Absorption spectra were obtained by means of a Cary Model 14R spectrophotometer and emission spectra by means of an Aminco spectrofluorometer. The emission spectrum of biacetyl is quite different in 50% ethanolwater medium from that in water alone. With 410-nm exciting light, the ratio of the phosphorescence to the fluorescence intensities at the respective peak emission wavelengths at 515 and 465 nm is about 2:1 in water, but only 1:1 in the mixed solvent. Correction for the fluorescence component was accordingly quite important in the study of the phosphorescence quenching in 50% ethanol-water medium. Two procedures were employed. In the first, use was made of the fact that the phosphorescence is entirely quenched on air saturation of the solution (saturation with pure oxygen produces no further change in the emission spectrum). It was thus possible to determine the ratio of the fluorescence intensity at 465 nm to that at 515 nm. The phosphorescence intensity in deaerated solutions containing complex was then calculated from the observed intensity at 515 nm, correcting for the contribution from the tail of the fluorescent emission by applying the value of the above ratio to the peak intensity of the fluorescence emission at 465 nm. This correction was variable, since a small amount of fluorescence quenching occurs at the higher complex concentrations used. The second procedure was that of analysis of the emission spectra into components, using a Du Pont 911 curve analyzer, followed by reading out the area under the phosphorescence component. The two methods agreed to within about 10%, an imprecision sufficient to make the quenching results uncertain at small complex concentrations.

The pH titration curve of quinoline in a 0.005 M solution of  $[Co(NH_3)_6]Cl_3$  in 20% ethanol-water is shown in Figure 1, along with that of a solution containing no quinoline. At a given pH, the difference between the plots gives the concentration of H<sup>+</sup> present as QH<sup>+</sup> and hence  $F_{QH^+}$ , the fraction of quinoline present in the acid form. The least-squares slope of a plot of  $1/F_{QH^+}$ vs.  $1/(H^+)$  gives  $K_a$  for the dissociation of QH<sup>+</sup> as 2.88  $\times 10^{-5} M$  (at 24°). The titration curve for the solution containing no quinoline indicates that the solvent effect on the pH readings is negligible.

It became apparent during this study that buffering of the solutions was necessary, since quantum yields were pH dependent, and without buffering the produced free ammonia altered the pH. Acetic acid-acetate buffers were therefore used. The calculated pH's in 20% ethanol-water, as determined by the procedure of Gutbezahl and Grunwald,<sup>18</sup> agreed well with our observed values.

The spectral changes observed in 20% ethanol-water with varying pH are consistent with the above acidbase equilibrium and are essentially the same as those previously reported in water.<sup>19</sup> In basic solution the spectrum consists of two bands with maxima at 275 and 313 nm. As the pH decreases, the lower energy transition shows an increased absorbance; there is an isosbestic point at 290 nm.

# **Biacetyl Sensitization**

Results. As the investigation proceeded, it became apparent that several variables are important in determining the sensitization quantum yield,  $\phi$ . First,  $\phi$ increases strongly with increasing alcohol content of the medium, as shown in Figure 2. The yield is virtually zero in water and rises to about 0.2 in 50% ethanol-water and 0.001 *M* complex. The figure further shows a strong dependence on the complex concentra-

- (16) C. A. Parker, Proc. Roy. Soc., Ser. A, 220, 104 (1953).
- (17) C. G. Hatchard and C. A. Parker, ibid., Ser. A, 235, 518 (1956).
- (18) B. Gutbezahl and E. Grunwald, J. Amer. Chem. Soc., 75, 565 (1953).
- (19) N. Mataga, Y. Kaifu, and M. Koyumi, Bull. Chem. Soc. Jap., 29, 373 (1956).

<sup>(15)</sup> M. F. Manfrin, G. Varani, L. Moggi, and V. Balzani, Mol. Photochem., 1, 387 (1969).



Figure 1. pH titration curves in 20% ethanol-water containing  $5 \times 10^{-3} M \operatorname{Co}(\mathrm{NH}_3)_{6}^{3+}$ , using HClO<sub>4</sub>: (O)  $3.38 \times 10^{-3} M$  quinoline, ( $\bullet$ ) no added quinoline, ( $\Delta$ ) calculated for  $K_{\mathtt{a}} = 2.9 \times 10^{-5} M$ , ( $\mathtt{A}$ ) calculated for blank assuming pH =  $-\log$  (HClO<sub>4</sub>).



Figure 2. Ethanol dependence of the biacetyl-sensitized decomposition of  $Co(NH_3)_6^{3+}$ ; natural pH: ( $\blacktriangle$ )  $1 \times 10^{-3} M$  complex, ( $\bullet$ )  $5 \times 10^{-3} M$  complex.

tion; the detailed role of this and of other variables was determined only for 50% ethanol-water solutions because of the difficulty in measuring  $\phi$  values in more aqueous media.

Figure 3 shows the dependence of  $\phi$  on the concentration of the complex in 50% ethanol-water;  $\phi$  rises to a maximum of 0.23 at 0.001 *M* complex, and then decreases to a limiting value of about 0.06 for concentrations above 0.005 *M*. The same graph also shows the plot of  $\phi_p^0/\phi_p$  vs. complex concentration, where  $\phi_p$  and  $\phi_p^0$  denote the phosphorescence yield in the presence and absence of complex, respectively. The lack of apparent quenching at complex concentrations below  $2.5 \times 10^{-4}$  *M* was reproducible and also was independent of ionic strength up to 0.01 *M*. The results can be fitted to a Stern-Volmer line of slope  $1.4 \times 10^3 M^{-1}$ ; quenching experiments in water yield data giving a slope of  $4.8 \times 10^4 M^{-1.2}$ 

The sensitization yield is also pH dependent. Fig-



Figure 3. Variation of biacetyl phosphorescence and sensitization yields with concentration of  $Co(NH_3)_{6^{3+}}$  in 50% ethanol-water: (•) sensitization yield (left ordinate), (O) phosphorescence yield (right ordinate).



Figure 4. pH dependence of the biacetyl-sensitized decomposition of  $Co(NH_3)_{6^{3+}}$ ;  $5 \times 10^{-3} M$  complex, 50% ethanol-water medium.

ure 4 summarizes this dependence in 50% ethanolwater. Use of the perchlorate salt of the complex, thus eliminating chloride ion, has no effect even in the presence of added acid, nor is  $\phi$  sensitive to complex concentration in the range 0.005-0.01 M.

Because of the large excess of biacetyl over complex, it was not possible to determine whether any significant consumption of the former occurred as the result of chemical reaction. In an indirect approach, a series of experiments was carried out with added 0.4 M methyl methacrylate monomer. In the case of the acetonephotosensitized reactions of Zeise's salt, it was found that this monomer intercepted radicals responsible for a redox component.<sup>20</sup> No significant change in  $\phi$  was

(20) P. Natarajan and A. W. Adamson, J. Amer. Chem. Soc., 93, 5599 (1971). found in the present case. This was true for solutions  $0.005 \ M$  in complex in either 50% ethanol-water or 10% ethanol-water (and pH 4.6-4.8), and for solutions  $0.001 \ M$  in complex in 50% ethanol-water.

Discussion. The above results confirm the initial report<sup>1</sup> that biacetyl photosensitizes the redox decomposition of  $Co(NH_3)_6^{3+}$  in nonacidified ethanol-water media. The results are also consistent with the later report<sup>2</sup> that little sensitization takes place in water medium or in acidified ethanol-water mixtures. The apparent conflict in the literature thus seems to be resolved.

The biacetyl-photoinduced decomposition of Co- $(NH_3)_{6^{3+}}$  observed under conditions of low acidity and high alcohol content of the solvent medium must involve at least two mechanisms, judging from the data of Figure 3. A qualitative mechanistic account is the following. We assume that triplet-state biacetyl does react with solvent ethanol to produce radicals capable of reducing the complex, and that at low complex concentrations most of the observed decomposition takes place by this path. The lack of effect of added methyl methacrylate monomer simply reflects, we assume, an improper choice of radical scavenger or of conditions. The second mechanism we take to be one of energy transfer from triplet-state biacetyl to complex, or a true sensitization. The quenching of biacetyl phosphorescence by the complex is nearly complete at 0.005 M complex and we therefore regard 0.06 as the maximum limiting yield for the sensitized decomposition. The two mechanisms are competitive at intermediate complex concentrations, the competition resulting in the observed maximum in  $\phi$ .

It is possible to write a detailed scheme along the above lines, for which the stationary-state analysis is consistent with the quantum yield data. However, in the absence of independent information regarding the kinetics of radical production and consumption, such a treatment is speculative. Depending on such assumed kinetics, the calculated sensitization yield may be smaller than 0.06, for example. Turning to the pHdependence studies, these were made using 0.005 Mcomplex, under which condition the yield of 0.06 may be entirely due to excitation energy transfer, so that the pH effect is to be assigned to changes in the sensitization or intersystem crossing efficiencies. If, however, an important contribution from a radical path is present even at this concentration, then the pH effect would have a quite different explanation.

In view of these complexities, we limit ourselves here to the conclusion that radical production via the biacetyl triplet state accounts for much of the observed decomposition of the complex and that the quenching of this state by the complex is accompanied by sensitization with an efficiency of at most 6% (assuming an intersystem crossing efficiency of unity for biacetyl; the



Figure 5. pH dependence of the quinoline-sensitized redox decomposition of  $\operatorname{Co}(\mathrm{NH}_3)_{6^{3+}}$  in 20% ethanol-water: ( $\bullet$ ) observed yield, (O) calculated using eq 1, ( $\bullet$ ) calculated assuming a triplet-state p $K_a$  of 5.4, ( $\Delta$ ) sensitization yields in 50% ethanol-water.

value in solution is reported to be  $0.99^{21}$ ). Some more general comments are made later.

# **Quinoline Sensitization**

Results. It was not possible to obtain sensitization yields for Q in a purely aqueous medium because of the small solubility of quinoline; however, the yield with QH<sup>+</sup>, using acidified solutions, is less than 0.002. The solubility problem was circumvented by using ethanolwater mixtures, and several effects are summarized in Figure 5. Unless otherwise specified, the medium is 20% ethanol-water. First, for Ar-purged solutions,  $\phi$  decreases from about 0.05 to about 0.0025 as the pH is decreased from 7 to 1. These results fit closely an equation of the form

$$\phi = \frac{F_{Q}\epsilon_{Q}\phi_{Q} + F_{QH} + \epsilon_{QH} + \phi_{QH} +}{F_{Q}\epsilon_{Q} + F_{QH} + \epsilon_{QH} +}$$
(1)

where F denotes fraction of quinoline as Q or as QH<sup>+</sup>  $(F_{\rm QH^+} = ({\rm H^+})/[({\rm H^+}) + K_{\rm a}]$ ,  $\epsilon$  denotes extinction coefficient, and  $\phi_{\rm Q}$  and  $\phi_{\rm QH^+}$  denote the separate sensitization yields for Q and QH<sup>+</sup>, respectively. The solid line in the figure is calculated using  $K_{\rm a} = 2.9 \times 10^{-5} M$ ,  $\phi_{\rm QH^+} = 0.0030$ , and a  $\phi_{\rm Q}$  value of 0.055. This  $K_{\rm a}$  value is the same as found from titration of quinoline. The ground-state  $pK_{\rm a}$  is reported to be 5.1 in ethanol as solvent, and that of the first triplet, 6.0;<sup>22</sup> the same shift

<sup>(21)</sup> J. LeMaire, J. Phys. Chem., 71, 2653 (1967).

<sup>(22)</sup> G. Porter and G. Jackson, Proc. Roy. Soc., Ser. A, 260, 13 (1961).

in pK<sub>a</sub> gives, in our medium, a triplet-state pK<sub>a</sub> of 5.4, a value entirely inconsistent with the data, as shown in the figure. Data for 50% ethanol-water as solvent are included in Figure 5. There is an increase in  $\phi$ , by 69% at pH 4.5 and by 32% at pH 2. The value for  $\phi_{QH+}$ appears not to change by much relative to 20% ethanolwater systems, but the data are not sufficient to determine a value for  $\phi_Q$ ,  $\phi_{QH^+}$ , or  $K_a$ . As a qualitative observation, increasing the ethanol concentration from 20 to 50% leads to increased absorption at 275 nm and a small decrease in absorption at 313 nm, which suggests that the ratio  $Q/QH^+$  has increased.

The sensitization yield is dependent upon the oxygen concentration. Under pH conditions such that 98% of the quinoline was present as QH<sup>+</sup>, pH 3.2, there was a 50% increase in  $\phi$  for argon-purged solutions as compared to air saturated ones, and at pH 6.3 so that 95%of the quinoline was present as Q, the increase was 40%. Unless otherwise indicated, all experiments were performed with deaerated solutions.

Finally, the sensitization yield was determined as a function of complex concentration. Figure 6 shows data plotted as  $1/\phi$  vs. 1/C, where C is the concentration of  $Co(NH_3)_6^{3+}$ . The ratio of intercept to slope for solutions  $1.7 \times 10^{-4} M$  in quinoline and at pH 3.2 is  $1.6 \times 10^4 M^{-1}$ , and for solutions  $3.4 \times 10^{-3} M$  in quinoline and at pH 6.3, this ratio is  $8.7 \times 10^3 M^{-1}$ . The respective intercepts give limiting quantum yields of 0.0025 and 0.051, corresponding to values of 0.002 and 0.054 on extrapolation to pure QH<sup>+</sup> and pure Q. The value for QH<sup>+</sup> averages the somewhat imprecise data for these low yields, and we regard it as being in substantial agreement with the value of 0.003 found from the pH dependence studies.

The emission behavior of quinoline is as follows. The emission spectrum at 77°K in 95% ethanol consists of a weak fluorescence centered at about 330 nm and a strong, structured phosphorescence in the region 400 nm to 600 nm. Quinolinium ion, under the same conditions, shows a strong fluorescence centered at 385 nm, with a slight structuring on the long-wavelength side. We see no phosphorescent emission in our 20% ethanolwater solutions at room temperature, and in neutral solutions the fluorescence is weak and partially masked by some solvent emission. The fluorescence yield is much higher in acid solutions, however, and appears as a strong blue emission centered at about 415 nm, ascribed to QH<sup>+</sup>.<sup>23</sup> We were limited to studies of QH<sup>+</sup> emission because of the weakness of that due to Q. The emission of QH<sup>+</sup> is not oxygen sensitive, but is quenched by relatively high concentrations of  $Co(NH_3)_6^{3+}$ . For solutions 1.7  $\times$  10<sup>-4</sup> M in quinoline and at pH 3.2, a plot of  $\phi_f^0/\phi_f$  vs. C gave a straight line of slope 36.6  $M^{-1}$ , where  $\phi_{\rm f}^{0}/\phi_{\rm f}$  is the ratio of the fluorescence intensities without and with complex present.

Unlike the case with biacetyl as sensitizer, the quinoline concentrations used were comparable to those of



Figure 6. Variation of quinoline sensitization yields with concentration of  $Co(NH_3)_{6^{3+}}$  in 20% ethanol-water: (•) pH 6.3, principal species is Q; (O) pH 2.7, principal species is QH+.

complex decomposition, and it was possible to determine whether any significant chemical change in the sensitizer took place. Two approaches were used. First, irradiation of a solution  $1.7 \times 10^{-4} M$  in quinoline,  $5 \times 10^{-3} M$  in complex, and at pH 4.89 to 4%decomposition of the complex (or  $2 \times 10^{-4} M \text{ Co}^{2+}$ produced) led to only small changes in the absorption spectrum. A small decrease in absorbance at 313 nm and a slight increase in the 250-290-nm region could be accounted for as resulting from small pH and solvent composition changes during deaeration; it appeared that less than 3% of the sensitizer was decomposed.

In a second experiment, the same solution as described above was photolyzed to 5% decomposition of the complex. A 2-ml aliquot was then diluted to 50 ml with 0.1 M HClO<sub>4</sub> and the fluorescence spectrum of the QH<sup>+</sup> present was compared with that obtained by applying the same procedure to an unphotolyzed solution. The two spectra were identical, and we conclude that no significant chemical change in quinoline accompanies its sensitization of the complex. The finding is consistent with the literature observation that quinoline is photochemically inert.<sup>24</sup>

Discussion. No free-radical path seems possible with quinoline as sensitizer. Excited-state quinoline should not be prone to hydrogen abstraction reactions and our direct observation is that negligible loss of quinoline occurs in sensitization experiments. The sensitization and quenching experiments should therefore be understandable in terms of the standard kinetic scheme of eq 2-12, where S and T denote singlet- and

excitation

$$S + h\nu \xrightarrow{a_{ss}} S^*$$
 (2)

(23) N. Mataga and S. Tsuno, Bull. Chem. Soc. Jap., 30, 368 (1957). (24) S. G. Hadley, J. Phys. Chem., 74, 3551 (1970).

1109

fluorescence emission

$$S^* \xrightarrow{e_{as}} S + h\nu$$
 (3)

deactivation by medium

$$S^* \xrightarrow{q_{ss}m} S$$
 (4)

deactivation by complex

$$S^* + C \xrightarrow{q_{M^c}} S + C^* \tag{5}$$

reaction from state populated by singlet energy transfer

$$C^* \xrightarrow{\phi_{s^c}} P$$
 (6)

intersystem crossing

$$S^* \xrightarrow{q_{st}} T$$
 (7)

radiationless deactivation

$$T \xrightarrow{q_{ts}m} S$$
 (8)

deactivation by complex

$$T + C \xrightarrow{q_{\omega^*}} C^* + S \tag{9}$$

deactivation by complex

$$T + C \xrightarrow{q_{ab}} C + S \tag{10}$$

reaction from state populated by triplet energy transfer

$$C^* \xrightarrow{\varphi_{tc}} P$$
 (11)

deactivation by oxygen

$$T + O_2 \xrightarrow{q_{ts}O_2} S$$
 (12)

triplet-state sensitized, respectively. The symbols used in eq 2-12 are those previously described.<sup>6</sup> Phosphorescence emission is not important at room temperature and is omitted. There are two sets of equations, one for Q and one for  $QH^+$ ; we assume, however, that only one species is present in a given case. Stationarystate analysis of eq 2-12 gives, for fluorescence quenching

$$\phi_i^0/\phi_f = 1 + \beta_f[\mathbf{c}] \tag{13}$$

where  $\beta_f = q_{ss}c/(e_{ss} + q_{ss}m + q_{st})$ , and for the singlet, S\*, sensitized decomposition

$$1/\phi_{\rm obsd} = \alpha + \beta/[c] \tag{14}$$

where  $\alpha = 1/\phi_{\rm s}^{\rm c}$ ,  $\beta = (e_{\rm ss} + q_{\rm ss}^{\rm m} + q_{\rm st})/\phi_{\rm s}^{\rm c}q_{\rm ss}^{\rm c}$  and  $\alpha/\beta = \beta_t$ . The fluorescence quenching experiments give  $\beta_t = 36.6 \ M^{-1}$  for QH<sup>+</sup>. If sensitization occurs only through S<sup>\*</sup>, the same value should result on taking the ratio of intercept to slope for the plot  $1/\phi vs. 1/c$ . The much larger value of  $1.6 \times 10^4 \ M^{-1}$  actually found strongly suggests that T rather than S<sup>\*</sup> is the excited sensitizer state involved; the conclusion is strongly reinforced by the observation that  $\phi$  is oxygen sensitive while  $\phi_t$  is not.

We take reaction 5 to be relatively unimportant at low complex concentrations and write the ratios  $q_{\rm st}/(e_{\rm ss} + q_{\rm ss}^{\rm n} + q_{\rm st})$  and  $q_{\rm ts}^{\rm s}/(q_{\rm ts}^{\rm s} + q_{\rm tc}^{\rm c})$  as  $\phi_{\rm st}$ , the intersystem crossing yield, and  $\phi_{\rm et}$ , the energy-transfer efficiency, respectively. Stationary-state analysis yields, for sensitization through T, the result

$$1/\phi = \alpha' + \beta'/[c]$$
 (15)

where  $\alpha' = 1/\phi_t c \phi_{et} \phi_{st}$ ,  $\beta' = (q_{ts}^m + q_{ts}^{O_2}[O_2])/\phi_t c \phi_{et}$  $\phi_{st}(q_{ts}^{c} + q_{ts}^{c^*})$  and  $\alpha'/\beta' = (q_{ts}^{c} + q_{ts}^{c^*})/(q_{ts}^{m} + q_{ts}^{c^*})$  $q_{ts}^{O_2}[O_2]$ ). The data of Figure 6 for deaerated solutions give  $(q_{st}c^* + q_{ts}c)/q_{ts}m$  as  $1.6 \times 10^4 M^{-1}$  and  $8.7 \times 10^3$  $M^{-1}$  for QH<sup>+</sup> and Q, respectively, (neglecting the small correction for the fact that at the two pH's a few percent of Q and QH<sup>+</sup> were present, respectively). The value of  $q_{ts}O_2[O_2]$  should be about 10<sup>6</sup> sec<sup>-1</sup> for aerated solutions if the rate is diffusion controlled, and our observed oxygen effects on  $\phi$  suggest that  $q_{ts}^{m}$  is about 10<sup>4</sup> sec<sup>-1</sup> for both Q and QH<sup>+</sup>; that is,  $\phi$  is roughly halved on aeration of a solution  $5 \times 10^{-3} M$  in complex. We therefore conclude that  $q_{ts}^{c} + q_{ts}^{c^*}$ , the bimolecular rate constant for quenching of T by complex, is of the order of  $10^8 M^{-1} \sec^{-1}$ , or only somewhat less than the diffusion-controlled limit.

The above analysis accounts reasonably well for the general observations, and the next level of detail concerns the pH effect on  $\phi$ . The data of Figure 5 were best explained on the basis that the ratio of  $Q^*$  to  $QH^{+*}$ produced on light absorption is determined by the ratio of light absorbed by ground-state Q to that absorbed by ground-state QH<sup>+</sup>; that is, the  $\phi$  vs. pH curve is reproduced assuming the  $K_{\rm a}$  value for ground-state quinoline. The implication is that the acid-base equilibration of either excited singlet- or triplet-state quinoline is slow compared to deactivating processes. This conclusion seems reasonable. The rate of relaxation of excited-state quinoline to the equilibrium ratio of  $Q^*$ to  $QH^{+*}$  corresponding to  $K_{a}^{*}$  is given, in first order, by  $k_r^* = k_1^* + k_{-1}^* [H^+]$ , where  $k_1^*$  and  $k_{-1}^*$  are the forward and reverse rate constants for the  $QH^{+*} \rightleftharpoons$  $Q^*$  and  $H^+$  reaction. The effect of excited-state acidbase equilibration on  $\phi$  should be greatest at a pH  $\simeq pK_{a}^{*}$  or at a pH of around 5.4, assuming  $pK_{a}^{*}$  to be somewhat larger than  $pK_{a}^{25}$  Thus, even if  $k_{-1}^{*}$  has a diffusion-controlled value,  $k_r$  should at best be comparable to the other rate constants of the system, and could be much smaller.

Quite apart from the above matter, it seems reasonable to take the data at low and at high pH as reflecting the behavior of QH\* and of Q\*, respectively. The appreciable difference in the sensitization behavior of these two forms of quinoline may derive from a difference in the  $\phi_{st}$  values. The emission studies described above suggest that  $\phi_{st}$  for Q is larger than for QH<sup>+</sup>,

(25) C. A. Parker, "Photoluminescence of Solutions," Elsiever, New York, N. Y., 1968.

The Journal of Physical Chemistry, Vol. 76, No. 8, 1972

judging from the larger phosphorescence to fluorescence ratio for Q as compared to QH<sup>+</sup>. Consistent with this effect of protonation, a 50% decrease in  $\phi_{st}$  due to hydrogen bonding has been reported for quinoline.<sup>26</sup> However, a more recent study reports no difference in  $\phi_{st}$  in alcoholic and hydrocarbon solvents.<sup>27</sup> A further point is that  $\phi_t^{c}$  should not depend significantly on whether the sensitizer species is Q or QH<sup>+</sup>, since the two triplet-state energies are nearly the same. Our ratio of  $\alpha'$  values then suggests that the ratio  $(\phi_{et}\phi_{st})_{QH}$  $(\phi_{et}\phi_{st})_{QH^+}$  is 0.051/0.0025 or 20. Alternatively, if we replace  $\phi_{et}$  by its defining expression and note that the ratio  $[(q_{ts}^{c} + q_{ts}^{c^*})/q_{ts}^{m}]_Q/[(q_{ts}^{c} + q_{ts}^{c^*})/q_{ts}^{m}]_{QH^+}$  is  $8.7 \times 10^3/1.6 \times 10^4$  or 0.54, then we can write

$$20 = (1/\alpha')_{Q}/(1/\alpha')_{QH^{+}} = (1/0.54) \frac{(q_{ts} \circ^{*} \phi_{st})_{Q}}{(q_{ts} \circ^{*} \phi_{st})_{QH^{+}}}$$

The difference between the limiting sensitization yields for Q and QH<sup>+</sup> must thus derive in part from changes either in  $q_{ts}e^*$  or in  $\phi_{st}$ . Until further information is known about the effect of protonation on  $\phi_{st}$ , the magnitude of the difference in the bimolecular quenching constant cannot be determined.

## **General Discussion**

Two questions were raised in the Introduction. With respect to the first, we have established some of the conditions under which absorption of light by biacetyl induces decomposition of  $Co(NH_3)_6^{3+}$ , and conclude that a chemical mechanism is important. Sensitization, that is, a process not involving net chemical change in the donor, is probably also present, but in low efficiency at best.

In answer to the more general question regarding photosensitized decompositions of  $Co(NH_3)_6{}^{3+}$ , we add quinoline to the list of sensitizers. It seems very likely that naphthalene is also one (although possibly 20% of the sensitization events were reported to accompany decomposition of the sensitizer<sup>3</sup>), as well as *trans*-4carboxylate stilbene (TSC).<sup>1</sup> It has not been established whether benzophenone can act as a true sensitizer for  $Co(NH_3)_6{}^{3+}$ ; such action does appear to occur with  $Cr(CO)_6$  as acceptor, in benzene as solvent.<sup>28</sup>

Table I summarizes some of the available results. It seems definite that sensitization can occur through either singlet or triplet donor excited states. The energy cutoff for the latter may be around the triplet-state energy for biacetyl, or 58 kcal  $mol^{-1}$ , but it is difficult to pick a cutoff energy for singlet excited-state sensitization.

We agree that the produced energetic form of the complex is probably not a hot ground state, since the reaction which occurs is not the thermal one (see ref 3); the nature of the produced excited state is presumably charge transfer (CT), again in view of the reaction being a redox decomposition. In all cases except naphthalene it seems necessary, on energetic grounds, to assume that a low-lying  ${}^{3}CT$  state of the complex is populated (see ref 1); in the case of naphthalene, the first  ${}^{1}CT$  state is energetically acceptable, but has not otherwise been demonstrated to be involved.

Another aspect is the following. The observation that  $\phi$  increases with increasing ethanol content seemingly constitutes an argument for the presence of a chemical mechanism. That is, increasing the ethanol concentration should increase the efficiency of hydrogen atom abstraction by a triplet-state sensitizer such

Table I:	Photosensitized	Decompositions	of	$C_0(NH_2)e^{3+}$
			01	

	Excite energy, k	d-state cal mol <sup>-1</sup>	
Sensitizer	Singlet	Triplet	Observation
TSC	74 <sup>a</sup>	50 <sup>6</sup>	Singlet-state sensitization
Biacetyl	62°	58°	Triplet-state sensitization, but inefficient.
Naphthalene	89	61	Singlet-state sensitization
QH <sup>+</sup>		62 <b>°</b>	Triplet-state sensitization, but inefficient.
Q	91 <sup>d</sup>	63°	Triplet-state sensitization
Benzophenone	74 <sup>d</sup>	69 <sup>d</sup>	Sensitization observed

<sup>a</sup> From position of tail of the first singlet-singlet absorption band: A. W. Adamson, A. Vogler, and I. Lantzke, *J. Phys. Chem.*, **73**, 4183 (1969). <sup>b</sup> J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1967. <sup>c</sup> Reference 6. <sup>d</sup> See p 297 of the reference of footnote b. <sup>e</sup> Reference 22.

as biacetyl or benzophenone, which is the effect observed. This reasoning evidently can be misleading, however, since qualitatively the same medium effect occurs with quinoline as sensitizer, although no radical path is now involved. There must therefore be a solvent effect unrelated to the ability of ethanol to act as a hydrogen atom donor.

From the kinetic point of view, this effect appears to be one of an increasing rate constant for energy transfer with increasing ethanol concentration. It is unlikely that the rate constant for encounters between solvated donor and complex is so strongly medium sensitive, and we believe that it is instead the efficiency of energy transfer *during* an encounter that is varying. The explanation may be one of reduced hydration of the complex with increasing ethanol content,<sup>29</sup> with consequently closer and more prolonged contact between donor and acceptor during each encounter and hence increased probability or a sensitization event occurring. That is, the sensitizer molecule may more easily replace ethanol than water in the immediate solvation sphere

- (27) S. G. Hadley, J. Phys. Chem., 75, 2083 (1971).
- (28) A. Vogler, Z. Naturforsch. B, 25, 1069 (1970).

<sup>(26)</sup> A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965).

<sup>(29)</sup> C. H. Langford and J. F. White, Can. J. Chem., 45, 3049 (1967).

of the complex ion. We suggest that the nature of the encounter complex deserves more attention than it has so far received. Varying the solvent medium may, for example, affect the efficiency of quenching differently from the efficiency of excitation energy transfer. Acknowledgment. These investigations were supported in part by Contract No. DA-ARO-D-31-124-G87 between the University of Southern California and the Department of the Army, Army Research Office (Durham).

# Vacuum-Ultraviolet Photolysis of the C<sub>4</sub>H<sub>6</sub> Isomers. IV. 1-Butyne

# by Kevin L. Hill and Richard D. Doepker\*

Department of Chemistry, University of Miami, Coral Gables, Florida 33124 (Received September 13, 1971)

Publication costs assisted by the National Science Foundation

The photolysis of 1-butyne was investigated, using xenon (147.0 nm) and krypton (123.6 nm) resonance radiation. The major products observed were hydrogen, acetylene, ethylene, allene, and vinylacetylene. Evidence is presented for the occurrence of primary processes forming atomic and molecular hydrogen:  $1-C_4H_6$ -yne +  $h\nu \rightarrow 2H + C_4H_4$ ,  $1-C_4H_6$ -yne +  $h\nu \rightarrow H + C_2H_4 + C_2H$ ,  $1-C_4H_6$ -yne +  $h\nu \rightarrow H_2 + 2C_2H_2$ ,  $1-C_4H_6$ -yne +  $h\nu \rightarrow H_2 + C_2H + C_2H_3$ . The formation of allene and a major fraction of the methyl radicals was attributed to the addition of a hydrogen atom to 1-butyne: H +  $1-C_4H_6$ -yne  $\rightarrow CH_3 + C_3H_4$ . The use of H<sub>2</sub>S, D<sub>2</sub>S, and CD<sub>3</sub>I as free radical interceptors demonstrated the presence of CH<sub>3</sub>, C<sub>2</sub>H, C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub>, and C<sub>3</sub>H<sub>3</sub> radicals.

# Introduction

In continuation of our vacuum-ultraviolet photochemical investigations to determine the modes of decomposition of electronically excited  $C_4H_6$  molecules,<sup>1-3</sup> the 147.0- and 123.6-nm photolysis of 1-butyne has been carried out. Previous study of the photochemistry of 1-butyne has been limited to a mercury-photosensitized decomposition by Kebarle.<sup>4</sup> Other alkynes which have received some attention in the vacuumultraviolet region are acetylene<sup>5,6</sup> and methylacetylene.<sup>7</sup> Stief, *et al.*,<sup>7</sup> observed that atomic hydrogen was formed in a primary process, during the 147.0-nm photolysis of propyne.

$$CH_3 - C = CH + h\nu \longrightarrow C_3H_3 + H.$$
(1)

The formation of acetylene and ethane was attributed to the following reaction sequence.

$$H + CH_3 - C = CH \longrightarrow CH_3 + C_2H_2 \qquad (2)$$

$$2CH_3 \longrightarrow C_2H_6$$
 (3)

The displacement of a CH<sub>3</sub> radical by an H atom had been shown previously by Safrany and Jaster.<sup>8</sup>

# **Experimental Section**

Materials. 1-Butyne (Matheson Co.) was purified by gas chromatography using a 16-ft dimethylsulfolane on Chromosorb column at  $25^{\circ}$ . An impurity of 0.004% acetylene was disclosed by gas chromatographic analysis, but this was removed by low-temperature distillation.  $D_2S$ ,  $CD_3I$ , and  $D_2$  were obtained from Merck Sharp and Dohme, Montreal, Canada, and used without further purification. Purification of other materials used has been described in previous studies.<sup>1-3</sup>

Irradiation. The irradiation procedure has been described previously.<sup>1</sup> The xenon and krypton lamps used were "titanium getter" lamps of the type described by Ausloos and Lias<sup>9</sup> and used in our recent work with cyclobutene.<sup>3</sup> Lamp intensities (147.0 nm) were measured by CO<sub>2</sub> actinometry<sup>10-12</sup> and were found to be in the range  $1.5 \times 10^{14}$ – $5 \times 10^{14}$  quanta/sec. The resulting CO was analyzed by mass spectrometry, and a quantum yield of unity was assumed for its formation.<sup>10-13</sup> At 123.6 nm, cyclobutene was used as

- (1) R. D. Doepker, J. Phys. Chem., 72, 4037 (1968).
- (2) R. D. Doepker and K. L. Hill, ibid., 73, 1313 (1969).
- (3) A. DeLeon and R. D. Doepker, *ibid.*, 75, 3656 (1971).
- (4) P. Kebarle, J. Chem. Phys., 39, 2218 (1963).
- (5) L. J. Stief, V. J. DeCarlo, and R. J. Matoloni, *ibid.*, 42, 3131 (1965).

(6) (a) S. Takita, Y. Mori, and I. Tanaka, J. Phys. Chem., 72, 4360 (1968);
(b) *ibid.*, 73, 2929 (1969).

(7) L. J. Stief, V. J. DeCarlo, and W. A. Payne, J. Chem. Phys., 54, 1913 (1971).

- (8) D. R. Safrany and W. Jaster, J. Phys. Chem., 72, 3323 (1968).
- (9) P. Ausloos and S. G. Lias, Radiat. Res. Rev., 1, 75 (1968).
- (10) B. H. Mahan, J. Chem. Phys., 33, 959 (1930).
- (11) P. Warneck, Discuss. Faraday Soc., No. 37, 57 (1964).
- (12) J. Y. Yang and F. M. Servedio, Can. J. Chem., 46, 338 (1968).
- (13) L. J. Stief and V. J. DeCarlo, J. Chem. Phys., 51, 3336 (1969).

C4H6 P. Torr	Additive (P, Torr)	Hı	CH	C3H3	C <sub>2</sub> H <sub>4</sub>	C2He	C <sub>8</sub> H <sub>8</sub>	CaH4ª	C4H4
1.0	None	0.27	0.04	0.11	0.14	0.23	0.09	0.52	0.37
10.0	None	0.20	0.04	0.12	0.12	0.13	0.05	0.25	0.33
1.0	$O_2(0,1)$	nd <sup>e</sup>	$t^d$	0.13	0.20			0.54	0.34
5.2	$O_2(0,5)$	nd	t	0.12	0.17			0.32	0.33
0.07	NO (0.007)	nd	0.02	0.12	0.09	0.01		0.78	0.33
0.5	NO $(0.05)$	nd	nd	0.12	0.09			0.50	0.33
1.0	NO (0.1)	0.27	nd	0.12	0.09			0.43	0.34
15.0	NO $(0.5)$	0.17	nd	0.12	0.09			0.30	0.33
10.0	NO (1.0)	0.14	nd	0.14	0.10			0.25	0.32
20.0	NO (2.0)	0.10	nd	0.12	0.09			0.21	0.33
<sup>a</sup> Allene.	$^{b} \Phi(C_{4}H_{4}) \pm 0.04.$ cr	nd = not de	termined.	d t = trace, 0	0.01.			1	

Table I: Photolysis of 1-Butyne (147.0 nm), Quantum Yields

Table II: Photolysis of 1-Butyne (123.6 nm), Quantum Yields

C4H6 P, Torr	Additive (P, Torr)	H2	CH	$C_2H_2$	C <sub>2</sub> H <sub>4</sub>	$C_2H_6$	$C_{2}H_{8}$	C3H4ª	C4H4
1.0	None	0.29	0.03	0.15	0.09	0.16	0.05	0.60	0.36
10.0	None	0.14	0.03	0.16	0.10	0.08	0.03	0.21	0.36
0.5	$O_2(0.03)$	$\mathbf{nd}^{c}$	nd	0.18	0.12			0.61	0.34
1.0	$O_2(0.05)$	nd	nd	0.17	0.12			0.50	0.32
2.5	$O_2(0.13)$	nd	nd	0.20	0.13			0.38	0.37
12.8	$O_2(0.7)$	nd	nd	0.19	0.12			0.22	0.34
0.07	NO (0.007)	nd	nd	0.16	0.08			0.66	0.35
1.0	NO (0.1)	0.22	nd	0.15	0.09			0.43	0.33
10.0	NO (1.0)	0.19	nd	0.17	0.10			0.19	0.36
<sup>a</sup> Allene.	$^{b} \Phi(C_{4}H_{4}) \pm 0.04.$	$^{\circ}$ nd = not de	termined.						

an actinometer assuming a value of 0.40 for the quantum yield of acetylene.<sup>3</sup> In all the above measurements a 550-cm<sup>3</sup> reaction vessel was used while holding conversions to within 0.05%.

The ultraviolet photolysis reported in this study was carried out in a 500-cm<sup>3</sup> Vycor reaction vessel, utilizing a Hanovia utility quartz medium-pressure lamp. All experiments were conducted at room temperature, to about 0.5% conversion. Two mercury-photosensitized experiments were carried out in a 1-l. Vycor reaction vessel using a Gelman-Camag low-pressure (253.7 nm) universal uv lamp. Photolysis times were 1.5 min in duration, equivalent to about 1% conversion.

Analysis. After irradiation, an aliquot of the sample was introduced into a dual-flame gas chromatograph and separation was achieved on a 25-ft 30% squalane column, or a 35 ft 15% dimethylsulfolane-8-ft 30% squalane combination column. The latter column was used primarily to check the purity of the reported vinylacetylene.

Noncondensable products were distilled at  $-210^{\circ}$ , collected, and analyzed with a CEC-21-103 C mass spectrometer. Products of special interest were separated by means of vapor chromatography, trapped with liquid nitrogen, and also analyzed with the CEC-21-103 C mass spectrometer.

## Results

Using  $CO_2$  as an actinometer the quantum yields of the major products from the 147.0-nm photolysis of 1butyne were determined. Table I reports the quantum yields of the products as determined in these experiments. Likewise, Table II reports similar quantum yields for the 123.6-nm photolysis of 1-butyne based on cyclobutene as an actinometer. At both of these wavelengths vinylacetylene appears to be independent of pressure as well as unaffected by the presence or absence of a radical scavenger. Allene, on the other hand, demonstrated a moderate pressure dependency.

In order to further examine the observed pressure effect observed in Tables I and II, 1-butyne was photolyzed in the presence of a large excess of nitrogen (147.0 nm) or Xe (123.6 nm), the results of which are given in Table III.

In addition to the data given in Tables I–III, a few general observations should be stated.

(1) When a radical scavenger was present, relative products yields were insensitive to irradiation time. This study corresponded to conversions of from 0.01 to 0.5% decomposition (based on the yield of vinyl-acetylene). Normal conversions were held to approx-

C4H6	Additive				-Relative yields	$C_4H_4 = 100-$		
P, Torr	(P, Torr)	CH4	$C_2H_2$	$C_2H_4$	$C_2H_6$	C <sub>3</sub> H <sub>8</sub>	C2H4ª	C4H6
				147.0 nm, 2	Ke			
0.3	None	9	29	34	72	25	180	10
0.3	$N_{2}(70)$	11	25	24	11	6	$17(0.33)^{c}$	15
0.3	$N_2$ (150)	10	24	24	9	5	9 (0.33)	18
0.3	$N_2$ (268)	7	24	20	11	6	6	14
				123.6 nm, 2	Kr			
0.2	Xe (1.3)	12	44	25	61	13	140	5
0.2	Xe (75)	15	39	26	nd <sup>d</sup>	5	18 (0.36)	12
0.2	Xe (160)	20	37	21	nd	3	9.2(0.35)	nd
<b>0</b> . $2$	Xe (500)	nd	36	23	nd	1	3.4	nd
<sup>a</sup> Allene.	<sup>b</sup> 1,2-Butadiene.	$^{c} \Phi(C_{4}H_{4}) \pm 0.07$	$^{d}$ nd = r	not determin	ed.			

Table III: Photolysis of 1-Butyne, Pressure Effect of Added "Inert"

Table IV. Photolysis (220-260 nm) of 1-Butyne in the Presence and Absence of Additives

CARE	Additive			Relativ	e yields, C <sub>2</sub> H <sub>2</sub>	= 100		
P, Torr	(P, Torr)	$CH_4$	$C_2H_4$	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	$C_3H_8$	C3H4"	$C_3H_4^{\circ}$
10	None	560	120	720	12	97	35	150
5.0	NO (0.25)	$nd^{c}$	110	<b>2</b>	5		3	350
10.0	NO (0.5)	nd	101	2	3		<b>2</b>	306
20.0	NO (1.0)	nd	98	1	8		4	240
10.0	$O_2(0.5)$	36	120	9	30	3	8	120
10.0	$H_{2}S(1.5)$	600	66	101	14	1	5	407

imately 0.02% when no radical scavenger was present to about 0.05% with either oxygen or nitric oxide present.

(2) An increase in NO from 5 to 20% of the butyne pressure had no noticeable effect on the relative yields of products observed in the vacuum-ultraviolet region.

(3) No analysis for 1,3-butadiene or the butenes was routinely performed in this study. 1,2-Butadiene was observed to the extent of nearly 10% of the vinylacetylene yields in both 147.0- and 123.6-nm photolysis.

(4) Small amounts of methylacetylene were observed in all vacuum-ultraviolet experiments. These yields were approximately 1-2% of the vinylacetylene. Slight increases were observed when NO was absent or when conversions exceeded the normal values.

Since the direct ultraviolet photolysis of 1-butyne has not been previously reported, a preliminary investigation was carried out as a part of this study. Some of these data are reported in Table IV.

In order to differentiate between a bimolecular reaction channel and a unimolecular one, common practice in radiation chemistry would call for the photolysis of a 1:1 mixture of 1-butyne- $h_6$ : 1-butyne- $d_6$ . Unfortunately, it was not economically possible to obtain 1butyne- $d_6$ . Therefore, in an attempt to elucidate the formation of hydrogen, allene, and 1,2-butadiene, a series of experiments was designed to substitute for the unavailability of 1-butyne- $d_6$ . The mercury-photosensitized dissociation of deuterium in the presence of 1-butyne (Table V) led to the formation of only allene as a major product when NO was present. Methane and ethane became important products along with 1-butene when the NO was omitted from the photolysis mixture.

<b>Fable V</b> :	Mercury-Photosensitized Dissociation of
Deuterium	in the Presence of 1-Butyne

of reactant, a		]	Major produc	ts	
mTorr		Ethanes	Allenes		
1-C <sub>6</sub> H <sub>6</sub> -yne	NO	$C_2H_6$	C₂H₅D	C <sub>8</sub> H <sub>4</sub>	C2H3D
200	80	0	0	5	95
200	0	78	22	5	95

In other experiments  $H_2S$  and  $D_2S$  were used as a diagnostic test for free radicals<sup>14</sup> (Tables VI and VII), while  $CD_3I$  was introduced in some 123.6 nm (Table VIII) primarily to examine the formation of allene and 1,2-butadiene.

1,2-Butadiene (approximately 10% of the vinylacetylene yield) was observed in the CD<sub>3</sub>I experiments. The presence of  $1,2-C_4H_3D_3$  was established through

(14) P. Ausloos and S. G. Lias, J. Chem. Phys., 44, 521 (1966).

CaHe	Additive							
P, Torr	(P, Torr)	Methane	Acetylene	Ethylene	Ethane	Allene	Hydroger	
				147.0 n	m, Xe			
1.0	$H_{2}S(0.1)$	300	50	60	58	190	ndª	
10.0	$H_{2}S(1.0)$	229	48	53	60	100	nd	
				123.6 n	m, Kr			
1.0	$H_{2}S(0.15)$	700	50	53	35	200	nd	
1.0	$D_2S(0.15)$	nd	38	46	35	168	65	
1.0	$D_{2}S(0.25)$	$\mathbf{nd}$	47	47	34	158	51	
1.0	$D_2S(0.36)$	nd	50	43	32	163	46	
1.0	$D_2S(0.60)$	$\mathbf{nd}$	51	46	31	173	50	

Table VI: Photolysis of 1-Butyne in the Presence of H<sub>2</sub>S (D<sub>2</sub>S)

**Table VII:** Isotopic Distribution of Product,  $1-C_4H_6$ -yne<sup>a</sup>-D<sub>2</sub>S Mixture at 123.6 nm

D2S P, Torr	H2	HD	D2	CH₄	CH₂D	C₃H₄	C₁H₂D
0.15	76	24		36	64	88	12
0.25	70	30		33	67	86	14
0.36	58	38	4	34	66	84	16
0.60	50	41	9	34	66	80	20
<sup>a</sup> 1-Buty	ne press	sure 1 Te	o <b>rr</b> .				

Table VIII: Photolysis of 1-Butyne (123.6 nm) in the Presence of  $\mathrm{CD}_3 I$ 

		Relative yields, vinylacetylene = $100$						
C <sub>4</sub> H <sub>6</sub>	CD <sub>8</sub> I	Acety-	Ethyl-	E4b	Pro-	A 11		
P, 10rr	P, Iorr	lene	ene	LIGANO	pane	Allene		
1.0	None	44	<b>22</b>	51	14	160		
1.0	0.2	44	23	80	8	83		
1.0	0.5	42	23	109	7	63		
1.0	1.0	39	25	132	5	49		
0.2	1.1	38	40	300	12	25		

mass spectral analysis, with best estimates indicating that it predominated over the  $1,2-C_4H_6$  produced. Further, the ethane formed (Table VIII) yielded an increasing D<sub>6</sub> product with increasing CD<sub>3</sub>I pressure. A ratio of  $C_2D_6/C_2H_3D_3 = 3/2$  was obtained for the equimolar mixture. The allene formed in these experiments showed less than 15% C<sub>3</sub>H<sub>3</sub>D.

#### Discussion

When 1-butyne (I.P. 10.18 eV)<sup>15</sup> absorbs a photon of energy 8.4 (147.0) or 10.0 eV (123.6 nm), only electronically excited neutral molecules will be produced.

$$1-C_4H_6-yne + h\nu \longrightarrow (C_4H_6)^*$$
(4)

If the lifetime of the resulting excited butyne molecule is less than the collision interval at the pressure range used in this study, fragmentation of this excited species will occur which is independent of total pressure. A long-lived excited molecule, on the other hand, would result in decreasing fragmentation with increasing total pressure.

Stief, et al.,<sup>5</sup> postulated the existence of a long-lived excited state for acetylene capable of collisional deactivation in the 147.0-nm photolysis of acetylene. Tanaka and coworkers<sup>6</sup> demonstrated this long-lived excited state of acetylene in the 147.0-nm acetylene-photosensitized decomposition of methane. Stief, De-Carlo, and Payne,<sup>7</sup> on the other hand, recently have shown evidence against any long-lived excited state in the 147.0-nm photolysis of propyne. Examination of Tables I and II indicates that only allene exhibits a pressure dependence characteristic of a product from a long-lived excited state of 1-butyne. However, this pressure effect is best explained through a hydrogen atom mechanism (see Allene Formation) as opposed to a long-lived excited-state decomposition.

Vinylacetylene Formation. It is noted in the Results section that vinylacetylene formation is independent of 1-butyne pressure and unaffected by the presence or absence of additives. The formation of vinylacetylene in the vacuum-ultraviolet photolysis of 1,3-butadiene,<sup>1</sup> 1,2-butadiene,<sup>2</sup> and cyclobutene<sup>3</sup> occurs through the elimination of two hydrogen atoms, either stepwise or simultaneously. This process applied to 1-butyne is depicted by the following reaction sequence

$$(C_4H_6)^* \longrightarrow H + (C_4H_5)' \tag{5}$$

$$(C_4H_5)' \longrightarrow H + C_4H_4 \tag{6}$$

where  $(C_4H_5)'$  is a fragment with excess internal energy. In order to be consistent with the data in Tables I-III, the lifetime of the  $(C_4H_5)'$  molecule must be less than the collision interval. This mode of formation is also consistent with the observation that vinylacetylene is observed in only trace amounts in the 220.0-260.0-nm photolysis of 1-butyne (Table IV). The photon energies in this range are insufficient for this process.

(15) T. Nakayania and K. Watanabe, J. Chem. Phys., 40, 558 (1964).

$$1-C_4H_{e}-yne + h\nu \longrightarrow 2H + C_4H_4 \qquad (7)$$
$$\Delta H = 139 \text{ kcal/mol}$$

A second channel leading to the formation of vinylacetylene might be expected through the direct elimination of molecular hydrogen from the photoexcited state.

$$1-C_4H_6\text{-yne} + h\nu \longrightarrow H_2 + (C_4H_4)' \tag{8}$$

Even with a photon energy of 195 kcal/einstein (147.0 nm), the resulting  $(C_4H_4)'$  molecule would possess the greater part of 160 kcal/mol excess energy. This excess energy would lead to additional fragmentation.<sup>5,6</sup>

$$(C_4H_4)' \longrightarrow C_2H_2 + C_2H_2 \tag{9}$$

$$\longrightarrow C_4H_2 + H_2$$
 (10)

$$\rightarrow C_2H_3 + C_2H$$
 (11)

Pressure quenching of the excess energy of the  $(C_4H_4)'$  molecule would be expected, but the lack of a pressure dependency on the vinylacetylene formation precludes that process. Thus, only a small part of the observed vinylacetylene could arise from molecular hydrogen elimination channel.

The reaction channel leading to diacetylene (reaction 10) cannot be excluded from consideration, since small amounts (10% of the total  $C_4H_4$  yield) may be masked in the analysis methods employed and analyzed as vinylacetylene.

Allene Formation. In the 147.0-nm photolysis of methylacetylene, Stief, DeCarlo, and Payne<sup>7</sup> postulated the formation of acetylene and ethane through a hydrogen atom reaction mechanism (see Introduction, reactions 1-3). Safrany and Jaster<sup>8</sup> had previously proposed that reaction 2 was a displacement of the methyl group by a hydrogen atom. Recently, in the vacuum-ultraviolet photolysis of cyclobutene,<sup>3</sup> a hydrogen atom sensitized isomerization process was established for the formation of 1,3-butadiene.

$$H + c - C_4 H_6 \longrightarrow (C_4 H_7)'$$
(12)

$$(C_4H_7)' \longrightarrow H + 1,3-C_4H_6 \tag{13}$$

This process was pressure dependent, decreasing rapidly as the total pressure increased from 0.1 to 5.0 Torr. Thus, it was proposed that the adduct  $(C_4H_7)'$ had a lifetime long enough to undergo collisional deactivation.

$$(C_4H_7)' + M \longrightarrow C_4H_7 + M$$
(14)

The resulting  $C_4H_7$  would no longer have sufficient energy to decompose.

The pressure dependency observed in the vacuumultraviolet photolysis of 1-butyne for allene formation shows similar characteristic to that of 1,3-butadiene formation in the photolysis of cyclobutane. This might suggest the following reaction sequence for allene formation in 1-butyne.

$$H + 1-C_4H_6-yne \longrightarrow (C_4H_7)'$$
(15)

$$(C_4H_7)' \longrightarrow CH_3 + C_3H_4$$
 (allene) (16)

$$(C_4H_7)' + M \longrightarrow C_4H_7 + M \qquad (17)$$

When a deuterium-1-butyne-mercury mixture was photolyzed with 253.7 nm (Table V), allene was the only major product observed when nitric oxide was present in the mixture. Mass spectral analysis of the allene product produced nearly 95% C<sub>3</sub>H<sub>3</sub>D. The predominance of C<sub>2</sub>H<sub>6</sub> in the ethane mixture for an unscavanged experiment demonstrates the elimination of the terminal methyl radical from the (C<sub>4</sub>H<sub>6</sub>D)\* molecule.

$$CH_{3}-CH_{2}-C=CH + D \longrightarrow$$

$$(CH_{3}-CH_{2}-\dot{C}=CHD)' \quad (18)$$

$$(CH_{3}-CH_{2}-\dot{C}=CHD)' \longrightarrow$$

$$CH_{3} + CH_{2}=C=CHD \quad (19)$$

The presence of  $C_2H_5D$  in the ethane mixture can be attributed to the formation of ethyl radical by a direct Hg-sensitized mechanism.

It has been noted that the formation of vinylacetylene is accompanied by the elimination of two hydrogen atoms. The addition of a hydrogen atom to 1-butyne is exothermic and will result in the fragmentation of the resulting molecule unless collisionally deactivated. As is seen in Table III, addition of nitrogen or xenon reduces the allene formation to within 5% of the vinylacetylene produced. Further, methyl iodide<sup>16</sup> is known to intercept H atoms with a second-order, room-temperature rate constant of approximately  $10^{13}$  cm<sup>3</sup> mol<sup>-1</sup> sec<sup>-1, 16c</sup>

$$CH_{3}I + H \longrightarrow HI + CH_{3}$$
 (20)

Estimating a rate constant for 1-butyne similar to that of propyne<sup>7</sup> at  $2 \times 10^{11}$  cm<sup>3</sup> mol<sup>-1</sup> sec<sup>-1</sup> suggests that methyl iodide should compete with 1-butyne for the available hydrogen atoms. Table VIII clearly displays a decreasing allene production with increasing methyl iodide pressure, which is consistent with the hydrogen atom reaction channel.

It may be noted here that the ineffectiveness of either NO or O<sub>2</sub> as hydrogen atom interceptors can be attributed to their third-order reaction channel with hydrogen atoms in the pressure range used in this investigation. For example, selecting a photolysis pressure of 10 Torr of 1-butyne and 1 Torr of nitric oxide and a value of the third-order rate constant of 2.26  $\times$  10<sup>16</sup> cm<sup>6</sup> mol<sup>-2</sup> sec<sup>-1 17</sup> for the addition of an H atom to NO,

The Journal of Physical Chemistry, Vol. 76, No. 8, 1972

<sup>(16) (</sup>a) H. M. Chadwell and T. Titani, J. Amer. Chem. Soc., 55, 1363 (1933); (b) E. Cremer, J. Curry, and M. Z. Polanyi, Z. Phys. Chem., Abt. B, 23, 445 (1933); (c) R. A. Holroyd, J. Amer. Chem. Soc., 91, 2208 (1969).

 <sup>(17) (</sup>a) M. Clyne and B. Thrush, Discuss. Faraday Soc., No. 33, 139 (1962);
 (b) Trans. Faraday Soc., 57, 1305 (1961).

the addition of hydrogen atoms to 1-butyne would be approximately 200 times faster than the addition to nitric oxide. Calculations in the case of oxygen give similar results.

A second free-radical interceptor was also used in this study. Ausloos and Lias<sup>14</sup> investigated the use of H<sub>2</sub>S as a radical interceptor in radiation chemistry. When 10% or more H<sub>2</sub>S is added to a normal hydrocarbon and the system photolyzed, the majority of the H, CH<sub>3</sub>, C<sub>2</sub>H<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, and other radicals abstract an H atom from H<sub>2</sub>S to form H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, respectively. In the cases where it has been applied in unsaturated hydrocarbons,<sup>1-3</sup> its use must be restricted to a diagnostic tool only, owing to unfavorable kinetic competition with the unsaturated molecule.

It can be seen in comparing the results given in Table VI to Tables I and II, that the yield of methane was greatly increased by the presence of  $H_2S$ , while allene appeared only slightly affected. These experiments establish the formation of methyl radicals within the system. On the other hand, the insensitive nature of the allene formation might not be anticipated. The reaction of hydrogen atoms with hydrogen sulfide (k = $4.2 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$  is approximately two times faster than the addition of hydrogen atoms to an equimolar concentration of 1-butyne. Since H<sub>2</sub>S pressures are normally of the order of from 10 to 20% of the butyne pressure, only a small decrease in allene would be predicted with the addition of hydrogen sulfide. Kebarle<sup>4</sup> has reported the formation of  $C_3H_3$  (propargyl) radicals in the mercury-photosensitized decomposition of 1-butyne, which if present in this system, might also be expected to react with hydrogen sulfide to produce allene. This indeed seems to be the case.

It may be seen in Table VI that the overall allene yields appears nearly independent of  $D_2S$  pressure. On the other hand, the yield of allene- $h_4$  (that which originates from the H atom-1-butyne reaction) decreased with increasing  $D_2S$  pressure. The formation of  $C_3H_3D$  is best explained as an abstraction reaction by  $C_3H_3$  radicals (see section on Radical Formation).

The direct formation of allene through a primary photochemical process can be excluded from consideration based on the high-pressure allene yield shown in Table III. These data would place an upper limit of approximately 0.02 for the quantum yield of allene formation from a primary reaction channel.

$$1-C_4H_6-yne + h\nu \longrightarrow CH_2 + C_3H_4 \qquad (21)$$

Acetylene and Ethylene. The 147.0-nm photolysis of the 1-butyne-nitric oxide system results in a  $C_2H_2/C_2H_4$ ratio of nearly 1.3. This ratio is independent of pressure or the addition of "inert" additives, but does increase to a higher value with 123.6-nm photons. The predominant reaction channel for the formation of ethylene and acetylene in the  $C_4H_6$  isomers thus far studied<sup>1-3</sup> has been attributed to a direct split of the excited molecule into ethylene and acetylene. It is interesting to note that such a process in the case of cyclobutane<sup>19</sup> and methylcyclopropane<sup>20</sup> results in the secondary decomposition of a  $C_2H_4$  fragment, and a distinctive pressure dependency is observed

$$c-C_4H_8 + h\nu \longrightarrow C_2H_4 + (C_2H_4)'$$
(22)

$$(C_2H_4)' \longrightarrow C_2H_2 + H_2$$
(23)

$$(C_2H_4)' + M \longrightarrow C_2H_4$$
(24)

where  $(C_2H_4)'$  is a molecule with excess internal energy. On the other hand, cyclobutene,<sup>3</sup> 1,3-butadiene,<sup>1</sup> and 1,2-butadiene<sup>2</sup> do not show a pressure effect on the  $C_2H_2/C_2H_4$  ratio that would be predicted by the cyclobutane mechanism. It appears that only a fraction of the ethylene formed in dissociation of the excited 1butyne has sufficient energy to eliminate a hydrogen molecule. The lifetime of this species must be shorter than the collision interval at the pressures used in this study.

$$1-C_4H_6-yne + h\nu \longrightarrow C_2H_2 + C_2H_4$$
(25)

$$\longrightarrow$$
 C<sub>2</sub>H<sub>2</sub> + C<sub>2</sub>H<sub>2</sub> + H<sub>2</sub> (26)

In comparing hydrogen and acetylene yields at the two vacuum-uv wavelengths, it can be concluded that the ratio of reaction 25 to reaction 25 increases with increasing photon energy. This would indeed be as expected.

A secondary source of acetylene may be attributed to a process similar to that for the formation of vinylacetylene.

$$(C_4H_5)' \longrightarrow C_2H_2 + C_2H_3 \tag{27}$$

Ethylene may also be produced by a process similar to the production of vinylacetylene.

$$(C_4H_5)' \longrightarrow C_2H + C_2H_4 \tag{28}$$

Since the ethynyl radical is not scavenged by nitric  $oxide^{2^{1}}$  but may abstract a hydrogen atom from an olefin,<sup>22</sup> additional acetylene may also arise from this reaction.

Hydrogen Formation. The hydrogen reported in the 147.0- and 123.6-nm photolyses of 1-butyne (Tables I and II) is produced through both the direct elimination of molecular hydrogen and a hydrogen atom abstraction mechanism.

One estimate based on the hydrogen yields  $(H_2)$  in the 123.6-nm photolysis in the presence of  $D_2S$ , Tables VI and VII, would indicate that the maximum molecular

(20) R. D. Doepker, J. Phys. Chem., 73, 3219 (1969).

<sup>(18)</sup> M. J. Kurylo, N. C. Peterson, and W. Braun, J. Chem. Phys., 54, 943 (1971).

<sup>(19) (</sup>a) R. D. Doepker and P. Ausloos, *ibid.*, **43**, 3814 (1965); (b) K. Obi, H. Akimoto, Y. Ogata, and I. Tanaka, *ibid.*, **55**, 3822 (1971).

<sup>(21)</sup> A. G. Sherwood and H. E. Gunning, ibid., 69, 1732 (1965).

<sup>(22)</sup> A. M. Tarr, O. P. Strausz, and H. E. Gunning, Trans. Faraday Soc., 62, 1221 (1966).

hydrogen yield is 25% of the vinylacetylene yield. Predominantly, this molecular hydrogen arises during the elimination of 2 mol of acetylene (reaction 26), or with the simultaneous formation of an ethynyl and a vinyl radical (reaction 11).

Radical Formation. The use of hydrogen sulfide as a diagnostic test for the presence of free radicals<sup>14</sup> has been successful in the earlier studies of the  $C_4H_6$  isomers.<sup>1-3</sup> Owing to the unavailability of 1-butyne- $d_6$ , it was necessary to photolyze 1-butyne in the presence of D<sub>2</sub>S. This system has many drawbacks related to the competitive kinetics involved. The use of H<sub>2</sub>S faces the same problems but not to the same degree.

Upon examination of Tables VI and VII in comparison to Tables I and II, it becomes apparent that a considerable yield of hydrogen atoms is produced in the photolysis of 1-butyne. The high HD yield, through a kinetically unfavorable reaction channel, points to a large steady state concentration of H-atoms.

The large increased yield of methane in the presence of  $H_2S$  and the presence of  $CH_3D$  methane in the  $D_2S$ experiments demonstrates a prominent concentration of methyl radicals in the photolysis system. The ethane yield seen in Table VI as well as small increases in acetylene and ethylene lead to the conclusion that ethyl, ethynyl, and vinyl radicals all play a role in the vacuum-ultraviolet photolysis of 1-butyne. Unfortunately, mass spectral analysis (when  $D_2S$  was used) of the  $C_2$  fraction failed to produce spectra that could be satisfactorily separated into the major components.

Table VII reveals the formation of  $C_3H_3D$ , which may well be formed through the abstraction of a D atom by a  $C_3H_3$  radical. In order to verify the presence of this radical, a 1:1 mixture of  $CD_3I + 1$ -butyne was photolyzed at both 147.0 and 123.6 nm. Upon analysis of the small 1,2-butadiene product with the mass spectrometer, the presence of  $CD_3CH=C=CH_2$ was clearly seen. This appeared to be the major part of the 1,2-butadiene formed in this system. Kebarle<sup>4</sup> demonstrated this methyl-propargyl reaction in his Hg-sensitized study. It must be emphasized here that the combination of a methyl radical with a propagyl radical leads to a 3:1 mixture of 1-butyne and 1,2butadiene. No analysis of the 1-butyne mixture was attempted.

Summary of Primary Processes. Based on the above discussion, values presented in the tables of data, and on the results of previously published and presently unpublished work on the  $C_4H_6$  isomers, estimates of the important primary processes can be attempted.

The formation of vinylacetylene through the elimination of two hydrogen atoms accounts for nearly all of the vinylacetylene observed.

$$1-C_4H_6-yne + h\nu \longrightarrow (C_4H_6)^*$$
 (4)

$$(C_4H_6)^* \longrightarrow 2H + C_4H_4 \tag{6a}$$

The Journal of Physical Chemistry, Vol. 76, No. 8, 1972

The quantum yield for this process is approximately 0.34 and shows at most only a slight increase with increasing photon energy.

A primary process leading to the formation of allene can be considered negligible, with an upper limit of a 0.02 quantum yield

$$(C_4H_6)^* \longrightarrow CH_2 + C_3H_4 \qquad (21a)$$

The formation of ethylene must be attributed to two major reaction channels.

$$(C_4H_6)^* \longrightarrow C_2H_2 + C_2H_4 \qquad (25a)$$

$$\longrightarrow$$
 H + C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H (28a)

If one considers that the total quantum yield for hydrogen atoms must exceed 0.8 (based on the low-pressure yield of  $C_3H_4$ ), reaction 28a would seem to be the most logical source of ethylene ( $\Phi = 0.10$ ).

Acetylene also required two reaction channels, one being reaction 25 and the other leading to the formation of molecular hydrogen.

$$(C_4H_6)^* \longrightarrow H_2 + 2C_2H_2 \qquad (9a)$$

Considering the estimated quantum yield of process 25 being apparently low, reaction channel 9a would be responsible for nearly all of the 0.13 quantum yield of acetylene. This process would indeed be expected to become increasingly important as photon energies increase. An increase in acetylene quantum yield is reflected in the data presented in Tables I and II.

Unfortunately, hydrogen yields cannot be completely separated into hydrogen atom or molecular hydrogen reaction channels with the data on hand. If, however, one considers the measured hydrogen to originate predominantly through a molecular hydrogen elimination process, then the addition of reaction 11a seems in order. The maximum quantum yield for this process would seem to approach a value of 0.20-0.25.

$$(C_4H_6)^* \longrightarrow H_2 + C_2H + C_2H_3 \qquad (11a)$$

Unaccounted for in the above summary is the presence of the ethyl and propargyl. The direct split of the excited  $(C_4H_6)^*$  molecule into ethynyl and ethyl radicals can be estimated at a quantum yield of 0.19 as a lower limit. This assumes that the yield of ethane in the H<sub>2</sub>S studies reflects a lower limit for the formation of ethyl radicals. Finally, the direct split into a methyl radical and a propargyl radical can only be approximated at 0.10 based on the total 1,2-butadiene yield.

Acknowledgment. The authors wish to thank Dr. G. J. Mains for many helpful suggestions and Dr. L. J. Stief for both some timely conversation and a preprint

of his work with propyne. Furthermore, the authors wish to acknowledge the National Science Foundation which supported this investigation under Grants No. NSF-GP-11265 and NSF-GP-20878, of which the latter made the purchase of the CEC-21-103 C mass spectrometer possible.

# **Pulse Radiolysis Study of Dimer Cation Formation of Aromatic**

# Hydrocarbons in Benzonitrile Solution

# by Akira Kira, Shigeyoshi Arai,\* and Masashi Imamura

The Institute of Physical and Chemical Research, Wako, Saitama 351, Japan (Received November 8, 1971) Publication costs assisted by the Institute of Physical and Chemical Research

Pulse radiolysis studies were made on several aromatic hydrocarbons in oxygenated benzonitrile solutions which were previously found to be appropriate for preparing solute cations. Absorption bands due to monomer cations were reduced with increase of the solute concentration, while corresponding increases in the intensity of the dimer cation bands were observed. Equilibrium constants for the dimer cation formation,  $M^+ + M \rightleftharpoons M_2^+$ , were evaluated to be  $5.2 \times 10^2$ ,  $1.7 \times 10^2$ ,  $5.2 \times 10$ , and  $2.9 \times 10 M^{-1}$  for naphthalene, perylene, 1,2-benzanthracene, and 9,10-dimethylanthracene, respectively, at  $17^\circ$  except for 1,2-benzanthracene at  $20^\circ$ . The tendency for stabilization was found to differ between the dimer cation formation and the excimer formation.

# Introduction

Dimer cations of organic compounds have been recently studied using  $\gamma$ -irradiated rigid matrices<sup>1-3</sup> and pulse radiolysis<sup>4-6</sup> as well as the esr method.<sup>7.8</sup> The extensive work by Badger and Brocklehurst<sup>1-3</sup> has accumulated optical spectral data of interest. However, the thermodynamic and kinetic data have not been reported except only for the cases of perylene<sup>7</sup> and pyrene.<sup>4-6</sup>

In the present study, the formation of dimer cations of several aromatic compounds in oxygenated benzonitrile solutions was demonstrated, and equilibrium constants were evaluated by means of pulse radiolysis.

#### **Experimental Section**

Chemicals. Naphthalene and anthracene were Tokyo Kasei's zone-refined reagents, and perylene was J. Hinton's zone-refined reagent. 1,2-Benzanthracene was chromatographically purified from Tokyo Kasei's reagent, meticulous care being taken to separate a compound with blue fluorescence that seemed to give an additional transient absorption on the pulse irradiation. 9,10-Dimethylanthracene (K & K) was also chromatographed. Biphenyl recrystallized three times from ethanol solutions was used as a second solute as will be explained later, and Tokyo Kasei's zone-refined biphenyl for the experiment on a biphenyl dimer cation. Benzonitrile was fractionally distilled under a reduced pressure.

Apparatus. The pulse radiolysis apparatus has been described elsewhere.<sup>9</sup> In the present experiments the wavelength region of the observation was expanded up to 1000 nm by using a Hamamatsu-TV's photomultiplier R-196 and a Nippon-Jarrell-Ash's monochromator Model 82-400. The energy of the electron pulses was 2.5 MeV, and the duration was  $0.8-2.1 \mu$ sec. The beam current was adjusted to give an appropriate intensity of the transient absorption.

#### Results

Experimental procedures were essentially the same as described in the previous paper.<sup>4</sup> Spectra and thermo-

(1) B. Badger, B. Brocklehurst, and R. D. Russell, Chem. Phys. Lett., 1, 122 (1967).

(2) B. Badger and B. Brocklehurst: (a) Trans. Faraday Soc., 65, 2576 (1969); (b) ibid., 65, 2578 (1969); (c) ibid., 65, 2588 (1969).

- (3) B. Badger and B. Brocklehurst, *ibid.*, 66, 2939 (1970).
- (4) A. Kira, S. Arai, and M. Imamura, J. Chem. Phys., 54, 4890 (1971).
- (5) M. A. J. Rodgers, Chem. Phys. Lett., 9, 107 (1971).
- (6) S. Arai, A. Kira, and M. Imamura, to be published.
- (7) T. C. Chiang and A. H. Reddoch, J. Chem. Phys., 52, 1371 (1970).
- (8) I. C. Lewis and L. S. Singer, ibid., 43, 2712 (1965).
- (9) A. Kira, S. Arai, and M. Imamura, Sci. Rep. Inst. Phys. Chem. Res., 47, 139 (1971).

dynamic and kinetic data were all observed for oxygenated benzonitrile solutions of hydrocarbons containing biphenyl as a second solute at the concentration (0.3 M) much higher than the solutes examined. Oxygenated benzonitrile solutions yield the absorption only due to solute cations on pulse irradiation, other major products such as triplet states and/or anions being completely removed by oxygen. When the concentration of the solute is relatively low, the yield of the solute cation decreases. However, addition of excess biphenyl was found to keep the total concentration of the solute cations constant and independent of the solute concentration. This fact may imply that a solvent cation is rapidly replaced by a biphenyl cation, which recombines with a negative species at a slower rate than a solvent cation does, while all biphenyl cations formed transfer their charges to solute molecules at solute concentrations used. Biphenvl had no effect on the observed absorption spectra.

Reactions 1 to 4 are considered to be complete during the pulse under the present conditions since neither a rapid decay nor a corresponding growth of an absorption was observed in the entire spectral regions of all solutions

$$S \rightarrow S^+$$
,  $e^-$ , other products (1)

$$S^+ + B \longrightarrow S^+ + B^+ \tag{2}$$

$$B^+ + M \longrightarrow B + M^+ \tag{3}$$

$$M^+ + M \rightleftharpoons M_2^+$$
 (4)

where S is a benzonitrile molecule, B is a biphenyl molecule, and M is a solute molecule. If the sum of the concentrations of both the monomer and dimer cations remains unchanged, the optical density, at various concentrations can be expressed by

$$(D - D_{\rm d}^{\circ})^{-1} = (1 + K[{\rm M}]) \{ (\epsilon_{\rm m} - \epsilon_{\rm d}) l C_0 \}^{-1} \quad (5)$$

where D is the optical density at the end of pulse,  $D_d^{\circ}$  is the optical density in the extreme case when all cations exist as the dimer cation,  $\epsilon_m$  and  $\epsilon_d$  are the extinction coefficients for the monomer and dimer cations, respectively, l is the optical path length,  $C_0$  is the sum of the concentrations of both cations, K is the equilibrium constant ( $K = [M_2^+]/[M^+][M]$ ). A plot of the lefthand side of eq 5 vs. [M] gives a straight line as shown in Figure 4 for 1,2-benzanthracene cations. Then the ratio of the slope to the intercept gives the equilibrium constant. Values of  $D_d^{\circ}$  could be determined directly if higher concentrations are available. In the cases of hydrocarbons with poor solubility the values were estimated by the extrapolation of a plot of D vs. 1/[M] to the ordinate.

It is necessary to examine whether the change in the transient spectra with the solute concentration is caused by the dimer cation formation or by other reactions with impurities, because there is a possibility that impurities with lower ionization potential scavenge the monomer cation and produce a new absorption. Dimer cation formation was deduced from careful observation on decay behavior of both the monomer and dimer cations. In general there should not be a large difference in the recombination rates of monomer and dimer cations as these rates are diffusion controlled. For example, the second-order decay constant of the pyrene dimer cation was found to be three-fourths of that of the pyrene monomer cation.<sup>4</sup> Therefore, provided the dimer cation is formed, the increase in the solute concentration will not accelerate the decay rate appreciably. In addition, the ratio of the intensity of the monomer band to that of the dimer band should remain constant over their decay periods if an equilibrium exists between them. On the other hand, undesirable impurities, if any, must enhance the decay of the monomer cation as the solute concentration is increased. When the dimer and monomer cations disappear by reactions 6 and 7

$$M^+ + Y^- \longrightarrow M + Y \tag{6}$$

$$M_2^+ + Y^- \longrightarrow 2M + Y \tag{7}$$

one can obtain the following equation

$$-\mathrm{d}D/\mathrm{d}t = \left\{ (k_{\rm m} + k_{\rm d}K[\mathrm{M}]) / l(\epsilon_{\rm m} + \epsilon_{\rm d}K[\mathrm{M}]) \right\} D^2 = kD^2 \quad (8)$$

where  $Y^-$  is a negatively charged species ( $[Y^-] = [M_2^+] + [M^+]$ ), and  $k_m$  and  $k_d$  are the rate constants of reactions 6 and 7, respectively. k is an apparent rate constant and its value is directly determined from a decay curve. Equation 8 can be rewritten as

$$k \{1 + (\epsilon_{d}/\epsilon_{m})K[M]\} = (k_{m}/l\epsilon_{m})\{1 + (k_{d}/k_{m})K[M]\}$$
(9)

The ratio,  $k_d/k_m$ , is evaluated by plotting values of the left-hand side against K[M].

Naphthalene. The transient spectra at the end of the pulse are shown in Figure 1. As the concentration increases, the absorption band at 710 nm declines, and the absorption band at 580 nm grows with an isosbestic point at 610 nm. The former is ascribed to the monomer cation<sup>10</sup> and the latter to the dimer cation. This conclusion is consistent with Badger and Brocklehursts' assignment<sup>1</sup> of the band at 571 nm to the dimer cation. Equation 5 was found to hold satisfactorily, and the equilibrium constant obtained is presented in Table I. The plot based on eq 9 is shown in Figure 2.

1,2-Benzanthracene. The spectra obtained are shown in Figure 3. The decay rate was seen to retard gradually by repetition of pulse irradiation. The spectra were mapped point by point from long to short wavelength by the photometric method, and the absorption at 880 nm was again recorded after the measurement at the shortest wavelength, 700 nm. The decay was

(10) T. Shida and W. H. Hamill, J. Chem. Phys., 44, 2375 (1966).


Figure 1. Transient spectra of naphthalene in oxygenated benzonitrile solutions containing 0.3 M biphenyl. Naphthalene concentrations: •, 2.2 mM;  $\bigcirc$ , 5.4 mM;  $\triangle$ , 11 mM; •, 22 mM;  $\Box$ , 54 mM. Pulse: 1.8  $\mu$ sec, 160 mA.



Figure 2. An example of the plot giving  $k_d/k_m$  according to eq 9 for the absorption at 710 nm of naphthalene cations.

Table I:	Equilibrium	Constants	and	Rate Parameters
----------	-------------	-----------	-----	-----------------

Compound	K, M <sup>-1</sup>	Temp, °C	$k_{\rm d}/k_{\rm m}^a$
Naphthalene	$(5.2 \pm 1.5)  imes 10^2$	17	0.5
1,2-Benzanthra- cene	$(5.2 \pm 1.5) \times 10$	20	···
Perylene	$(1.7 \pm 0.5) \times 10^2$	17	1.4
9,10-Dimethyl- anthracene	$(2.9\pm0.9)\times10$	17	1.0
Anthracene	$\sim 30$	16	
trans-Stilbene	$\sim 10$	25	
Pyrene <sup>b</sup>	$(2.7 \pm 0.2)  imes 10^2$	20	0.75
<sup>a</sup> See text. <sup>b</sup> Referen	nce 4.		

apparently slower than measured before, but the optical density at the end of the pulse was identical as shown



Figure 3. Transient spectra of 1,2-benzanthracene in oxygenated benzonitrile solutions containing 0.3 M biphenyl. 1,2-Benzanthracene concentrations: •,  $4.2 \text{ m}M; \Box$ ,  $20 \text{ m}M; \Delta$ , 42 mM; O, 100 mM. Pulse: 0.8  $\mu$ sec, 160 mA. Double symbols at 880 nm are points taken after a series of measurements from 920 to 700 nm (see text).

in Figure 3. The retardation was not recovered by reoxygenation. The higher the solute concentration was, the more remarkably the retardation was observed to be. However, its mechanism is not understood at the moment. When an insufficiently purified sample was used, the absorption band at 880 nm decayed rapidly and a long-lived absorption with a peak at 740 nm appeared. This result is obviously different from that observed for the dimer formation.

The absorption with a peak at 880 nm and with a shoulder at 800 nm appearing preferentially at low concentrations accords with the absorption due to the monomer cation of 1,2-benzanthracene observed in rigid matrices.<sup>11</sup> The spectrum for the solution of 100 mM 1,2-benzanthracene may be regarded as close to that of the dimer cation. A spectral survey from 450 to 700 nm revealed that no remarkable absorption peak due to the dimer cation exists in this wavelength region. Both the monomer and dimer cations seemed to have intense absorption in the vicinity of 400 nm. However, precise measurement was not achieved because of the absorption of the solute. The absorption intensity of the monomer band near 510 nm decreased with increasing solute concentration, while the intensity of the

#### (11) T. Shida, private communication.



Figure 4. An example of the plot to evaluate K based on eq 5 for the absorption at 880 nm of 1,2-benzanthracene cations.

absorption in the region of 550 nm apparently increased. The plot based on eq 5 is shown in Figure 4.

Perylene. Perylene could be investigated only up to 10 mM because of its limited solubility. Spectral change is shown in Figure 5. The intense band of the perylene monomer cation at 450 nm<sup>12</sup> was reduced, and the absorption in the region of 600 to 700 nm was raised a little with increasing solute concentration. Another set of data revealed that a weak band with a peak at 740 nm is more pronounced at low concentrations than at high concentrations. This fact indicates that the band is not the charge-resonance band, contrary to the earlier suggestion.<sup>3</sup>

Decay curves fit the second-order rate law and eq 9 is satisfied.

Anthracene and 9,10-Dimethylanthracene. The absorption of the anthracene monomer cation which has a peak at 740 nm<sup>10</sup> was found to decrease at high concentrations as shown in Figure 6, curve A, and the corresponding increase of the absorption was observed in a region of 500 to 670 nm. However, the decrease in optical density at 740 nm was relatively small even for the nearly saturated solution of about 50 mM. 9,10-Dimethylanthracene has a higher solubility and therefore spectral change with concentration is more distinct than anthracene as shown in Figure 6, curve B. An absorption band with a peak at 680 nm, which can be ascribed to the monomer cation, turned to a broader one with a peak at a shorter wavelength as the concentration was increased. This change may be regarded as due to the formation of the dimer cation, though an isosbestic point is not clearly recognized. The decay behavior of the cations supports this conclusion.

Other Compounds. Biphenyl and trans-stilbene were also examined briefly. The optical density of the monomer cation band of trans-stilbene at 480 nm<sup>12</sup> decreased



Figure 5. Transient spectra of perylene in oxygenated benzonitrile solutions containing 0.3 M biphenyl. Perylene concentrations: •, 1.0 mM;  $\Box$ , 5.0 mM;  $\bigcirc$ , 10.3 mM. Pulse: 0.8  $\mu$ sec, 120 mA.

from 0.45 to 0.38 as the concentration was increased from 7.8 to 78 mM. The decay of the monomer cation fits the first-order rate law, being different from other hydrocarbon cations. Rate constants were found to be  $2.2 \times 10^5$  and  $2.1 \times 10^5 \text{ sec}^{-1}$  for 7.8 and 78 mM solutions, respectively. Almost identical values of the decay rate for these two solutions exclude the possibility that the first-order decay results from any impurity in *trans*-stilbene, although the mechanism of the decay is not explained readily. The decrease of the monomer cation absorption is very likely caused by the dimer cation formation.

In the case of biphenyl the concentration of the cations could not be kept constant independently of the solute concentration because of the lack of a suitable second solute. Therefore, spectra were simply compared between 6 mM and 0.3 M solutions. Both spectra after appropriate normalization coincided well with each other within experimental errors. This may suggest that the biphenyl dimer cation is hardly produced at a room temperature.

## Discussion

The present results suggest that dimer cation formation is probably a general property of cations of catacondensed aromatic hydrocarbons in fluid solutions. Other conjugated molecules of which dimer cations

(12) T. Shida and W. H. Hamill, J. Chem. Phys., 44, 4372 (1966).



Figure 6. Transient spectra of anthracene (A) and 9,10-dimethylanthracene (B) in oxygenated benzonitrile solutions containing 0.3 M biphenyl. (A)  $\bullet$ , 4.3 mM;  $\bigcirc$ , 43 mM; (B)  $\bullet$ , 4.1 mM;  $\Box$ , 13.5 mM;  $\triangle$ , 27.0 mM;  $\bigcirc$ , 91 mM. Pulse: (A) 2.1  $\mu$ sec, 80 mA; (B) 2.1  $\mu$ sec, 120 mA.

have been observed in rigid matrices<sup>1-3</sup> may be regarded as having a possibility for dimer formation at room temperature. The occurrence of the dimerization of cations might, thus, be taken into consideration in the interpretation of radiation chemical phenomena in irradiated organic substances.

Equilibrium constants and rate parameters obtained are listed in Table I. Values of  $-\Delta G$  calculated from K are listed along with  $-\Delta G$  and  $-\Delta H$  of the excimer formation in Table II. Since values of  $-\Delta G$  for the excimers of naphthalene and 9,10-dimethylanthracene have not been reported, the former was tentatively estimated to be close to those of its methyl derivatives.<sup>13</sup> The latter is expected to be very small, if  $-\Delta S$  is as large as those of other compounds. The values of  $-\Delta G$ for dimer cations spread from the largest for naphthalene to the smallest for 9,10-dimethylanthracene. On the contrary,  $-\Delta G$  values of the excimer formation are classified into two groups, the extraordinary large value for pyrene and the smaller values for others.

Badger and Brocklehurst<sup>14,15</sup> have calculated the equilibrium constant of the dimer cation, regarding  $-\Delta H$  as a half of the energy of the charge resonance band and assuming  $-\Delta S$  as the same as that of the excimer formation. Their predicted values are different from our present results for which errors are less than a factor of 10. The heats of formation of dimer cations evaluated experimentally for perylene in dichloromethane<sup>7</sup> and pyrene in benzonitrile<sup>6</sup> are smaller than those estimated under the assumption that  $-\Delta H$  is half of the energy of the charge resonance band. However,

Table II :	Comparison of $-\Delta G$ (kcal/mol) and $-\Delta H$
(kcal/mol)	between Dimer Cations and Excimers

Compound	$- \text{Dimer} \\ - \Delta G^a$	$\begin{array}{c} \text{cation} - \\ -\Delta H \end{array}$	$\frac{-\Delta G}{\Delta G}$	mer <sup>a</sup> - ΔΗ
Naphthalene	3.6		(0.4)	5.8
Pyrene	3.3	7.10	4.1	9.4
Perylene	3.0	8.60	e	е
1,2-Benzanthracene	2.3		0.9	6.0
9,10-Dimethyl-	1.9		(<1)	4.4
anthracene				

<sup>a</sup> Values at the temperatures listed in Table I. <sup>b</sup> Reference 6. <sup>c</sup> Reference 7. <sup>d</sup> Reference 13. The values in parentheses are estimated. See text. <sup>e</sup> Though the excimer fluorescence was reported, thermodynamic data have not been determined.

their values are based on the data obtained in nonpolar hydrocarbon matrices. The equilibrium constant probably depends on polarity of the solvent; that is, a solvent with a lower dielectric constant may favor a larger value of the equilibrium constant. The effect of the solvent on the dimer cation formation is now under investigation. Further, our spectral data indicate that Badger and Brocklehursts' assignment<sup>3</sup> of the band at 750 nm as the charge resonance of the pervlene dimer cation may be erroneous. If the difference of solvent between dichloromethane and benzonitrile is neglected,  $-\Delta S$  of the perylene dimer cation formation is calculated to be 19  $\pm$  4 cal/mol-deg from  $-\Delta H$  in Chiang and Reddochs' work and  $-\Delta G$  in this work. Although thermodynamic parameters have not been reported for the pervlene excimer, most of the reported values of  $-\Delta S$  for the excimer formation of aromatic hydrocarbons are in the vicinity of 20 cal/mol-deg.<sup>13</sup>

Precise discussion of the electronic spectra of dimer cations is best made on the basis of data obtained with the rigid matrix method, which provides spectra over a wider wavelength region and with higher accuracy in intensity. However, we should like to point out that two kinds of changes in the spectral shape were observed. One is that an intense band of the monomer cation is replaced by a new dimer cation band at a shorter wavelength as is observed for naphthalene. Pyrene is similarly classified. The steep rise below 430 nm in the spectral shape of the pyrene dimer cation may imply the existence of an intense band concealed by the absorption of pyrene. The other type of change, as seen in anthracene and 1,2-benzanthracene, is a minor shift of the monomer cation band to a shorter wavelength with a reduction of intensity.

(15) B. Badger and B. Brocklehurst, Nature, 219, 263 (1968).

<sup>(13)</sup> J. B. Birks, (a) Progr. Reaction Kinet., 5, 181 (1970); (b) "Photophysics of Aromatic Molecules," Wiley-Interscience, London, 1970, p 354.

<sup>(14)</sup> The value of the equilibrium constant of naphthalene excimer is wrongly cited in ref 15 because of the confusing symbol in the original paper.

As a method of studying dimer cations, pulse radiolysis has the following merits: the dimeric nature is proved and the equilibrium constant is evaluated; an isosbestic point can be confirmed. However, the effect of an impurity and restriction of solubility become a serious problem for measurements at high concentrations. This method is practically useful for compounds for which the equilibrium constant for the dimer cation formation is higher than about ten. If the temperature is lower, the equilibrium constant must increase, and therefore observation becomes easier.  $\Delta H$  and  $\Delta S$ can be determined from values of equilibrium constants at different temperatures. Such studies are now in progress.

Acknowledgment. We wish to thank Dr. T. Shida for showing us his unpublished spectral data of aromatic hydrocarbon ions.

## **Reactions of Energetic Positronium Atoms in Solutions**<sup>1</sup>

## by Lawrence J. Bartal, J. Blair Nicholas, and Hans J. Ache\*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061 (Received July 9, 1971)

Publication costs borne completely by The Journal of Physical Chemistry

The lifetime spectra of positrons in solutions of Sn(IV), Sn(II), Pb(II), Cd(II), Zn(II), Tl(I), and Na salts were studied as a function of solute concentration. No significant changes in the two lifetimes,  $\tau_1$ , and  $\tau_2$ , observed in these spectra, could be noticed over a wide range of solute concentrations. The corresponding intensities  $I_2$  dropped sharply with solute concentration, eventually levelling off and becoming constant at higher solute concentrations. These saturation values of  $I_2$  are characteristic for each compound and decrease in the order Na > Tl > Zn > Cd > Sn(II) > Pb(II). The data are discussed in terms of a proposed oxidation of "hot" positronium atoms by the solute.

## Introduction

The study of the mechanisms involved in the reactions of hydrogen atoms is undoubtedly of the greatest importance for the understanding of various parameters which determine the progress of chemical reactions in general. One area which has been recently the subject of much experimental and theoretical interest is the mechanism of the reduction processes involving electron transfer in aqueous solutions.

In most of these investigations, hydrogen atoms have been produced mainly by two techniques: (a) in the gas phase by a high-frequency discharge and subsequent introduction of the hydrogen atoms into the aqueous solution<sup>2</sup> and (b) by irradiation of the aqueous solution with ionizing radiations.<sup>3</sup> This work has led to the determination of the rate constants for the reduction of several ions by hydrogen atoms in aqueous solution, and by comparison of these reaction rates and the rates of other known analogous reactions, probable mechanisms were proposed.<sup>4</sup> The above techniques for the production of hydrogen atoms, however, allowed the hydrogen atoms to become thermalized before they could react. Consequently, these methods did not permit the study of a very important parameter in these reduction reactions, the effect of the kinetic energy of the reactant on the progress of the reaction.

A technique which has been widely employed to produce energetic hydrogen atoms is the generation of "hot" tritium recoil atoms via nuclear reactions. It has been put to use extensively for the investigation of "hot" tritium reactions in a great variety of substrates and phases.<sup>5</sup> This method, which relies on radiation detection for the identification of the products into which the radioactive tritium has been incorporated, cannot be applied to the study of energetic hydrogen atoms with inorganic solutes in aqueous solutions, where the tritium cannot be expected to form a stable reaction product with the solute species. Con-

- (1) Work supported by the U.S. Atomic Energy Commission.
- (2) G. Czapski and G. Stein, J. Phys. Chem., 63, 850 (1959).
- (3) See, e.g., M. Anbar and D. Meyerstein, Nature (London), 206, 818 (1965).

<sup>(4)</sup> For reviews, see (a) H. Taube, Advan. Inorg. Chem. Radiochem.,
1, 1 (1959); (b) J. Halpern, Quart. Rev., Chem. Soc., 15, 207 (1961);
(c) N. Sutin, Annu. Rev. Nucl. Sci., 12, 285 (1962). For compilation of rate constants for the reactions of hydrogen atoms with inorganic and organic compounds in aqueous solution, see M. Anbar and P. Neta, Int. J. Appl. Radiat. Isotopes, 18, 493 (1967).

<sup>(5)</sup> A. P. Wolf, Advan. Phys. Org. Chem., 2, 201 (1964).

sequently, we have searched for a method which would allow us to study the reactions of hydrogen-like species while they still possess kinetic energies in order to elucidate the role of kinetic energy in hydrogen-like atom reactions in solutions.

On the basis of the results presented in this paper, we feel that the reactions of the positronium atom (Ps), which is the bound state of a positron and electron  $(e^+e^-)$ , can provide us with the desired information.

Ps can be formed in two ground states, singlet or para Ps, with antiparallel orientation of the spins of the positron and electron, which has an average intrinsic (annihilation) lifetime of  $1.25 \times 10^{-10}$  sec, and triplet or ortho Ps (parallel spin orientation) which exhibits an average intrinsic lifetime of  $1.4 \times 10^{-7}$  sec. These lifetimes are extremely short so that the chemistry of the Ps cannot be observed in the usual way by product analysis. But unlike other radioactive tracers, the lifetimes of the Ps species in matter and their mass annihilation mechanisms depend on the chemical environment and serve to characterize them. Thus, by applying nuclear physical methods it is possible to study the reactions of the Ps atoms.<sup>6</sup> Since the Ps atoms, when formed, may have, in accordance with the Ore model, kinetic energies ranging from 6.8 eV down to thermal energies, it seems quite possible that a fraction of the Ps atoms might well undergo chemical interactions while still possessing appreciable amounts of kinetic energy.

Experimental evidence that Ps reacts chemically in solutions at energies above thermal is quite rare and practically limited to the results obtained by Tao and Green<sup>7</sup> in aqueous oxy acids. Oxidation reactions involving thermal Ps atoms have been postulated in several systems,<sup>8-13</sup> but very little evidence for oxidation at high energies has been presented thus far.<sup>13,14</sup> In the following study we have systematically investigated "hot" Ps reactions which lead presumably to an oxidation of Ps by single electron transfer.

## **Experimental Section**

Purity and Source of Reagents. Samples of purified grade  $Pb(NO_3)_2$  and reagent grade  $ZnCl_2$  were obtained from Baker and Adamson Co. Reagent grade  $CdCl_2$ , crystalline  $SnCl_2$ , and purified grade  $NaClO_4$  were purchased from Fisher Scientific Company. Research grade  $Pb(ClO_4)_2 \cdot 3H_2O$  and  $TlClO_4$  were from K and K Laboratory, and anhydrous reagent grade  $SnCl_2$  was obtained from Matheson Coleman and Bell. Samples of all reagents were used without further purification for both the concentration and temperature studies.

Preparation of Samples. Specially designed sample vials for the concentration studies (cylindrical glass tubes 100 mm long and 10 mm i.d.) were filled with 0.5 ml of sample solution to which was added  $3-5 \ \mu$ Ci of carrier free <sup>22</sup>Na (obtained from ICN in 0.5 *M* HCl solution). The solution was subsequently diluted with

the appropriate solvent throughout the concentration study. Before the start of lifetime measurements each sample vial was thoroughly degassed and sealed under vacuum.

Samples prepared by dissolving reagents in solvents other than water (*i.e.*, pyridine and acetone) were prepared in a manner similar to that described in the preceding paragraph.

A minimum amount of HCl was used to prevent precipitation of basic forms of tin and zinc compounds in the solutions studied.

Samples for the temperature study were prepared in the same manner as described for the concentration studies. The temperature of the system was maintained at  $\pm 0.5^{\circ}$  by immersing the sealed sample vial in an oil bath specially designed for use in timing measurements.

Positron Lifetime Measurements. The lifetime measurements followed the standard procedure using delayed coincidence techniques as previously described.<sup>10</sup> By applying constant fraction timing discrimination, an optimum resolving time of 0.35 nsec was achieved, as characterized by the full-width half-maximum of the prompt spectrum of a <sup>60</sup>Co source. The data obtained in the delayed coincidence spectrum were fitted by the method of least squares to determine the annihilation lifetimes. The lifetime spectra were decomposed into two or three components. The decomposition into two components resulted, however, in a better fit to the experimental curves. Consequently, it was concluded that the results can be best described by a two-component analysis. The calculations were performed on an IBM 360/50-65 computer, using computational methods developed by Cumming<sup>15</sup> or Tao.<sup>16</sup> The intensities were calculated by normalizing the areas under each of the components to that of the entire distribution. The intensity is then given by the ratio of the area of each component to that of the total area under the distribution curve. Correction for the small amount of posi-

- (9) H. Horstman, J. Inorg. Nucl. Chem., 27, 1191 (1965).
- (10) T. L. Williams and H. J. Ache, J. Chem. Phys., 50, 4493 (1969).
- (11) V. I. Goldanskii, V. G. Firsov, and V. P. Shantarovich, Dokl. Akad. Nauk SSSR, 155, 636 (1964).
- (12) S. J. Tao and J. H. Green, J. Chem. Soc. A, 408 (1968).
- (13) J. E. Jackson and J. D. McGervey, J. Chem. Phys., 38, 300 (1963).
- (14) G. Trumpy, Phys. Rev., 118, 668 (1960).
- (15) J. D. Cumming, BNL Report No. 6470.
- (16) S. J. Tao, IEEE Trans. Nucl. Sci., 175 (1968).

<sup>(6)</sup> For references, see (a) J. Green and J. Lee, "Positronium Chemistry," Academic Press, New York, N. Y., 1964; (b) V. I. Goldanskii, At. Energ. Rev., 6, 3 (1968); (c) J. D. McGervey in "Positron Annihilation," A. T. Stewart and L. O. Roellig Ed., Academic Press, New York, N. Y., 1967, p 143; (d) J. A. Merrigan, S. J. Tao, and J. H. Green, Tech. Org. Chem., in press; (e) H. J. Ache, Angew. Chem., Int. Ed. Engl., in press.

<sup>(7)</sup> S. J. Tao and J. H. Green, J. Phys. Chem., 73, 882 (1969).

<sup>(8)</sup> J. D. McGervey, H. Horstman, and S. DeBenedetti, Phys. Rev., 124, 1113 (1961).

tron annihilation occurring in the walls of the sample vials was made.

## **Results and Discussion**

As mentioned in the Introduction, Ps atoms formed in the Ore gap may have a maximum kinetic energy of 6.8 eV down to thermal energies. Thus the first question is to determine whether Ps atoms undergo reactions such as oxidation-reduction reactions with simple metal cations in aqueous solutions while they still possess excess kinetic energy. Interactions of a Ps atom with a substrate can be categorized into two distinct classes of reactions. The first can be described as a physical interaction and includes pickoff, *i.e.*, annihilation of the positron bound in the Ps atom with a "strange" electron and triplet-singlet spin conversion or vice versa.<sup>6</sup> More recently, however, convincing evidence was presented that the Ps atom is "chemically stable" and may also undergo chemical reactions such as oxidation, reduction, substitution, addition, and compound formation.<sup>7-15,17-23</sup>

In order to simplify the issue, we have chosen systems containing no paramagnetic species so that the spin conversion process can be neglected. Consequently, possible interactions between Ps and the molecules in solution will include only pickoff and chemical reaction.

Information about the energy at which the chemical reaction occurs can be extracted from positron lifetime measurements. Formation of Ps, subsequent self-annihilation of para Ps, and the annihilation of free positrons will occur within a relative short period of time after the birth of the positron. Because of the finite resolution of the conicidence equipment, para Ps selfannihilation and free positron annihilation will give rise to a component in the lifetime spectra with a short composite lifetime,  $\tau_1$ . The energetic ortho Ps, however, like any other hot atom, has two alternatives. It may undergo chemical reactions while still hot or lose its excess kinetic energy by moderating collisions, becoming a thermalized Ps atom and reacting as such. In pure water there seems to be very little indication of "hot" Ps reactions,<sup>24</sup> and the thermalized or nearly thermalized species annihilate solely via pickoff,<sup>6</sup> with an annihilation rate characteristic for water,  $\lambda_{aq}$ , which is the sum of the self-annihilation rate of the ortho Ps,  $\lambda_t,$  and  $\lambda_p,$  the pickoff annihilation rate of water, i.e.,  $\lambda_{aq} = \lambda_p + \lambda_t$ , wherein

$$\lambda_{\rm p} = K_{\rm pickoff} [\rm H_2O]$$

 $(K_{\text{pickoff}} = \text{the rate constant of the pickoff process in water and [H<sub>2</sub>O] = water concentration). Thus$ 

$$\lambda_{aq} = \lambda_t + K_{pickoff}[H_2O] = 5.6 \times 10^8 \text{ sec}^{-1}$$

or

$$\tau_{\rm ac} = 1/\lambda_{\rm ac} = 1.78$$
 nsec

The Journal of Physical Chemistry, Vol. 76, No. 8, 1972

That is to say, the self-annihilation (intrinsic) lifetime of ortho Ps is shortened by a certain amount due to the pickoff process;  $\tau_{aq}$  is substantially different from  $\tau_1$ , which is usually about 0.4 nsec; and the result is the appearance of a long-lived component with an average lifetime  $\tau_2 = \tau_{aq}$  in the time spectra. The intensity of this component,  $I_2$ , can be correlated to the number of ortho Ps atoms initially formed.

Let us now consider the case of a solute which reacts chemically, *e.g.*, by oxidation, only with "hot" Ps atoms, *i.e.*, the threshold energy of the reaction lies above thermal energies, and the deficient energy has to be supplied by the kinetic energy of the Ps. In this case, the reaction has to take place shortly after the birth of the Ps atom before it has time to lose its kinetic energy.

The product formed in the chemical reactions, e.g., in the case of oxidation, is the free positron, which will annihilate almost as soon as it is formed. Thus, the lifetime of the ortho Ps will be shortened by the amount of time it takes for the Ps atom to become thermalized, and it will become indistinguishable from that of the free positrons or para Ps; *i.e.*, it will drop out of the second component and apppear as a part of the shortlived component. The only observable evidence is then a reduction of the intensity,  $I_2$ , of the second component (no change of  $\tau_2$ ).

If, on the other hand, the chemical reaction (oxidation) occurs at thermal energies, the chemical reaction rate  $\lambda_{ox}$  has to be added to the pickoff and self-annihilation rates, and the overall annihilation rate,  $\lambda_2$ , will be in this case equal to the sum of the three rates  $\lambda_{ox} + \lambda_p + \lambda_t$ , resulting in a shortening of the lifetime  $\tau_2$ . Since the chemical reaction rate  $\lambda_{ox}$  is directly related to the solute concentration,  $\tau_2$  will decrease with increasing solute concentration.

In aqueous solutions of Sn(II), Pb(II), Cd(II), Zn(II), Tl(I), and Na salts, no significant changes can be noticed in the two lifetimes  $\tau_1$  and  $\tau_2$  over a wide solute concentration range (up to 2 *M* concentration). They remain practically constant at  $\tau_1 \sim 0.4$  nsec and  $\tau_2 \sim 1.7$  nsec.

From the fact that in the present case no change in the long lifetime  $\tau_2$  is observed with an increase in solute concentration, it follows that thermalized ortho

- (17) S. J. Tao, Phys. Rev. Lett., 14, 935 (1965).
- (18) J. D. McGervey and S. Benedetti, Phys. Rev., 114, 495 (1959).
- (19) R. E. Green and R. E. Bell, Can. J. Phys., 35, 398 (1957).
- (20) J. H. Lee and G. J. Celitans, J. Chem. Phys., 44, 2506 (1966).
- (21) D. A. L. Paul, Can. J. Phys., 37, 1059 (1959).

(22) V. I. Goldanskii, F. I. Dalidchik, and G. K. Ivanov, High Energ. Chem., 3, 142 (1964).

(23) V. I. Goldanskii and A. D. Mokrushin, Khim. Vys. Energ., 2, 93 (1967).

(24) Although reactions of "hot" Ps atoms with the solvent molecules cannot be entirely excluded, it seems that the cross sections of these reactions are relatively small. This is probably due to a different kind of interaction, most likely Ps compound formation, similar to that postulated in aqueous oxy acid systems by Tao and Green.<sup>7</sup>

### **Reactions of Energetic Positronium Atoms**

Ps atoms do not react to any significant extent with the surrounding molecules in thse systems except by pickoff, leading eventually to their annihilation. These findings are further substantiated by temperature studies, where the positron annihilation data reveal no change in  $\tau_2$  or  $I_2$  over the whole temperature range from 25 to 85°.

The intensities,  $I_2$ , however, drop drastically with an increase in solute concentration and approach a lower limit (or saturation value),  $I_2^{\text{sat}}$ , which is characteristic for each individual compound.

As seen in Figure 1, the following order for  $I_2^{\text{sat}}$  is observed: Na > Tl > Zn > Cd > Sn(II) > Pb(II). The decrease of the intensity,  $I_2$ , of the long-lived component, without a simultaneous decrease of  $\tau_2$ , must consequently be the result of a reduced number of thermalized ortho Ps atoms present which can annihilate *via* pickoff.

In addition to the reactions of "hot" Ps atoms, as discussed above, some other processes which could possibly lead to a reduction of  $I_2$  without a simultaneous decrease of  $\tau_2$  have to be considered. (a) In the presence of a solute, a positron might rapidly lose most of its kinetic energy in one or few collisions with the solute species. Thus, the number of collisions undergone in the Ore gap, where positronium formation is energetically possible, is greatly reduced and less positronium is formed. (b) The positron can undergo positron compound formation with the solute species at energies above or within the Ore gap. The annihilation lifetime of the formed positron compound is expected to be extremely short, and the overall result is again a reduction of positronium formation. (c) After positronium formation has taken place, ortho Ps is converted to para Ps by the solute species.

Reactions a and b are processes which compete with the positronium formation process, and the dependence of  $I_2$  on solute concentration should follow the following equation

$$I_2 = I_2^0(1 + KM)$$

where  $I_{2^{0}}$  = intensity of second component in pure solvent, K = a constant, and M = the molarity of solution, as discussed in detail by Green and Bell.<sup>19</sup> This model, however, cannot satisfactorily explain the saturation values for  $I_{2}$  at higher solute concentrations as observed in the present investigations (Figure 1).

The same can be said for reaction c (spin conversion) unless the reaction is a threshold reaction, *i.e.*, it occurs only with hot positronium atoms. Spin conversion, however, has been observed in the past only in the presence of paramagnetic species. None of the solutes studied in this investigation is paramagnetic. In addition, angular correlation measurements have not provided any evidence for spin conversion in any of these solutions.



Figure 1. Intensities of the long-lived component,  $I_2$ , vs. solute concentrations in aqueous solutions of  $(\blacklozenge)$ Pb(ClO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O, (O) CdCl<sub>2</sub>, ( $\bigtriangleup$ ) SnCl<sub>2</sub> (in 1.18 *M* HCl), (O) TlClO<sub>4</sub>, (O) NaClO<sub>4</sub>, (I) ZnCl<sub>2</sub> (in 0.047 *M* HCl).

Thus, a more likely explanation seems to be that the drop in  $I_2$  is the result of reactions of ortho Ps atoms at energies above thermal (vide supra). The appearance of the saturation region for  $I_2$  can then be easily understood in terms of the postulated "hot" mechanism. Since Ps atoms are formed with various amounts of kinetic energy, it seems only logical to assume that the observed  $I_2^{\text{sat}}$  represents the number of Ps atoms formed with kinetic energies below the threshold energy for the Ps reaction. Thus, the relative reduction in the intensity of the long-lived component,  $(I_2^0 - I_2^{\text{sat}})/I_2^0$ , is the fraction of Ps atoms formed with kinetic energies above the threshold energy of the long-lived component, it is atoms formed with kinetic energies above the threshold energy ( $I_2^0$  = intensity of the long-lived component).

An interesting question arises as to the nature of the species and the mechanisms involved in these "hot" reactions. From the data obtained in aqueous solutions of various sodium salts,<sup>25</sup> it is clear that the above effect must be associated with the cations of the salts. The changes in  $\tau_2$  or  $I_2$  introduced by the  $\text{ClO}_4^-$  or  $\text{Cl}^-$  ions have been found to be negligible under these experimental conditions. The simplest way of describing the interaction between the Ps and cation in solution might be via an oxidation reaction involving single clectron transfer

$$A^+ + Ps \longrightarrow e^+ + A$$

In solutions the cations are solvated and the use of ionization potentials to assess the thermicity of the reaction will not be very satisfactory. Indeed, the  $(I_2)$  data reveal no relation between the ionization potential of the cations involved and the observed  $I_2^{\text{sat}}$ .

A better approach would be to correlate the electron affinities of the cations (in solutions) to the individual  $I_2^{\text{sat}}$ . Unfortunately, these data are not available.

<sup>(25)</sup> M. Bertolaccini, A. Bisi, and L. Zoppa, Nuovo Cimento B, 156, 237 (1966).



Figure 2.  $I_2^{eat}$  vs. standard oxidation potentials and arbitrary energy distribution function of Ps atoms.

A very important feature of the chemical reactions of Ps atoms is that they never reach equilibrium. The short lifetime of the positrons, their low concentrations, and their continuous slowing down to lower kinetic energies prevent the establishment of any equilibrium. Thus, no chemical or physical parameter measured under equilibrium conditions can be used in positronium chemistry without limitations.

Although Ps in solution differs considerably in this respect from the usual oxidation-reduction reactions, the standard oxidation potential should be expected to be a useful guide insofar as it indicates the electron affinity of the solute ion and thus the threshold energy of the oxidation reaction. It should be pointed out, however, that this is only a first approximation and it should be valid only for cases where the oxidation occurs via a single electron transfer and not for more complex redox systems, such as  $MnO_4^-$  or  $NO_3^-$ .

In Figure 2 the  $I_2$  saturation values are plotted as a function of the standard oxidation potentials of the cations. The resulting curve suggests indeed a qualitative correlation between threshold energies and such potentials, possibly owing to partial correlation of a negligible contribution of entropy factors and reverse energy barriers. A serious drawback in this approach, however, is that most of the potentials quoted in this study refer to average energies released in multielectron transfer and are not the single-electron potential which would apply more properly to Ps reactions. This may have introduced relatively large uncertainties.

Despite these obvious shortcomings, it is interesting to note that the extrapolation of the curve as  $I_2 \rightarrow 0$ (Figure 2) suggests a hypothetical "oxidation potential" for Ps between about 0 and 0.1 V, which coincides closely with that postulated by McGervey, *et al.*,<sup>8</sup> who arrived at this result from the observation of the rate of oxidation reactions of thermalized Ps species. Consistent with this hypothesis is our observation that in systems such as Sn(IV), Cu(II), and Hg(II), which have a standard oxidation potential greater than 0.0 V,  $I_2$  approaches 0% at solute concentrations of about 0.3 *M* and  $\tau_2$  decreases simultaneously, indicating that oxidation occurs with "hot" as well as with thermal Ps atoms.

Thus far it seems that our findings support the contention that in the solutions studied in the present investigation the chemical interactions between solute and Ps atoms occur mainly *via* an oxidation mechanism at Ps energies above thermal. It further follows that if the threshold energy for the oxidation is greater than thermal, as postulated for the systems in this study, the maximum fraction of Ps atoms which can be oxidized is given by  $(I_{2^0} - I_{2^{\text{sat}}})/I_{2^0}$ .

Accordingly, in a solution containing several species, capable of reacting with "hot" Ps atoms, the one with the lowest threshold energy should determine the saturation intensity  $I_2^{\text{sat}}$ . This has been experimentally tested and confirmed in aqueous solutions of Pb(NO<sub>3</sub>)<sub>2</sub> which contain two species known to react with Ps, Pb<sup>2+</sup>, and NO<sub>3</sub><sup>-</sup>.  $I_2$  was found to level off at higher solute concentrations to a plateau which corresponds to the saturation value observed in aqueous NaNO<sub>3</sub> solutions<sup>19</sup> (Figure 3).

If one assumes that the threshold energies involved in the reactions between Ps and the dissolved compounds are directly proportional to the numerical values of the standard oxidation potentials of their cations, an energy distribution function for the positronium atoms can be derived as shown in Figure 2. Unfortunately, the oxidation potentials do not provide an absolute energy scale so that the energy axis on this plot can only be arbitrary. It seems, however, that the energy distribution assumes a fairly rectangular shape at energies close to thermal.

Information about the reaction cross sections could be obtained from the relative changes of  $(I_2^0 - I_2)/(I_2^0 - I_2^{\text{sat}})$  as a function of solute concentration.

Unfortunately, at the present time very little is known about the exact nature of the reactant and consequently about its concentration in the solutions under investigation.

In order to assess the effects of the various parameters such as dissociation of ions, activity of the ions, solvation and/or complex formation, and viscosity of the solution, a series of experiments was started which included positron lifetime measurements of metal salts dissolved in different solvents. Some preliminary results are shown in Figure 4, where the intensity,  $I_2$ , of the long-lived component is plotted as a function of the molarity of  $SnCl_2$  in water, acetone, and pyridine. (No changes of  $\tau_2$  have been observed under these conditions.) Although undoubtedly the viscosity, the degree of dissociation, and the nature of the formed solvation complexes or its adducts will be clearly different in various solutions, the observed ratios  $(I_{2^{0}} - I_{2})/(I_{2^{0}} - I_{2})$  $I_{2^{\text{sat}}}$  remain practically unchanged over the whole concentration range (Figure 5). The observed indepen-



Figure 3. Intensity  $I_2$  vs. solute concentration in aqueous solutions of  $(\oplus)$  PbNO<sub>3</sub>,  $(\bigstar)$  Pb(ClO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O,  $(\bigstar)$  NaNO<sub>3</sub>. Data for NaNO<sub>3</sub> were taken from ref 19.



Figure 4. Intensities  $I_2$  in solutions of SnCl<sub>2</sub> in various solvents: ( $\bullet$ ) SnCl<sub>2</sub> in acetone, ( $\bullet$ ) SnCl<sub>2</sub> in pyridine, ( $\bullet$ ) SnCl<sub>2</sub> in 1.18 *M* HCl.

dence of the reaction rate on viscosity is expected for reactions which occur at higher kinetic energies and provides further evidence for a "hot" reaction mechanism. These results, however, seem also to indicate that Ps quenching in these systems is largely independent of whether there occurs an actual extensive separation of cation and anion, as in strongly polar solvents, or whether they are bonded in a single molecule as in nonpolar solvents.

A similar phenomenon has been previously observed<sup>2b</sup> in the case of the  $CuCl_2$  system, where the rate constant of (thermal) positronium reactions with  $CuCl_2$  is the same (at equal solute concentration and normalized to



Figure 5.  $(I_2^0-I_2)/(I_2^0-I_2^{sat})$  in solutions of SnCl<sub>2</sub> in various solvents  $(I_2^0 = \text{intensity observed in pure solvent})$ :  $(\nabla)$  SrCl<sub>2</sub> in acetone,  $(\spadesuit)$  SnCl<sub>2</sub> in pyridine,  $(\blacksquare)$  SnCl<sub>2</sub> in 1.18 *M* HCl.

the same viscosity) in water, acetone, and tetrahydrofuran regardless of the sharp reduction of conductivity during transition from water to the other two solvents. More experimental work will be required to substantiate these preliminary results in other systems, but should this evidence stand up in time, then it seems that the positronium reaction could offer an opportunity to study valence states independently of the complicating phenomena of dissociation and solvation.

## Summary

The experimental resluts presented in this paper strongly support an important aspect in positronium chemistry, that Ps atoms can react chemically at energies above thermal as well as at thermal energies. For oxidation reactions which occur between simple metal cations and Ps, the oxidation potentials of the species involved serve as a rough guideline for the threshold energy of the reaction and the maximum fraction of Ps reacting, which could be related to the changes in the intensity,  $I_{2^0} - I_{2^{\text{sat}}}$ .

It is hoped that a combination of positron lifetime and angular distribution or Doppler broadening measurements<sup>26</sup> will provide us with a tool to assess directly the energy Ps possesses when it annihilates and thus the energies at which the "hot" Ps reactions occur.

(26) V. H. Hsu and C. S. Wu, Phys. Rev. Lett., 18, 889 (1967).

# An Investigation of the Low Energy Singlet-Triplet and Singlet-Singlet

**Transitions in Ethylene Derivatives by Ion Impact<sup>1</sup>** 

### by John H. Moore, Jr.

Department of Chemistry, University of Maryland, College Park, Maryland 20742 (Received November 22, 1971) Publication costs assisted by the National Science Foundation

The lowest energy singlet-triplet and singlet-singlet transitions in ethylene and some of its simple derivatives have been investigated using the technique of ion-impact energy-loss spectroscopy. The energy of maximum transition intensity has been measured and the magnitude of the singlet-triplet splitting between the T and V states has been determined. In 1,3-butadiene a transition at 4.9 eV was observed in addition to the known transition to the lowest triplet state at 3.2 eV.

### Introduction

The ethylene molecule is the simplest olefin, and as a result this molecule and its derivatives are often studied in order to understand the properties of the carboncarbon double bond and the effects of nearby substituents on the nature of the bond. Spectroscopic studies of ethylene and its derivatives are frequently hampered by the relative intensities of several of the most important transitions. The  $\pi^* \leftarrow \pi$  transition from the ground state to the lowest triplet state (T  $\leftarrow$  N) is particularly weak even for a singlet-triplet transition. This is apparently the result of a large difference between the ground state and excited state geometries which permits very little Franck-Condon overlap between the two configurations. By contrast both the spin-allowed  $\pi^* \leftarrow \pi$  transition (V  $\leftarrow$  N) and the first Rydberg transition ( $R \leftarrow N$ ) are dipole-allowed and are intense features in the optical and electron-impact spectrum. However, the V  $\leftarrow$  N transition consists mostly of continuum and is usually overlapped by the  $R \leftarrow N$ bands.<sup>2</sup> Electronic selection rules for transitions induced by ion impact differ from optical selection rules, and for this reason a study has been made of a series of substituted ethylenes using the technique of ion-impact energy-loss spectroscopy.

In an ion-impact spectrometer a change in the internal energy of a sample molecule is detected by measuring the kinetic energy lost by an ion which has been inelastically scattered from the molecule. The spectrometer used in these experiments is similar in design and operation to a modern electron impact spectrometer. The instrument has been described in detail previously<sup>3</sup> and will not be discussed here; however, it may be useful to consider some of the characteristics of ion-impact induced electronic transitions.

For collision energies of up to several kiloelectronvolts, the duration of an ion-molecule collision is sufficiently long to permit electron exchange between the ion and the target molecule to occur with relatively large probability. As a result singlet-triplet transitions are easily excited by ion impact. In addition, for the type of inelastic process being investigated here, it has been observed that scattering occurs only into a small solid angle in the forward direction. This is in contrast to electron impact wherein the scattering is more nearly isotropic. As a result it is possible to detect a larger fraction of the inelastically scattered current in an ion scattering experiment than is the case for electron scattering. Thus while the selection rules for ion-impact spectroscopy are expected to be similar to those which apply to low-energy electron-impact spectroscopy, weak transitions are often more easily detected in an ion spectrometer than in an electron spectrometer.

### Results

Electronic transitions induced by proton and He<sup>+</sup> impact on ethylene and a variety of alkyl- and halogensubstituted ethylenes as well as vinyl methyl ether and 1,3-butadiene have been investigated. The collision energy was about 3.0 keV, and the energy resolution was about 0.35 eV. The sample gas pressures were in the vicinity of 10 mTorr. The reported spectral peak positions are the averages of measurements made on at least five different spectra.

Energy-loss spectra of He<sup>+</sup> inelastically scattered from the various ethylenes are presented in Figure 1. With the exception of 1,3-butadiene, the most intense feature in each of these spectra is a peak at about 4 eV which corresponds to the transition to the lowest-lying triplet state,  $T \leftarrow N$ . Using his method of high pressure oxygen-induced optical absorption, Evans observed the absorption maximum of the  $T \leftarrow N$  transition in ethylene at 4.6 eV.<sup>4</sup> In the ion-impact energy-loss

<sup>(1)</sup> Work supported by grants from the National Science Foundation and the Research Corp.

<sup>(2)</sup> For a recent review on the ethylene spectrum see: A. J. Merer and R. S. Mulliken, Chem. Rev., 69, 639 (1969).

<sup>(3)</sup> J. H. Moore, Jr., J. Chem. Phys., 55, 2760 (1971).

<sup>(4)</sup> D. F. Evans, J. Chem. Soc., 1735 (1960).





Figure 1. 3.0-keV He<sup>+</sup>-impact energy-loss spectra of ethylene, some simple substituted ethylenes, and 1,3-butadiene. The sample gas pressure was about 10 mTorr. These spectra were taken using a count-rate meter and the maximum scattered signal strength was typically about 50 counts/sec.

spectrum this peak occurs at 4.3 eV. The energy of the maximum singlet-triplet excitation produced by ion impact on the alkyl-substituted ethylenes is very

Figure 2. 3.0-keV proton-impact energy-loss spectra of ethylene, some simple substituted ethylenes, and 1,3-butadiene. The sample gas pressure was about 10 mTorr. The maximum scattered signal strength was typically about 150 counts/sec.

little changed from the maximum in the ethylene spectrum. For the chloro-substituted ethylenes the  $T \leftarrow N$  peak is at somewhat lower energies than in ethylene

Molecule	$T \leftarrow N$ max, eV	T ← N other measurements	V + N max, eV	V←N. other measurements	$\Delta E$ , eV
Ethylene	4.3	4.6 (4)	7.8	7.6 (8)	3.5
		4.4 (9)		7.7 (7, 9, 14)	
Butene-1	4.3		7.3	7.1 (10, 15)	3.0
cis-Butene-2	4.2	(16)	7.2-7.5	7.1 (10, 15)	3.0-3.3
		4.3(7)			
trans-Butene-2	4.2		7.5	7.0 (10, 15)	3.3
Vinyl chloride	4.0		6.9	6.75 (8)	2.9
1,1-Dichloroethylene	3.9		6.9	6.45 (8)	3.0
Tetrachloroethylene	4.2			6.3? (8)	
1,1-Difluoroethylene	4.6		7.6	7.5 (17)	3.0
Vinyl methyl ether	4.2		6.7		2.5
1,3-Butadiene	3.2	3.2(4)	6.1	5.9 (15)	2.9
		3.3 (7)		5.8-6.1(7)	

Table I: Energy-Loss Peak Positions in the Ion-Impact Spectra of Simple Ethylene Derivatives<sup>a</sup>

<sup>a</sup> Other measurements are listed in the form: optical results/electron-impact results. References are given in parentheses.  $\Delta E$  represents the singlet-triplet splitting between the T and V states as measured peak-to-peak.

and in 1,1-difluoroethylene the peak occurs at higher energy.

In butadiene the lowest triplet state moves to lower energy and the peak of the T  $\leftarrow$  N transition is at 3.2 eV. In addition a peak appears at 4.9 eV which corresponds to a transition to a state which lies below the lowest energy singlet state. Evans has reported singlet-triplet absorptions peaking at 3.2 and 3.9 eV.<sup>4</sup> He suggests that the triplet states are <sup>3</sup>B<sub>u</sub> and <sup>3</sup>A<sub>g</sub>, respectively. However, these two states are theoretically predicted to lie at 3.9 and 4.6 eV by Pariser and Parr<sup>5</sup> and at 3.4 and 4.4 eV by Sidman.<sup>6</sup> In the low-energy electron-impact spectrum obtained by Oosterhoff, *et al.*,<sup>7</sup> there are peaks at 3.3 and 3.8 eV and a very weak transition at about 4.8 eV.

Proton-impact spectra are presented in Figure 2. Electron-exchange scattering cannot occur in a protonmolecule collision since the proton does not have an electron and as a result only singlet-singlet transitions occur in these spectra.

There are two intense transitions in the 6-9-eV region of both the optical and electron-impact spectrum of ethylene—the first Rydberg transition,  $R \leftarrow N$  and the  $\pi^* \leftarrow \pi$  transition to the <sup>1</sup>B<sub>1u</sub> state, V  $\leftarrow$  N. The intensity maximum of the V - N transition is reported to be at 7.6 eV in the optical spectrum and 7.7 eV in the electron-impact spectrum.<sup>7.9</sup> The first peak in the ionimpact spectrum of ethylene is at 7.8 eV. The disparity between these measurements is probably caused by variations in the intensity of the  $R \leftarrow N$  and other underlying transitions. In contrast to the ethylene case, the  $R \leftarrow N$  and  $V \leftarrow N$  transitions in transbutene-2 produce two well-separated peaks at 6.2 and 7.5 eV, respectively. In 1,3-butadiene the V - N transition at 6.2 eV falls well below the Rydberg transitions.

## Discussion

The peak energies of the transitions to the lowest triplet state and the corresponding singlet state of each of the sample molecules are presented in Table I. Peak energy measurements from optical and low-energy electron-impact spectra are included for comparison. Since the T state and the V state of ethylene and its simple derivatives have the same electronic configuration (excepting the difference in electron spin multiplicity), the energy difference between these two states is a quantity of interest. As indicated in Table I, the singlet-triplet splitting as measured peak-to-peak is 3.5 eV in ethylene and decreases to about 3.0 eV in most of the substituted ethylenes.

The V  $\leftarrow$  N maxima in the ion-impact spectra is higher in energy than in the corresponding optical and electron-impact spectra. It is of interest to note that this trend holds for ethylene in which the R  $\leftarrow$  N and V  $\leftarrow$  N bands are superimposed, as well as for *cis*- and *trans*-butene-2 in which these two bands are reasonably well separated.<sup>10</sup>

Anomolous intensity behavior in the 7–8-eV region of the ethylene spectrum has been observed by other investigators. Ross and Lassettre<sup>11</sup> have suggested that an electronic quadrupole transition at 7.45 eV may

- (5) R. Pariser and R. G. Parr, J. Chem. Phys., 21, 767 (1953).
- (6) J. W. Sidman, ibid., 27, 429 (1957).

- (10) J. T. Gary and L. W. Pickett, ibid., 22, 599 (1954).
- (11) K. J. Ross and E. N. Lassettre, ibid., 44, 4633 (1966).

<sup>(7)</sup> H. H. Brongersma, J. A. v.d. Hart, and L. J. Oosterhoff, "Fast Reactions and Primary Processes in Chemical Kinetics," S. Claesson, Ed., Interscience, New York, N. Y., 1967, p 211.

<sup>(8)</sup> G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966.

<sup>(9)</sup> J. P. Doering and A. J. Williams III, J. Chem. Phys., 47, 4180 (1967).

be contributing to the apparent intensity of the  $V \leftarrow N$ peak. A recent theoretical work by Buenker, *et al.*,<sup>12</sup> discusses the  $V \leftarrow N$  bands of ethylene in terms of the electronic and geometrical structure of excited states in 7-8-eV region. They conclude that verticle transitions are forbidden for the  $V \leftarrow N$  excitation. If the  $V \leftarrow N$ peak corresponds to a nonvertical transition, it would not be surprising to learn that the position of the intensity maximum is a function of the excitation mechanism.

One of the most interesting features of the spectra observed in this work is the intense transition at 4.9 eV in 1,3-butadiene. It seems probable that this is a singlet-triplet transition; however, the appearance of this feature in the He<sup>+</sup>-impact spectrum and its absence from the proton-impact spectrum does not prove that the upper state of this transition is a triplet. Robin, et al.,<sup>13</sup> postulate the presence of a CH\*  $\leftarrow \pi$ , "mystery band" in the butadiene spectrum at about 5 eV. This assignment seems unlikely for the transition observed here since no feature in the other ethylene spectra can be readily identified with the olefin mystery band. Also since the mystery band is a spin-allowed transition, it would be expected to appear in the proton-impact spectrum.<sup>14-17</sup>

- (12) R. J. Buenker, S. D. Peyerimhoff, and H. L. Hsu, Chem. Phys. Lett., 11, 65 (1971).
- (13) M. B. Robin, R. R. Hart, and N. A. Kuebler, J. Chem. Phys., 44, 1803 (1966).
- (14) J. A. Simpson and S. R. Mielczarek, ibid., 39, 1606 (1963).
- (15) L. C. Jones and L. W. Taylor, Anal. Chem. 27, 228 (1955).
- (16) G. P. Semeluk and R. D. Stevens, Can. J. Chem., 49, 2452 (1971).
- (17) G. Bélanger and C. Sandorfy, J. Chem. Phys., 55, 2055 (1971).

# **Primary Processes in Excited Charge-Transfer Systems**

### by N. Orbach, R. Potashnik, and M. Ottolenghi\*

Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel (Received September 7, 1971) Publication costs assisted by the U.S. National Bureau of Standards

The relative yields of triplet state, fluorescent exciplex, and radical ions, generated by the interaction of an excited acceptor (pyrene or anthracene) with N,N-diethylaniline (DEA) as donor, are followed using fast laser photolysis techniques. The effects of temperature and solvent polarity on the relative yields of the products are examined. In nonpolar solvents the data are found to be inconsistent with a mechanism in which intersystem crossing takes place from the relaxed exciplex, in competition with fluorescence. In polar systems, part of the observed pyrene triplet ( ${}^{3}P^{*}$ ) is generated by the relatively slow recombination:  $P^{-} + DEA^{+} \rightarrow {}^{3}P^{*} + DEA$ . However, most of  ${}^{3}P^{*}$  is already present at the end of the laser pulse, prior to any substantial decay of  $P^{-}$  and DEA<sup>+</sup>. It is suggested that the principal path of intersystem crossing in both polar and nonpolar solvents is a fast process competing with vibrational or solvent relaxation of the excited system.

### Introduction

The primary process of intersystem crossing (ISC) from the singlet to the triplet manifold is of major importance in determining the physical and chemical consequences of light absorption by molecules. However, apart from the familiar effects of enhanced ISC due to interactions of the excited molecule with heavy atom or paramagnetic neighbors, very little is known concerning other environmental effects on the rate of crossing to the triplet state.

Recently,<sup>1</sup> the importance of charge-transfer interactions in enhancing ISC have been shown in relation to the quenching of the fluorescence of aromatic molecules by electron donors or acceptors. Pulsed laser photolysis experiments were carried out: (a) in nonpolar solvents, where the excited state donor (D)-acceptor (A) interaction is associated with the generation of a fluorescent exciplex  $(A^-D^+)^*$ ,<sup>2</sup> e.g.

$${}^{1}A^{*} + D \longrightarrow {}^{1}(A^{-}D^{+})^{*} \longrightarrow A + D + h\nu$$
 (1)

(b) in polar liquids, where deactivation is associated with the formation of solvated radical  $ions^{2,3}$ 

(1) C. R. Goldschmidt, R. Potashnik, and M. Ottolenghi, J. Phys. Chem., 75, 1025 (1971).

<sup>(2)</sup> H. Leonhardt and A. Weller, Ber. Bunsenges. Phys. Chem., 67, 791 (1963).

<sup>(3) (</sup>a) H. Knibbe, D. Rehm, and A. Weller, *ibid.*, 72, 257 (1968); (b)
M. Koizumi and H. Yamashita, Z. Phys. Chem. (Frankfurt am Main),
57, 103 (1968); (c) K. Kawai, N. Yamamoto, and H. Tsubomura,
Bull. Chem. Soc. Jap., 42, 369 (1969); (d) K. H. Grellmann, A. R.
Watkins, and A. Weller, J. Lumin., 1, 2, 678 (1970).

$${}^{1}A^{*} + D \longrightarrow A_{s}^{-} + D_{s}^{+}$$
 (2)

Both processes were found<sup>1</sup> to be accompanied by comparable high yields of intersystem crossing to the <sup>3</sup>A\* state. The relatively fast ( $\tau < 20$  nsec) growth of the absorbance attributed to <sup>3</sup>A\* was interpreted in terms of a rapid generation of the triplet state, suggesting a process which does not occur from the relaxed exciplex competing with fluorescence, nor (in polar systems) via the  $A^- + D^+ \rightarrow {}^{3}A^* + D$  recombination process. The suggested (fast) ISC mechanism, which is in variance with the commonly accepted paths, can in principle be questioned in nonpolar systems by arguing that the triplet and the exciplex have, coincidentally, identical absorption spectra.<sup>1,4</sup> In such a case the process:  $(A^-D^+)^* \xrightarrow{ISC} {}^{3}A^* + D$  will not be associated with a net change in absorbance. Consecutively, no growing-in of 3A\*, matching the decay of  $(\Lambda^{-}D^{+})^{*}$ , will be observed. Similar arguments may also be presented in polar solvents, the absorptions of  $A_{s}^{-}$  and  $D_{s}^{+}$  replacing those of the exciplex. To avoid such ambiguities and to obtain a further insight into the charge-transfer induced intersystem crossing, we have extended the experimental observations, analyzing the effects of solvent and temperature on the relative vields of ions, exciplex and triplet state. The results will be shown to support the "fast" mechanism of intersystem crossing, suggesting that the triplet state is populated from nonrelaxed excited states of the exciplex. The data will also bear on the general problem of vibrational deactivation in solution.

## **Experimental Section**

The pulsed N<sub>2</sub> (3371 Å) laser photolysis apparatus<sup>5</sup> and the steady-state fluorimeter<sup>6</sup> have been previously described. Low-temperature experiments were carried out by placing the sample cell within a metal block, both inside a special quartz dewar equipped with appropriate optical windows. The required low temperature was obtained by pouring liquid nitrogen into a container in thermal contact with the metal block. After equilibration, the temperature was maintained within 1°K for at least 10 min.

Chemicals employed were anthracene (Fluka puriss.), pyrene (Fluka, zone refined), and DEA (BDH, vacuum distilled). All solvents employed (toluene, methylcyclohexane, isopentane, methanol and acetonitrile) were Matheson, spectroquality products. Tetracyanobenzene (TCNB) an Eastman Kodak product, was used after subsequent recrystallizations.

Samples were deaerated by consecutive freeze and thaw cycles or by bubbling  $N_2$  gas through the solutions.

### Results

I. Effects of Temperature on Exciplex and Triplet Yields in Nonpolar Solvents. Experiments were carried out in which anthracene and pyrene (acceptors) were



Figure 1. Steady-state fluorescence of pyrene-DEA and anthracene-DEA exciplexes. Left side: [anthracene] =  $1.1 \times 10^{-2} M$ ; [DEA] = 0.5 M; excitation = 379 nm. Right side: [pyrene] =  $10^{-3} M$ ; [DEA] = 0.5 M; excitation = 337 nm.

excited in the presence of the common DEA donor. Characteristic fluorescence spectra, recorded under steady-state excitation, in a solution of  $1.1 \times 10^{-2} M$ anthracene and 0.5 M DEA in toluene at 320°K and 215°K, are shown in Figure 1. Upon lowering the temperature the 480 nm exciplex emission band undergoes a red shift and a decrease in intensity. At 215°K the 425 nm peak of the anthracene fluorescence can be observed, indicating that, at this temperature,  $\sim 25\%$ of the excited anthracene molecules fluoresce before undergoing the reaction with DEA. Small corrections for incomplete quenching at lower temperatures (determined from the residual amounts of unquenched anthracene fluorescence) were therefore introduced when plotting (Figure 2) the relative fluorescence intensity  $(\phi_f^{r})$  vs. temperature. Figure 3c shows the effects of temperature on the exciplex emission lifetime measured in the same sample by pulsed laser excitation. In Figure 2 the temperature dependence of the relative anthracene triplet state yields  $(\phi_{isc}^{r})$  is also presented. The latter were estimated in the laser experiments, by recording the absorbance change at the characteristic 430-435-nm peak of 3A\*, after the decay of the exciplex (>100 nsec after pulsing). As in the case of  $\phi_{f}^{r}$ , also  $\phi_{isc}^{r}$  has been corrected (at low temperatures) for incomplete quenching of 'A\* by DEA. Thus, the plots in Figure 2 represent the relative fluorescence and ISC yields associated with the quenching process.

Temperature effects similar to the above have also been observed for the pyrene-DEA system in either toluene or in a 1:1 isopentane-methylcyclohexane solvent mixture (Figure 4). Due to the relatively long lifetime of the lowest excited pyrene singlet state ( $\sim 400$  nsec), fluorescence quenching was complete

<sup>(4)</sup> R. Potashnik, C. R. Goldschmidt, M. Ottolenghi, and A. Weller, J. Chem. Phys., 55, 5344 (1971).

<sup>(5)</sup> C. R. Goldschmidt, M. Ottolenghi, and G. Spein, Isr. J. Chem., 8, 29 (1970).

<sup>(6)</sup> J. Feitelson, J. Phys. Chem., 68, 391 (1964).



Figure 2. Relative yields of exciplex fluorescence excited at 379 nm  $(\phi_l r)$  and intersystem crossing  $(\phi_{ise} r)$  as a function of temperature, for the interaction between excited anthracene and DEA in toluene; [anthracene] =  $1.1 \times 10^{-2} M$ , [DEA] = 0.5 M. The data have been corrected for the fraction of unquenched anthracene molecules, using the expressions:  $\phi_l r = [1/X]$  (F) and  $\phi_{ise} r = 1 [D_t - (1 - X)D_t^a]$ , where X is the fraction of excited molecules which have been quenched by DEA, F is the relative fluorescence intensity,  $D_t$  and  $D_t^a$  are, correspondingly, the anthracene triplet absorbance observed at 430 nm, in the presence and absence of DEA.



Figure 3. Half-lives of the decay of exciplex fluorescence as a function of temperature. (a) Pyrene-DEA in 1:1 isopentane: 2-methylbutane; [pyrene] =  $10^{-2} M$ , [DEA] = 0.5 M. (b) Pyrene-DEA in toluene (same concentrations). (c) Anthracene-DEA in toluene; [anthracene] =  $1.1 \times 10^{-2}$ , [DEA] = 0.5 M.

down to below 170°K, so that no corrections for incomplete quenching were necessary in this case. Excimerization could be neglected in view of the large excess of DEA (0.5 *M*) relative to the pyrene concentration (10<sup>-3</sup> *M*), leading to a rate ratio of  $(k_{1P*+DEA}/k_{1P*+P}) \simeq 2 \times 10^3$ . It should be finally pointed out that the low temperature limit of the plots in Figures 2 and 4 was imposed by the lower limits of the solvents fluidity.



Figure 4. Relative fluorescence  $(\phi_t^r)$  and triplet  $(\phi_{isc}^r)$  yields in pyrene–DEA systems as a function of temperature. Concentrations, same as Figure 1.

The Quenching of Excited Pyrene by DEA in II. Polar Solutions. a. General Pulsed-Photochemical Patterns. Dilute  $(2 \times 10^{-5} M)$  solutions of pyrene in acetonitrile, in the presence of  $2 \times 10^{-2} M$  DEA, were exposed to pulsed laser excitation. At the above concentrations, the pyrene monomer fluorescence is totally quenched via the diffusion controlled reaction with DEA, while excimerization (rate constant  $\sim 2.4 \times 10^{9}$  $M^{-1}$  sec<sup>-1</sup>) can be neglected. The absorbance change recorded at the end of the laser pulse (20 nsec after triggering) is shown in Figure 5b. The spectrum consists of three superimposed bands with maxima around 490, 470, and 415 nm. The initial change in absorbance is subsequently followed by a decay of the 490 and 470nm bands, and by a growing-in process in the 415-nm region. The transient spectrum recorded 2 µsec after pulsing is also shown in Figure 5b. In Figure 5a the spectra reported in the literature for the P- and DEA+ ions, as well as for the pyrene triplet state, are reported.

It is evident that absorption bands attributable to the three species: P<sup>-</sup>, DEA<sup>+</sup>, and <sup>3</sup>P<sup>\*</sup> are present at the end of the laser pulse, *i.e.*, all species are formed within less than  $\sim 20$  nsec. The subsequent decay of the ions obeys second-order kinetics with a bimolecular rate constant of  $\sim 2 \times 10^{10} M^{-1} \sec^{-1}$ . Simultaneously, a growing-in of the characteristic 415-nm triplet band takes place, suggesting the process

$$P^{-} + DEA^{+} \longrightarrow {}^{3}P^{*} + DEA \qquad (1)$$

Unfortunately, a quantitative comparison between the half lives of the ions decay and that of the triplet development could not be carried out. This was due to the very small fraction of the growing absorbance



Figure 5. Transient spectra in the laser photolysis of pyrene solutions in acetonitrile. (a) Spectra of radical cation (I), anions (II) and pyrene triplet (III) according to: (I) T. Shida and W. H. Hamill, J. Chem. Phys., 44, 2369 (1966); E. J. Land and G. Porter, Trans. Faraday Soc., 59, 2027 (1963). (II) W. I. Aalbersberg, G. J. Hoytink, E. I. Mackor, and W. P. Weijland, Mol. Phys., 2, 3049 (1959); J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, J. Phys. Chem. 69, 628 (1965). (III) G. Porter and M. W. Windsor, Proc. Roy. Soc. Ser. A, 245, 238 (1958); Z. Teitelbaum, R. Potashink, and M. Ottolenghi, Mol. Photochem., 3, 107 (1971). (b) Transient spectra of 2 imes 10<sup>-5</sup> M pyrene-2 imes 10<sup>-2</sup> M DEA in acetonitrile at room temperature. Key: -O-, 20 nsec after triggering;  $-\bullet$ , 2 µsec after triggering. (c) Transient spectra in a pyrene-DEA acetonitrile solution [concentrations as in (b)] in the presence of  $1.5 \times 10^{-3} M$  TCNB. Key: --O-, 20 nsec after triggering; -----, 400 nsec after triggering.

as well as to the superimposed decay of the triplet which, under our experimental conditions, interferes with the analysis of the growing-in kinetics. Because of the same reason it was impossible to obtain an accurate value for the ratio between the decay rate of the  $P^-$  absorbance at 490 nm and the corresponding growing-in of <sup>3</sup>P\* at 415 nm, from which the relative contributions of process (1) and the parallel path

$$P^- + DEA^+ \longrightarrow P + DEA$$
 (2)

could have been estimated.

Pulsed laser experiments in acetonitrile were also carried out in the presence of a low concentration (1.5) $\times$  10<sup>-3</sup> M) of a second acceptor (TCNB) which was added to the pyrene  $(2 \times 10^{-5} M)$ -DEA  $(2 \times 10^{-2})$ M) system. In view of the practically diffusion controlled rate constant (1.6  $\times$  10<sup>10</sup>  $M^{-1}$  sec<sup>-1</sup>) of the reaction between <sup>1</sup>P\* and DEA, it could be assumed that at least 90% of the quenching of <sup>1</sup>P\* was still carried out by DEA, with only a minor contribution from the process with TCNB. In fact, the transient spectrum at the end of the laser pulse obtained in the presence of TCNB (Figure 5c) is practically identical with that observed in the absence of TCNB. However, the slow second-order decay of the 490-nm band is now replaced by a fast ( $\tau_{1/2} \simeq 30$  nsec) exponential decay, which is accompanied by a matching growing-in of a band around 460 nm. In view of the known spectrum of the negative ion of TCNB (Figure 5a), the new process is readily attributed to the charge-transfer reaction

$$P^- + TCNB \longrightarrow P + TCNB^-;$$
  
 $k \simeq 2 \times 10^{-10} \sec^{-1} M^{-1}$  (3)

The growing-in of the absorbance in the microsecond range around 415 nm, attributed to reaction 1, is not observed in the presence of TCNB. This is in keeping with the total elimination of  $P^-$  via reaction 3.

b. Temperature Dependence of Triplet and Radical Ions Yields. Experiments for the determination of the temperature dependence of the relative triplet and ions yields in the pyrene-DEA system were carried out in methanol which maintains its fluidity over a relatively large temperature range. Upon lowering the temperature, a rise in the initial 415-nm absorption and a simultaneous drop in the 495- and 450-nm bands of  $P^-$  and DEA<sup>+</sup> is observed, confirming that the 415-nm band, attributed to <sup>3</sup>P<sup>\*</sup>, does not belong to any of the ions. The relevant data are shown in Figure 6. All yields were derived from absorbance measurements at the end of the laser pulse and are thus free from any contribution of processes 1 and 2.

## Discussion

a. Exciplex Formation and Intersystem Crossing in Nonpolar Solvents. The experimental data presented in Figures 2 and 4 for both pyrene and anthracene show a symmetric relation between the drop in the exciplex fluorescence and the corresponding rise in the triplet yield. This should actually be expected assuming that intersystem crossing and exciplex fluorescence are the only important deactivation routes in low-polarity systems. It should be pointed out, however, that the above data do not support a mechanism in which intersystem crossing takes place from the relaxed exciplex  $^{1}(A^{-}D^{+})^{*}$  in competition with fluorescence. Such a mechanism, *i.e.* 

$$^{1}(A^{-}D^{+})^{*} \xrightarrow{K_{f}} A + D + h\nu_{f}$$

and

$$(A^-D^+)^* \xrightarrow{K_{iec}} {}^{s}A^* + D$$

leads to the expressions

$$\phi_{f} = \frac{k_{f}}{k_{f} + K_{iso}} = k_{f}\tau; \quad \phi_{isc} = \frac{k_{iso}}{k_{f} + k_{iso}} = k_{iso}\tau \quad (4)$$

for the fluorescence and triplet yields correspondingly. Since in our systems  $\phi_f$  and  $\phi_{isc}$  exhibit a marked temperature sensitivity in ranges where  $\tau$  is only slightly affected by temperature (Figures 2, 3 and 4), the assumed mechanism would imply that a drop in  $k_f$  is always compensated by a rise in  $k_{iso}$  which will keep  $\tau$  unchanged. Such a coincidence is unreasonable, especially if it is maintained for two different acceptors in two different solvents. We conclude that the formation of the fluorescent exciplex state and intersystem crossing are two competing (rather than consecutive) processes. Schematically

$${}^{1}\mathbf{A}^{*} + \mathbf{D} \longrightarrow$$

$${}^{1}(\mathbf{A}^{-} \cdot \mathbf{D}^{+})^{\ddagger} \longrightarrow {}^{k_{\text{isc}}} {}^{3}\mathbf{A}^{*} + \mathbf{D}$$

$${}^{1}(\mathbf{A}^{-} \cdot \mathbf{D}^{+})^{\ddagger} \longrightarrow {}^{k_{f}}\mathbf{A} + \mathbf{D} + h\nu \quad (5)$$

where  $(A^{-}D^{+})^{\ddagger}$  denotes a nonrelaxed excited complex which can either deactivate to the fluorescent  $(A^{-}D^{+})^{\ast}$ state or undergo intersystem crossing to <sup>3</sup>A<sup>\*</sup>. It is the competition between these two processes which determines the temperature dependence of  $\phi_{t}$  and  $\phi_{isc}$ , which are thus given by

$$\phi_f = \frac{k_d}{k_d + k_{isc}}; \quad \phi_{isc} = \frac{k_{isc}}{k_d + k_{isc}} \tag{6}$$

The temperature dependence of  $\phi_f$  and  $\phi_{isc}$  in a range where  $\tau$  is relatively unaffected by temperature is now explained by the fact that  $\tau = 1/k_f$  is not included in the expressions of  $\phi_f$  and  $\phi_{isc}$ .

It is interesting at this point to reexamine the data of Mataga and Murata,<sup>7</sup> concerning the temperature dependence of the fluorescence of the tetracyanobenzene-toluene electron donor-acceptor (EDA) complex. Upon lowering the temperature from 293° to 212°, the CT fluorescence yields decreases by a factor of  $\sim 3$ while the fluorescence decay time drops by only 10%. In this respect, as well as for different other features,<sup>7</sup> the EDA complex behaves very similarly to the exciplexes of the present work. Thus, rather than invoking a drop in the radiative transition probability with a coincidental matching increase in the nonradiative transition probability of the relaxed EDA complex, fast radiationless transitions from non-relaxed excited states may be responsible for the experimental observations of Mataga and coworkers.

b. Intersystem Crossing and Ionization in Polar Solvents. The mechanism of the "fast" intersystem cross-



Figure 6. Relative yields of ions  $(\phi_P^{-r} \text{ and } \phi_{DEA}^{+r})$  and triplet state  $(\phi_{iee}^{r})$  in the laser photolysis of pyrene-DEA in methanol. Concentrations: [pyrene] = 2.5.  $\times 10^{-4}$ , [DEA] = 0.125 *M*.  $\phi_P^{-r}$  was estimated directly from the absorbance change at 490 nm.  $\phi_{DEA}^{+r}$  was obtained from the absorbance change around 465 nm, after substracting the contribution of P<sup>-</sup> (see Figure 5a). Similarly,  $\phi_{iee}^{r}$  was estimated from the absorbance change at 415 nm, correcting for the contribution of the ions at this wavelength.

ing in polar solvents (*i.e.*, the fraction  ${}^{3}A^{*}$  which is not formed via reaction 1) should be discussed in terms of the temperature effects presented in Figure 6. The most striking observation is the analogy between the effect of temperature on the triplet yield in the polar (Figure 6) and the nonpolar (Figures 2, 4) media. This clearly suggests a common, polarity independent, ISC mechanism, which leads to the same expression 6 for  $\phi_{isc}$  and, consequently, to a similar dependence of  $\phi_{isc}$ on T. It should be pointed out that the analogy between  $\phi_{isc}$  (T) in polar and nonpolar media cannot be extended in a simple way to the complementary processes of ionization  $(\phi_i)$  and exciplex formation  $(\phi_i)$ . This is due to the fact that according to (5) (neglecting a temperature dependent radiationless deactivation of  $(A^{-}D^{+})^{*}$ ) each excited complex which fails to yield <sup>3</sup>A<sup>\*</sup> will finally fluoresce. However, in a polar medium, ionic recombination processes within an initially formed ion pair<sup>3d</sup> may affect the final yield of ions. The scheme

$${}^{1}A^{*} + D \longrightarrow {}^{1}(A^{-}D^{+})^{\pm} \xrightarrow{k_{isc}} {}^{3}A^{*} + D$$

$$\downarrow^{k_{d}}$$

$$A + D \xleftarrow{k_{r}} (A_{s}^{-} \cdots D_{s}^{+}) \xrightarrow{k_{s}} A_{s}^{-} + D_{s}^{+}$$
(7)

will lead to the expression

(7) N. Mataga and Y. Murata, J. Amer. Chem. Soc., 91, 3144 (1969).

$$\phi_{i} = \left\{ \frac{k_{d}}{k_{d} + k_{isc}} \right\} \left\{ \frac{k_{s}}{k_{s} + k_{r}} \right\}$$
(8)

It is to the temperature dependence of the additional  $k_{\rm s}/(k_{\rm s}+k_{\rm r})$  that we attribute the different temperature effects on the yields of exciplex (Figures 2, 4) and ions (Figure 6). It is difficult to account quantitatively for the temperature dependence of  $k_s/(k_s + k_r)$ . (It is likely that  $k_s$  represents not only the rate of ion pair dissociation<sup>3d</sup> but also reflects the rate of escape from geminate ions recombination in a secondary, diffusional, photochemical cage<sup>8</sup>). However, it is reasonable to attribute the "wells" in the curves of  $\phi_{p}$ -<sup>r</sup> and  $\phi_{\text{DEA}^{+}}$  in Figure 6 to two opposite temperature effects. That on  $k_d/(k_d + k_{isc})$  which will decrease the ion pair  $(A_s - \cdots D_s)$  yield upon lowering the temperature, and that on  $k_s/(k_s + k_r)$  which, due to the increasing polarity at low temperatures (for methanol D = 32at room temperature and D = 58 at  $180^{\circ}$ K), will increase the probability of obtaining the separated ions from each ion pair formed. In fact, the initial drops in  $\phi_{DEA^+}$  and  $\phi_{p^-}$ , observed upon lowering the temperature, match the corresponding rise in  $\phi_{isc}$ <sup>r</sup> (Figure 6) exactly as  $\phi_{f}$  does (Figures 2 and 4). At still lower temperatures the effect is balanced by the rise in  $k_{\rm s}$  $(k_s + k_r)$ , giving rise to the "wells." A plateau is finally reached when  $k_s \gg k_r$ .

(c) Primary Processes in Excited Charge-Transfer systems. The conclusion that intersystem crossing, following excited donor-acceptor interactions, takes place from nonrelaxed states, calls for a more detailed description of the principal processes involved in the interaction. The following scheme is proposed as a general model, accounting for the primary phenomena in the systems of the present work.

#### Scheme I

$^{1}A^{*} + D \longrightarrow (^{1}A^{*}D)$	(population of locally excited singlet state)
$({}^{1}A^{*}D) \longrightarrow {}^{1}(A^{-}D^{+})_{vs}^{\ddagger}$	(internal conversion to nonre- laxed CT singlet state)
$^{1}(A^{-}D^{+})_{vs}^{\pm} \longrightarrow ^{1}(A^{-}D^{+})_{s}^{\pm}$	(vibrational relaxation $(k_v)$ )
$^{1}(A^{-}D^{+})_{v_{8}}^{\pm} \longrightarrow ^{3}A^{*} + D$	(intersystem crossing $(k_{isc})$ )
$(A^-D^+)_{\mathfrak{s}} \xrightarrow{\mathfrak{s}} A + D + h\nu_{\mathfrak{s}}$	(fluorescence of partially relaxed exciplex)
$(A^-D^+)_{s}^{\ddagger} \longrightarrow (A^-D^+)^{\ast}$	(solvent relaxation, nonpolar solvents $(k_s)$ )
$(A^-D^+)^* \longrightarrow A + D + h\nu$	(fluorescence of totally relaxed exciplex $(k_f)$ )
$(A^-D^+)_s^{\pm} \longrightarrow A_s^- + D_s^+$	(solvent relaxation followed by ionization, polar solvents)

The initially formed locally excited state  $({}^{1}A*D)$  can be described in a first approximation by the wave function

$${}^{1}\Psi_{\text{LE}} = a\Psi^{1,3}(A^{-}D^{+})^{*} + b\Psi({}^{1}A^{*}D); (b \gg a)$$

in which  $\Psi^{1,3}$  (A<sup>-</sup>D<sup>+</sup>)\* and  $\Psi$  (<sup>1</sup>A\*D) represent the contributions of the corresponding zero-order charge-

transfer and locally excited ( ${}^{1}L_{\alpha}$  for anthracene and  ${}^{1}L_{b}$  for pyrene) states. Fast internal conversion to the singlet CT state

$${}^{1}\Psi_{CT} = c\Psi^{1,3}(A^{-}D^{+})^{*} + d\Psi({}^{1}A^{*}D); \quad (c \gg d)$$

will subsequently take place. The initially formed CT state is denoted by  ${}^{1}(A^{-}D^{+})_{vs}^{\pm}$  to account for the excess of vibrational and solvent-relaxation energies. The value of the excess energy, approximated by the difference between the energy of  ${}^{1}A^{*}$  and that of the O-O transition of the relaxed exciplex emission in a nonpolar solvent, is  $\sim 0.6$  eV for anthracene-DEA and  $\sim 0.5$  eV for pyrene-DEA. Two different relaxation processes will then take place. An intramolecular vibrational deactivation  $(k_v)$ , followed by a slower solvent reorganization  $(k_s)$  around the dipolar structure of  ${}^{1}(A^{-}D)_{s}^{\pm}$ . The solvent relaxation process suggested for excited EDA complexes by Mataga and Murata<sup>7</sup> has been recently directly observed by Egawa, et al. via low-temperature time-resolved fluorescence experiments in the nanosecond range.<sup>9</sup> We suggest that intersystem crossing takes place in competition with vibrational relaxation rather than with the thermal solvent reorientation. Pending direct pulsed photolysis experiments with picosecond time resolution, this assumption cannot be rigorously verified in a direct way. However, the fact that intersystem crossing in polar solvents, where ionization replaces exciplex fluorescence, is of the same order of efficiency and exhibits a similar temperature dependence as in nonpolar systems, strongly supports the proposed mechanism. This is due to the fact that prior to solvent reorganization, the nature of the  $(A-D+)_s = CT$  state will be practically independent of the static dialectric constant of the medium. The principal interaction with the solvent will then involve electronic polarization.

A rationalization of the fact that intersystem crossing takes place from  ${}^{1}(A^{-}D^{+})_{vs}^{\dagger}$  but is not observed from  ${}^{1}(A^{-}D^{+})^{*}$ , should be sought in the general expression for the rate constant of a radiationless transition (ISC in the present case)

$$k_{\rm isc} = P_{\rho}CF$$

where  $P_{\rho}$  is the density of states factor, C is the electronic factor and F is the Franck-Condon factor.<sup>10</sup> In our present systems the large value of  $k_{isc}$  arises from the inclusion of a charge transfer character in the triplet state wave function

$${}^{3}\Psi = e\Psi^{1,3}(A^{-}D^{+})^{*} + f\Psi({}^{3}A^{*}D)$$

The experimental results presented above have been interpreted by assuming that  $k_{isc}$  is large for higher

<sup>(8)</sup> R. M. Noyes, J. Amer. Chem. Soc., 77, 2042 (1955).

<sup>(9)</sup> K. Egawa, N. Nakashima, N. Mataga, and Ch. Yamanaka, Chem. Phys. Lett., 8, 108 (1971).

<sup>(10)</sup> For a review see: J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970.

vibrational states but is negligible for the 0-point energy level of  ${}^{1}\Psi_{CT}$ . Such a behavior may be explained by assuming that a higher triplet state,  $T_x$ , (or states:  $T_{\nu}, T_{z}, \ldots$ ), rather than the lowest one  $(T_1)$  is responsible for intersystem crossing. A plausible possibility is that  $T_z$  is the lowest charge-transfer triplet  ${}^{3}\Psi_{CT}$ , for which  $e \gg f$ . The high efficiency of the  ${}^{1}\Psi_{CT} \rightarrow {}^{3}\Psi_{CT}$ radiationless transition (followed by rapid internal conversion to <sup>3</sup>A\*) will be due to the common high CT character of  ${}^{1}\Psi_{CT}$  and  ${}^{3}\Psi_{CT}$  leading to the very small energy gap between the two states, which will increase the Franck-Condon factor F. If  ${}^{3}\Psi_{CT}$  lies above  ${}^{1}\Psi_{CT}$ , <sup>11</sup> high vibronic levels but not the zero point state of the  ${}^{1}\Psi_{CT}$  exciplex, will be active in the radiationless process. It is also possible that  $T_{\mathbf{X}}$  is an upper locally excited triplet of the complex, exhibiting a higher CT character and a lower CT singlet-triplet energy gap than those corresponding to  $T_1$ . The involvement of higher triplet states has been previously proposed to account for the effects of temperature on the fluorescence of aromatic molecules in solution.<sup>12</sup> Thermal activation of the relaxed  $S_1$  state to higher vibrational levels leads to the enhancement of intersystem crossing. We should note, however, that in the present charge-transfer systems the temperature effect is in the opposite direction. Namely, the triplet yields decrease upon increasing temperature. As pointed above, this behavior is attributed to the competition between ISC and thermal relaxation. This situation is therefore different from that prevailing for most aromatic molecules in solution, where intersystem crossing in a relatively slow process which may efficiently compete with fluorescence but not with thermal deactivation from higher vibrational levels of  $S_1$ . We should finally add that the dependence of nonradiative decays on the initial vibrational excitation<sup>13</sup> can be interpreted in terms of Franck-Condon<sup>14</sup> and density of states<sup>15</sup> factors, without invoking intermediate electronic states such as  $T_x, T_y, \ldots$  In the systems of the present work we are inclined at present to prefer the intermediate triplet-state mechanism. However, further experimental and theoretical work will be required to account quantitatively for the rates of ISC in excited chargetransfer systems.

According to the above model the S-shaped curves, representing the effects of temperature on  $\phi_{isc}$ ,  $\phi_{i}$  and (partially) on  $\phi_i^{r}$ , are attributed to the temperature dependence of the ratios  $k_{\rm isc}/(k_{\rm d} + k_{\rm isc})$  and  $k_{\rm d}/(k_{\rm d} +$  $k_{isc}$ ). Since we are dealing with intersystem crossing from nonthermalized states, we may assume that  $k_{isc}$ is independent of temperature. In such a case the complete temperature effect will be due to the temperature dependence of the thermal deactivation rate constant,  $k_d$ , which we have identified as the vibrational relaxation parameter  $k_{\rm v}$ . Accordingly, the S-shaped behavior of  $k_v/(k_z + k_{isc})$  implies that  $k_v(T)$  exhibits a high-temperature upper limit  $k_v^{\max}(T)$  as well as a nonzero low-temperature limiting value,  $k_{x}^{\min}(T)$ . Thus, if the above interpretation of the data of the present work proves to be correct, it actually leads to the first experimental observation of temperature effects on the vibrational relaxation of electronically excited molecular systems in liquids. This calls for further work on radiationless processes in excited charge transfer systems.

Acknowledgment. This work was carried out under the sponsorship of the U.S. National Bureau of Standards.

(11) S. Iwata, J. Tanaka, and S. Nagakura, J. Chem. Phys., 47, 2203 (1967).

(12) R. G. Bennett and P. J. McCartin, *ibid.*, 44, 1969 (1966); A. Kearvell and F. Wilkinson, J. Chim. Phys., 66, 125 (1969); P. F. Jones and A. R. Calloway, *ibid.*, 66, 110 (1969).

(13) B. K. Selinger ar.d W. R. Ware, J. Chem. Phys., 53, 3160 (1970);
C. S. Parmenter and M. W. Schuyler, Chem. Phys. Lett., 6, 339 (1970);
E. W. Schlag and H. V. Weyssenhoff, J. Chem. Phys., 51, 2508 (1969).

(14) R. D. Levine, tc be published.

(15) A. Nitzan, J. Jortner, and P. M. Rentzepis, Chem. Phys. Lett., 8, 445 (1971); A. Nitzan and J. Jortner, to be published.

# Infrared Spectra and Dielectric Properties of Crystalline Hydrogen Cyanide

## by P. F. Krause and H. B. Friedrich\*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52240 (Received October 28, 1971) Publication costs assisted by the National Science Foundation

The infrared absorption intensities of the librational modes of the low-temperature phase of crystalline HCN and DCN have been measured. An interpretation of the measured intensities in terms of a dipolar coupling model suggests that the intrinsic dipole moment of HCN is significantly reduced in going from the gaseous to the crystalline state. The measured intensities were used to compute the static dielectric constant and the longitudinal-transverse splitting of the librational modes. Both calculations were in good agreement with the observed values.

### Introduction

We shall discuss in this paper measurements of the absorption intensities of the librational modes of crystalline HCN, the relationship between the measured intensities and the transverse-longitudinal mode splitting, the static dielectric constant, and the intrinsic dipole moment of HCN in the crystal. Several previous discussions<sup>1-7</sup> of the intensities of external modes in molecular crystals suggest that the interpretation of the intensities in terms of intrinsic moments is plausible for the librational modes in cases where the intrinsic dipole moment is fairly large, *i.e.*, for OCS,<sup>2</sup> ClCN, and BrCN,<sup>3</sup> and for HCl and HBr.<sup>7</sup> In cases where the intensity results solely from induced moments, such as the translational modes of N<sub>2</sub>,<sup>4,5</sup> CO<sub>2</sub>,<sup>4,6</sup> HCl,<sup>7</sup> and HBr,<sup>7</sup> the agreement between the observed and predicted intensities has been less satisfactory. However, the total intensity of the two translational modes of  $CO_2$ was found<sup>6</sup> to be in good agreement with that predicted.

The HCN crystal is similar to those of HCl and HBr in that the intermolecular interaction may involve hydrogen bonding. Also similar are the dramatic differences between the internal mode intensities in the gas and crystalline phases. Since the results of the intensity measurements<sup>7</sup> in crystalline HCl and HBr suggested a decrease in the intrinsic dipole moment relative to the gas phase, we have performed similar measurements on crystalline HCN to provide an additional test of the plausibility of the model used to interpret the measurements.

Two crystalline phases of HCN have been identified. The low-temperature phase is orthorhombic<sup>8</sup> ( $C_{2v}^{20}$ , *Imm*) with unit cell dimensions a = 4.13, b = 4.85, and c = 4.34 Å; the phase change occurs at about 170°K to a tetragonal modification ( $C_{4v}^9$ , *I4mm*) with a = 4.63and c = 4.34 Å. The phase change was first detected by specific heat measurements;<sup>9</sup> no discontinuity was observed in the earlier dielectric constant measurements.<sup>10</sup> Except for a contraction of the *b* axis and an expansion of the *a* axis, the two phases are similar in that the crystal consists of chains collinear with the c axis.<sup>8</sup>

The correlation diagram for the *Imm* phase is shown in Figure 1. The infrared- and Raman-active modes are the two internal stretching modes, the two bending modes, and two librational modes  $(B_1 \text{ and } B_2)$ . Since there is but one molecule per primitive cell, there are no translational optic modes. The internal-mode infrared<sup>11,12</sup> and Raman<sup>13</sup> spectra are in agreement with those predicted, except that the splitting of the bending mode does not appear unambiguously. The Raman spectra of the low-temperature phases of HCN and DCN show strong bands at 173 and 163  $cm^{-1}$ , respectively, along with weaker, more diffuse bands centered at 240 and 220  $cm^{-1}$ , respectively. The bands at 173 and 163  $\rm cm^{-1}$  have been assigned<sup>13</sup> to the unsplit librational modes in HCN and DCN, respectively. It is not too surprising that the bands are not split, since the a and b axes are not very different in the orthorhombic phase.

### **Experimental Section**

The HCN was prepared by addition of aqueous  $H_2SO_4$  (1:1) to aqueous NaCN (3 g of NaCN in 3 ml of  $H_2O$ ). It was dried by passage through three U tubes containing CaCl<sub>2</sub> heated to 35°. The DCN was pre-

- (1) O. Schnepp, J. Chem. Phys., 46, 3983 (1967).
- (2) H. B. Friedrich, *ibid.*, 47, 4269 (1967).
- (3) H. B. Friedrich, ibid., 52, 3005 (1970).
- (4) A. Ron and O. Schnepp, *ibid.*, 46, 3991 (1967).
- (5) R. V. St. Louis and O. Schnepp, ibid., 50, 5177 (1969).
- (6) K. G. Brown and W. T. King, *ibid.*, 52, 4437 (1970).
- (7) R. E. Carlson and H. B. Friedrich, ibid., 54, 2794 (1971).
- (8) W. J. Dulmage and W. N. Lipscomb, Actz Crystallogr., 4, 330 (1951).
- (9) W. F. Giauque and R. A. Ruehrwein, J. Amer. Chem. Soc., 61, 2626 (1939).
- (10) C. P. Smyth and S. A. McNeight, *ibid.*, 58, 1723 (1936).
- (11) R. E. Hoffman and D. F. Hornig, J. Chem. Phys., 17, 1163 (1949).
- (12) G. E. Hyde and D. F. Hornig, *ibid.*, 20, 647 (1952).
- (13) M. Pezolet and R. Savoie, Can. J. Chem., 47, 3041 (1969).



Figure 1. Correlation diagram for the Imm phase of crystalline HCN.

pared similarly using  $D_2O$  and  $D_2SO_4$  and also by the addition of aqueous KCN (1 g of KCN in 3 ml of  $D_2O$ ) to thoroughly dried  $P_2O_5$  at 0°. Further purification was accomplished by vacuum distillation.

Polycrystalline films were prepared by bleeding the gas through a needle valve at about  $5 \times 10^{-3}$  mmol/min and depositing on a single-crystal silicon window mounted in an Andonian liquid helium dewar equipped with high-density polyethylene outer windows. The window was kept at 130°K during the deposition to allow some annealing while depositing the film.

The film thickness was measured using an interference fringe technique;<sup>14</sup> the thickness is given by

$$l = N\lambda/2n \tag{1}$$

where l is the film thickness,  $\lambda$  the constant wavelength used to monitor the deposition, N the number of fringes, and n the index of refraction of the film. Depositions were monitored on a Perkin-Elmer 421 spectrophotometer with  $\lambda$  varying from 2.6 to 3.7  $\mu$ m. The 4000-600-cm<sup>-1</sup> region was also scanned using this instrument to verify the purity of the film; no features other than those due to HCN or DCN were observed.

All far-infrared spectra were recorded with a Beckman IR-11 spectrophotometer equipped with a pyroelectric crystal (triglycine sulfate) detector. The necessity of using the single-beam mode to measure intensities is illustrated in Figure 2, where two spectra of a 1.2-µm thick film of crystalline HCN are shown. The solid-line spectrum was obtained with the radiation chopped only between the source and the sample; the dashed-line spectrum was recorded in the double-beam mode, with the radiation also modulated between the sample and the detector. Since the sample was at 10°K and the detector at room temperature, the apparent absorption in the double-beam case is considerably enhanced when the ratio of the source to detector black body emissions is low, as is true in this region of the spectrum. All of the data to be reported here were obtained with the radiation chopped only between the source and the sample.



Figure 2. Infrared spectra of crystalline HCN; —, single beam; ---, double beam.

For all measurements the spectrum was recorded at either 10 or 77°K; the sample was then evaporated by warming the window and the background spectrum recorded after recocling the window. The background was drawn in as described previously,<sup>7</sup> and the integrated areas were measured using either a polar planimeter or calculated by adding areas of trapezoids. The integrated intensity,  $\Gamma$  (cm<sup>2</sup>/mmol) was calculated from the equation

$$\Gamma = (\rho l)^{-1} \int \ln (I_0/I) d \ln \omega$$
 (2)

where  $\rho$  is in millimoles per cubic centimeter, l is in centimeters, and  $\omega$  is the frequency in reciprocal centimeters. Values of the intensity

$$A = (\rho l)^{-1} \int \ln (I_0/I) d\omega \qquad (3)$$

were also computed using the approximate relation  $A \approx \Gamma \omega_0$ , where  $\omega_0$  is the band center.

Replots of typical experimental spectra for HCN and DCN are shown in Figures 3 and 4. Figure 3 shows the spectra of 2.04- $\mu$ m thick films of pure HCN at 10 and 77°K. The peak absorptions of 176 cm<sup>-1</sup> at  $10^{\circ}$ K and 173 cm<sup>-1</sup> at 77°K agree well with previous infrared and Raman measurements.<sup>13</sup> The spectra of two films containing HCN-DCN mixtures are shown in Figure The solid-line spectrum is of a film containing 95%4. HCN at 77°K; the band maximum is shifted to 171  $cm^{-1}$  and the intensity of the high-frequency shoulder has increased relative to pure HCN. The dashed-line spectrum is of a film containing 70% DCN (as determined by relative intensities of the internal modes). Here  $\omega_0$  is at 164 cm<sup>-1</sup> and the high-frequency shoulder at about 215  $cm^{-1}$ . If there were no coupling to the translational acoustic modes and if the librational mode were harmonic,  $\omega_0$  of pure DCN would be at 156 cm<sup>-1</sup>.

Since the x = 0 selection rule does not apply to the

(14) J. L. Hollenberg and D. A. Dows, J. Chem. Phys., 34, 1061 (1961).



Figure 3. Spectra of HCN; --, 10°K; ---, 77°K.



Figure 4. Spectra of mixed HCN-DCN films; —, 95% HCN; ---, 70% DCN.

mixed crystal and since the observed spectrum of the mixed crystals is not separable into HCN and DCN contributions, the extraction of intensities from the experimental spectrum is dependent on the model chosen. We choose here to assume the observed intensity in the mixed crystal is the sum of the intensities expected for pure HCN and DCN; this assumes that the intensity per molecule is independent of dynamical coupling. With this assumption, the HCN and DCN intensities were computed from the measured total intensity  $A_{\rm T}$ , using eq 4. Here  $F_{\rm H}$  and  $F_{\rm D}$  are the mole fractions of

$$A_{\rm T} = F_{\rm D}A_{\rm DCN} + F_{\rm H}A_{\rm DCN}I_0'/I_0 \qquad (4a)$$

$$A_{\mathrm{T}} = F_{\mathrm{H}}A_{\mathrm{HCN}} + F_{\mathrm{D}}A_{\mathrm{HCN}}I_{0}/I_{0}' \qquad (4\mathrm{b})$$

HCN and DCN, respectively;  $I_0$  and  $I_0'$  are the moments of inertia of HCN and DCN.

The measured intensities for pure HCN films at about 10 and at 77°K are listed in Table I, and the intensities obtained for HCN and DCN using eq 4 are shown in Table II. The error limits given are the 95% confidence limits of the means.

 Table I:
 Experimental Absorption Intensities of the

 Librational Mode of Pure HCN

la	A <sup>b</sup> (10°K)	A <sup>b</sup> (77°K)
1.02	3440	4270
1.02	2920	
1.93	3220	
1.93	3390	
1.99	4230	4930
1.99	4130	4030
2.04	3080	4090
2.04	3050	3640
Av	$3430 \pm 400$	$4190~\pm~580$

<sup>a</sup> Film thickness in micrometers calculated using eq 1 with n = 1.41 at 3700 cm<sup>-1</sup>. <sup>b</sup> Intensity in darks (cm<sup>-1</sup>/mmol). Calculated from eq 2 using  $A \approx \omega_0 \Gamma$ .  $\omega_0 = 176$  and 173 cm<sup>-1</sup> at 10 and 77°K, respectively. The density,  $\rho_{\tau} = 38.15$  mmol/cm<sup>3</sup> (ref 8).

Table II :	Experimental	Absorption	Intensities	of	Mixed
HCN-DCI	N Films⁴				

ω <sup>b</sup>	lc	$F_{\rm D}{}^{d}$	AHCN <sup>e</sup>	A DCN <sup>e</sup>
165	2.04	0.70	3450	2740
<b>16</b> 5	2.10	0.82	4690	3830
164	2.16	0.77	3980	3250
164	2.64	0.83	3950	3230
164	1.08	0.84	3590	2940
			Av 3930 $\pm$ 480	$3200~\pm~410$

<sup>a</sup> All data for films at 77°K. <sup>b</sup> Frequency in reciprocal centimeters. <sup>c</sup> Path length in micrometers. See Table I. <sup>d</sup> Mole fraction of DCN calculated from relative internal mode intensities. <sup>e</sup> Intensity in reciprocal centimeters per millimole.

### **Experimental Errors**

There is a possibility that systematic errors exist in each of the terms in eq 2. First, the density,  $\rho$ , which we have used is that derived from the crystal structure determination<sup>8</sup> at 153°K; this density is the upper limit to that of the film actually prepared. Although some error may be introduced by no correction for thermal expansion, it is not likely to be as serious as the assumption that the film contains perfect polycrystals with no vacancies. The density also enters indirectly into our calculation of the film thickness using eq 1 in that the index of refraction is a computed value which depends on the density.

The influence of the value of  $\rho$  on the intensities computed from the experimental data is shown in Table III. The value of  $\bar{n}$  was calculated as described in the next section. As the density is decreased, the value of the film thickness calculated from eq 1 is increased, so the resulting correction to the numbers shown in Tables I and II is fairly small, even for a 20% reduction in the density.

A more serious error arises from reflection corrections, since the difference between the index of refraction of

 Table III:
 Dependence of Measured Intensity on

 Film Density
 Particular State

ρ <sup>a</sup>	$\hat{n}^b$	$R_1^c$	$R_{\mathbf{A}}^{d}$
38.15	1.41	1.00	1.00
34.3	1.36	1.04	1.07
30.0	1.31	1.08	1.18

<sup>a</sup> Assumed density in millimoles per cubic centimeter. <sup>b</sup> Average index of refraction at 3700 cm<sup>-1</sup>. <sup>c</sup> Factor by which film thickness in Tables I and II must be multiplied. <sup>d</sup> Factor by which intensities in Tables I and II must be multiplied.

the silicon window and of the film is quite large. In order to estimate the necessary correction, a calculation similar to that of Maeda and Schatz<sup>15</sup> was performed. First, the optical constants were calculated using

$$\hat{n}^{a}(\omega) = n_{\omega}^{\ \alpha} + (\rho/2\pi^{2})\sum_{i}A_{i}^{\ \alpha}/(\omega_{i}^{2} - \omega^{2} + i\omega\gamma_{i}) \quad (5)$$

where  $\hat{n}^{\alpha}(\omega)$  is the complex index of refraction along the  $\alpha$ th crystallographic direction at frequency  $\omega$ ,  $n_{\omega}^{\alpha}$  is the high-frequency index of refraction,  $A_{i}^{\alpha}$  is the intensity in reciprocal centimeters per millimole of the *i*th band polarized along the  $\alpha$ th axis, and  $\gamma_{i}$  is the damping factor. The values of the parameters used for the calculation of the optical constants are shown in Table IV. The values of the internal mode intensities<sup>16</sup> used were not corrected for reflection effects, but since we are interested here only in the 176-cm<sup>-1</sup> region, no serious errors will result. For the calculation in eq 5, the components of the  $\nu_{2}$  and  $\nu_{L}$  intensities on the *a* and *b* axes were taken to be the same (see next section).

Table IV :	Parameters for Optical Constant Calculation				
Mode	$\omega^a$	$A^b$	γ		
<i>v</i> 3	3128	44820	30		
$\nu_1$	2101	6570	6		
$2\nu_2$	1626	3690	7		
<b>v</b> 2	828	6440	9.5		
٧L	176	$A_{L}$	10		

<sup>a</sup> All frequencies in reciprocal centimeters. <sup>b</sup> Band intensity in reciprocal centimeters per millimole, with  $\rho = 38.15 \text{ mmol/cm}^3$  (see text).

The average of the computed optical constants, nand  $\kappa$ , were then used to calculate<sup>17</sup> an "observed" spectrum. The area of this spectrum was then calculated using the same procedures used for the experimental spectra. The results of some typical calculations are shown in Table V. The values of  $A_L$ , the sum of the two librational mode intensities, calculated from the observed spectra are less than the input values of  $A_L$ ; the ratio of the input and calculated intensities depends somewhat on the magnitude of the intensity and the film thickness, and it is strongly dependent on the index of refraction of the substrate. Since the experimental data shown in Table I yield an observed intensity of about 3400 cm<sup>-1</sup>/mmol and were obtained with an average film thickness of 1.5  $\mu$ m and a silicon substrate with  $n_{\omega} = 3.42$ , the correction factor taken from Table V is 1.55. This results in a corrected experimental intensity of 5300  $\pm$  600 cm<sup>-1</sup>/mmol.

Table V:	Reflection Cor	rections		
$n_w^a$	lp	$A_{L}^{c}$	$A_{\rm L}$ (calcd)	R <sup>d</sup>
3.42	1.0	3000	1840	1.63
3.42	1.5	4000	2620	1.53
3.0	1.5	4000	2750	1.45
2.0	1.5	4000	3430	1.17
1.5	1.5	4000	3950	1.01
3.42	1.0	5000	3140	1.59
3.42	1.25	5000	3180	1.57
3.42	1.50	5000	3220	1.55
3.42	1.75	5000	3270	1.53
3.42	1.50	7000	4880	1.43

<sup>a</sup> Index of refraction of window. <sup>b</sup> Film thickness in micrometers. <sup>c</sup> Input librational mode intensity (see Table IV). <sup>d</sup> Factor by which observed intensity must be multiplied to yield true intensity.

### **Dipolar Interactions in Crystalline HCN**

(A) Dipolar Coupling Model. The dipolar coupling model we shall use is based on the formalism of Mandel and Mazur<sup>18</sup> and Decius<sup>19</sup> and is the same as that we have previously used.<sup>3,7</sup> The dipolar field propagation tensor,  $T^{ij}$  is defined as

$$T_{\alpha\beta}{}^{ij} = \nabla_{\alpha}\nabla_{\beta}(R^{ij})^{-1} \tag{6}$$

where  $R^{ij}$  is the distance between sites *i* and *j*. The total dipole moment is given by

$$\mathbf{p} = (\mathbf{U} - \alpha \mathbf{S})^{-1}(\mathbf{m} + \alpha^{0} \mathbf{E})$$
(7)

where  $\mathbf{S}^{ij} = \Sigma T^{ij}$ ,  $\boldsymbol{\alpha}$  is the polarizability tensor, **m** is the intrinsic dipole moment, and **U** is the unit tensor. The total interaction energy is given by

$$V_{d} = \frac{1}{2}\mathbf{m}\mathbf{S}(\mathbf{U} - \alpha\mathbf{S})^{-1}\mathbf{m} - \mathbf{E}(\mathbf{U} - \alpha\mathbf{S})^{-1}\cdot\mathbf{m} + \mathbf{O}(\mathbf{0}\mathbf{E}^{2}) \quad (8)$$

No quadrupole terms are included, since they do not contribute to the calculated intensity of librational modes in this case.

The field propagation tensor, S, was evaluated by two methods, and the results are shown in Table VI.

- (15) S. Maeda and P. N. Schatz, J. Chem. Phys., 35, 1617 (1961).
- (16) P. Krause, H. B. Friedrich, and A. Bandy, unpublished results.
  (17) O. S. Heavens, "Optical Properties of Thin Solid Films," Butterworths, London, 1955.
- (18) M. Mandel and P. Mazur, Physica, 24, 116 (1958).
- (19) J. C. Decius, J. Chem. Phys., 49, 1387 (1968).

The first column shows the result of summing all terms in a spherical shell of 70-Å radius. The second column gives the contribution of the Lorentz field,  $4\pi/3\bar{v}$ , where  $\bar{v}$  is the volume of the primitive cell. The third column gives the depolarization field for a slab-shaped crystal with the *ab* plane transverse. The sums of the first three terms are shown in column 4; the values computed by the method of deWette and Schacher<sup>20</sup> are shown in column 5, and it is seen that the two methods are in good agreement as has previously been found.<sup>7</sup> Note that although the crystallographic unit cell is orthorhombic, the contribution to **S** from the terms inside the sphere is nearly zero, since the three cell dimensions are not very different.

Table	VI: Calcu	Calculated S Tensor for $HCN^{a}$						
	$\mathbf{S}_{sph}^{b}$	<b>S</b> L <sup>c</sup>	$\mathbf{S}_{\mathbf{p}}^{d}$	8°	s'			
aa	0.00186	0.09637	0	0.09823	0.09822			
bb	-0.00015	0.09637	0	0.09622	0.09607			
cc	-0.00170	0.09637	-0.2891	-0.1944	-0.1943			

<sup>a</sup> All values in (ångströms)<sup>-3</sup>. <sup>b</sup> Sum of terms in spherical shell of 70-Å radius. <sup>c</sup>  $4\pi/3v$ , where v = 47.47 Å<sup>3</sup>/molecule. <sup>d</sup> Surface polarization term,  $-4\pi/v$ , for the *ab* plane transverse. <sup>e</sup> Sum of first three terms. <sup>f</sup> Obtained from the procedure of ref 20.

(B) Dielectric Constant. Although single-crystalline HCN should be pyroelectric, presumably the dielectric constant measured<sup>10</sup> for polycrystalline HCN involves no zero-field polarization. The high-frequency dielectric constant,  $\varepsilon_{\infty}$ , is given by<sup>21</sup>

$$\boldsymbol{\varepsilon}_{\infty} = \mathbf{U} + \frac{4\pi}{v} [(\mathbf{U} - \boldsymbol{\alpha} \mathbf{S})^{-1} \cdot \boldsymbol{\alpha}]$$
(9)

where **U** is the unit tensor, v the volume per primitive cell, and  $\alpha$  the electronic polarizability. Since we need consider only transverse cases, the **S** tensor to be used here is obtained from Table VI with the surface polarization term omitted.

Although the site symmetry of the HCN crystal suggests that  $\alpha_{zz}$  may be different than  $\alpha_{yy}$ , we have used the gas-phase polarizabilities to compute  $\mathbf{e}_{\infty}$  as shown in Table VII. The static dielectric constant may be computed using<sup>15,22</sup>

$$\epsilon_0 = \epsilon_{\infty} + (\rho/\pi^2) \sum (\bar{n}_i A_i / \omega_i^2) \qquad (10a)$$

or

$$n_0 = n_{\infty} + (\rho/2\pi^2) \sum A_i/\omega_i^2$$
 (10b)

In eq 10a, n for isotropic substances is defined<sup>15</sup> as

$$\dot{n} = \int n\alpha d\omega / \int \alpha d\omega \qquad (11)$$

where  $\alpha$  is the absorption coefficient,  $4\pi \varkappa \nu$ . For our case of nonisotropic but polycrystalline films we have taken  $\bar{n}$  to be

$$\bar{n} = \int \sum n_i \alpha_i d\omega / \int \sum \alpha_i d\omega_i$$
(12)

where the summation is over the components on the three crystallographic axes. The value of  $\epsilon_0$  obtained from eq 10a is shown in the second column of Table VII; the value obtained using eq 10b is shown in the third column. Since the two values should be the same,<sup>22</sup> the close agreement shown in Table VII suggests that the value of  $\bar{n}$  for the librational mode (1.31) is appropriate. The experimental values<sup>10</sup> of  $\epsilon_0$  at 87°K are 2.35, 2,39, and 2.33 at 50, 5, and 0.5 kHz, respectively.

Table VII:	Calculated Dielectric Constant					
	e a a	eg <sup>b</sup>	e0 <sup>C</sup>			
a	1.685	2.151	2.178			
b	1.680	2.146	2.173			
с	2.806	2.837	2.829			
ē	2.057	2.378	2.393			

<sup>a</sup> Calculated using eq 9 with v = 47.47 Å<sup>3</sup>/molecule,  $\alpha_{\perp} = 1.92$ , and  $\alpha_{\parallel \parallel} = 3.92$  Å<sup>3</sup> ("Landolt-Bornstein Zahlenwerte und Functionen," Vol. I, Part 3, Springer-Verlag, Berlin, 1951, p 510). <sup>b</sup> Calculated using eq 10a with  $\bar{\pi} = 1.31$  and the parameters of Table IV with  $A_{\rm L} = 5300$ . <sup>c</sup> Calculated using eq 10b.

Although the close agreement between the calculated and observed values of  $\epsilon_0$  suggests at least that the order of magnitude of our experimental value of  $A_{\rm L}$  is correct, the calculated dielectric constant does depend on several assumptions. For example, one might expect the polarizability along the chain axis to be somewhat different than the gas-phase value. If the parameters used in Table VII are used to compute  $\bar{\epsilon}_0$  with  $\alpha_{11} = 3.5$  instead of 3.92, the calculated value of  $\bar{\epsilon}_0$  becomes 2.33 instead of 2.39. The computed  $\bar{\epsilon}_0$  is also fairly sensitive to the lattice mode frequency. If  $\omega_{\rm L} =$ 173 cm<sup>-1</sup>, as it is at 77°K, then  $\epsilon_0 = 2.40$ . As the temperature is raised,  $\omega_L$  shifts<sup>13,23</sup> to 162 cm<sup>-1</sup> at 180°K (above the phase change), and the calculated value of  $\bar{\epsilon}_0$  becomes 2.45. In general, as the temperature is raised, both the density and the lattice mode frequencies will decrease. The density change tends to decrease  $\bar{\epsilon}_0$  as the temperature rises, but the frequency changes tend to increase  $\bar{\epsilon}_0$ .

(C) Calculated Intensities. The calculated intensity is given by<sup>7</sup>

$$\Gamma = (8\pi^3 Na/3hc) |\langle 0|\mathbf{Bm}|1\rangle^2$$
(13)

where **B** =  $(\mathbf{U} - \alpha \mathbf{S})^{-1}$ , and the corresponding experimental value<sup>22,24</sup> is given by

(20) F. W. deWette and G. E. Schacher, Phys. Rev. A, 137, 78 (1965).

- (21) R. Frech and J. C. Decius, J. Chem. Phys., 51, 5315 (1969).
- (22) S. Maeda and P. N. Schatz, *ibid.*, 36, 571 (1962).
- (23) R. Savoie, private communication.
- (24) K. H. Illinger and C. P. Smyth, J. Chem. Phys., 35, 392 (1961).

The Journal of Physical Chemistry, Vol. 76, No. 8, 1972

IR SPECTRA AND DIELECTRIC PROPERTIES OF CRYSTALLINE HCN

$$\Gamma = (\rho l)^{-1} \int n \ln (I_0/I) d \ln \omega \qquad (14)$$

For a particular unit cell  $(\kappa = 0)$  normal coordinate,  $Q\gamma$ , the matrix element in eq 13 is given by

$$(\partial(\mathbf{Bm})/\partial Q\gamma)\langle 0|Q\gamma|1\rangle$$

To avoid including the frequency in the computed intensity, we prefer to make use of  $A \approx \omega_0 \Gamma$  and compute the intensity, A, using

$$A\gamma = [Na\pi/3000c^2\bar{n}\gamma](\partial \mathbf{p}/\partial Q\gamma)^2$$
(15)

where  $\bar{n}$  is defined by eq 12 and the experimental value of  $A\gamma$  is given by eq 3.

According to eq 7 and 8, the dipole derivative is given by

$$(\partial \mathbf{p}/\partial Q\gamma) = \mathbf{B}(\partial \mathbf{m}/\partial Q\gamma) + \mathbf{B}(\partial \alpha/\partial Q\gamma)\mathbf{SBm}$$
 (16)

The calculated values for the dipole derivatives as a function of the magnitude of the intrinsic dipole moment, m, are shown in Table VIII. The first two columns give the dipole derivatives and intensities calculated for the librational modes with  $\alpha$  and  $(\partial \alpha / \partial Q)$  both zero; *i.e.*, no induced moments are included. The third and fourth columns give the corresponding values with the induced moments included. The term in eq 16 containing  $(\partial \alpha / \partial Q)$  results in  $(\partial \mathbf{p} / \partial Q)$  being somewhat different for the *ab* and *ac* planes transverse, for example. The values shown in Table VIII are the average values for the two possible transverse orientations for each mode.

Table VIII:	Calculated Dipole Derivatives and Intensities						
Mode	$(\partial m/\partial Q)^a$	A <sup>b</sup>	$(\partial p/\partial Q)^c$	$A^{d}$			
Bı	23 (m)	2530	29.5 (m)	4160			
$\mathbf{B}_2$	23 (m)	2530	29.4 (m)	4140			
$B_1 + B_2$		5060		8300			
me	$3.06 \pm$	0.17	$2.39 \pm$	0.13			

<sup>a</sup> Calculated from eq 16 with  $\alpha$  and  $(\partial \alpha / \partial Q) = 0$ . <sup>b</sup> Intensity computed from  $(\partial m / \partial Q)$  with m = 2.99 D: D. E. Stogryn and A. P. Stogryn, *Mol. Phys.*, **11**, 371 (1966). <sup>c</sup> Calculated from eq 16 with  $\alpha_{||}$  and  $\alpha_{\perp} = 3.92$  and 1.92 Å<sup>3</sup>, respectively. <sup>d</sup> Intensity computed from  $(\partial p / \partial Q)$  with m = 2.99 D (see the reference of footnote b). <sup>e</sup> Value of m in debyes required to fit the experimental value of A (5300 ± 600 cm<sup>-1</sup>/mmol) with  $\bar{\pi} =$ 1.31.

Although neglect of all induced moments results in a computed intrinsic dipole moment essentially the same as the gas-phase value, the calculation which includes the classical induced moments suggests that the intrinsic moment in the crystal is less than the gas-phase value, in agreement with the conclusions reached for the HCl and HBr crystals.<sup>7</sup>

(D) Longitudinal-Transverse Splitting. The longitudinal mode frequency may be computed<sup>25</sup> using the first term of eq 8 to give

$$\lambda_i = \lambda_i^0 - (\partial \mathbf{m} / \partial Q_i) \mathbf{S} (\partial \mathbf{p} / \partial Q_i)$$
(17)

where we have substituted  $\mathbf{p} = (\mathbf{U} - \mathbf{\alpha}\mathbf{S})^{-1}\mathbf{m}$ . Here  $\lambda_i = 4\pi^2 \nu_i^2$  and  $\lambda_i^0$  refers to the frequency of the *i*th mode to be expected in the absence of dipolar coupling. The longitudinal-transverse splitting for the mode polarized along the *a* axis, for example, is given by

)

$$\lambda_{\rm L} = \lambda_{\rm T} - (\partial \mathbf{m}/\partial Q)(\mathbf{S}_{bc} - \mathbf{S}_{ab})(\partial \mathbf{p}/\partial Q) \qquad (18)$$

where the subscripts on S indicate which plane is transverse.

We have evaluated  $\lambda_{\rm L}$  using the two models used in Table VIII. First, we have calculated the splitting using  $(\partial \mathbf{m}/\partial Q)$  from Table VII with several values of m and, to be consistent, with  $(\partial \mathbf{p}/\partial Q) = (\partial \mathbf{m}/\partial Q)$  in eq 18. The results are shown in Table IX. Note that if the value of m calculated from the experimental intensities is used, *i.e.*, 3.06, the calculated  $\omega_{\rm L}$  is 267 cm<sup>-1</sup>. Savoie has measured<sup>23</sup>  $\omega_{\rm L}$  to be at 249 cm<sup>-1</sup> with  $\omega_{\rm T} =$ 176 cm<sup>-1</sup>. The value of m required to fit the experimental value of  $\omega_{\rm L}$  is 2.68. Thus, the values of m obtained from the intensities and from the L0–T0 splitting are not in good agreement.

Table IX: Calculated	Calculated Longitudinal Mode Frequency				
$m^a$	$\omega L^b$	ωL <sup>c</sup>			
3.06	267	287			
2.90	259	278			
2.68	249	266			
2.39	236	250			

<sup>a</sup> Intrinsic dipole moment in debyes. <sup>b</sup> Longitudinal mode in reciprocal centimeters calculated using eq 18 with  $(\partial p/\partial Q) = (\partial m/\partial Q)$ .  $\omega_{\rm T} = 176$  cm<sup>-1</sup>. <sup>c</sup> Calculated using eq 18 with  $\omega_{\rm T} = 176$  cm<sup>-1</sup>.

In contrast, if eq 18, along with the value of  $(\partial \mathbf{p}/\partial Q)$ from Table VIII, is used to compute  $\omega_{\rm L}$ , the value of  $\omega_{\rm L}$  computed from the intensity data agrees very well with the observed value, *i.e.*, with m = 2.39, the computed  $\omega_{\rm L}$  agrees with the experimental value. The values of  $\omega_{\rm L}$  for the two librational modes, B<sub>1</sub> and B<sub>2</sub>, are computed to be the same for all cases.

### Discussion

The model we have used to interpret our results is certainly open to question, since it is based on the classical interaction of point dipoles. Nevertheless, since the dielectric constant and particularly the longitudinal mode calculation are in agreement with the dipole derivatives we have obtained from the measured intensities, the model used is at least self-consistent. Since the observables relate to the polarization or the dipole moment per unit volume, it is clear than an interpretation of our results in terms of a molecular dipole mo-

(25) H. B. Friedrich and R. E. Carlson, J. Chem. Phys., 53, 4441 (1970).

ment in the crystal is dependent on the model used to relate the polarization to the molecular property which is not directly observable.

If the intrinsic dipole moment is indeed lower in the crystal than in the gas phase, then we must consider what effect nonclassical interactions will have on the measured intensities. Although we know of no way to make accurate *ab initio* calculations to determine m in the crystal, we can discuss<sup>7</sup> in general terms the influence of covalent intermolecular bonding on the librational mode intensities. The intrinsic dipole moment of a molecule in the crystal may be represented as

$$\mathbf{m} = \mathbf{m}^{0}(R) + \mathbf{m}'(R, R', \theta)$$
(19)

where  $\mathbf{m}^0$  is the gas-phase moment which is a function only of the intramolecular distances, R; m' represents all changes which occur when the crystal is formed and, in general, will be a function of R', the intermolecular distances,  $\theta$ , the relative orientations in the crystal, and R. If m' is independent of  $\theta$ , then eq 19 may be written in terms of an orientation vector,  $\Lambda$ , and the scalar moments as

$$\mathbf{m} = \mathbf{\Lambda} m = \mathbf{\Lambda} [m^0(R) + m'(R, R')]$$
(20)

It may then be shown<sup>7</sup> that

$$(\partial \mathbf{p}/\partial Q) = [(\partial \mathbf{B}/\partial Q)\mathbf{\Lambda} + \mathbf{B}(\partial \mathbf{\Lambda}/\partial Q]m + \mathbf{B}\mathbf{\Lambda}(\partial m'/\partial Q)$$
 (21)

which is the same as eq 16, since  $(\partial R'/\partial Q) = 0$  for librational modes.

Some indication of the validity of the assumptions used above is provided by the measured value of the intensity of the internal bending mode in the gas and crystalline phases. Thus, the gas-phase value<sup>12</sup> for  $(\partial m/\partial Q)$  is 57 esu. Using only the second term of eq 16,  $(\partial p/\partial Q_2)$  is predicted to be 70 esu in the crystal; the value derived from the experimental intensity shown in Table IV is 75 esu. Thus, for the bending mode, most of the change in the intensity can be accounted for without including an explicit dependence of m' on  $\theta$  in eq 19. The stretching mode intensities, however, are drastically different in the gas and crystal phases, indicating that m' is strongly a function of R'.

In our discussions we have made use only of the intensity data obtained at about  $10^{\circ}$ K. The total band intensity increased somewhat at  $77^{\circ}$ K, but most of the increase is attributable to the high-frequency wing. Since we have no quantitative explanation for this increase, we have used only the  $10^{\circ}$ K data.

The spectra of the mixed HCN-DCN films show a continuous decrease of  $\omega_0$  as the mole fraction of DCN increases. The band is broadened considerably, but the total band intensity is roughly the same as would be predicted on the basis of a sum of pure crystal intensities. Despite the fact that the dynamics and selection rules for the mixed films are quite different than for pure crystals, since most of the intensity of the librational mode is due to the intrinsic moment, it is not too surprising that the intensity per molecule remains relatively constant in the mixed films.

Acknowledgment. We are grateful to Professor R. Savoie for helpful discussions and for providing us with the results of his measurements of the longitudinal modes prior to publication. This work was supported by the National Science Foundation.

# **Region of Water**<sup>1</sup>

### by W. F. Murphy and H. J. Bernstein\*

Division of Chemistry, National Research Council of Canada, Ottawa, Canada (Received October 26, 1971) Publication costs assisted by the National Research Council of Canada

The Raman spectra for some isotopic forms of liquid water  $(H_2O, D_2O)$ , and the OH region of HOD) have been obtained in the stretching region, separated into their isotropic and anisotropic components, and decomposed into a series of symmetric bands. The number of bands, their approximate frequency positions, and their depolarization ratios were dictated on the basis of a simple model for liquid water involving two molecular species having either four or three hydrogen bonds. The results provide a self-consistent description of the observed Raman spectra. They are also qualitatively consistent with the infrared spectra and the effect of temperature on these spectra.

### Introduction

The structure of liquid water is a very complex problem, which has been treated from several points of view.<sup>2a-e</sup> Vibrational spectra<sup>2d</sup> have been used to support various models, and a specific region of interest has been the stretching region. We restrict ourselves here to consideration of this region for water and its deuterated analogs.

A suitable model for describing the stretching region observed in the infrared and Raman spectra of these liquids should provide a rationale for the following experimental results. (1) The intensity distribution for liquid  $H_2O$  (and  $D_2O$ ) in the infrared spectrum<sup>3</sup> is significantly different from that for the corresponding Raman spectrum.<sup>4</sup> (2) The depolarization ratio of the Raman spectrum changes across the band.<sup>5</sup> (3) There is a significant difference<sup>6</sup> between the contours observed in the infrared and Raman spectra of HOD. (4) The recent availability of improved Raman techniques led to the observation of a high-frequency shoulder in the Raman spectrum of  $H_2O$ , HOD, and  $D_2 O.^7$ (5) Any model should explain the observed temperature dependence<sup>4,8</sup> of these bands.

We shall describe here a simple model for water structure which can account for these results. This model combines features of previously published water models, as indicated below. The spectral features will be described in terms of vibrational stretching modes of two types of hydrogen-bonded water molecules. These are the fully bonded tetracoordinated species and the species of the tricoordinated type which has a free OH. The suitability of this model was demonstrated for both the isotropic and anisotropic components of the observed Raman spectra. This requires not only that the total intensity be described in terms of the model, but also the intensity of these individual components, that is, the depolarization ratio throughout the band.

## **Experimental Procedure and Data Handling**

The Raman spectra of liquid H<sub>2</sub>O, D<sub>2</sub>O, and 5 mol % H<sub>2</sub>O in D<sub>2</sub>O were recorded using the data system developed in this laboratory. The samples were at room temperature and in a  $1 \times 1 \times 5$  cm fused silica cell. The source was a CRL argon laser operating at 4880 A with a power of about 700 mW. A Spex 1400 double monochromater and EMI 6256 photomultiplier were used with photon-counting detection. The two polarized components of the scattered light were measured by using a Polaroid HN-22 analyzer in the scattered beam and recording the spectra of the light polarized parallel and perpendicular to the polarization vector of the incident light, which was fixed perpendicular to the optical axis of the spectrometer. In terms of the generally accepted scattering geometry conventions,<sup>9</sup> these are the Y(ZZ)X and Y(ZY)Xcomponents, respectively. The spectra were obtained several times and remained constant to within the statistical counting errors.

The spectra were first processed using a program

- (6) H. R. Wyss and M. Falk, Can. J. Chem., 48, 607 (1970).
- (7) G. E. Walrafen, J. Chem. Phys., 52, 4176 (1970).

<sup>(1)</sup> Issued as NRCC No. 12515.

<sup>(2) (</sup>a) D. Eisenberg and W. Kauzman, "The Structure and Properties of Water," Cxford University Press, London, 1969; (b) R. A. Horne, Ed., "Structure and Processes in Water and Aqueous Solutions," Wiley, New York, N. Y., 1971; (c) J. Lee Kavanau, "Water and Solute-Water Interactions," Holden-Day, San Francisco, Calif., 1964; (d) a comprehensive literature review of the vibrational spectra of liquid water is presented in K. M. Cunningham, Ph.D. Thesis, Yale University, 1971.

<sup>(3)</sup> A. N. Rusk, D. Williams, and M. R. Querry, J. Opt. Soc. Amer.,
61, 895 (1971); R. E. Frech, Ph.D. Thesis, University of Minnesota,
1968.

<sup>(4)</sup> G. E. Walrafen, J. Chem. Phys., 47, 114 (1967).

<sup>(5)</sup> J. W. Schultz and D. F. Hornig, J. Phys. Chem., 65, 2131 (1961).

<sup>(8)</sup> J. Schiffer and D. F. Hornig, *ibid.*, 49, 4150 (1968).

<sup>(9)</sup> T. C. Damen, S. P. S. Porto, and B. Tell, Phys. Rev., 142, 570 (1966).



Figure 1. Parallel polarized component of the Raman spectrum of liquid  $H_2O$  in the OH stretching region; observed and corrected spectra.

which corrects the measured intensities for the dead time losses due to the finite pulse pair resolution time of the counting system, subtracts the dark count, converts the data to a linear frequency shift scale which includes correction for the periodic scanning error of our spectrometer, and finally corrects the observed intensities for the spectral sensitivity of the spectrometer system. The special importance of the sensitivity correction in this type of study is obvious from Figure 1, which shows the uncorrected input and corrected output data. Certainly any meaningful quantitative discussion of the shape of this band must be based on data which have undergone such a correction.

The isotropic and anisotropic components of the scattering spectrum were derived from the parallel and perpendicular components following a procedure similar to that described by Scherer.<sup>10</sup> Thus, if a band is completely depolarized ( $\rho_s = 3/4$ ), it will have only an anisotropic component, while a completely polarized band ( $\rho_s = 0$ ) will have only an isotropic component. A partially polarized band ( $0 < \rho_s < 3/4$ ) will have components in both spectra. Furthermore, it is expected from band contour considerations<sup>11</sup> that the bandwidth of the anisotropic component.

No further processing of the data was applied before using it in the band-fitting procedure. In particular, the data were not smoothed or otherwise treated to eliminate noise.

The band decomposition was carried out using a modification of the band-fitting program developed by Jones and coworkers.<sup>12</sup> This program was altered to allow use with Raman spectra and extended to allow selected band parameters to be held fixed or linearly related to one another.



Figure 2. Water species and related vibrational modes which contribute to the OH stretching region.

The Model. The model is based on the assumption that liquid water is made up of predominantly one type of water molecule which is tetracoordinated via hydrogen bonds with four other water molecules<sup>2c</sup> (see Figure 2). This structure corresponds to that of crystalline ice, and the bands in the vibrational spectrum of the solid are quite narrow.<sup>13</sup> In the liquid, however, a distribution of configurations involving differences in bond lengths and angles occurs (see, e.g., ref 2c), and this results in the observation of broad bands in the vibrational spectra. For our purpose we assume this tetracoordinated species has approximate  $C_{2v}$  symmetry, and its spectrum to a good first approximation is independent of coupling beyond the first coordination shell.<sup>14</sup>

The stretching vibrations of this species may thus be classified as symmetric and asymmetric modes having frequencies  $\nu_1$  and  $\nu_3$ , respectively. The symmetric mode is expected to have an intense Raman band which is highly polarized ( $\rho_{s} < 0.25$ ), while the asymmetric mode should be weaker and virtually completely depolarized ( $\rho_s \simeq 3/4$ ). On the other hand,  $\nu_3$  is expected to be stronger than  $\nu_1$  in the infrared spectrum due to the complementary nature of infrared and Raman intensities. The anisotropic Raman spectrum (Figure 3) has a maximum at  $3455 \pm 5 \text{ cm}^{-1}$  which is thus associated with the asymmetric stretching frequency,  $\nu_3$ . It is expected then that the observed frequency for the OH vibration of tetracoordinated HOD at  $3400 \pm 5$  $cm^{-1}$  (see below) will be the average of the symmetric and asymmetric frequencies of H<sub>2</sub>O

$$\nu_{\rm OH}({\rm HOD}) = (1/2)(\nu_1 + \nu_3)$$
 (1)

Using the above values for  $\nu_3$  and  $\nu_{OH}(HOD)$ , the

(10) J. R. Scherer, S. Kint and G. F. Bailey, J. Mol. Spectrosc., 39, 146 (1971).

(11) A. E. Douglas and D. H. Rank, J. Opt. Soc. Amer., 38, 281
(1948); I. I. Sobelman, Izv. Akad. Nauk SSSR, Ser. Fiz., 17, 554
(1953).

(12) J. Pitha and R. N. Jones, "Optimization Methods for Fitting Curves to Infrared Band Envelopes," NRC Bulletin No. 12, National Research Council of Canada, Ottawa, 1968.

(13) J. E. Bertie and E. Whalley, J. Chem. Phys., 40, 1637 (1964);
 M. J. Taylor and E. Whalley, *ibid.*, 40, 1660 (1964).

(14) G. E. Walrafen in "Hydrogen-Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor and Francis, London, 1968. symmetric frequency of H<sub>2</sub>O is estimated to be about 3345 cm<sup>-1</sup>, roughly intermediate between the two strong features observed in the isotropic spectrum. These features then could be explained by Fermi resonance between the overtone of the bending vibration at  $1640 \pm 5$  cm<sup>-1</sup> and the symmetric stretching vibration.<sup>5</sup> If these features are part of a Fermi doublet, say  $\nu_A$  and  $\nu_B$ , then their average frequency should be the same as that for the unperturbed frequencies, <sup>15</sup> *i.e.* 

$$(1/_2)(\nu_{1A} + \nu_{1B}) = (1/_2)(\nu_1 + 2\nu_2)$$
 (2)

Therefore, substituting for  $\nu_1$  from eq 1 into eq 2 gives

$$\nu_{1A} + \nu_{1B} = 2\nu_2 - \nu_2 + 2\nu_{OH}(HOD) = 6625 \pm 25 \text{ cm}^{-1}$$
 (3)

In the Raman spectrum of tetracoordinated hydrogenbonded H<sub>2</sub>O in the OH stretching region, one should therefore observe a partially polarized Fermi doublet whose frequencies are symmetric about 3312 cm<sup>-1</sup>. For D<sub>2</sub>O ( $\nu_2 = 1210$ ,  $\nu_3 = 2540$ , and  $\nu_{OD}(HOD) =$ 2500 cm<sup>-1</sup>), parallel reasoning gives  $\nu_{1A} + \nu_{1B} =$ 4880  $\pm$  25 cm<sup>-1</sup>.

The predicted spectrum of the tetracoordinated species thus can explain several of the experimental results listed above. The two strong features in the Raman effect are due to the Fermi resonance of  $\nu_1$  with the first overtone of  $\nu_2$ , the difference between the infrared and Raman spectrum is due to the change in relative intensity of  $\nu_1$  and  $\nu_3$ , and the change in depolarization ratio across the band is due to the contribution from the depolarized  $\nu_3$ .

However, on the basis of this species alone, the spectrum of HOD in the OH (and OD) region would be expected to be a single band with little difference between the infrared and Raman contours. Also, another type of OH stretching vibration is necessary to explain the high-frequency shoulder observed in all of these spectra. One choice for the source of this shoulder is the scattering due to a free OH bond, *i.e.*, one not participating in a hydrogen bond. Since we have assumed that liquid water is mainly made up of tetracoordinated molecules, ( $\sim C_{2v}$ ), the free OH could occur most easily in the next most probable species, a molecule  $(C_s)$  with three hydrogen bonds<sup>14</sup> (see Figure 2). As indicated in Figure 2, we assume that the stretching frequencies of the tricoordinated species with two bonded OH's are close enough to those of the tetracoordinated species that their bands will be obscured by the more intense bands of the latter. Thus, the spectrum of this tricoordinated species will be neglected.

The tricoordinated species with one bonded OH will then have a high-frequency band associated with the free OH vibration. In addition, it will have a bonded OH vibration at lower frequency, which, in fact, provides an explanation for the difference between the infrared and Raman spectra of HOD. As shown by Wyss and Falk,<sup>6</sup> the infrared frequency at the band intensity maximum is different in value from that observed in the Raman spectrum, namely 3400 and 3420  $cm^{-1}$ , respectively. This behavior can be explained on the basis that this band is made up of two unresolved bands due to the bonded OH vibrations of tetra- and tricoordinated HOD molecules. This shift in band maxima between Raman and infrared is caused by the difference in the contribution of the tricoordinated species to the total intensity of the band; *i.e.*, this band is relatively weaker in the absorption spectrum. This intensity relation is justified by noting that free OH stretching modes are weaker relative to bonded OH bands in the infrared compared to the Raman. This fact is extended to postulate that bonded OH stretching vibrations in waters with a free OH will also be weaker in the infrared compared to the bonded OH bands of tetracoordinated molecules. Thus, in the infrared band there is little intensity contribution from the tricoordinated species, giving an estimate of  $\nu_{OH}$ - $(HOD) = 3400 \text{ cm}^{-1}$  for the tetracoordinated species.<sup>16</sup> The frequency of the tricoordinated bonded OH band is sufficiently higher than  $3400 \text{ cm}^{-1}$  to give the observed Raman maximum at  $3420 \text{ cm}^{-1}$ .

Thus, for HOD we expect a band at  $3400 \text{ cm}^{-1}$  due to the OH vibration of the tetracoordinated species, the free OH vibration at 3620-3640 cm<sup>-1</sup>, and a third band, intermediate in frequency, due to the bonded OH vibration of the tricoordinated species. These latter two are expected to be relatively weak in the infrared. Similarly, for H<sub>2</sub>O, in addition to the bands of the tetracoordinated species, two bands due to the tricoordinated species are expected. The shoulder attributed to the free OH in H<sub>2</sub>O and the shoulder due to OH in HOD are observed at very nearly the same frequency. By analogy, the frequencies of the bonded OH in the tricoordinated species of H<sub>2</sub>O and HOD are expected to be nearly the same. These bands are also expected to be weak in the infrared.

On the basis of these two species, then, the observed frequency and intensity properties of the infrared and Raman spectra of the isotopic forms of liquid water may be rationalized. The temperature behavior of these spectra will be considered in the Results and Discussion.

Band-Fitting Procedure. This model was used as the basis of a band-fitting or band-decomposition procedure in an attempt to reproduce the observed Raman profiles (Figures 3, 4, and 5). The band contours were approximated by symmetric Gaussian Lorentzian prod-

<sup>(15)</sup> G. Placzek, "Rayleigh and Raman Scattering," U. S. Atomic Energy Commission UCRL-TRANS-526(L), 1962, pp 139-145; translated from "Marx Handbuch der Radiologie," Vol. 6, Part II, 2nd ed, Akademie Verlagsgesellshaft, Leipzig, 1934, pp 205-374.

<sup>(16)</sup> The temperature dependence of the infrared spectrum of HOD<sup>6</sup> leads to a better estimate of  $\nu_{OH}(HOD) = 3390 \text{ cm}^{-1}$ . However, this should make little difference in our results.



Figure 3. Isotropic (above) and anisotropic (below) components of the Raman spectrum of  $H_2O$ , showing observed spectrum and results of band decomposition procedure. The intensity calibration marks are the same in both spectra.

uct functions of the type

$$I(\nu) = \frac{x_1 \exp(-x_4(\nu - x_2)^2)}{1 + x_3(\nu - x_2)^2}$$

The parameters  $x_1$ ,  $x_3$ , and  $x_4$  were varied as necessary in the least-squares procedure in order to attain a best fit. The band position,  $x_2$ , was constrained to be equal for the isotropic and anisotropic components of a single band.

For a set of parameters for which convergence was achieved, an important criterion for goodness of fit was the requirement that the bandwidth of the anisotropic component be greater than that for the isotropic component of a given band. The positions of the bands due to the tetracoordinated species were forced to maintain the fixed or relative range of values estimated above. Different sets of frequency values for the two bands of the tricoordinated species were then tried until a mutually consistent set was obtained which reproduced the spectra of all the isotopic species.

The additional band shown in the HOD spectrum  $(ca. 3000 \text{ cm}^{-1} \text{ in Figure 5})$  is due to D<sub>2</sub>O. The band parameters were found by fitting a D<sub>2</sub>O spectrum taken under comparable experimental conditions. These values were then used to estimate the background in the HOD spectrum.

Previous results' and our own preliminary investigation indicated that there is no unexpected difference between the contours of the OH and the OD bands of HOD. We thus did not consider the OD band in detail. We are confident that it may be decomposed in a manner strictly analogous to our OH results.

### **Results and Discussion**

The results of the fitting procedure are plotted in Figures 3, 4, and 5, and listed in Table I. Note that the total calculated intensity is plotted in the figures; it



Figure 4. Isotropic (above) and anisotropic (below) components of the Raman spectrum of  $D_2O$ , showing the observed spectrum and results of band decomposition procedure. The intensity calibration marks are the same in both spectra.



Figure 5. Isotropic (above) and anisotropic (below) components of the Raman spectrum of HOD, showing the spectrum and results of band decomposition procedure. The intensity calibration marks are the same in both spectra. Bands centered below  $3000 \text{ cm}^{-1}$  are due to D<sub>2</sub>O.

is usually obscured by the noise of the experimental data. These results are considered to provide a satisfactory confirmation of the model.

The frequency positions of the component bands have in general an estimated error of  $10-20 \text{ cm}^{-1}$ . The best fit of the observed contour of H<sub>2</sub>O was found for  $\nu_{1A} + \nu_{1B} = 6615 \text{ cm}^{-1}$  and for D<sub>2</sub>O, 4860 cm<sup>-1</sup>, which is well within the accuracy of the values estimated using eq 3.

The ratio between corresponding frequencies for  $H_2O$  and  $D_2O$  is relatively constant, as expected. However, since this was a criterion for the selection of frequency estimates for the tricoordinated species, the significance of this point is diminished.

The requirement on the relative bandwidths of the isotropic and anisotropic components of a partially

			-	Bar	d parameters				
			Peak height	Frequency	Lorentzian	Gaussian	Width,		Depolariza-
Species	Vibration	Component	$\boldsymbol{x_1}$	<i>x</i> <sub>2</sub> , cm <sup>-1</sup>	23	24	cm -1	Band area	tion ratio
					(a) H <sub>2</sub> O				
Tetra	$\nu_{1\mathbf{A}}$	Iso	43400	3215	$6 imes 10^{-5}$	$2 imes 10^{-6}$	220	$1.1 \times 10^{7}$	0.04
		Aniso	1560		$6 \times 10^{-6}$	$2 imes 10^{-6}$	245	$5.0 imes10^{5}$	
Tetra	<b>V</b> 1B	Iso	35700	3400	$2 imes 10^{-5}$	$4 imes 10^{-5}$	219	$8.4 imes10^6$	0.14
		Aniso	5250		$5 \times 10^{-7}$	$4  imes 10^{-5}$	255	$1.4  imes 10^6$	
Tetra	v <sub>3</sub>	Aniso	6040	3455	$9 imes10^{-6}$	$4  imes 10^{-6}$	200	$1.6 imes10^6$	3/4
Tri	₽bonded	Iso	8720	3545	$9 \times 10^{-7}$	$1 \times 10^{-4}$	140	$1.3 imes10^6$	0.26
		Aniso	3180		$5  imes 10^{-23}$	$1 \times 10^{-4}$	157	$5.3 imes10^{5}$	
Tri	Viree	Iso	6200	3635	$3 imes 10^{-20}$	$3 \times 10^{-4}$	100	$6.6  imes 10^5$	0.12
		Aniso	1100		$2 imes 10^{-10}$	$4  imes 10^{-4}$	79	$9.3 imes10^4$	
					(b) D <sub>2</sub> O				
Tetra	<b><i>V</i>1A</b>	Iso	25000	2372	$2  imes 10^{-4}$	$3  imes 10^{-5}$	123	$3.6 imes10^6$	0.014
		Aniso	400		$3 \times 10^{-4}$	$4 imes 10^{-5}$	108	$5.2 imes10^4$	
Tetra	νıB	Iso	20000	2488	$3 \times 10^{-8}$	$1 \times 10^{-4}$	162	$3.5 imes10^6$	0.06
		Aniso	1340		$3 \times 10^{-7}$	$1 \times 10^{-4}$	161	$2.3 imes10^{5}$	
Tetra	V3	Aniso	5000	2540	$2 \times 10^{-4}$	$4 imes 10^{-6}$	139	$9.6 imes10^{5}$	3/4
Tri	Phonded	Iso	2500	2610	$6 \times 10^{-16}$	$3 \times 10^{-4}$	92	$2.5 imes10^{5}$	0.40
		Aniso	2220		$9 \times 10^{-7}$	$3 \times 10^{-4}$	81	$2.2 imes10^{5}$	
Tri	Viree	Iso	2900	2680	$3 \times 10^{-4}$	$1 \times 10^{-4}$	93	$3.1 imes10^5$	0.25
		Aniso	1340		$4 \times 10^{-12}$	$4 \times 10^{-4}$	91	$1.2 imes10^5$	
				(c)	HOD-OH Stretch				
Tetra	₽ОН	Iso	9523	3400	$5 imes 10^{-6}$	$2 imes 10^{-6}$	223	$2.4 imes10^6$	0.21
		Aniso	2640		$6 imes 10^{-b}$	$1 \times 10^{-5}$	225	$7.0 imes10^{5}$	
Tri	Phonded	Iso	4374	3530	$5 \times 10^{-7}$	$9 \times 10^{-6}$	176	$8.2 imes10^{5}$	0.15
		Aniso	810		$3 \times 10^{-7}$	$9 imes 10^{-6}$	177	$1.5 imes10^{5}$	
Tri	Vfree	Iso	1930	3625	$2  imes 10^{-10}$	$5 imes 10^{-5}$	77	$1.6  imes 10^{5}$	0.03
		Aniso	135		$8  imes 10^{-4}$	$1 \times 10^{-3}$	39	$5.8 imes10^3$	

Table I:	Numerical Results of	Band-Decomposition	Procedure for Raman S	pectra of Isoto	pic Forms of Liquid Water
----------	----------------------	--------------------	-----------------------	-----------------	---------------------------

polarized band is, in general, well satisfied. This breaks down only for weaker bands which are not well defined in one or the other component. In addition, the comparison between the relative bandwidths of bands associated with different vibrations is encouraging. The free OH should have the least perturbation from its environment, and the bands attributed to it are, as expected, the narrowest. The bonded OH in the tetracoordinated species is expected to have the greatest range of environmental perturbations and thus the broadest bands, as observed.

The intensity ratio of the Fermi components in the isotropic part of the spectra of  $H_2O$  and  $D_2O$  is not unrealistic. However, it is difficult to account for this ratio changing by a factor of 3–4 in the anisotropic part. Although a change of this type is not precluded theoretically,<sup>16</sup> a change of this magnitude has not been reported.<sup>17</sup> Also, there are other factors which might contribute to the large change in this ratio. One of these could be that the anisotropic components of these bands are weak and not well defined in the spectra; thus, the fit for these bands cannot be expected to have a high degree of accuracy. Another could be that the model assumption of identical tetracoordinated species does not adequately explain the details of the

Fermi interaction. A further factor could be that the assumption of symmetrical bands which forms the basis for the band decomposition procedures may be poor in this case.

Another possible objection to these results is the large values of  $\nu_3 - \nu_1$  found from the band analysis of liquid H<sub>2</sub>O and D<sub>2</sub>O. However, if the change in geometry and change in potential function cannot be predicted, the change in  $\nu_3 - \nu_1$  on going from gas to liquid cannot be specified. It can be shown that if only an increase in H-O-H angle takes place, as would be expected if the molecule becomes more tetrahedral in the liquid, then  $\nu_3 - \nu_1$  will be larger in the liquid phase than in the gas. However, since unpredictable changes in cross-term potential force constants may also take place, it is not possible to predict the sign or magnitude of  $\nu_3 - \nu_1$ .

The rationalization of the temperature dependence of these bands in terms of this model is quite straightforward. It has been reported<sup>4,8</sup> that the high-frequency sides of the contours of these bands increase in

<sup>(17)</sup> E.g., from the data for the Fermi doublet of  $CS_2$  it can be shown that this ratio changes by about a factor of 2: W. R. Hess, H. Hacker, H. W. Schrötter, and J. Brandmüller, Z. Angew. Phys., 27, 233 (1969).

intensity with respect to the low-frequency sides as the sample temperature is increased. Walrafen, in fact, reported an "isosbestic point" for H<sub>2</sub>O at 3460  $cm^{-1.4}$  Since the thermodynamically less stable tricoordinated hydrogen-bonded species would be expected to increase in relative concentration with increasing temperature, their respective bands at 3545 and  $3635 \text{ cm}^{-1}$ , which are on the high-frequency sides of the contour, would be expected to increase in intensity, as reported. Thus, as can be seen from Table I, the frequency for the isosbestic point is consistent with our results. Similar arguments hold for the isosbestic point of HOD at 3470 cm<sup>-1</sup>.<sup>18</sup> However, the present model is not capable of supporting a quantitative discussion of the temperature effects, first, because of the simplifying assumptions discussed above and second, because the complicating effect of hot bands involving intermolecular modes of vibration was

ignored. Consideration of the effect of these hot bands in general and on the Fermi doublet in particular is felt to be beyond the level of sophistication of this model.

In conclusion, we have demonstrated that the chosen model satisfies the several requirements outlined above and that the band-fitting procedure verifies its suitability for understanding the bond-stretching region of liquid water. We realize that this model is a simplified description of a very complex system, and it must be emphasized that we do not insist that this is the only model which can be used to interpret these data. Certainly, any model which is consistent with the requirements set out in the Introduction could be an acceptable alternative to this one. However, we feel that the virtue of the model considered here lies in its simplicity.

(18) K. A. Hartman, J. Phys. Chem., 70, 270 (1966).

## **Measurement of Longitudinal Relaxation Times for Spin-Decoupled Protons**

## by Michael J. Gerace and Karl F. Kuhlmann\*

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755 (Received November 2, 1971) Publication costs assisted by the National Science Foundation

The saturation recovery method has been employed to obtain the longitudinal relaxation time for spin-decoupled protons. The methyl group  $T_1$  for a solution of methanol in dimethyl- $d_6$  sulfoxide was the same for samples decoupled either by double irradiation (0.62  $\pm$  0.02 sec) or by the addition of acid (0.64  $\pm$  0.02 sec).

The measurement of the longitudinal proton relaxation time  $T_1$  for a single-lined nmr spectrum has provided information concerning molecular motion. Knowledge of relaxation times of different chemically shifted nuclei in the same molecule can render additional information, but their attainment in the presence of spin-spin coupling is usually a difficult task. Not only does each line in the spectrum have to be assigned to a particular spin state, but the initial state from which the spin relaxes must be established.<sup>1</sup> Moreover, the return rate of an individual spectral line to equilibrium is not governed by a single exponential decay.<sup>2</sup> Some of these problems have been avoided by using pulse-Fourier-transform techniques;<sup>3</sup> however, this method requires instrumentation which is not always available.

Theoretically,  $T_1$  can be obtained from decoupled spectra,<sup>4</sup> provided the spectrum is of first order. That is, when two nonequivalent sets of homonuclear spin-

coupled protons are decoupled *via* double irradiation, unambiguous relaxation times for either proton can be obtained. We have used the saturation recovery method to demonstrate the feasibility or measuring relaxation times for such a system using standard highresolution nmr equipment.

An experimental method for the determination of proton relaxation times by the saturation recovery technique is reported by Van Geet and Hume.<sup>5</sup> We have made the following modifications of the method

<sup>\*</sup> Address correspondence to this author at the Department of Chemistry, Stanford University, Stanford, Calif. 94305.

<sup>(1)</sup> J. E. Noggle, J. Chem. Phys., 43, 3304 (1965).

<sup>(2)</sup> A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 294.

<sup>(3)</sup> R. L. Vold and J. S. Waugh, J. Chem. Phys., 48, 3831 (1968).

<sup>(4)</sup> K. F. Kuhlmann, D. M. Grant, and R. K. Harris, *ibid.*, 52, 3439 (1970).

<sup>(5)</sup> A. L. Van Geet and D. H. Hume, Anal. Chem., 37, 983 (1965).

contained therein. We employ a standard Varian HR-60 nmr spectrometer locked on external sulfuric acid. The sweep oscillator is replaced by a Monsanto Model 3100-A digital frequency synthesizer in order to minimize signal drift. A decoupling rf field  $H_2$  is applied to the center of the chosen multiplet, while the sweep frequency is adjusted to correspond exactly with the resonance position of the resulting single peak. Saturation is induced by switching  $H_1$  to its maximum value with a relay. When saturation is complete, the  $H_1$ field is decreased to about 0.02 mG, and the recovery is monitored on a Varian Model C 1024 time-averaging computer. Although we have modified the experimental arrangement used by Van Geet and Hume, in principle the introduction of an  $H_2$  field to their instrumentation should lead to the same result.

The relaxation time is computed by a least-squares fit of the experimental curve with the equation

$$v = v_{\infty}(1 - e^{-t/T_1})$$

Since the data points are equally spaced,  $v_{\infty}$  can be determined by the method of Guggenheim.<sup>6</sup> An initial distortion in the recovery curves, also seen by other workers,<sup>5,7,8</sup> requires deletion of the first 15% of each curve. The calculations are facilitated by direct transmission of the data to a time-shared computer with a Binary-ASCII translator.<sup>9</sup> The calculated  $T_1$  values are taken as the average of five separate measurements. It is found that  $T_1$  is insensitive toward changes in  $H_2$ , provided decoupling is complete; but if  $H_2$  is not large enough, the recovery curve becomes distinctly nonexponential and the apparent value of  $T_1$  varies with  $H_2$ . On the other band, the signal-to-noise ratio is greatest at low values of  $H_2$ , and thus an optimum value of the latter quantity can be found by trial.

A 25 mol % solution of methanol in dimethyl- $d_6$  sulfoxide was examined at 27°. Since our major interest was in applications to systems with  $T_1$  values in the neighborhood of 1 sec, an undegassed sample was purposely used in the present experiment. The high-resolution proton magnetic resonance spectrum showed a downfield quartet and an upfield doublet, both with splittings of about 5 Hz, the centers of which were separated by 57 Hz. These figures give assurance that the spectrum is of first order. Proceeding as described above, we employed an  $H_2$  value of about 4 mG and found  $T_1$  for the undegassed sample to be  $0.62 \pm 0.02$  sec, which, as expected, is considerably shorter than that observed<sup>10</sup> in degassed liquid methanol.

Addition of acid to the system accelerates proton exchange so that spin-spin splittings are not observed. We therefore also measured  $T_1$  for a sample of the above solution containing 0.1 m p-nitrobenzoic acid (chosen for its convenience as a weighable solid, soluble in methanol). For the single methyl resonance in this case we obtained  $T_1 = 0.64 \pm 0.02$  sec, which checks to within experimental uncertainty the figure for the magnetically decoupled system. Thus, the second rf field does not affect the measurement of longitudinal relaxation times in spin-decoupled systems.

Experiments of the type described herein should facilitate relaxation studies of chemically shifted protons (or fluorines). In principle, the method can be applied to more complicated spin systems with the aid of triple resonance and noise-decoupling techniques.

Acknowledgment. The authors greatly appreciate the financial support of the National Science Foundation and of the Advanced Research Projects Agency of the Department of Defense under Contract No. F44620-68C-0015. The encouragement and interest of Dr. W. H. Stockmayer is gratefully acknowledged.

(8) A. L. Van Geet, Anal. Chem., 40, 304 (1968).

(10) T. Fukumi, Y. Arata, and S. Fujiwara, J. Chem. Phys., 49, 4196 (1968).

<sup>(6)</sup> E. A. Guggenheim, *Phil. Mag.*, 2 (7), 538 (1926); see, for example, D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill, New York, N. Y., 1962, p 222.

<sup>(7)</sup> J. E. Anderson and R. Ullman, J. Phys. Chem., 71, 4133 (1967).

<sup>(9)</sup> IDM Corp., Hanover, N. H.

## New Electrochemical Measurements of the Liquidus in the LiF-BeF<sub>2</sub> System.

Congruency of Li<sub>2</sub>BeF<sub>4</sub><sup>1</sup>

### by K. A. Romberger, J. Braunstein,\* and R. E. Thoma

Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830 (Received August 2, 1971) Publication costs assisted by the Oak Ridge National Laboratory

Emf measurements of cells with transference provide a method for precise determinations of the liquidus in binary salt systems if the emf is stable, reproducible, and responsive to the change of activity of a component in the melt accompanying a phase change in one of the half cells. The method is described as applied to new measurements of the liquidus of the system LiF-BeF<sub>2</sub> at compositions between 0.12 and 0.58 mole fraction BeF<sub>2</sub> with a precision of about  $\pm 0.0002$  mole fraction BeF<sub>2</sub> and  $\pm 0.2^{\circ}$ . The direction of the emf change at the onset of precipitation provides virtually unequivocal distinction between a peritectic, eutectic, or congruent melting point. Our measurements indicate congruency of Li<sub>2</sub>BeF<sub>4</sub> with a melting point of 459.1°. The maximum in the liquidus lies close to the eutectic of Li<sub>2</sub>BeF<sub>4</sub>-LiF, hence is difficult to establish by conventional means. The LiF-Li<sub>2</sub>BeF<sub>4</sub> eutectic occurs at 0.3280 mole fraction BeF<sub>2</sub> and 458.9°.

## Introduction

Extensive investigations of phase equilibria in the system LiF-BeF2<sup>2</sup> have been motivated by its practical importance in the development of molten salt nuclear reactors,<sup>3</sup> its structural significance as a weakened analog of silicate systems,<sup>4</sup> and its importance in testing theories of ionic liquids.<sup>5</sup> Methods of investigation have included direct observation of crystallizing melts, thermal analysis, thermal gradient quenching, petrography, X-ray diffractometry, and high temperature centrifugation. The results of various studies of the system using these methods, together with a critical evaluation of the results of different investigators, have been summarized by Thoma, et al.,<sup>2</sup> who described the main features of the phase diagram. Disparities regarding the detailed structure of portions of the liquidus in the results of some investigators are attributable to the hygroscopicity of BeF<sub>2</sub> and LiF-BeF<sub>2</sub> mixtures, to the difficulty of purification of the materials, and to the fact that application of many of the methods of investigation requires deduction of equilibrium behavior from nonequilibrium measurements, e.g., thermal analysis. Thus it has proved difficult to establish with certainty some features of the phase diagram, such as the congruency or incongruency of melting of the compound Li<sub>2</sub>BeF<sub>4</sub>.

In this paper we describe new measurements of the liquidus of the LiF-BeF<sub>2</sub> system, employing an emf cell with transference in a method which approaches extremely closely a true equilibrium measurement. Like any concentration cell with transference the system is not in fact at equilibrium because of the irreversible process of diffusion or flow occurring across the porous barrier. However, it has been demonstrated repeatedly in cells of this type that this (constrained) irreversible

process has no discernible effect on the reversible processes occurring in the cell. As a matter of fact, nearly any cell can be considered in some respects to be a concentration cell with transference. Thus in the cell containing  $H_2$  and Ag-AgCl electrodes, it is necessary to constrain interdiffusion of dissolved  $H_2$  and AgCl. In the transference cell employed in the present study, emf measurements are made in molten salt mixtures of one or two phases and the phases are isothermal and in equilibrium with each other during the measurement. It is in this sense that the term equilibrium is employed throughout this paper in connection with the transference cell measurements.

Emf methods have been applied previously to the establishment of phase diagrams or solubility limits,<sup>6</sup> but probably not with the accuracy which has been demonstated in this system. The method used here employs a concentration cell with transference<sup>7</sup> which permits virtual equilibrium determination of the phase boundaries either isothermally at successive compositions, or with constant overall composition at successive temperatures. More important, it provides very precise means

(6) H. A. Øye, Acta Chem. Scand., 18, 361 (1964); H. R. Bronstein, J. Phys. Chem., 73, 1320 (1969).

<sup>(1)</sup> Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

<sup>(2)</sup> R. E. Thoma, H. Insley, H. A. Friedman, and G. M. Hebert, J. Nucl. Mater., 27, 166 (1968).

<sup>(3)</sup> W. R. Grimes, Nucl. Appl. and Tech., 8, 137 (1970).

<sup>(4)</sup> V. M. Goldschmidt, Shr. Norske Vid. Akad. Oslo I, Mat. Naturv. Klasse, 8, 7 (1926).

<sup>(5)</sup> J. Braunstein, K. A. Romberger, and R. Ezell, J. Phys. Chem., 74, 4383 (1970).

<sup>(7)</sup> K. A. Romberger and J. Braunstein, *Inorg. Chem.*, 9, 1273 (1970); Molten Salt Reactor Program Semiann. Progr. Rept., Oak Ridge National Laboratory, ORNL-4548, p 161 (1970); ORNL-4449, p 138 (1969).

for determining the topology of the liquidus, resolving closely spaced invariant points, and characterizing a eutectic, peritectic or congruent melting point without dependence on the accuracy of absolute measurements of composition or temperature. However, the method also lends itself readily to accurate absolute measurements, with internal consistency checks, and is capable of wider exploitation than has been the case to date.

We believe that our results demonstrate unequivocally the congruency of melting of the solid compound  $Li_2BeF_4$ , a characterization which was difficult to establish by other methods because of the proximity of the congruent melting point of  $Li_2BeF_4$  to the  $LiF-Li_2BeF_4$ eutectic. The method should be applicable also to other alkali fluoride beryllium fluoride systems and to other binary salt systems, such as  $LiF-ThF_4$ , for which suitable electrodes are available, and can probably be adapted to many multicomponent systems as well.

### **Experimental Section**

The liquidus of the LiF-BeF<sub>2</sub> system was redetermined at compositions between 12 and 59 mol % BeF<sub>2</sub> by means of an all-metal concentration cell with transference<sup>7</sup>

$$\begin{array}{c|c} \mathbf{Be} \begin{vmatrix} \mathbf{LiF} & \mathbf{LiF} \\ \mathbf{BeF_2} & \mathbf{BeF_2} \end{vmatrix} \mathbf{Be} \qquad (A)$$
$$\mathbf{I} \quad \mathbf{II} \end{cases}$$

Beryllium electrodes dip into molten  $\text{LiF-BeF}_2$  mixtures of differing composition. One compartment, holding about 2 cm<sup>3</sup> of melt, serves as a reference half cell (I). It is separated by a fritted disk from the bulk compartment (II) containing about 50–200 cm<sup>3</sup> of melt.

The cell is identical with one described previously<sup>7</sup> except that silica was replaced by molybdenum for construction of the crucible and stirrer and by nickel for the electrode compartments and frits. The molvbdenum crucible is contained in an outer silica envelope which is cemented to a water-cooled nickel flange by means of Silastic RTV 731 adhesive sealant. A nickel cover plate, provided with risers terminating with Swage-Lok fittings to permit entry of electrodes, electrode compartments, stirrer, thermocouple well, and cover gas inlet, is bolted to the flange, employing a Teflon O-ring as a gasket. The cell could thus be evacuated or maintained under a small positive pressure of dried helium. Weighed additions of salt (LiF,  $BeF_2$ , or a pre-mixed composition) were introduced into the cell, under a protective gas atmosphere, through a ball valve assembly in the cover plate. Electrodes are beryllium metal cylinders attached to nickel rods by means of a gold-nickel braze. They are insulated from each other and from the metal parts of the cell by Teflon sleeves in the cooled upper portion of the cell assembly. Temperature was measured with a National Bureau of Standards calibrated platinum platinum-rhodium (10%) thermocouple and a chromelalumel thermocouple that had been compared with it.

Optical grade single crystal LiF from Harshaw and vacuum distilled  $BeF_{2}^{8}$  were employed.

Since the cell is all metal (except for the Teflon insulators in a cool region), and makes use of only a single kind of electrode (beryllium) by virtue of being a concentration cell with transference, it is remarkably free from sources of contamination of the materials. Stirring provides a uniform temperature in the melt. There was no evidence of mass transfer or corrosion of the electrodes, and the electrodes maintained their dimensional stability during experiments of several months duration. The nickel electrode compartments remained noble with respect to the beryllium electrodes by about 0.5 V with no tendency of the cell emf to run down, suggesting the absence of electronic conduction. In a further test for the presence of electronic conduction or reduced (subvalent) species, analysis of melt in which the beryllium electrode had been immersed showed that the reducing power was below the limit of detection, putting an upper limit of about 0.1 mol % on reduced species as Be<sup>0</sup> (there would be no way from this analysis to distinguish whether reduced species, if present, were  $Be^0$  or  $Be^+$ ). This low concentration of reduced species, if present, has negligible effect on the emf measurements in this cell.

The composition of the melt in the reference half cell (I) was established by filling it via suction from accurately weighed melt prepared in the bulk compartment. The depth of the melt in the reference compartment was determined within  $\pm 1$  mm by using the precalibrated Be electrode within it as a depth probe to sense electrical contact between the electrode and the nickel compartment. The melt height in the reference compartment was maintained from 3 to 6 mm above that in the bulk compartment by raising the reference compartment when salt was added to the bulk compartment. Hence a small amount of salt flowed from the reference compartment (I) to the bulk (II), preventing back diffusion and composition changes in the small reference compartment. Periodic checks were made of the salt level in the reference compartment during the course of an experiment. From the dimensions of the small reference compartment and its melt depth, the amount of material contained within it was readily calculated. The error introduced in the calculation of the bulk composition because of the reference compartment correction is a function of the disparity of the two compositions. For this reason the bulk and reference compartment compositions were adjusted to similar values so that the absolute error introduced from this correction was  $< \pm 0.0001$  mole fraction. Accuracy of the bulk melt composition could be maintained to

<sup>(8)</sup> We thank B. F. Hitch for distilling the BeF<sub>2</sub>.

 $\pm 0.0002$  mole fraction BeF<sub>2</sub>. The accuracy of the weighed-in compositions could be verified by a cycle consisting of measurement of the emf followed by addition of first LiF and then BeF<sub>2</sub> (or mixtures of known composition) to return to the calculated initial composition and reproduce the initial emf. Before starting a series of isothermal composition changes, the reference compartment was emptied by gas pressure and refilled with material of known composition from the bulk compartment in order to establish a reference composition for verifying the melt composition at the liquidus.

Application of the Emf Method to Determination of the Liquidus. The emf, E, of cell (A) may be written,<sup>7</sup> at the constant temperature T

$$2FE = \int_{I}^{II} [(1 - t_{Be})d\mu_{BeF_{2}} - 2t_{Li}d\mu_{LiF}] = \int_{I}^{II} t_{Li} \left(\frac{1 + x}{1 - x}\right) d\mu_{BeF_{2}} = -\int_{I}^{II} t_{Li} \left(\frac{1 + x}{x}\right) d\mu_{LiF} \quad (1)$$

where  $t_{\text{Li}}$  is the transference number of lithium ion (relative to fluoride), x is the mole fraction of BeF<sub>2</sub>, and  $\mu_{\text{BeF}_2}$  and  $\mu_{\text{LiF}}$  are the chemical potentials of BeF<sub>2</sub> and LiF. If the composition of molten salt in the reference half cell is held fixed while that in the bulk compartment (II) is varied, the isothermal change of emf with composition is

$$2F\left(\frac{\partial E}{\partial x}\right)_{T} = t_{\text{Li}} \left(\frac{1+x}{1-x}\right) \left(\frac{\partial \mu_{\text{BeF}_{2}}}{\partial x}\right)_{T}$$
(2a)

$$= -t_{\rm Li} \left(\frac{1+x}{x}\right) \left(\frac{\partial \mu_{\rm LiF}}{\partial x}\right)_T \qquad (2b)$$

Since the derivatives on the right-hand side of equations (2a) and (2b) are, respectively, positive and negative for the homogeneous binary mixture, the emf decreases monotonically and continuously as the melt in the bulk compartment is enriched in LiF so long as only one phase (liquid) is present. When the melt of the binary mixture becomes saturated with a solid of fixed composition, however, its composition (and hence the chemical potentials of the components) remains unchanged on further isothermal addition of solute, and the slope of an emf composition plot must become zero. It is therefore possible to determine the liquidus composition on an isotherm from the sharp change of slope of the emf-composition curves, as shown in Figure 1a. (There will be a discontinuity in the slope even if solid solution is formed, although the slope will not then become zero.)6

If the temperature of the cell is changed while the total composition in the bulk compartment is held constant, with the composition in the reference compartment adjusted so that no phase change occurs there as the temperature is changed, the emf change in the



Figure 1. Evaluation of liquidus temperature and composition from change of slope of emf-composition plots and emf-temperature plots. (a) Emf at a series of compositions spanning the liquidus at constant temperature  $(T = 607.5^{\circ})$ . (b) Emf at a series of temperatures spanning the liquidus at fixed overall composition  $(X = 0.2997 \text{ mole fraction BeF}_2)$ .

temperature region in which the melt in the bulk compartment remains a single phase may be written

$$2F\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_{\mathrm{single \ phase}} = 2F\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_{x} = \frac{\mathrm{d}}{\mathrm{d}T}\int_{\mathrm{I}}^{\mathrm{II}} t_{\mathrm{Li}} \left(\frac{1+x}{1-x}\right) \left(\frac{\mathrm{d}\mu_{\mathrm{BeF}_{2}}}{\mathrm{d}x}\right)_{T} \mathrm{d}x \quad (3)$$

When the temperature of the cell drops to and below the liquidus, the emf change, for temperatures and compositions along the liquidus, becomes

$$\left[\frac{\mathrm{d}E}{\mathrm{d}T}\right]_{\mathrm{liquidus}} = \left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_{x} + \left(\frac{\mathrm{d}E}{\mathrm{d}x}\right)_{T} \left[\frac{\mathrm{d}x}{\mathrm{d}T}\right]_{\mathrm{liquidus}}$$
(4)

Thus there is again a discontinuity in slope as the system passes through the liquidus, as illustrated in Figure 1b by a plot of equilibrium emf values at a series of temperatures.

It should be reemphasized that these measurements are virtual equilibrium measurements, at a succession of fixed temperatures, and are not cooling curves; *i.e.*, time is not a variable. Supercooling is not a problem since, once nucleation took place, the liquidus was determined equally well from emf measurements at a series of increasing temperatures until the liquidus temperature was crossed from below. Once solid was present, liquidus temperatures obtained with increasing and decreasing temperature agreed. However, it was also possible in some cases to obtain a reproducible metastable phase boundary along the metastable extension of the LiF liquidus.

In eq 4, the first term in the right-hand side generally is small in magnitude relative to the second term, as seen by the shallow slope in the one-phase region in Figure 1b. The sharpness of the slope change on passing through the liquidus is thus determined by the second term. It will be noted that where the liquidus is steep and the factor  $[dx/dT]_{liquidus}$  is small,  $(\partial E/\partial x)_T$  in eq 2 will tend to be large. On the other hand, where


Figure 2. Schematic representation of temperature-composition and temperature-emf plots expected for eutectic (a), congruent melting point (b), and peritectic (c).

 $(\partial E/\partial x)_T$  is small, corresponding to small values of  $(\partial \mu_{BeF_2}/\partial x)_T$  (see eq 2), the slope of the liquidus will tend to be shallow, *i.e.*,  $[dx/dT]_{liquidus}$  will be large. The method therefore does not lose sensitivity in the region of either a steep or shallow liquidus, as may occur in the analysis of cooling curves.

Characterization of an Invariant Point as a Eutectic, Congruent Melting Point or Peritectic. The formation of a congruently melting compound, eutectic, or peritectic on precipitation of a solid phase may be established by the direction of change of emf on passing through the liquidus, as illustrated schematically in Figure 2. If a cell containing melt of composition corresponding exactly to either a eutectic or a congruent melting point is cooled, no abrupt change of slope occurs in an emf-temperature plot on passing through the liquidus because the composition of the liquid phase remains unchanged. However, by cooling through the liquidus cells in which the initial compositions of liquid in compartment II span the composition at the invariant point, the distinction between the two can be made. If the invariant point is a eutectic, then upon crossing the liquidus, the melt compositions and emf's will converge to the value corresponding to the eutectic composition and then remain constant. When the invariant point is a congruently melting compound, the compositions and emf's below the liquidus will diverge for initial melt compositions spanning the compound composition. These two kinds of invariant points are also distinguished from each other by their melting characteristics, since the eutectic temperature will be the lowest melting and the compound temperature the highest melting of the series. These two cases are illustrated schematically in Figure 2a.

These two cases are in direct contrast to that of an incongruently melting compound which gives rise to a peritectic point. Here the temperature of the liquidus continues to drop as the initial melt composition crosses the peritectic composition, since the melt composition and hence the cell emf consistently change in the same direction. The magnitude of the slope of the emf-composition plot changes (abruptly) at the peritectic point (since the slope of the liquidus is discontinuous) but not its sign, since the liquid com-



Figure 3. Change of Emf with time on cooling through about  $0.1^{\circ}$  below the liquidus at compositions near X = 0.3333 mole fraction BeF<sub>2</sub>. Key:  $\rightarrow$ , indicates that Li<sub>2</sub>BeF<sub>4</sub> is the precipitating phase;  $\leftarrow$ , indicates that LiF is the precipitating phase.

position continues to change in the same direction. This latter case is illustrated in Figure 2b.

Although it is in principle possible to carry out a series of nearly equilibrium measurements at a series of closely spaced temperatures, establishment of the precise shape of the liquidus in the region near the composition  $Li_2BeF_4$  was accomplished by measuring the emf as a function of time during cooling. This was expeditious because of the very shallow slope of the liquidus in this region, and the large enthalpy of fusion of Li<sub>2</sub>BeF<sub>4</sub>.<sup>9</sup> In order to lower the temperature by as much as  $0.1^{\circ}$ below the liquidus, the corresponding composition change in the melt would require precipitation of so much solid as to impede stirring and thermal equilibration in the cell. Thus, although the emf measurements in this case were not made at complete phase equilibrium, the total temperature change during obtaining these cooling curves was of the order of 0.1°, so that the departure from equilibrium was extremely small. Figure 3 shows the changes of emf with time on cooling 17 mixtures of composition near 0.33 mole fraction  $BeF_2$ . It is apparent that a change in direction occurs between melts 96 and 97 corresponding to 0.3337 and 0.3329 mole fraction BeF<sub>2</sub>, probably at 97 (0.3329). These compositions were calculated from weights of components added to the cell, but the congruency of the melting point is established by the shape of the family of emf plots rather than from absolute composition and temperature measurements. The composition of the congruently melting compound calculated

<sup>(9)</sup> T. B. Douglas and W. H. Payne, J. Res. Nat. Bur. Stand., Sect. A, 73, 499 (1969).

from these results is  $0.3333 \pm 0.0004$  mole fraction BeF<sub>2</sub>. The stoichiometry of crystalline Li<sub>2</sub>BeF<sub>4</sub> has been established previously, by X-ray diffraction, as 0.33333 mole fraction BeF<sub>2</sub>.<sup>10</sup>

Plots 104 through 107 establish the eutectic of LiF and  $Li_2BeF_4$ . Although it would normally be difficult to establish precisely the small composition interval between the eutectic and the compound, this composition difference can be determined quite accurately from the emf difference, relative to a common reference half cell, between the compositions of the eutectic and the compound. The dependence of emf on composition can be determined with easily weighable quantities of components, and in this region of the phase diagram the change of emf with composition is  $(\partial E/\partial x)_T =$ 1405 mV. An easily observed change of 0.14 mV thus corresponds to a composition change of 0.0001 mole fraction. Thus the composition difference between the LiF-Li<sub>2</sub>BeF<sub>4</sub> eutectic and the Li<sub>2</sub>BeF<sub>4</sub> congruent melting point can be established as  $\Delta x = 0.0057 \pm$ 0.0003 mole fraction BeF<sub>2</sub>, more accurately than the absolute composition can be determined. Similarly, the temperature difference can be established, with the aid of measured values of  $(\partial E/\partial T)_x$ , as  $\Delta T = 0.2^\circ$ , although direct measurements of this small temperature difference would be difficult to obtain.

The liquidus points obtained in this manner are shown together with the equilibrium results in the vicinity of the  $Li_2BeF_4$  melting point in Figure 4. The equilibrium data include a metastable point on the LiF liquidus of melt supersaturated with  $Li_2BeF_4$  (which often showed a tendency toward supercooling). The position of this metastable point further establishes that the equilibrium LiF liquidus lies to the left of the composition  $Li_2BeF_4$ .

A revised phase diagram for the system  $\text{LiF-BeF}_2$ is given in Figure 5, based on the new equilibrium liquidus data<sup>11</sup> obtained from emf measurements of the cell (A), emf-time cooling curves over an interval of about 0.10° below the liquidus, and previously reported identification of the solid phases and subsolidus transitions in this system.<sup>2,10</sup>

#### Discussion

The LiF-BeF<sub>2</sub> phase diagram follows the pattern of the other alkali fluoride (MF)-beryllium fluoride systems in that the apparent relative stability of the  $(MF)_2BeF_2$  solid compound decreases in the order Cs > Rb > K > Na > Li until Li<sub>2</sub>BeF<sub>4</sub> is only barely congruent.

The results of our investigation of the LiF-BeF<sub>2</sub> liquidus demonstrate for the first time unequivocally that  $\text{Li}_2\text{BeF}_4$  melts congruently. The precision of the experimental methods for establishing the relative differences in composition-temperature relationships fixes as well the values for the LiF-Li<sub>2</sub>BeF<sub>4</sub> eutectic at LiF-BeF<sub>2</sub> (0.6724 - 0.3276 mole fraction), mp 458.9



Figure 4. The region of the LiF-BeF<sub>2</sub> liquidus near the melting point of Li<sub>2</sub>BeF<sub>4</sub>. (·), Data obtained from emf-time cooling curves (0.1° interval). ( $\triangle$ ,O), Equilibrium measurements. The lowest open circle (O) is a metastable point on the LiF liquidus of a melt supersaturated with Li<sub>2</sub>BeF<sub>4</sub>.

 $\pm$  0.2°, with great accuracy. Its proximity to the composition of Li<sub>2</sub>BeF<sub>4</sub> indicates the cause of previously unsuccessful attempts to ascertain the melting-freezing behavior of  $Li_2BeF_4$ , for in none of the previous methods were incremental in situ changes of composition employed. Considering the usual precision which previously typified temperature measurements in these investigations, such attempts would have been fruitless. The results of the current investigation confirm the approximate accuracy of the liquidus as described previously on the basis of data available at that time in a report from this laboratory.<sup>2</sup> In providing this confirmation by the (independent) electrochemical method, they also confirm that the melting point of  $BeF_2$  is not the high temperature value as is still contended by some Russian investigators,<sup>12</sup> but rather is, as one of us (Thoma, ref 2) has reported previously, near 555°.

The electrochemical method has been shown here to be capable of yielding highly precise liquidus data which, when combined with the isothermal emf data obtained with cell (A), will be used to extend the thermodynamic analysis of this and related systems.

In a previous discussion of nonideality in alkali fluoride-alkaline earth fluoride mixtures, we reported that the limiting excess chemical potential interaction parameter,  $\lim_{X_{BeF2} \to 0} (\mu_{LiF}^E/X^2)$ , for LiF in LiF-BeF<sub>2</sub> (-5.5 kcal/mol) was in agreement with values for the other MF-BeF<sub>2</sub> systems when compared according to the

<sup>(10)</sup> J. N. Burns and E. K. Gordon, Acta Crystallogr., 20, 135 (1966).

<sup>(11)</sup> A complete tabulation of the equilibrium temperatures and compositions will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

<sup>(12)</sup> V. I. Belousov and L. N. D. Siderov, Zh. Fiz. Khim., 44, 254 (1970).



Figure 5. Revised phase diagram of the system LiF-BeF2.

conformal ionic solution (CIS) theory.<sup>5</sup> The important parameter in CIS theory is the difference of the reciprocal cation-anion distances in the two salts. The additional liquidus data reported here permit a more extensive investigation of the nonideality. The ideal liquidus curve for LiF, calculated from its melting point, heat of fusion, and heat capacity under the assumption that the components are LiF and Li<sub>2</sub>BeF<sub>4</sub> with the  $BeF_4^{2-}$  ion undissociated, leads to striking agreement (within  $1-2^{\circ}$ ) with the measured liquidus for compositions up to 50 mol % Li<sub>2</sub>BeF<sub>4</sub> (25 mol % BeF<sub>2</sub>) in LiF. (At higher BeF<sub>2</sub> contents increasingly positive deviations are found, with interaction parameters of the order of + 2 kcal/mol.) Bredig<sup>13</sup> has called our attention to a number of common cation binary mixtures of a fluoride with a large tetrahedral anion in which deviations from ideality are small over an extended range of composition. Caution must be urged, however, before attempting to interpret the solution behavior of alkali fluoride-beryllium fluoride mixtures solely in terms of ideally mixing complex ions. Thus in the solvent sodium fluoride, the limiting interaction parameter  $\lim_{X_{BeF_2} \to 0} (\mu_{NaF} E / X_{BeF_2}^2)$  is -8.5 kcal/ mol, also in agreement with CIS. This value is 3.5 kcal/mol more negative than the limiting NaF-Na<sub>2</sub>- $BeF_4$  interaction parameter that would correspond to the hypothetical ideal mixture  $Na^+(F^-, BeF_4^{2-})$ . The ideal mixing model would predict virtually identical values  $(-2RT_{\rm MF})$  of  $\lim_{X_{\rm BeF_2} \to 0} (\mu_{\rm alkF} E / X_{\rm BeF_2}^2)$  for all of the alkali fluoride-fluoroberyllate mixtures, whereas in fact the limiting interaction parameters generally appear to vary uniformly with the CIS distance parameter.<sup>5</sup> While there is little question that there are strong  $Be^{2+}-F^-$  interactions in these mixtures and that  $Be^{2+}$  is tetrahedrally surrounded by  $F^{-}$  ions,<sup>14</sup> a quantitative explanation of the solution energetics in terms of the complex tetrafluoroberyllate ion is still lacking, and many of the features of these solutions are in accord with the application of CIS theory to alkali, beryllium, and fluoride ions.

(13) M. A. Bredig, private communication.

(14) A. S. Quist, J. B. Bates, and G. E. Boyd, J. Phys. Chem., 76, 78 (1972).

# Theory for a Homogeneous Reaction following a

# **Quasireversible Electrode Reaction**

#### by Dennis H. Evans

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (Received September 50, 1971) Publication costs assisted by the National Science Foundation

Theory is developed for the electrochemical mechanism involving the irreversible homogeneous chemical reaction of the product of a quasireversible heterogeneous electron-transfer reaction at an electrode surface. A numerical method is employed to obtain theoretical current-potential curves for cyclic voltammetry. Correlations of peak potential, current function, and wave shape with dimensionless kinetic parameters are presented and discussed. Theory for cyclic voltammetry with an irreversible second-order reaction of the product of the electrode reaction is also presented. It is found that the electron-transfer reaction will be sufficiently rapid to permit use of earlier theories which assume reversible behavior if  $k_t C_0^{*(m-1)} < k_s^2/100\pi D$ , where  $k_t$  is the rate constant for the chemical reaction,  $C_0^*$  is the bulk concentration of the reactant, *m* is the order of the following chemical reaction,  $k_s$  is the standard heterogeneous electron transfer rate constant, and *D* is the common diffusion coefficient employed in the calculations. Experimental results from several earlier papers are discussed in the light of the above criterion, and it is shown that some of the earlier data were affected by both the following chemical reaction and limited reversibility of the electron-transfer reaction.

Numerous examples of the occurrence of homogeneous chemical reactions coupled to the heterogeneous electron-transfer reaction at an electrode have been reported and theory has been developed for many of the simpler reaction schemes for experimental techniques such as polarography, chronopotentiometry, cyclic voltammetry, and the double potential step method. One of the most common types involves a chemical reaction following the electrode reaction (EC mechanism) as shown in reactions 1 and 2.<sup>1</sup> The substance Z is not

$$R \xrightarrow{kf} Z$$
 (2)

electroactive in the potential range of interest and it does not react with O. The quantities  $k_s$  and  $\alpha$  are the standard heterogeneous electron-transfer rate constant (referred to  $E^{0}_{O,R}$ ) and the electron-transfer coefficient, respectively. In this work it is assumed that the chemical reaction is irreversible.

Normally the simplifying assumption is made that reaction 1 is reversible, *i.e.*,  $k_s$  is large enough to ensure that reaction 1 will achieve equilibrium throughout the time scale of the experiment.<sup>2-4</sup> Hence, the Nernst equation may be used in conjunction with the surface concentrations of O and R to obtain the potential of the electrode. It is the purpose of the present paper to explore the effects of irreversibility (finite  $k_s$ ) of reaction 1 on the observed electrode response.

One rather obvious special case has been recognized for a long time. When  $k_s$  is very small, sufficient activation overpotential occurs to render reaction 1 totally irreversible, *i.e.*, the rate of the reverse reaction is completely negligible. In this case, the response of the electrode is independent of the fate of R and the following reaction has no effect.

When reaction 1 is reversible, the following chemical reaction has the effect of shifting the polarographic  $E_{1/2}$  to more positive potentials.<sup>2</sup> Analogous shifts in the chronopotentiometric quarter-wave potential  $(E_{\tau/4})$ and the peak potential in cyclic voltammetry  $(E_{\rm p})$  are observed.<sup>3,4</sup> The behavior of systems in which reaction 1 is not completely reversible is as yet unknown, though a few calculations have been presented earlier.<sup>5</sup> In general, finite values of  $k_s$  should result in smaller potential shifts than predicted for completely reversible behavior. In some cases  $k_s$  may be large enough to ensure reversibility when the forward rate of reaction 2 is small, but the limited reversibility of reaction 1 will exert its effect as  $k_i$  becomes large. It would be helpful to know whether the theory which assumes reaction 1 to be reversible<sup>2-4</sup> may be safely employed for given values of  $k_{\rm f}$  and  $k_{\rm s}$ . This paper provides quantitative answers to these questions for the techniques of chronopotentiometry and cyclic voltammetry. In addition,

<sup>(1)</sup> Reaction 1 is written as a reduction, and the theoretical expressions in this paper will be developed for reductions. Modification of the results to pertain to oxidations requires a few obvious changes of sign for potentials and currents.

<sup>(2) (</sup>a) D. M. H. Kern, J. Amer. Chem. Soc., 76, 1011 (1954); (b)
P. Kivalo, Acta Chem. Scand., 9, 221 (1955); (c) J. Koutecky, Collect. Czech. Chem. Commun., 20, 116 (1955).

<sup>(3)</sup> P. Delahay, C. C. Mattax, and T. Berzins, J. Amer. Chem. Soc., 76, 5319 (1954).

<sup>(4)</sup> R.S. Nicholson and I. Shain, Anal. Chem., 36, 706 (1964).

<sup>(5) (</sup>a) W. G. Stevens, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1966; (b) R. S. Nicholson, Proceedings of the Fourth International Congress on Polarography, Prague, 1966, p 69.

a scheme involving the dimerization of R is discussed for the case of cyclic voltammetry.

Although shifts in  $E_{1/2}$  were the first means by which EC mechanisms were studied and shifts in  $E_{\tau/4}$  and  $E_{\rm p}$ have occasionally been used for this purpose, the more powerful two-step techniques such as current-reversal chronopotentiometry,<sup>6,7</sup> peak current ratio measurements in cyclic voltammetry,<sup>4</sup> and the double potential step method<sup>8</sup> have almost completely displaced the potential-shift methods. Of these three, current-reversal chronopotentiometry and the double potential step method produce data independent of  $k_s$  and  $\alpha$ . Only gross reversibility is required.

The genesis of the present investigation lay in our use of potential shifts as corroborative evidence in conjunction with cyclic voltammetric studies of moderately rapid dimerization reactions.<sup>9</sup> It was necessary to verify that  $k_s$  was sufficiently large to ensure that the peak potentials were not being affected by limited reversibility.

#### **Cyclic Voltammetry**

The "digital simulation" technique of Feldberg<sup>10</sup> was used to obtain theoretical current-potential curves. In this technique the Fick's law diffusion equations for O and R, appropriately modified to include reaction 2, are treated numerically to obtain the surface concentrations of O and R which permit computation of the current utilizing the electrochemical rate equation<sup>11</sup>

$$i = nFAk_{s} \left\{ C_{O(X=0)} \exp\left[\frac{-\alpha nF(E-E^{0})}{RT}\right] - C_{R(X=0)} \exp\left[\frac{(1-\alpha)nF(E-E^{0})}{RT}\right] \right\}$$
(3)

where *i* is the current, *F* is the faraday, *A* is the electrode area, and  $C_{O(X=0)}$  and  $C_{R(X=0)}$  are the surface concentrations.

The initial potential for the simulation was always at least 165/n mV more positive than  $E^0$  or  $E_p$ , whichever was the more positive. This was large enough to ensure that the peak potentials and current function were independent of the particular value of initial potential chosen. The simulations were performed using less than 0.26/n mV change in potential per time unit. Thus the simulations required more than 600 iterations (time units) to proceed from the initial potential to the peak potential.

A dimensionless heterogeneous electron-transfer rate parameter,  $\Psi_{ev}$ , was defined in accordance with Nicholson<sup>12</sup>

$$\Psi_{\rm ev} = (D_{\rm O}/D_{\rm R})^{\alpha/2} (k_{\rm s}/\sqrt{\pi D_{\rm O} a})$$
(4)

The quantity a is related to the sweep rate, v, by the expression

$$a = nFv/RT \tag{5}$$

In the simulations a common diffusion coefficient was used, *i.e.*,  $D = D_0 = D_R$ . This is not a requirement of the simulation technique, but it was done for the sake of convenience. Some simulations were performed with  $D_0 = 2D_R$ , and results consistent with eq 4 were obtained. The dimensionless chemical reaction rate parameter is  $k_t/a$ .

To test the accuracy of the simulation technique, the values of the parameters in the program were adjusted to duplicate conditions for which cyclic voltammetric theory was already available. These simulations were in accord with earlier results for reversible electron transfer with no following reaction,<sup>4</sup> reversible electron transfer with irreversible following reaction,<sup>4</sup> and quasireversible electron transfer with no following reaction.<sup>12</sup>

Simulations were then performed for numerous values of  $\Psi_{cv}$  and  $k_f/a$  using  $\alpha = 0.5$ . Typical currentpotential curves are shown in Figure 1. The current function may be used to compute the current using the relationship<sup>4</sup>

$$i = nFAC_{\circ}^* \sqrt{D_0 a} \sqrt{\pi} \chi(at)$$
 (6)

where  $C_0^*$  is the bulk concentration of O and  $\sqrt{\pi}\chi(at)$  is the current function.

Values of  $n(E_p - E^0)$  are presented in Figure 2. For a reversible electron-transfer reaction ( $\Psi_{cv} \rightarrow \infty$ , dashed curve),  $n(E_p - E^0)$  is approximately -28.5 mV for small  $k_t/a$ , and it varies 29.6 mV per decade of  $k_t/a$  for large  $k_t/a$ . For small  $k_t/a$  and finite  $\Psi_{cv}$ , the peak potentials correspond to the case of quasireversible electron transfer with no following chemical reaction. The chemical reaction can cause large positive shifts in  $n(E_p - E^0)$  only if  $\Psi_{cv}$  is fairly large. When  $\Psi_{cv}$  is small, the electron transfer is almost completely irreversible and the disappearance of the product R has little effect on the potential, as may be seen from the lower curves in Figure 2.

The shapes of the current-potential curves were also examined. Large values of  $\Psi_{\rm cv}$  and small  $k_{\rm f}/a$  give curves of a nearly reversible shape<sup>4</sup> with  $n(E_{\rm p/2} - E_{\rm p})$ approximately equal to 56.5 mV. For large values of  $\Psi_{\rm cv}$  and large  $k_{\rm f}/a$ , the waves develop a "superreversible" shape with  $n(E_{\rm p/2} - E_{\rm p})$  being less than 56.5 mV. For smaller values of  $\Psi_{\rm cv}$ , one sees a regular progression from a quasireversible shape at small  $k_{\rm f}/a$  toward the totally irreversible shape<sup>4</sup>  $[n(E_{\rm p/2} - E_{\rm p}) = 47.7/\alpha n$ mV] as  $k_{\rm f}/a$  increases. Since the simulations become quite lengthy for large  $k_{\rm f}/a$ , no curves were computed

(6) O. Dracka, Collect. Czech. Chem. Commun., 25, 338 (1960).

- (7) A. C. Testa and W. H. Reinmuth, Anal. Chem., 32, 1512 (1960).
- (8) W. M. Schwarz and I. Shain, J. Phys. Chem., 69, 30 (1965).

(10) S. W. Feldberg in "Electroanalytical Chemistry," Vol. 3, Marcel Dekker, New York, N. Y., 1969, pp 199-296.

(11) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience, New York, N. Y., 1954, pp 32-36.

(12) R.S. Nicholson, Anal. Chem., 37, 1351 (1965).

<sup>(9)</sup> J. P. Zimmer, J. A. Richards, J. C. Turner, and D. H. Evans, Anal. Chem., 43, 1000 (1971).



Figure 1. Current-potential curves for cyclic voltammetry with and without a first-order following chemical reaction for three levels of reversibility of the electron-transfer reaction as indicated by  $\psi_{\rm cv}$  (defined in eq 4). Only the cathodic sweep was calculated because the emphasis in this paper is on large values of  $k_t/a$  for which no anodic peak is observed in the cyclic experiment.



Figure 2. Peak potential for cyclic voltammetry as a function of the dimensionless kinetic parameter for the first-order following chemical reaction,  $k_f/a$ , for various values of  $\psi_{ev}$  (numbers on curves) as defined by eq 4. Dashed curve corresponds to a reversible electron-transfer reaction.

for  $k_t/a > 10^2$ . Nevertheless, it appears that both the shape and position of the waves eventually become identical with those for an electrochemically irreversible process<sup>4</sup> as  $k_t/a \rightarrow \infty$ .

For practical evaluation of cyclic voltammetric data, the curves in Figure 2 are inconvenient. It is more desirable to construct plots of  $n(E_p - E^0)$  vs. log (a) for given values of  $k_s/\sqrt{\pi D}$  and  $k_t$ . An example is given in Figure 3 in which  $k_s/\sqrt{\pi D}$  is taken as 100 sec<sup>-1/2</sup>. As log (a) becomes large (rapid scan rates), the peak potential is governed by the limited electron-transfer rate and  $n(E_p - E^0)$  decreases 29.6/ $\alpha n$  mV per decade change in scan rate.<sup>4</sup> When  $k_t$  is small,  $n(E_p - E^0)$ approaches the value expected for a reversible process (-28.5 mV) as log a decreases. For larger values of DENNIS H. EVANS

Figure 3. Peak potential for cyclic voltammetry as a function of scan rate for a given degree of reversibility  $(k_s\sqrt{\pi D} = 100 \text{ sec}^{-1/2})$  and various values of  $k_f$ . Data obtained from Figure 2.

100 sec-1/1

c

-50

-100

n(E<sub>p</sub>-E<sup>o</sup>), mv

4= IO

 $k_i$ , the expected positive shift of  $n(E_p - E^0)$  is observed at slow scan rates.

log a

Curves like those in Figure 3 were constructed for other values of  $k_{\rm s}/\sqrt{\pi D}$ . Larger values move the  $k_t \rightarrow \infty$  line to the right, causing a greater separation between the region of scan rates where the peak potential is governed by the limited rate of electron transfer and the region where the chemical reaction exerts its effect. For smaller values of  $k_{\rm s}/\sqrt{\pi D}$ , the  $k_t \rightarrow \infty$  line moves to the left and both effects must be taken into account at most scan rates.

A general condition may be found in which the electron-transfer reaction is rapid enough and/or the chemical reaction is slow enough that a region of scan rates exists in which the peak potential agrees with that predicted for reversible electron transfer with irreversible following chemical reaction. This condition is given approximately by

$$k_{\rm f} \le k_{\rm s}^2 / 100 \pi D \tag{7}$$

In the case given in Figure 3,  $k_f$  must be less than or equal to  $100 \text{ sec}^{-1}$ . When this is so, the values of  $n(E_{\rm p}-E^0)$  for scan rates less than the scan rate where the chemical kinetic parameter,  $k_f/a$ , is unity ( $a < 10^2$ in this case) are within 2 mV of the values predicted for a reversible electron-transfer reaction with irreversible following chemical reaction.<sup>4</sup> At scan rates greater than the scan rate where  $k_f/a$  is unity, the peak potentials conform to theory for a quasireversible process without following reaction. In other words, the region of scan rate in which the peak potential is governed by the following chemical reaction is well separated from the region in which the peak potential is governed by the limited rate of electron transfer. When inequality 7 is not satisfied, both factors must be taken into account over a considerable range of scan rates, as may be seen by examining the curves for  $k_f > 10^2$  given in Figure 3.



Figure 4. Peak current function for cyclic voltammetry as a function of the dimensionless kinetic parameter for the first-order following chemical reaction,  $k_t/a$ , for various values of  $\psi_{ev}$  (numbers on curves) as defined by eq 4: ---, a reversible electron-transfer reaction; ---, an electrochemically irreversible process.

The peak current function also shows a small but significant dependence upon the rate of the electron-transfer reaction<sup>12</sup> and the rate of following chemical reactions.<sup>4</sup> Values of the peak current function for various values of  $\Psi_{ev}$  and  $k_f/a$  are shown in Figure 4. The current function possesses its characteristic value for a reversible process, 0.4464, when  $k_t/a$  is small, and it increases toward the characteristic irreversible value,<sup>4</sup> 0.4958, as  $k_{\rm f}/a$  becomes large. When  $\Psi_{\rm cv}$  is very small, the peak current function is given by the value for an electrochemically irreversible reaction,  $\frac{4}{viz}$ , 0.4958 $\sqrt{\alpha}$ (lowest line in Figure 4). For intermediate values of  $\Psi_{\rm ex}$ , the current function displays a smooth variation from its value for a quasireversible electron-transfer reaction when  $k_f/a$  is small, to its value for an electrochemically irreversible reaction  $(0.4958\sqrt{\alpha})$  as  $k_{\rm f}/a \rightarrow$ œ

Because many following chemical reactions are not first order and cannot be made pseudo-first order, it was decided to simulate a typical case of a second-order following chemical reaction. The case chosen is given by the reaction scheme

$$O + ne \stackrel{k_{B}, \alpha}{\longrightarrow} R \tag{8}$$

$$2R \xrightarrow{\chi_2} D$$
 (9)

Theory for the specific case where reaction 8 is reversible was given by Olmstead, Hamilton, and Nicholson.<sup>13</sup> The simulation procedure was the same as was used for the first-order following reaction.<sup>14</sup> Peak current functions were within 0.001 and values of  $n(E_{\rm p} - E^0)$  were within 0.2 mV of the values of Olmstead, Hamilton, and Nicholson when  $\Psi_{\rm ev}$  was taken as 10<sup>6</sup>.

Values of  $n(E_p - E^0)$  for this mechanism are presented in Figure 5 for numerous values of  $\Psi_{ev}$  and the



Figure 5. Peak potential for cyclic voltammetry as a function of the dimensionless kinetic parameter for the second-order following chemical reaction,  $k_2C_0^*/a$ , for various values of  $\psi_{ev}$  (numbers on curves) as defined by eq 4. Dashed curve corresponds to a reversible electron-transfer reaction.

chemical kinetic parameter  $k_2C_0^*/a$ , where  $C_0^*$  is the bulk concentration of O. The dependence of the peak potential on kinetic parameters is quite similar to that observed for the first-order case (Figure 2). In addition, the trends in the shape of the current-potential curves and the peak current function parallel the behavior observed for the first-order case.

Again, conditions may be found in which the peak potential will be given quite accurately by the theory for an irreversible second-order reaction following a reversible charge transfer. The appropriate inequality is approximately

$$k_2 C_0^* < k_s^2 / 100 \pi D \tag{10}$$

### Chronopotentiometry

A cumbersome but exact equation for chronopotentiometric potential-time curves corresponding to the reaction scheme given by reactions 1 and 2 may be obtained by introducing the known expressions<sup>3</sup> for the surface concentrations of O and R into eq 3. Numerous chronopotentiograms were computed, and it was found that the quarter-wave potential and the shape of wave depend on the kinetic parameters in a manner completely analogous to that discussed above for cyclic voltammetry. Again, if inequality 7 is satisfied, one can be certain that a region of transition times exists for which the theory for a reversible electron transfer with irreversible following reaction<sup>3</sup> is accurate.

<sup>(13)</sup> M. L. Olmstead, R. G. Hamilton, and R. S. Nicholson, Anal. Chem., 41, 260 (1969).

<sup>(14)</sup> The values of  $k_2$  reported in this paper are defined by the rate equation<sup>10</sup>  $-dC_R/dt = 2k_2C_R^2$ . Olmstead, Hamilton, and Nicholson<sup>13</sup> omit the factor of 2. Therefore, all values of  $k_2$  reported in their paper must be divided by 2 for comparison with the present paper.

In the case of chronopotentiometry, it is possible to show rigorously what was only inferred from the simulations of cyclic voltammograms; *viz.*, as the rate of the following chemical reaction becomes exceedingly rapid, the equation for the chronopotentiometric wave is identical with that for an electrochemically irreversible process<sup>15</sup> (small  $k_s$ ), though in fact  $k_s$  may be quite large.

### Discussion

Numerous investigators have interpreted the position of a wave on the potential axis utilizing theory which assumes that the electron-transfer process is reversible. With the theoretical information from the present work, we will ascertain what effect if any the limited reversibility of the electron-transfer reaction may have had on the experimental results.

Jaenicke and Hoffmann<sup>16</sup> used chronopotentiometry to study the oxidation of ascorbic acid. Current reversal experiments indicated that the rate constant for the reaction of dehydroascorbic acid (probably hydration) was 340 sec<sup>-1</sup>. However, the dependence of  $E_{\tau/4}$  on transition time was not in agreement with theory for reversible electron transfer with a following chemical reaction.<sup>3</sup> In the range of transition times between 10 and 0.1 sec ( $k_{f}\tau$  from 3400 to 34)  $E_{\tau/4}$  varied about 20 mV per decade compared to the predicted 15 mV. In going from a transition time of 0.1 sec to 0.01 sec, an additional 45 mV shift was observed. Thus, this is a case where  $E_{\tau/4}$  is governed by both the following chemical reaction and the limited rate of the electron-transfer reaction, with the latter being more important at short transition times. A more complete analysis of this case is not warranted owing to the very limited amount of data available and the possibility that uncompensated resistance may have affected the current-time curves. Jaenicke and Hoffmann recognized the limited reversibility of the electrode reaction and they did not attempt to extract kinetic information from the  $E_{\tau/4}$ data.

A chronopotentiometric study of the oxidation of p-aminophenol<sup>17,18</sup> utilized the shape and position of potential-time curves to obtain the rate constant for a following chemical reaction. The reaction was rather slow ( $k_{\rm f} = 0.1 \, {\rm sec^{-1}}$ ), and only very modest reversibility of the primary electrode reaction is required. From inequality 7 the apparent value of  $k_s$  should be greater than 0.02 cm/sec. Current-reversal chronopotentiograms' demonstrate that the process is not very reversible, the difference between the potentials of the anodic and cathodic waves indicating an apparent  $k_{s}$  of the order of  $10^{-4}$  cm/sec.<sup>19</sup> Thus, the current-potential curves were governed by both the following chemical reaction and limited reversibility, a fact consistent with the lack of agreement between  $k_f$  obtained from potential data<sup>17,18</sup> and  $k_f$  obtained from current-reversal chronopotentiometry.7

In most applications of cyclic voltammetry to the

study of electrode reactions with following chemical reactions, the kinetic information is obtained from the ratio of peak currents. Shifts in peak potentials have been noted, but a quantitative interpretation of the shifts has rarely been given. In a recent study of the reduction of  $\alpha.\beta$ -unsaturated ketones,<sup>9</sup> a dimerization following reversible charge transfer was postulated. Analysis of peak current ratios yielded a dimerization rate constant of  $1.8 \times 10^5 \text{ l.}/(\text{mol sec})$  using  $1.0 \times 10^{-8}$ M bulk concentration of ketone. Applying inequality 10, we conclude that  $k_8$  must be greater than about 0.4 cm/sec ( $D = 3 \times 10^{-6}$  cm<sup>2</sup>/sec) in order to be able to use the theory for reversible electron transfer with following chemical reaction<sup>13</sup> to interpret the dependence of  $E_{p}$  on scan rate. From the peak separation at rapid scan rates (>30 V/sec), it was found that  $k_s > 1$  cm/sec, which indicates that the electron-transfer reaction is sufficiently reversible. This is supported by the observation<sup>9</sup> that the variation in  $E_p$  with changes in scan rate is in excellent agreement with that predicted assuming a reversible electron-transfer reaction.

Polarography has been the most widely applied technique for the study of following chemical reactions by means of shifts in potential. Though the theory for polarography was not developed in the present work, the similarity in the requirements for reversibility in chronopotentiometry and cyclic voltammetry (inequalities 7 and 10) encourages us to use the same requirement in analysis of the polarographic results, *viz.*,  $k_f$  $< k_s^2/100\pi D$ .

The early data of Kern<sup>2</sup> concerning ascorbic acid oxidation cannot be treated, as he was unable to evaluate  $k_t$  though he did observe a dependence of  $E_{1/2}$  on drop time in agreement with the theory which assumes reversible electron transfer. More informative is the polarographic study of the reduction of the mercury-(II)-EDTA complex in the presence of magnesium ions.<sup>20</sup> The following chemical reaction is the complexation by magnesium ions of the EDTA which is liberated in the initial electrode reaction. Thus, the following chemical reaction is pseudo-first order when the magnesium concentration is much larger than the concentration of mercury-EDTA complex. The rate of the chemical reaction may be controlled by varying the magnesium concentration.

The largest pseudo-first-order rate constant calculated from the experimental data was  $320 \text{ sec}^{-1}$ . Using inequality 7, it is computed that  $k_s$  must be greater

(15) P. Delahay and T. Berzins, J. Amer. Chem. Soc., 75, 2486 (1953).

(19) (a) L. B. Anderson and D. J. Macero, *ibid.*, 37, 322 (1965);
(b) F. H. Byerlein and R. S. Nicholson, *ibid.*, 40, 286 (1968).

<sup>(16)</sup> W. Jaenicke and H. Hoffmann, Z. Elektrochem., 66, 814 (1962).

<sup>(17)</sup> W. K. Snead and A. Remick, J. Amer. Chem. Soc., 79, 6121 (1957).

<sup>(18)</sup> A. C. Testa and W. H. Reinmuth, Anal. Chem., 32, 1518 (1960).

<sup>(20)</sup> D. M. H. Kern, J. Amer. Chem. Soc., 81, 1563 (1959).

than 0.7 cm/sec, assuming the diffusion coefficient of the mercury-EDTA complex to be 5  $\times$  10<sup>-6</sup> cm<sup>2</sup>/sec. Goffert, et al.,<sup>21</sup> have provided polarographic information on the reduction of mercury(II)-EDTA and the anodic wave for EDTA. Using the theory of Koutecky<sup>22</sup> for quasireversible polarographic waves, it was estimated that the apparent  $k_{\rm s}$  was only  $10^{-3}$  cm/sec at the same pH used by Kern.<sup>20</sup> Thus the electrode reaction is not sufficiently reversible to allow use of the theory which assumes reversible electron transfer. In fact the dependence of  $E_{1/2}$  on magnesium ion concentration was considerably less than theoretical, an observation which prompted Kern to speculate that the electron-transfer reaction was not sufficiently reversible.<sup>20</sup> The above calculations fully vindicate this speculation.

One of the most successful applications of the polarographic method was reported by Koryta and Zabransky,<sup>23</sup> who studied the oxidation of cadmium amalgam in the presence of EDTA. The cadmium electrode reaction is highly reversible, and these authors reported good agreement with theory for the dependence of  $E_{1/2}$ on drop time, EDTA concentration, and pH. The largest pseudo-first-order rate constant computed from their data was  $10^7 \text{ sec}^{-1}$ . Using inequality 7 and D = $10^{-5} \text{ cm}^2/\text{sec}$ , it is concluded that  $k_s$  must be greater than 100 cm/sec in order to have sufficient reversibility. Typical values of  $k_s$  for the cadmium(II)-cadmium amalgam electrode reaction are in the range 0.1–1.0 cm/sec.<sup>24</sup> It would appear that the data of Koryta and Zabransky<sup>23</sup> correspond to a case where both limited reversibility and following chemical reaction control  $E_{1/2}$ . However, the latter effect must be dominant, as the data agree within experimental error with theory which assumes a reversible electron-transfer reaction.

The cases discussed above demonstrate that limited reversibility of the electrode reaction often affects data obtained for the EC mechanism. The criteria embodied in inequalities 7 and 10 must be satisfied for a given system before utilizing theory based on assumed reversibility of the electrode reaction. Otherwise, the potential of the wave will be influenced by both factors and the theoretical curves presented in this paper must be employed.

Acknowledgments. This research was supported by the National Science Foundation through Grant No. GP-19579. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

- (22) J. Koutecky, Collect. Czech. Chem. Commun., 18, 597 (1953).
- (23) J. Koryta and Z. Zabransky, ibid., 25, 3153 (1960).
- (24) N. Tanaka and R. Tamamushi, *Electrochim. Acta*, 9, 963 (1964).

<sup>(21)</sup> J. Goffert, G. Michel, and G. Duyckaerts, Anal. Chim. Acta, 9, 184 (1953).

# Multicomponent Diffusion in a System Consisting of a Strong Electrolyte

Solute at Low Concentrations in an Ionizing Solvent

by L. A. Woolf

Diffusion Research Unit, Research School of Physical Sciences, Australian National University, Canberra, A.C.T., Australia (Received August 2, 1971)

Publication costs assisted by L. A. Woolf

Diffusion in a solution composed of a strong electrolyte and a solvent which also ionizes must be described by the flow equations for a three-component system when the ions of the solute and solvent are at similar concentrations. A theory is developed to predict values of the diffusion coefficients for the flows of neutral components. The theory is adequate to describe diffusion in the system (particularly when the concentrations of the solute ions are either much greater than or much less than those of the solvent ions) and indicates large values for the cross-term diffusion coefficients when all ionic concentrations are comparable.

It is usual to describe diffusion in a two-component system consisting of a strong electrolyte solute, 1, dissolved in an ionizing solvent, 0, by Fick's first law

$$(J_i)_{\mathbf{R}} = -(D_i)_{\mathbf{R}}(\partial c_i/\partial x) \qquad (i = 0, 1)$$

where the flows  $J_i$  are measured with respect to a reference frame, R,  $D_i$  denotes the diffusion coefficient, and  $(\partial c_i/\partial x)$  is the local gradient of concentration  $c_i$ . Following a suggestion by Woolf, Miller, and Gosting,<sup>1</sup> experiments by Mills<sup>2</sup> showed Fick's law was inadequate to describe the flows of the neutral components when the stoichiometric concentration of 1 was close to that of the ions which come from partial ionization of the solvent. Since then theoretical methods have been developed to predict diffusion coefficients in systems of three (or more) components when two weak or strong electrolyte components have an ion in common.<sup>3,4</sup>

This paper shows how a theory based on that of ref 3 can be used to calculate values of diffusion coefficients in a three-component system consisting of a partly dissociated solvent and two fully dissociated electrolytes not having any ions in common but each having an ion in common with the solvent. In so doing the qualitative prediction of ref 1 is confirmed and given a quantitative basis.

#### Theory

The system to be considered contains a partially ionized substance, 0, with a degree of dissociation,  $\alpha$  (composed of  $\nu_{04}$  ions of A of valence  $z_4$  and  $\nu_{05}$  ions of B of valence  $z_5$ ) and a completely ionized substance, 3,  $C_{\nu_{26}}$  $D_{\nu_{R}}$ . These dissociate according to eq 1 and 2

$$A_{\nu_{04}}B_{\nu_{05}} = \nu_{04}A^{z_4} + \nu_{05}B^{z_5}$$
(1)

$$C_{\nu_{36}}D_{\nu_{37}} = \nu_{36}C^{z_6} + \nu_{37}D^{z_7}$$
(2)

The system can also be described as consisting of substance 0 and the substances 1 and 2, which ionize fully as, respectively

$$A_{\mu_{14}}D_{\mu_{17}} = \nu_{14}A^{z_4} + \nu_{17}D^{z_7}$$
(3)

$$C_{\nu_{25}}B_{\nu_{25}} = \nu_{26}C_{\cdot}^{z_6} + \nu_{25}B^{z_6}$$
(4)

On either description of the composition of the system it must contain five constituents—the neutral molecules 0 and the four ions, 4, 5, 6, and 7. However, the number of independent components for diffusion is two.<sup>5</sup> Because the theoretical development requires interrelationships between ionic and neutral component chemical potentials, it is necessary to describe the system in terms of the three neutral solutes 0, 1, and 2 which ionize according to (1), (3), and (4). Reaction 1 is assumed to be sufficiently rapid to ensure local chemical equilibrium.<sup>6</sup> All flows and related coefficients are referred to the solvent-fixed frame of reference.<sup>7</sup>

The chemical potentials  $\mu_i$  and their gradients  $X_i$ (=  $-\text{grad }\mu_i$ ) of the solutes 0, 1, and 2 are defined in terms of ionic chemical potentials by

$$\mu_i = \sum_{j=4}^7 \nu_{ij} \mu_j \qquad (i = 0, 1, 2) \tag{5}$$

$$X_{i} = \sum_{j=4}^{7} \nu_{ij} X_{j} \qquad (i = 0, 1, 2)$$
(6)

with  $\nu_{06} = \nu_{07} = \nu_{16} = \nu_{16} = \nu_{24} = \nu_{27} = 0$ . Conserva-

(1) L. A. Woolf, D. G. Miller, and L. J. Gosting, J. Amer. Chem. Soc., 84, 317 (1962).

- (2) R. Mills, J. Phys. Chem., 66, 2716 (1962).
- (3) R. P. Wendt, *ibid.*, 69, 1227 (1965).
- (4) D. G. Miller, ibid., 71, 616 (1967).

(5) There are three independent relations between the five concen-7 7

trations:  $\sum_{i=4}^{l} c_i z_i = 0$ ,  $c_0 \overline{V}_0 + \sum_{i=4}^{l} c_i \overline{V}_i = 1$ , and  $K_{\overline{W}} = c_i^{\mu_{ind}} c_5^{\mu_{\gamma_b}} / c_0$ where  $K_{\overline{W}}$  is the equilibrium constant for (1) and the  $c_i$ 's are concentrations in mol cm<sup>-3</sup>. Also see ref 7.

(6) Compare with W. H. Stockmayer, J. Chem. Phys., 33, 1291 (1960).

(7) J. G. Kirkwood, R. L. Baldwin, P. J. Dunlop, L. J. Gosting, and G. Kegeles, *ibid.*, 33, 1505 (1960). tion of charge and mass for (1), (3), and (4) provide, respectively, the restrictions

$$\sum_{j=4}^{7} \nu_{ij} z_j = 0 \qquad (i = 0, 1, 2) \tag{7}$$

$$c_{j} = \sum_{i=0}^{2} \alpha_{0i} \nu_{ij} c_{i} \qquad (j = 4, 5, 6, 7) \qquad (8)$$

where

$$\alpha_{01} = \alpha_{02} = 1 \text{ and } \alpha_{00} = \alpha \tag{9}$$

The dependence of the macroscopic velocities  $u_t$  of the neutral components 0, 1, 2 on those of the constituent ions may be defined by

$$\sum_{i=0}^{2} \nu_{ij} c_i u_i = c_j u_j \qquad (j = 4, 5, 6, 7) \qquad (10)$$

The flows  $J_t$  of the neutral components or ions are related to these velocities

$$J_i = c_i u_i$$
  $(i = 1, ..., 7)$  (11)

Thus (8)-(11) provide

$$\sum_{i=1}^{2} \nu_{ij} J_i = J_j \qquad (j = 4, 5, 6, 7) \qquad (12)$$

(The terms in  $J_0$  have been omitted from (12) since  $J_0 = 0$  is used here to define the solvent-fixed frame of reference for the flows and velocities.)

Entropy Production. For this system of four ions the entropy production due to isothermal diffusion is

$$T\sigma = \sum_{j=4}^{7} J_{j}X_{j} + fE \sum_{j=4}^{7} z_{j}J_{j}$$
(13)

where  $\sigma$  is the local entropy production per unit volume, T the absolute temperature,  $f = 10^{7}F$  (F is the Faraday) and E is the local electric field. By using (12), (7), and (6) in (13) the ionic flows are replaced and the coefficient of fE eliminated

$$T\sigma = \sum_{i=1}^{2} J_i X_i \tag{14}$$

The linear laws relating the flows and forces may therefore be written in terms of either ionic or neutral component phenomenological coefficients. In the former instance

$$J_{i} = \sum_{j=4}^{7} l_{ij}(X_{j} + z_{j}fE) \qquad (i = 4, 5, 6, 7) \quad (15)$$

where the  $l_{ij}$  are ionic phenomenological coefficients.<sup>4</sup>

Diffusion in multicomponent electrolyte systems is almost invariably described in terms of flows of neutral solutes. Experimental and theoretical flow equations for the present system may be written as

$$J_{i} = -\sum_{j=1}^{2} D_{ij} \operatorname{grad} c_{j} = \sum_{j=1}^{2} L_{ij} X_{j} \qquad (i = 1, 2) \quad (16)$$

where the  $D_{ij}$  define neutral solute diffusion coefficients

and the  $L_{ij}$  corresponding phenomenological coefficients. These coefficients are related by

$$D_{ij} = \sum_{k=1}^{2} L_{ik} \mu_{kj} \qquad (i, j = 1, 2) \qquad (17)$$

where

$$\mu_{kj} = \partial \mu_k / \partial c_j \qquad (k, j = 1, 2) \qquad (18)$$

In the following section the  $l_{ij}$  of (15) are related to the  $D_{ij}$  of (16).

Relations between  $D_{ij}$  and  $l_{ij}$ . The condition of zero net electric current flow requires here that

$$\sum_{j=4}^{7} z_j J_j = 0 \tag{19}$$

and enables the term fE in (15) to be replaced so that

$$J_{i} = \sum_{l=4}^{7} X_{i} \left[ l_{il} - \frac{\sum_{j=4}^{7} \sum_{k=4}^{7} l_{ij} l_{kl} z_{j} z_{k}}{\sum_{m=4}^{7} \sum_{n=4}^{7} l_{mn} z_{m} z_{n}} \right]$$

$$(i = 4, 5, 6, 7) \quad (20)$$

The  $z_i$  in (20) are replaced using (7) in the form

$$z_i = a_{i7} z_7$$
 (i = 4, 5, 6, 7) (21)

with  $a_{47} = -\nu_{17}/\nu_{14}$ ,  $a_{57} = -(\nu_{04}/\nu_{05})a_{47}$ ,  $a_{67} = -(\nu_{25}/\nu_{14})a_{47}$  $\nu_{26}a_{57}$ , and  $a_{77} = 1$ . Using (21) and defining

$$\Omega_{tl} = l_{tl} - \frac{\sum_{j=4}^{7} \sum_{k=4}^{7} l_{tj} l_{kl} a_{j7} a_{k7}}{\sum_{m=4}^{7} \sum_{n=4}^{7} l_{mn} a_{m7} a_{n7}}$$

(i, l = 4, 5, 6, 7)(22)

enables (20) to be rearranged in the form

$$J_{i} = \sum_{l=4}^{7} \Omega_{il} X_{l} \qquad (i = 4, 5, 6, 7)$$
(23)

The ionic chemical potentials  $X_{l}$  in (23) are related through (6) by

$$X_{i} = \sum_{j=0}^{2} a_{ij} X_{j} + a_{i7} X_{7} \qquad (i = 4, 5, 6, 7) \quad (24)$$

where the coefficients  $a_{ij}$  have the values  $a_{40} = a_{42} =$  $a_{52} = a_{70} = a_{71} = a_{72} = 0, a_{41} = 1/\nu_{14}, a_{50} = 1/\nu_{05},$  $a_{51} = -(\nu_{04}/\nu_{14})a_{41}, a_{60} = -\nu_{25}/(\nu_{05}\nu_{26}), a_{61} = -(\nu_{04}/\nu_{14})a_{41}$  $\nu_{14}a_{60}, a_{62} = 1/\nu_{26}$ . Using (24) and the identity<sup>8</sup>

$$\sum_{l=4}^{i} a_{l7} \Omega_{il} = 0 \qquad (i = 4, 5, 6, 7) \qquad (25)$$

in (23) gives<sup>9</sup>

(8) Reference 3, footnote 12.

(8) Reference 3, footnote 12. (9) The Gibbs-Duhem equation in the form  $X_0 = -(1/c_0) \sum_{j=1}^{2} c_j X_j$ 

has been used to eliminate the term in  $X_0$  from (24).

$$J_{i} = \sum_{j=1}^{2} \sum_{l=4}^{7} a_{lj} \Omega_{il} X_{j} \qquad (i = 4, 5, 6, 7) \qquad (26)$$

where

$$a_{ij}' = a_{ij} - (c_j/c_0)a_{i0}$$

The flows of neutral solutes are obtained through (12) (putting p = i + 3)

$$\nu_{ip}J_i = \sum_{j=1}^2 \sum_{l=4}^7 X_j \Omega_{pl} a_{lj}' \qquad (i = 1, 2) \qquad (27)$$

These latter flows are related to the neutral solute diffusion coefficients using (16) and (18)

$$\nu_{ip}D_{ij} = \sum_{k=1}^{2} \sum_{l=4}^{7} a_{lk}' \Omega_{pl} \mu_{kj} \qquad (i, j = 1, 2) \quad (28)$$

Evaluation of the  $\Omega_{pl}$  involves the approximations<sup>10</sup>

$$l_{ij} = 0 \quad (i \neq j) \qquad (i, j = 4, 5, 6, 7)$$

$$l_{ii} = \lambda_i^{\circ} c_i / (|z_i| F^2 \times 10^7) \qquad (i = 4, 5, 6, 7)$$
(29)

Here  $\lambda_i^{\circ}$  is the limiting equivalent conductance in cm<sup>2</sup> ohm<sup>-1</sup> equiv<sup>-1</sup> and the Faraday is in coulomb equiv<sup>-1</sup>. Use of the first of (29) in (22) gives

$$\Omega_{il} = \delta_{il} l_{il} - l_{il} l_{ll} a_{i7} a_{l7} / S \qquad (i, l = 4, 5, 6, 7) \quad (30)$$

where

$$S = \sum_{k=4}^{7} a_{k7}^{2} l_{kk}$$

and  $\delta_{il} = 1$  (i = l) or 0  $(i \neq l)$ .

#### Discussion

In relating the preceding equations with experiment it is convenient to examine three concentration regions.

Mutual Diffusion. When  $c_6$ ,  $c_7 \gg c_4$ ,  $c_5$  all of  $\Omega_{t4}$ and  $\Omega_{t5}$  (i = 4-7) in (23) may be shown via (30) to be much less than any of  $\Omega_{t6}$  or  $\Omega_{t7}$  (i = 4-7) so that  $J_j \approx$ 0 (j = 4, 5) and

$$J_{i} = \Omega_{i6} X_{6} + \Omega_{i7} X_{7} \qquad (i = 6, 7) \qquad (31)$$

Because of the requirements of electrical neutrality  $J_6$ and  $J_7$  are then not independent and may be shown by a similar route to that used by Miller<sup>4</sup> to give a limiting law expression for the mutual diffusion coefficient. This result is in qualitative agreement with experiments of Mills who found that with decreasing solute concentration mutual diffusion persisted in two aqueous solutions to solute concentrations of about  $10^{-7}$  mol cm<sup>-3</sup>.

Tracer Diffusion. When  $c_6$ ,  $c_7 \ll c_4$ ,  $c_5$  (and ions 6 and 7 do not significantly affect the equilibrium between the solvent and ions 4 and 5),  $J_6$  and  $J_7$  are essentially independent. It is reasonable to assume that the chemical potential gradients of ions 4 and 5 will be much less than those gradients for ions 6 and 7, so that  $\partial c_4 / \partial x$  and  $\partial c_5 / \partial x$  are effectively zero; eq 23 then reduces once more to (31).

Because results are available for the flows of bromide ion in the H<sub>2</sub>O-MgBr<sub>2</sub> system, it is convenient to write an explicit expression for  $J_7$  using 4, 5, 6, and 7 to denote the hydrogen, hydroxyl, magnesium, and bromide ions, respectively. The expression is shortened by using the equation for the limiting value of the tracer diffusion coefficient  $D_t$  of an ion i,  $D_t^{\circ} = [RT/(F^2 \times 10^7)](\lambda_t^{\circ}/|z_t|)$ , where R is the gas constant, and by noting that at very low concentrations it is reasonable to assume

$$-X_i = (\partial \mu_i / \partial x) = (\partial \mu_i / \partial c_i)(\partial c_i / \partial x); \quad \mu_i =$$
$$\mu_i^\circ + RT \ln c_i \quad (i = 4, 5, 6, 7)$$

Thus

$$-J_{7} = D_{7}^{\circ} \left\{ \frac{\partial c_{7}}{\partial x} - \frac{c_{7}a_{77}}{S(F^{2} \times 10^{7})} \times \left[ \frac{\lambda_{6}^{\circ}a_{67}}{z_{6}} \frac{\partial c_{6}}{\partial x} + \frac{\lambda_{7}^{\circ}a_{77}}{z_{7}} \frac{\partial c_{7}}{\partial x} \right] \right\} \quad (32)$$

For the present example of H<sub>2</sub>O-MgBr<sub>2</sub> at 298°K  $a_{67} = -2$ ,  $a_{77} = 1$ ,  $z_6 = 2$ ;  $z_7 = -1$ ,  $\lambda_6^\circ = 53.05$ , and  $\lambda_7^\circ = 78.14.^{11}$  The term in square brackets in (32) has an estimated maximum value of about 50 ( $\partial c_7/\partial x$ ) and so long as  $c_7 \leq c_4$ , S is of the order  $5 \times 10^{-8}$ . Thus

$$-J_7 = D_7^{\circ} (\partial c_7 / \partial x) (1 - 10^9 c_7) \quad (c_7 \ll 10^{-10} \text{ mol cm}^{-3})$$

and for  $c_7 < 10^{-11}$  mol cm<sup>-3</sup> the diffusion of ion 7 (and ion 6) closely approximates tracer diffusion. This is in reasonable accord with the results of Mills<sup>2</sup> who obtained values of  $D_7 \approx D_7^{\circ}$  within experimental error<sup>12</sup> over the concentration range  $4 \times 10^{-9}$  to  $6 \times 10^{-11}$ mol cm<sup>-3</sup>. It is also in agreement with the result predicted from the Onsager limiting law for tracer diffusion.<sup>13</sup>

Three-Component Diffusion. When the concentrations of all the ionic species are comparable, it is no longer possible to eliminate transport coefficients or chemical potential gradients from (20). Equation 28 must then be used to evaluate the multicomponent diffusion coefficients of the neutral solutes chosen to represent the diffusing system. By defining

$$\mu_{k} = \mu_{k}^{\circ} + RT \ln \prod_{j=4}^{7} (c_{j})^{\nu_{kj}} \qquad (k = 0, 1, 2)$$

assuming all activity coefficients to be unity, and using (8), (9), the second equation of footnote 5, putting

$$\alpha \ll 1$$
 and assuming  $\sum_{j=1}^{n} c_j \overline{V}_j \ll 1$  there results

<sup>(10)</sup> These approximations are virtually exact for the concentration region where (28) describes diffusion in a system comprising a strong electrolyte solute in water (see ref 3, p 1231).

<sup>(11)</sup> R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 2nd ed (revised), 1965, p 465.

<sup>(12)</sup> The diffusion measurements of ref 3 were made in water having a specific conductance about ten times higher than that of pure water. Therefore the results at  $10^{-10}$  mol cm<sup>-3</sup> and lower concentrations may be in error.

<sup>(13)</sup> L. J. Gosting and H. S. Harned, J. Amer. Chem. Soc., 73, 159 (1951).

$$\mu_{kj} = (\partial \mu_k / \partial c_j) = RT \delta_{kj} \left( \frac{\nu_{kq}}{c_k} + \frac{\nu_{kr}^2 \overline{V_o}^2}{\alpha_{00} \nu_{or} + c_k \nu_{kr} \overline{V_o}} \right) \quad (33)$$

(q = 8 - k; r = k + 3; k = 0, 1, 2; j = 4, 5, 6, 7). Substitution of (33) in (28) and expansion of the summations leads after some algebra to the results

$$D_{11} = \frac{RT}{\nu_{14}} \left( \frac{\nu_{17}}{c_1} + \frac{\nu_{14}^2 \bar{V}_0^2}{\alpha_{00} \nu_{04} + c_1 \nu_{14} \bar{V}_0} \right) \times (a_{41} \Omega_{44} + a_{51} \Omega_{45} + a_{61} \Omega_{46})$$

$$D_{22} = \frac{RT}{\nu_{25}} \left( \frac{\nu_{26}}{c_2} + \frac{\nu_{25}^2 V_0^2}{\alpha_{00}\nu_{05} + c_2\nu_{25} \overline{V}_0} \right) a_{62}\Omega_{56}$$
(34)  

$$D_{12} = (\nu_{25}/\nu_{14})(\Omega_{46}/\Omega_{56})D_{22}$$
  

$$D_{21} = (\nu_{14}/\nu_{25})D_{11}(a_{41}\Omega_{54} + a_{51}\Omega_{55} + a_{61}\Omega_{56})/(a_{41}\Omega_{44} + a_{51}\Omega_{45} + a_{61}\Omega_{46})$$

Values of  $D_{ij}$  calculated from (34) for the system  $H_2O-MgBr_2$  at 25° are given in Table I.<sup>14</sup> The  $\lambda_i^{\circ}$  were from ref 11,  $\alpha$  was calculated to be 1.8068  $\times 10^{-9}$  (based on an ionic product for water of  $10^{-20}$  mol<sup>2</sup> cm<sup>-6</sup>),  $\bar{V}_0 = 18.069$  cm<sup>3</sup> mol<sup>-1</sup>,  $\nu_{04} = \nu_{05} = \nu_{14} = \nu_{17} = \nu_{26} = 1$ ,  $\nu_{25} = 2$ ,  $a_{41} = 1$ ,  $a_{51} = -1$ ,  $a_{61} = a_{62} = 2$ .

Table I:	Diffusion Coefficients in the System
H <sub>2</sub> O-HBr	$-Mg(OH)_2$ at 25° (1 = HBr, 2 = $Mg(OH)_2$ ) <sup><i>a</i></sup>

$C_1$	$C_2$	$D_{11}$	$D_{12}$	$D_{21}$	$D_{22}$
$2 imes 10^{-6}$	$1 \times 10^{-6}$	0.005	-0.001	-0.001	0.000
$2 imes 10^{-7}$	$1 \times 10^{-7}$	0.053	-0.007	-0.015	0.002
$2  imes 10^{-8}$	$1 \times 10^{-8}$	0.515	-0.683	-0.146	0.194
$2 imes 10^{-9}$	$1  imes 10^{-9}$	4.176	-5.513	-1.185	1.565
$2 imes10^{-10}$	$1 \times 10^{-10}$	11.705	-15.285	-3.323	4.339
$2 \times 10^{-11}$	$1 \times 10^{-11}$	5.079	-6.035	-1.442	1.713
$2 imes 10^{-12}$	$1 \times 10^{-12}$	1.785	-1.532	-0.507	0.435
$2 imes 10^{-13}$	$1 \times 10^{-13}$	1.317	-0.965	-0.374	0.274
<sup>a</sup> Concent D <sub>ij</sub> in cm <sup>2</sup> s	rations, $C_1$ , ec <sup>-1</sup> $\times$ 10 <sup>5</sup> .	C2 in mo	l cm⁻³; d	iffusion co	efficients

Sundelof<sup>15</sup> has shown that  $D_{ij} \rightarrow 0$  as  $c_i \rightarrow 0$   $(i \neq j, c_j \neq 0)$ ; (16) reduces then to  $J_i = -D_{ii}(\partial c_i/\partial x)$  and  $D_{ii}$  may be identified as the tracer diffusion coefficient of species *i*. For the present system the results in Table I for the  $D_{ij}$   $(i \neq j)$  indicate that the experimental measurements made by Mills<sup>2</sup> for the diffusion of bromide ion down to concentrations as low as  $10^{-11}$  g-ion cm<sup>-3</sup> do not represent true tracer diffusion.

Unfortunately, it is not possible with this treatment in terms of flows of neutral salts to calculate values of the diffusion coefficient measured by Mills. That author used isotopically labeled bromide ion to follow diffusion in the system. As the concentration of the solute component was made progressively more dilute a breakdown from mutual diffusion to, apparently, tracer diffusion was observed. The method used by Mills measured only the overall flow of the labeled bromide ions and did not enable determination of the contributions to this flow by concentration gradients of other species. A correlation between the present calculations given in Table I and the results of Mills is. however, possible. At the higher concentrations  $(10^{-7})$ mol cm<sup>-3</sup>) of two of the ionic species (since  $c_4$  and  $c_5$  are fixed) three-component diffusion makes only a small contribution to the overall flows. With decreasing concentration the effects of the three-component diffusion increase rapidly reaching a maximum near  $10^{-10}$ mol  $cm^{-3}$  where the concentrations of all the ionic species present are virtually the same. With further decrease in concentration of two of the ionic species the contribution of the three-component diffusion to the overall flows decreases. The major part of the ionic transfer must then be due to tracer diffusion.

The large variations in magnitude of the  $D_{ij}$  in Table I are probably due to describing diffusion in the system in terms of flows of neutral solutes rather than the more physically realistic flows of ions. It is experimentally feasible in multicomponent electrolyte systems to determine ionic diffusion coefficients  $d_{ij}$  defined for a system of n ions by the flow equations<sup>16-18</sup>

$$j_i = -\sum_{j=1}^n d_{ij}(\partial c_j/\partial x) \qquad (i = 1, n)$$

These  $d_{ij}$  may be readily related to the corresponding neutral salt coefficients  $D_{ij}$  and thence to phenomenological coefficients  $L_{ij}$ . Unfortunately, experimental measurements are not available to allow the usefulness of this avenue of approach to be determined.

(17) J. R. Vinograd and J. W. McBain, J. Amer. Chem. Soc., 63, 2008 (1941).

(18) E. R. Gilliland, R. F. Baddour, and D. J. Goldstein, Can. J. Chem. Eng., 35, 10 (1957).

<sup>(14)</sup> In the present terminology the system is written as  $H_2O-HBr-Mg(OH)_2$  to identify its components 0, 1, and 2, respectively.

<sup>(15)</sup> L. O. Sundelof, Ark. Kemi, 20, 369 (1963).

<sup>(16)</sup> Ionic diffusion coefficients have been defined previously in a different and not equivalent form by Vinograd and McBain<sup>17</sup> and Gilliland, Baddour, and Goldstein.<sup>18</sup>

# Catalytic Polarographic Current of a Metal Complex.<sup>1,2</sup> VIII. Effect

# of Weakly Complexing Supporting Electrolytes

by Josip Čaja, Hubert C. MacDonald, Jr., E. Kirowa-Eisner, Lowell R. McCoy, and Harry B. Mark, Jr.\*

Department of Chemistry, University of Cincinnati,<sup>3</sup> Cincinnati, Ohio 45221 (Received April 7, 1971) Publication costs borne completely by The Journal of Physical Chemistry

The polarographic reduction of Ni(II) in the presence of *p*-phenylenediamine (PPDA) has been studied in noncomplexing and in weakly complexing electrolytes. Catalytic prewaves, similar to those previously reported with *o*-phenylenediamine (OPDA), are observed only in the latter case. The reaction mechanism is believed to involve an aquated nickel-anion complex formed in the bulk of the solution and the adsorbed organic ligand. A good correlation is found between the prewave currents obtained with OPDA and Ni(II) in various electrolytes, and the rate of ligand exchange reported by others between corresponding nickelanion complexes and a large organic anion. Experimental data for the PPDA and OPDA-Ni(II) systems agree qualitatively with the predictions of kinetic equations derived for an electrode reaction between a nickel-anion complex and an adsorbed ligand. Experimental data are also presented describing the polarographic results obtained with Ni(II) and isomers of the naphthalenediamines and with an inorganic ligand, N<sub>3</sub><sup>-</sup>.

#### Introduction

Previous investigations have shown that the prewaves observed during the polarographic reduction of Ni(II) in the presence of o-phenylenediamine (OPDA) result from the formation of an electrochemically active complex involving the adsorbed ligand.<sup>2b,d,e</sup> The term prewave arises from the fact that these waves occur at potentials positive to that of the main, irreversible hexaaquonickel wave. Electrochemical kinetic studies <sup>2d-f</sup> conducted in noncomplexing supporting electrolytes have demonstrated that the observed dependence of the prewave height on a variety of experimental variables conforms well with that theoretically predicted for the following reaction mechanism

$$Ni(H_2O)_{6^{2+}} + OPDA_{ads} \xrightarrow{k_{cham}} Ni(OPDA)_{ads}^{2+} \xrightarrow{k_{s1}} Ni^0 + OPDA_{ads}$$
(1)

Because the adsorbed ligand is regenerated by the reduction of the surface complex, the prewaves are also referred to as catalytic prewaves.

Efforts to relate the "apparent rate constants," calculated in kinetic studies, to the outer Helmholtz potentials,  $\phi_2$ , were not completely successful. Although qualitative agreement with the theoretical requirements for this reaction was obtained in relatively dilute ( $\leq 0.5 M$ ) supporting electrolytes, quantitative evaluations of the  $\phi_2$  effects showed that a net charge value of 1+ must be assigned to the reactant involved in the rate-determining step rather than the value of 2+ indicated by reaction 1. Also, in more concent

trated electrolytes, the prewave currents increased with increasing electrolyte concentrations rather than decreasing as predicted by theory. While various explantations have been offered for these unexpected results, these remain conjectural at this time.

In view of the above situation, studies of the ligand catalyzed reduction of Ni(II) have been extended to other ligands to provide a broader base of experimental information. This paper presents data obtained with the *p*-phenylenediamine (PPDA)-Ni(II) system. Particular emphasis will be placed on the unusual results obtained with this combination of reactants in supporting electrolytes containing the alkali metal acetates. A reaction mechanism involving a complexation reaction between the hexaaquonickel ion and the anion of the supporting electrolyte prior to the formation of the surface complex with an adsorbed ligand will be discussed as an alternate to that given in reaction 1. The ligand-catalyzed reduction of Ni(II) by the isomers of the naphthalenediamines and by an inorganic ligand,  $N_3^-$ , will also be described.

(3) Initial studies done at the University of Michigan, Ann Arbor, Michigan.

<sup>(1)</sup> This research was supported in part by Grants No. NSF GP-6425, GP-9307, and GP-27216 from the National Science Foundation.

<sup>(2)</sup> For other papers in this series, see (a) H. B. Mark, Jr., and C. N. Reilley, J. Electroanal. Chem., 4, 189 (1962); Anal. Chem., 35, 195 (1963); (b) H. B. Mark, Jr., J. Electroanal. Chem., 7, 276 (1964); (c) H. B. Mark, Jr., L. R. McCoy, E. Kirowa-Eisner, and H. C. MacDonald, Jr., J. Phys. Chem., 72, 1083 (1968); (d) L. R. McCoy, H. B. Mark, Jr., and L. Gierst, *ibid.*, 72, 4637 (1968); (e) H. B. Mark, Jr., and L. R. McCoy, Rev. Polarogr., 14, 122 (1968); (f) L. R. McCoy and H. B. Mark, Jr., J. Phys. Chem., 73, 953 (1969); (g) L. R. McCoy and H. B. Mark, Jr., *ibid.*, 73, 2764 (1969); (h) H. C. MacDonald, Jr., and H. B. Mark, Jr., *ibid.*, 74, 3140 (1970); (i) J. Čaja and H. B. Mark, Jr., Anal. Lett., 3, 543 (1970).

#### **Experimental Procedures**

In general, the experimental procedures were conducted in accordance with routine practices which have been described elsewhere.<sup>2,4</sup>

Except for the organic diamines and the NaN<sub>3</sub>, all reagents were of reagent quality. The PPDA was purified by treating a saturated methylene chloride solution with activated charcoal. After filtration, the filtrate was heated and cyclohexane was added until PPDA crystals started to form. The resulting mixture was then cooled and filtered. This recrystallization procedure was repeated four times. The various naphthalenediamines were recrystallized twice from ethanol. Sodium acetate was used as received; sodium propionate was recrystallized twice from water. Sodium azide was recrystallized twice from ethanol.

All polarographic measurements were made at the end of the drop life, mechanically maintained at  $4.40 \pm 0.05$  sec. The rate of mercury flow, measured in water, was 2.18 mg/sec at a mercury column height of 100 cm.

Surface concentrations of adsorbed PPDA were calculated from differential capacitance measurements made at a dme. The experimental procedures have been described in a previous paper.<sup>2f</sup> The calculations were made using a computer program<sup>5a</sup> similar to that used by Mohilner and Mohilner.<sup>5b</sup>

### **Polarographic Data**

Polarograms obtained with PPDA and Ni(II) in 0.1 M KCl are shown in Figure 1 together with a typical prewave produced by OPDA in the same electrolyte. It is apparent that greater concentrations of PPDA than of OPDA are required to yield an electrochemical effect. Further, PPDA does not produce a prewave in this electrolyte but rather causes a gradual displacement of the entire wave front in a positive direction as the concentration of the ligand is increased. The results obtained with PPDA and Ni(II) in 1.0 M NaOAc are shown in Figure 2. Here, a prewave similar in appearance to that observed with the OPDA-Ni(II) system emerges as the concentration of the ligand is increased. Similar results are obtained when sodium propionate is substituted for sodium acetate.

The suppression of the PPDA-Ni(II) prewave height with increasing concentrations of sodium acetate in the supporting electrolyte is shown in Figure 3. This behavior is qualitatively similar to that previously reported for the OPDA-Ni(II) system.<sup>2d</sup> This result supports the existence of a rate-controlling chemical reaction at the electrode surface. A decrease in the negative value of the outer Helmholtz potential,  $\phi_2$ , with increasing electrolyte concentrations should reduce the prewave height if, indeed, such a rate-limiting surface reaction were involved. Further support for this contention is found in the fact that substitution of lithium acetate for sodium acetate results in an increase in the height of the PPDA-Ni(II) prewave in a manner



Figure 1. Comparison of polarograms obtained with PPDA and OPDA;  $5 \times 10^{-4} M$  Ni(II) in 0.1 *M* KCl: (---) 1.6  $\times$  10<sup>-4</sup> *M* OPDA, (----) PPDA, concentrations as indicated.



Figure 2. Dependence of prewave current on bulk PPDA concentration; 1.0 M NaOAc,  $10^{-2} M$  Ni(II).



Figure 3. Dependence of prewave current on NaOAc concentration;  $5 \times 10^{-4} M$  PPDA,  $10^{-3} M$  Ni(II).

consistent with the differences in  $\phi_2$  potentials reported for electrolytes containing these cations by Dandoy and Gierst.<sup>6</sup>

The difference between the results obtained with the alkali metal acetates and with the alkali metal salts of strong acid anions is not restricted to the PPDA-Ni(II) system. Some enhancement of the OPDA-Ni(II)

<sup>(4)</sup> L. Meites, "Polarographic Techniques," Interscience, New York, N. Y., 1965.

<sup>(5) (</sup>a) R. LaBudde, private communication, 1968; (b) D. M. Mohilner and P. R. Mohilner, J. Electrochem. Soc., 113, 992 (1968).
(6) J. Dandoy and L. Gierst, J. Electroanal. Chem., 2, 116 (1961).

![](_page_87_Figure_1.jpeg)

Figure 4. Variation in prewave height with electrolyte anion present; 0.1 M electrolyte,  $5 \times 10^{-3} M$  Ni(II),  $10^{-4} M$  OPDA.

![](_page_87_Figure_3.jpeg)

Figure 5. Polarogram of  $10^{-3} M \operatorname{Ni}(II)$  in 0.1  $M \operatorname{NaN}_{2}$  solution, no organic ligand present.

prewave is also obtained with acetate electrolytes. Figure 4 shows the prewaves obtained with the latter reactants in a number of electrolytes. Here, the prewave is distinctly higher in the presence of the acetate ion than in all other solutions with the exception of that containing N<sub>3</sub><sup>-</sup>. The N<sub>3</sub><sup>-</sup> case represents a very different situation, as is evident from Figure 5, where a prewave is shown to be obtained in the absence of any organic ligand in a solution of sodium azide alone. As both the acetate and the azide anions are generally considered no more strongly adsorbed than is the bromide ion,<sup>7-9</sup> the prewave enhancement shown in Figure 4 in electrolytes containing the first two ions cannot be attributed to a simple  $\phi_2$  effect.

A limited amount of data has also been recorded with four isomers of the naphthalenediamines. Polarograms obtained with these materials and Ni(II) are given in Figure 6. Only those amines having adjacent amino groups produce prewaves. No comparative study has yet been made to determine whether the acetate ion affects the prewave heights observed with these ligands.

### Interpretation of the Polarographic Data

The data presented here make it evident that the reduction of Ni(II) can proceed by a number of paths.

![](_page_87_Figure_10.jpeg)

Figure 6. Polarograms obtained with isomers of naphthalenediamine and  $5 \times 10^{-3} M$  Ni(II) in 0.1 M NaOAc: (----) 1,2-NDA, (----) 2,3-NDA, (----) 1,5-NDA.

Dandoy and Gierst in their analysis of the reduction of the hexaaquonickel ion<sup>6</sup> concluded that the electroactive species was a less highly hydrated ion existing in equilibrium with the hexaaquo form. It is not unreasonable to consider that the reduction of the nickel ion in the presence of the azide ion may involve the formation of a more easily reduced mixed aquo-azo complex. The N<sub>3</sub><sup>-</sup> anion is not strongly adsorbed at a mercury surface,<sup>9</sup> and a reaction mechanism involving the adsorbed anion is not likely even though this possibility cannot be excluded if it can be shown that the reaction rate is sufficiently large. In the case of the organic amines, there is little doubt that the adsorbed ligand is directly involved in a surface reaction of the type shown in reaction 1. In the earlier work with OPDA in noncomplexing electrolytes, there was little evidence of any specific effect other than a  $\phi_2$  effect arising from the choice of a particular electrolyte. In this study, however, the highly specific results obtained in acetate solutions strongly suggest that this anion is a partner in the reaction. It is to this possibility that the following discussion is largely directed.

Ligand Exchange Rates. The nickel ion is known to form a complex of the type  $Ni(H_2O)_5X^+$  with the acetate anion (as  $X^-$ ).<sup>10</sup> The formation constants for this as well as those of a number of other complexes of the same type are given in Table I. It is apparent from these data that the magnitude of the formation constant does not in itself offer a basis for predicting the existence of an electroactive complex. If this were true, the use of an electrolyte containing the fluoride ion should

<sup>(7)</sup> D. C. Grahame and B. A. Soderberg, J. Chem. Phys., 22, 499 (1954).

<sup>(8)</sup> L. Gierst, private communication of unpublished results, 1970.

<sup>(9)</sup> F. C. Anson, private communication of unpublished results 1970. A recent study does indicate that  $N_3^-$  is more strongly adsorbed than  $Cl_3^-$ , however. C. V. D'Alkaine, E. R. Gonzalez, and R. Parsons, J. Electroanal. Chem. Interfacial Electrochem., 32, 57 (1971).

<sup>(10)</sup> L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, Burlington House, London, 1964, p 336.

provide the greatest prewave enhancement, whereas an examination of Figure 4 shows the opposite to be true. The answer to this apparent paradox is suggested by the recent ligand-exchange rate studies by Funahashi and Tanaka,<sup>11</sup> who determined the formation constants for a number of mixed aquo-anion complexes of Ni(II) and the ligand-exchange rate constants of these complexes and of the hexaaquo ion with the organic ligand 4-(2-pyridylazo)resorcinol, shown below as HL<sup>-</sup>

$$\begin{array}{c|c} \operatorname{Ni}(\mathrm{H}_{2}\mathrm{O})_{6}^{2^{+}} + 2\mathrm{HL}^{-} \\ + \mathrm{X}^{-} \\ \\ & \\ \operatorname{Ni}(\mathrm{H}_{2}\mathrm{O})_{5}\mathrm{X}^{+} + 2\mathrm{HL}^{-} \end{array} \begin{array}{c} {}^{k_{\mathrm{H}_{2}}\mathrm{o}^{\mathrm{L}}} \\ & \\ & \\ \operatorname{Ni}(\mathrm{H}_{2}\mathrm{O})_{5}\mathrm{X}^{+} + 2\mathrm{HL}^{-} \end{array}$$
(2)

The data presented by these authors are also given in Table I. The exchange rate is clearly greater for the acetonickel complex than it is for the hexaaquonickel ion. Moreover, the hexaaquonickel ion has a greater ligand-exchange rate than does the fluoronickel complex. The azo complex has the highest exchange rate of any shown here. The above data strongly suggest that the acetonickel complex may react more rapidly with the adsorbed ligand than does the hexaaquonickel ion. If this is true for the PPDA-Ni(II)-acetate system, the reaction sequence may be more properly written as

$$\operatorname{Ni}(\mathrm{H}_{2}\mathrm{O})_{6} + \mathrm{X}^{-} \underbrace{\underset{k_{\mathrm{b}}}{\overset{k_{\mathrm{f}}}{\longrightarrow}}} \operatorname{Ni}(\mathrm{H}_{2}\mathrm{O})_{5}\mathrm{X}^{+} + \mathrm{H}_{2}\mathrm{O} \qquad (3)$$

$$\operatorname{Ni}(\operatorname{H}_{2}\operatorname{O})_{5}X^{+} + \operatorname{L}_{ads} \xrightarrow{k_{h}} \operatorname{Ni}(\operatorname{H}_{2}\operatorname{O})_{5}L^{2+}_{ads} + X^{-} \quad (4)$$

$$\underset{L_{soln}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{sonn}}{\overset{L_{son$$

An alternative to the rate-limiting chemical combination step in reaction 4 can also be considered. A transition product, Ni(H<sub>2</sub>O)<sub>5</sub>LX,<sup>+</sup> may be the actual electroactive species, with X<sup>-</sup> regenerated only after the electron-transfer reaction. Kinetic calculations carried out under the condition that  $k_e \gg k_h$  will not be able to distinguish between these alternate paths, as the L<sub>ads</sub> and X<sup>-</sup> regeneration rate will be the same either by the electrochemical reduction or by the prior chemical reaction.

If the adsorption equilibrium between  $L_{ads}$  and  $L_{soin}$  is attained quickly, it is not difficult to derive the dependence of the prewave limiting current arising from reactions 3, 4, and 5 on the reactant concentrations and on time, at a plane electrode under conditions of semiinfinite linear diffusion. This derivation is given

<b>Table I:</b> The Formation Equilibrium Constants, H	Кх,	for
$Ni(H_2O)_{5}X$ Complexes <sup><i>a</i></sup> and the Homogeneous		
Ligand-Exchange Rate Constants, $k_{x}^{L}$ , with		
4-(2-Pyridylazo-)resorcinol <sup>b</sup>		

x	$Log K_x$	$k_{\mathbf{x}}^{\mathbf{L}},$ $M^{-1} \sec^{-1}$
$\mathbf{F}^{-}$	1.1	$1.1  imes 10^3$
$\mathbf{PF_{6}}^{-}$	0	
Cl-	Very weak	
Br-	-0.12	
I-	0	
ClO4-	0	
NO3-	0	
Acetate	0.74	$4.5 imes10^3$
SCN-	1.76, 1.50	
$N_3^-$	0.66	$1.1 imes10^4$
S2O32-	2.06	
(H <sub>2</sub> O)		$1.7 imes10^3$
Reference 10.	<sup>b</sup> Reference 11.	

in the Appendix to this paper. The results of this derivation appear below.

$$i = nFA \frac{\sqrt{D}}{\sqrt{t}} \left[ \frac{K_s[\mathbf{X}^0]}{1 + K_s[\mathbf{X}^0]} \times \exp(k_f[\mathbf{X}^0]t) \right] [M^0] \exp\lambda^2 \operatorname{erfc} \lambda \quad (6)$$

where  $[X^0]$  is the bulk concentration of the anion (in large excess with respect to the concentration of the aquo-anion complex of nickel) and  $[M^0]$  is the bulk concentration of the nickel ion. The parameter  $\lambda$  is defined as

$$\lambda = k_{\rm h}[{\rm L}]_{\rm ads} \sqrt{t} / \sqrt{D} \tag{7}$$

The value of  $\lambda$  can, in principle, be calculated from the ratio of the current given by eq 6 to that of the diffusion-limiting current given by the classical expression<sup>12</sup>

$$i_{\rm d} = nFA\sqrt{D}[{\rm M}^{\rm o}]/\sqrt{\pi}\sqrt{t} \qquad (8)$$

When this is done, the following relationship is obtained

$$\frac{i}{i_{\rm d}} = \sqrt{\pi} \alpha \exp(k_{\rm f}[{\rm X}^{\rm 0}]t) \lambda \exp\lambda^2 {\rm erfc} \lambda$$

or

$$\left[\frac{\exp(-k_{t}[\mathbf{X}^{0}]t)}{\alpha}\right]\frac{i}{i_{d}} = \lambda \exp\lambda^{2} \operatorname{erfc}\lambda$$
(9)

where

$$\alpha = \frac{K_s[X^0]}{1 + K_s[X^0]} \tag{10}$$

(11) S. Funahashi and M. Tanaka, Inorg. Chem., 8, 2159 (1969).

(12) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience, New York, N. Y., 1954, p 51. If the procedure used in deriving eq 6 and 9 are applied to the reactions shown in eq 1, an expression differing from eq 9 only in the absence of the bracketed group of terms in the left member of eq 9 is obtained<sup>13</sup>

$$i/i_{\rm d} = \lambda \, \exp\lambda^2 \mathrm{erfc}\lambda$$
 (11)

with  $\lambda$  again defined as shown in eq 7.

In practice, a better accord with the polarographic case can be achieved by substituting  $\sqrt{7/3D}$  wherever the diffusion term is found<sup>14</sup> or, better, by using the relationship between  $i/i_d$  and  $\lambda$  given by Koutecky's<sup>15</sup> more rigorous treatment of the electrode as an expanding plane. Aside from mathematical considerations, a more serious difficulty attends the use of eq 9. It is evident from Figure 7 that account must also be made for a competing reaction with the hexaaquo (or subhexaaquo) nickel ion. Except in guite concentrated solutions of weakly complexing electrolytes or in dilute solutions of noncomplexing electrolytes where the aquated ion is the sole electroactive species, the actual situation would more likely involve a "mixed" electrode reaction not correctly described by either eq 9 or 11 alone.

A comparison of eq 9 and 11 shows that a "correction" in the form of the bracketed terms in the left member of eq 9 must first be applied to the experimentally determined value for  $i/i_d$  before the value of  $\lambda$  can be properly found from the identical function at the right of both equations. Failure to do so when a significant proportion of the electrode current is derived from the reaction between the adsorbed organic ligand, L, and the metalarion complex will produce an erroneously high value for  $\lambda$ . The degree of error will increase as the electrolyte anion concentration is increased. When these erroneous values of  $\lambda$  are plotted against the  $\phi_2$  values for the electrolytes to yield the charge value for the reacting species in the manner described by Gierst,<sup>16</sup> it follows that erroneous charge values will also be obtained. Indeed, when this was done for the PPDA-Ni(II)-propionate system, a charge of about +0.5was obtained.

The same reasoning provides an explanation for the fact that the prewave current first decreases and then rises or remains static as the concentration of the electrolyte is increased. At low electrolyte concentrations, little of the more easily reduced aquo-anion complex is present, and the predominant reaction is the reduction of the simple aquated ion. Increasing electrolyte concentrations results in a supression of the prewave current by decreasingly negative values of  $\phi_2$ .<sup>2d</sup> As the concentration of the electrolyte is further increased. reduction of the aquo-anion complex becomes the major electrode process and the contribution of the group of terms enclosed in brackets in eq 6 becomes increasingly important. The increase in electrode current with increasing anion concentration then overshadows the effect of the double-layer potential. It should be noted

![](_page_89_Figure_8.jpeg)

Figure 7. Effect of acetate and perchlorate anions on prewaves obtained with  $10^{-3} M$  PPDA and  $5 \times 10^{-3} M$  Ni(II): (----) 1.0 M NaOAC, (----) 1.0 M NaClO<sub>4</sub>, (----) 1.0 M NaClO<sub>4</sub>, no PPDA present.

here that the complex nature of eq 6 makes an adjustment of the reactant concentrations for concentration polarization caused by the  $\phi_2$  potential a difficult matter. No attempt will be made therefore to treat the data in a quantitative manner from this standpoint.

Equation 6 was derived with the assumption that a 1:1 relationship exists in the reaction between the ionic nickel species and the adsorbed organic ligand. If another combining ratio actually existed, this equation should be modified to include an exponent for  $[L]_{ads}$ which would reflect this fact. At low bulk ligand concentrations, where a Henry's law relationship can be assumed to exist between bulk and surface concentrations, it is evident by inspection of eq 7 that the slope of a plot of  $\log \lambda$  against the log of the bulk ligand concentration should equal this stoichiometric coefficient. In this case, unlike that described above, errors arising from a mixed reaction or failure to correct  $i/i_d$  are not too serious. As each set of polarographic measurements is made in one electrolyte and at one time of measured drop life, the terms enclosed in brackets at the left of eq 9 simply become a "constant" for the entire set. At low values of  $i/i_d$ , where a near linear relationship exists between this ratio and  $\lambda$ , values of  $\lambda$  derived from either eq 9 or 11 would differ merely by a proportionality constant. This constant would have no effect on the slope of the plot and, therefore, no effect on the value of the stoichiometric coefficient found in this manner. When this exercise was performed for the PPDA-Ni(II) reactants in 1.0 M sodium acetate and in 0.5 M sodium propionate, a slope of unity was found,<sup>17</sup> indicating a 1:1 relationship. A linear relationship would be expected

- (13) L. R. McCoy, Ph.D. Thesis, University of Michigan, 1967.
- (14) J. E. B. Randles, Can. J. Chem., 37, 238 (1959).
- (15) J. Koutecky, Collect. Czech. Chem. Commun., 18, 597 (1953).
- (16) L. Gierst, Trans. Sym. Electrode Processes, 109 (1959).
- (17) H. C. MacDonald, Jr., Ph.D. Thesis, University of Michigan, 1969.

from eq 6 between the prewave current and the nickel ion concentration. This has been found to hold experimentally with these reactants and electrolytes.<sup>17</sup>

Adsorption State of PPDA. Because the experimental evidence supported the existence of a surface reaction between some species of nickel ion and adsorbed PPDA molecules, surface concentrations of PP-DA have been determined as a function of bulk ligand concentration and of the type and concentration of the supporting electrolyte.

It is evident, as already noted with reference to Figure 1, that considerably greater bulk concentrations of PPDA than of OPDA are required for an equivalent electrochemical effect. This fact could be explained either by a slower reaction rate or by a less favorable adsorption equilibrium for PPDA, resulting in a lower surface concentration of this ligand. Similarly, the greater prewave height observed in acetate electrolytes would be expected if it could be shown that PPDA was more strongly adsorbed from this electrolyte. Figure 8 shows that the ligand, PPDA, is more strongly adsorbed (in the potential range of interest to the prewave) than is OPDA, and no significant increase in adsorption is found in sodium acetate solutions as compared to that found in sodium perchlorate solutions. Thus, the observed polarographic results cannot be explained by differences in the adsorption properties of PPDA and OPDA.

The degree of protonation of the ligand is a matter of concern, as only the nonprotonated ligand has been found to participate in the surface reaction.<sup>2a,b,17,18</sup>

 Table II: Acid Constants and Formation Equilibrium

 Constants for Various Amine Ligands with Ni(II)

Ligand	$pK_a$	Log K
En	10.09ª	$K_1, 7.52; K_2, 6.28; K_3, 4.26$
Aniline	4.60ª	
Pyridine	5.23ª	$K_1, 1.78; K_2, 1.05; K_3, 0.31$
o-Phenylenediamine	4.5ª	$2^{\circ}$ (1:1 complex)
m-Phenylenediamine	4.9ª	No data
<i>p</i> -Phenylenediamine	6.10	No data
1,2-Naphthalenediamine	4.50 <sup>b</sup>	No data
2,3-Naphthalenediamine	4.30	No data
1,8-Naphthalenediamine	4.380	No data
1,5-Naphthalenediamine	4.210	No data

<sup>a</sup> A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen, London, 1962. <sup>b</sup> P. H. Grantham, E. K. Weisberger, and J. H. Weisberger, J. Org. Chem., 26, 1008 (1961); A. Bryson, J. Amer. Chem. Soc., 82, 4862 (1960). <sup>c</sup> Reference 13.

Table II shows that the  $pK_{a_2}$  of PPDA is sufficiently high that the pH must be maintained just below the precipitation point for the nickel ion (about 8.0 for the concentrations used in these experiments) to ensure that

![](_page_90_Figure_9.jpeg)

Figure 8. Comparison of surface concentrations of PPDA and OPDA on mercury in 0.1 M NaOAc and NaClO<sub>4</sub> electrolytes;  $10^{-2} M$  ligand: (×) PPDA and NaOAc, (□) PPDA and NaClO<sub>4</sub>, ( $\Delta$ ) OPDA and NaOAc, (○) OPDA and LiClO<sub>4</sub>.

the greater part of the ligand is present in its free base form. At one point in these investigations, it was felt that the prewave current increase observed in acetate media might be due to a "surface buffering" condition. In unbuffered electrolytes, an increase in the hydrogen ion concentration in the diffuse layer resulting from the negative charge on the electrode<sup>19</sup> could increase the degree of protonation of the adsorbed ligand (and, hence, cause a reduced electrochemical activity) to a degree which would not be predicted from the direct measurement of the bulk pH of the electrolyte. Consideration of simple double layer theory shows that this idea is incorrect. The following experiment shows this also. When the height of the prewave was measured as a function of pH in 0.1 M sodium perchlorate the inflection point of the prewave current-pH curve was found to lie at a pH value of 6.2, a value agreeing well with that shown for the  $pK_{a_2}$  for this ligand in Table II. The coincidence of these values shows there is no "surface buffering" effect in this case.

Unlike the surface concentration and the degree of protonation of the adsorbed ligand, which can be measured reasonably well and correlated with their effects on the prewave current, another factor of possible significance in these surface reactions remains largely unexplored. The orientation of the adsorbed ligand may have an appreciable effect on its ability to participate in a surface reaction. While no unambiguous information is available on this point, the surface concentrations of PPDA present in some of the polarographic measurements are sufficiently high that surface crowding should assure that at least some fraction of the surface concentration is present in a vertical rather than a planar orientation. Inspection of Figure 2 suggests that a vertical position may be the more chemically

<sup>(18)</sup> It has been shown by other investigators that protonation of organic amine ligands reduces the rate of ligand replacement in Ni(II) systems by at least  $10^{4}$ ; *i.e.*, the reaction is much slower than that of the unprotonated ligand: D. L. Rabenstein and R. J. Kula, *J. Amer. Chem. Soc.*, 91, 2492 (1969); J. C. Cassatt and R. G. Williams, *ibid.*, 90, 6045 (1968).

<sup>(19)</sup> K. M. Joshi and R. Parsons, Electrochim. Acta, 4, 129 (1961).

active one, as the prewave only begins to exhibit its characteristic form at high ligand concentrations. If the PPDA molecule reorients from a favorable vertical position to an inactive planar position at more positive potentials (in a manner similar to that found for aniline by Damaskin, *et al.*<sup>20</sup>), again surface crowding would exercise an opposing effect, resulting in a shift of the prewave front to more positive potentials as the ligand concentration is increased (as shown in Figure 1). At this time, however, any effect of ligand orientation on the speed of the chemical reaction remains conjectural.

Effect of the Chemical Properties of the Ligand on the Prewave. The ligand-catalyzed reduction of the nickel ion has been studied using amines having widely different base strengths and complexing abilities. These include pyridine, aniline, ethylenediamine, and m-phenylenediamine,  $^{2a,b}$  as well as the naphthalenediamines, PPDA, and OPDA described in this paper. Although the adsorptivities and, hence, surface concentrations of OPDA, PDDA, and pyridine on Hg are qualitatively similar,  $^{2b,13,17}$  the prewave currents obtained in solutions containing the same bulk ligand concentrations are very different. If no other evidence were available, this would offer proof that the ligand takes a direct part in the rate-determining step.

The magnitude of the prewave current does not correlate with the basicity of the ligand. The  $pK_{a_2}$  values of the monoprotonated forms of these amines together with their known stability constants with Ni(II) are given in Table II. The base strengths of OPDA and of aniline are essentially the same, but aniline does not exhibit electrocatalytic activity. The 1,2, 2,3, and 1,5 isomers of naphthalenediamine and OPDA have nearly the same base strengths, but 1,5-naphthalenediamine, unlike the others, does not produce prewaves with Ni-(II) (see Figure 6). It is of interest to note that while the stronger bases, pyridine and PPDA, do cause prewaves, the anodic shifts of the prewave potentials and the magnitudes of the prewave currents are considerably less than those observed with ligands having adjacent amino groups, e.g., OPDA.<sup>28,13,17</sup>

Thus, in general it appears that the weaker bases with two adjacent functional groups have greater formation constants and/or rate constants of formation for complexation with Ni(II) than do ligands of similar base strength which can satisfy only one coordination site. Although the stronger bases, pyridine and PPDA, are capable of forming electroactive species, it appears that the nature or structure of the complexes formed with monodentate ligands does not provide as great a decrease in the reduction overpotential as does the intermediate formed with the bidentate ligands.

#### Summary

The data presented in this and in previous papers show that the reduction of Ni(II) can proceed in a number of ways which are energetically favored over the direct reduction of the hexaaquonickel ion. Aromatic diamines such as OPDA which have adjacent amino groups are adsorbed at a mercury surface, where they form electroactive complexes with the aquated nickel ion, resulting in a large decrease in the reduction overpotential of Ni(II). Isomers such as PPDA, with more distant functional groups, are adsorbed as strongly but do not react as rapidly with the aquated nickel ion. The reaction rate is changed in cases where certain aquo-anion nickel complexes are present in the solution. This explains the enhancement of the catalytic prewaves observed with Ni(II) and PPDA (and OPDA) in acetate and propionate electrolytes when these are contrasted with those observed in noncomplexing electrolytes such as the perchlorates. A theoretical analysis of the former case is made difficult by the fact that a mixed reaction occurs and by the complexity of the mathematical relationship.

The catalytic prewaves obtained with the naphthalenediamines are similar in all respects to those obtained with the phenylenediamines. The prewaves produced by the anion  $N_3^-$  appear to be similar to those observed with SCN<sup>-</sup>. No effort has been made to treat this reaction from a theoretical standpoint, but the reaction sequence in this case is probably quite complex.<sup>21,22</sup>

No correlation is observed between the base strengths or the complex formation constants with Ni(II) and the electrocatalytic effects of the various organic ligands. Concentration polarization of  $H^+$  in the diffuse double layer by the negatively charged electrode apparently has no effect on the degree of protonation of the absorbed PPDA and OPDA molecules beyond that predictable by simple measurement of the pH of the electrolyte. A good correlation has been found between the prewave currents measured with Ni(II) and OPDA in solutions containing various anions and the ligandexchange rates reported for complexes of Ni(II) containing these anions with the monoionic form of 4-(2pyridylazo)resorcinol.

#### Appendix

Derivation of Kinetic Equations for an Electrochemical Reaction between a Metal-Anion Complex and an Adsorbed Ligand. The dependence of the electrode current on the reactant concentrations and on time under the condition of semiinfinite linear diffusion will be derived for the following reaction sequence

<sup>(20)</sup> B. B. Damaskin, I. P. Mishutushkina, V. M. Gerovich, and R. I. Kaganovich, Zh. Fiz. Khim., 38, 976 (1964).

<sup>(21)</sup> Similar prewaves are observed for the complexing anions  $SCN^{-}$  and  $S_2O_3^{2-}$  (see Table I for the K values). Gierst and Petit<sup>22</sup> have shown for the  $SCN^{-}$  prewave that the  $SCN^{-}$  [not the Ni(II)] is actually reduced and, therefore, the mechanism is much more complex than the electrocatalysis of Ni(II) discussed here. The N<sub>3</sub><sup>-</sup> does not seem to have this added complication.

<sup>(22)</sup> L. Gierst and F. Petit, private communication of unpublished results, 1970; F. Petit, Ph.D. Thesis, La Faculte des Science de Paris, 1968.

$$\mathbf{M}^{m+} + \mathbf{X}^{n-} \underbrace{\overset{k_{l}}{\underset{k_{\mathbf{b}}}{\longrightarrow}}} \mathbf{M} \mathbf{X}^{(m-n)+}$$
(A1)

$$MX^{(m-n)+} + L_{ads} \xrightarrow{k_{h} (slow)} ML_{ads}^{m+} + X^{n-} \quad (A2)$$

$$ML_{ads}^{m+} + me \xrightarrow{k_{e}} M^{0} + L_{bdv} \quad (A3)$$

The derivation will be made with the assumptions that (1) the electron transfer rate,  $k_{\rm e}$ , is much greater than the chemical rate,  $k_{\rm h}$ ; (2) the concentration of the ligand, [X], is much larger than that of the complex [MX]; and (3) at least near-equilibrium surface concentrations of the adsorbed ligand, [L]<sub>ads</sub>, are present at all times. The first of these permits the reverse reaction for eq A2 to be ignored. The second assumption is generally satisfied where the anion is derived from the supporting electrolyte. The third assumption requires careful examination, as the adsorption of large organic molecules may be slow. It has been shown that this assumption can be safely made for one large organic molecule, OPDA, where its concentration is in excess of about  $2 \times 10^{-4} M$ .<sup>13</sup>

In the following operations, the bulk concentrations of the reactants will be indicated by the superscript zero. Charge values will be omitted. The concentration of the metal-anion complex can now be given in terms of the reactant concentrations and the stability constant,  $K_s$ , as

$$[MX] = \frac{K_{s}[X^{0}]}{1 + K_{s}[X^{0}]}[M] = \alpha[M]$$
(A4)

where

$$\alpha = \frac{K_{s}[X^{0}]}{1 + K_{s}[X^{0}]} \tag{A5}$$

In keeping with the method generally used by Delahay,<sup>23</sup> a new quantity, u, will be defined as

$$u = [MX^{0}] - [MX] = \alpha[M^{0}] - [MX]$$
 (A6)

Fick's equation, modified for kinetic terms, becomes

$$\frac{\partial M}{\partial t} = \frac{D\partial^2 M}{\partial x^2} - k_{\rm f}[{\rm M}][{\rm X}^0] - k_{\rm b}[{\rm MX}] \quad ({\rm A7})$$

Combining eq A6 and A7, one obtains

$$\frac{\partial u}{\partial t} = \frac{-D\partial^2 u}{\partial x^2} - \gamma \alpha M^0 + \gamma u \qquad (A8)$$

where

$$\gamma = k_{\rm b} - k_{\rm f} \frac{[{\rm X}^0]}{\alpha} = k_{\rm f} [{\rm X}^0] \tag{A9}$$

The LaPlace transform of A9 can be readily solved for the quantity,  $\bar{u}_{x,s}$  to give

$$\bar{u}_{x,s} = \theta \exp{-x \sqrt{\frac{s+\gamma}{D}}} + \frac{\gamma \alpha [M^0]}{s(s+\gamma)} \quad (A10)$$

where  $\theta$  is to be evaluated from the boundary conditions. The flux,  $\Phi_{0,s}$ , is defined as

$$\Phi_{0,s} = -D\partial u/\partial x \tag{A11}$$

where x = 0. Differentiating eq A10 and setting x = 0 then yields

$$\Phi_{0,s} = \theta \sqrt{D} \sqrt{s + \gamma} \tag{A12}$$

A separate definition for the flux can also be obtained at the electrode surface from the rate of the chemical reaction if this rate controls the electrode process. Assuming a 1:1 relationship between MX and  $L_{ads}$ , one then obtains

$$\Phi_{0,t} = k_{h} [MX]_{0,x} [L]_{ads}$$
(A13)

Equations A13 and A6 can then be combined and the LaPlace transformation taken to give

$$\Phi_{0,s} = \frac{\beta \alpha [M^0]}{s} - \beta \bar{u}$$
 (A14)

 $\mathbf{where}$ 

$$\beta = k_{\rm h} [\rm L]_{ads} \tag{A15}$$

Equations A12 and A14 may now be equated and solved for  $\theta$ . The latter value can then be inserted into eq A10, permitting a solution for the desired quantity,  $\bar{u}_{0,s}$ .

$$u_{0,s} = \alpha [M^0] \left[ \frac{\beta}{s(\sqrt{D\sqrt{s+\gamma}}+\beta)} + \frac{\gamma\sqrt{D}}{s\sqrt{s+\gamma}(\sqrt{D\sqrt{s+\gamma}}-\beta)} \right]$$
(A16)

The inverse transformation of eq A16 then gives

$$u_{0,t} = \alpha[M^{0}] - \alpha[M^{0}] \exp\gamma t \times \exp\frac{\beta^{2}}{\sqrt{D}} t \operatorname{erfc} \frac{\beta}{\sqrt{D}} \sqrt{t} \quad (A17)$$

Equation A17 can then be combined with eq A6 and A13 to give

$$\Phi_{0,t} = \beta |\alpha[\mathrm{M}^0] \exp \gamma t \; \mathsf{X}$$

 $\exp \frac{\beta^2 t}{D} \operatorname{erfc} \frac{\beta}{\sqrt{D}} \sqrt{t}$  (A18)

(23) Reference 12, p 417.

Reinserting previously defined values for constants and simplifying, one finally obtains

$$\Phi_{0,t} = \frac{\sqrt{D}}{\sqrt{t}} \alpha[M^0] \exp k_t [X^0] t \lambda \, \exp \lambda^2 \text{erfc} \lambda \quad (A19)$$

where

$$\lambda = \frac{\beta}{\sqrt{D}}\sqrt{t} = \frac{k_{\rm h}[{\rm L}]_{\rm ads}}{\sqrt{D}}\sqrt{t} \qquad (A20)$$

The current is given by

$$i = nFA\Phi_{0,t} \tag{A21}$$

# Oxidation Pathways of 2,2'-Benzothiazolinone Azines. I. Electrochemistry

#### by Jiří Janata and Michael B. Williams

P. & P. Laboratory, I.C.I. Ltd., The Heath, Runcorn, Cheshire, England (Received October 7, 1971) Publication costs assisted by Imperial Chemical Industries Ltd.

2,2'-Benzothiazolinone azines are oxidized at a platinum electrode in two steps to the radical cation and dication, respectively. The value of the apparent semiquinone formation constant K' characterizing the stability of the radical cation depends on the acidity of the solution because of the protonation of both neutral azine and of the dication. The dication has been found to decompose autocatalytically yielding the radical cation, ketone, imine, and nitrogen as final products. The decomposition mechanism which is also acidity dependent has been proposed.

Oxidation of 2,2'-benzothiazolinone azines and related compounds has been studied extensively both by chemical<sup>1</sup> and electrochemical<sup>2</sup> methods. Because of some discrepancies between reported electrochemical parameters of these compounds and stabilities of their higher oxidized states we have reexamined their behavior in media which would not interfere with oxidation processes at more positive potentials. We have observed that the oxidation pattern is profoundly affected by the acidity of the medium and, to a lesser extent, by the concentration of water. All derivatives were found to be sufficiently soluble in aqueous and nonaqueous acetonitrile which offers a relatively wide potential range. Most of the measurements have been done on 2,2'-(3-methylbenzothiazolinone) azine as a model compound. Intermittent checks on the behavior of other derivatives were made to ensure that they follow the same pattern.

### **Experimental Section**

All azines studied in this work were synthesized and purified by methods described by Huenig, et al.<sup>1</sup> 3-Methylbenzothiazolinone hydrazone was prepared according to Besthorn<sup>3</sup> and recrystallized from methanol (mp 142°); the supporting electrolyte used in nonaqueous acetonitrile was 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB). The salt itself was prepared by mixing aqueous solutions of ammonium tetrafluoroborate with tetrabutylammonium hydroxide and recrystallizing the precipitate twice from 1:1 ethanol-water mixture. Spectroscopic grade (BDH) acetonitrile was distilled from  $P_2O_5$  and stored over activated molecular sieves Linde Type 4A. All electrochemical experiments were carried out under nitrogen purified over a Cu catalyst and molecular sieves. The nitrogen was presaturated with acetonitrile vapor.

The potentiostat used in this work was noncommercial, based on operational amplifiers.<sup>4</sup> A Wavetek function generator Model 110 and Tectronix storage oscilloscope Model 549 were used for fast-sweep cyclic voltammetry. The platinum rotating disk electrode (RDE) had a stationary area of 0.020 cm<sup>2</sup> (measured by traveling microscope). Because of a small but significant wobble on the shaft, no absolute current measurements have been made with this electrode. Unless stated otherwise the speed of rotation of the electrode was 1320 rpm. The reference electrode for aqueous acetonitrile was Ag-AgCl, in saturated KCl. Silver wire in 0.01 M AgNO<sub>3</sub> acetonitrile solution served as

<sup>(1)</sup> S. Huenig, H. Balli, H. Conrad, and A. Schott, Justus Liebigs Ann. Chem., 676, 36 (1964).

<sup>(2)</sup> S. Huenig, H. Balli, H. Conrad, and A. Schott, *ibid.*, 676, 52 (1964).

<sup>(3)</sup> E. Besthorn, Ber. Bunsenges. Phys. Chem., 43, 1579 (1910).

<sup>(4)</sup> E. R. Brown, T. G. McCord, D. E. Smith, and D. De Ford, Anal. Chem., 38, 1119 (1966).

the reference electrode for nonaqueous studies. All experiments were carried out at  $25.00 \pm 0.05^{\circ}$ .

A Perkin-Elmer spectrophotometer Model 350 was used for optical measurements.

#### Results

Acidity Dependence of the Main Redox System. Reactions dominating the oxidation-reduction pattern of the azines are as follows

![](_page_94_Figure_5.jpeg)

The dissociation constant of the equilibrium I-IV has been determined spectrophotometrically (in 1:1 cellosolve-water mixture) as  $pK_1 = 1.8$ . The second protonation constant  $K_2$ , which is expected to be close to  $K_1$ , has not been determined, but it has been observed that the spectrum of the dication changes with acidity of the solution. Thus, the absorption maximum shifts gradually from 515 nm in 0.19 M H<sub>2</sub>SO<sub>4</sub> to 505 nm in 1.87 M H<sub>2</sub>SO<sub>4</sub>. On the other hand, no change in the visible or uv spectrum of II has been observed over the range 0.1 to 3 M H<sub>2</sub>SO<sub>4</sub>.

The dependence of the half-wave potentials of the first and second waves and of the logarithm of the apparent semiquinone formation constant K' on concentration of sulfuric acid is shown in Figure 1. Since the definition of pH scale is not valid for the media used in this work, the dependence of half-wave potentials on the acidity cannot be interpreted in the usual way.<sup>5</sup> It should be noted, however, that the curves for the half-wave potentials (Figure 1) are symmetrical, which implies that the same number of protons are involved in both steps.

A summary of half-wave potentials and of apparent semiquinone formation constants of 3-methyl-, 3-ethyl-, and 3-ethyl-6-sulfonate derivatives in unbuffered aqueous and nonaqueous acetonitrile are given in Table I. The second wave of 2,2'-(3-ethyl-6-sulfonate benzothiazolinone) azine is poorly developed in both media because of coating of the RDE with insoluble dication<sup>2</sup> IV.

Oxidation at RDE and Cyclic Voltammetry. Two one-electron oxidation steps should produce two waves

![](_page_94_Figure_10.jpeg)

Figure 1. Dependence of half-wave potentials and apparent semiquinone formation constant K' on concentration of H-SO<sub>4</sub> in 3:1 acetonitrile-water mixture. The concentration of I is  $2.46 \times 10^{-4} M$ .

![](_page_94_Figure_12.jpeg)

Figure 2. Dependence of the ratio of limiting currents on the square root of speed of rotation  $\omega^{1/2}$  (in radians sec<sup>-1</sup>) for (a) nonaqueous acetonitrile, (b) 3:1 acetonitrile-water mixture, (c) 3:1 acetonitrile-water mixture, 1 *M* H<sub>2</sub>SO<sub>4</sub>. Concentration of I is 5.0 × 10<sup>-4</sup> *M*.

of equal height. In fact the ratio of the two limiting currents,  $i_1/i_2$ , changes with experimental conditions. Plots of limiting current of the first wave against square root of speed of rotation ( $\omega^{1/2}$ ) are linear under all conditions studied which indicates that this oxidation step is diffusion controlled. On the other hand, the ratio  $i_1/i_2$  in nonaqueous (a) or neutral (b) medium changes with the speed of rotation (Figure 2). In acid aqueous acetonitrile (c) the ratio remains constant but is less than unity.

The ratio of limiting currents is also affected by the concentration of water. It can be seen from Figure 2 curves a and b that the concentration of water determines whether this ratio increases or decreases with  $\omega^{1/2}$ . Furthermore, the relative position of these two curves depends on the concentration of the depolarizer. There is no doubt that water plays an important role in

(5) L. Meites, "Polarographic Techniques," 2nd ed, Interscience, New York, N. Y., 1965, p 248.

		-3:1 acetonitrile-wat	er		Nonaqueous acetoniti	ile <sup>a</sup>
	$\frac{E^{1/2}I_/II^b}{mV}$	$E^{1/2}$ II/III <sup>b</sup> mV	$10^{-8} \times K'$	${E^{1/2}}_{\mathrm{I/II}^c}{\mathrm{mV}}$	${E^{1/2}}_{\mathrm{II}/\mathrm{III}^c}{}_{\mathrm{mV}}$	$10^{-8} \times K'$
3-Methyl-	465	945	1.35	225	742	5.08
3-Ethyl-	463	950	1.78	210	723	4.78
3-Ethyl-6-	550	985 (?)	0.22(?)	232		
sulfo-						

<b>Fable I</b> :	Summary of Half-Wave	Potentials and Semiquinone Formation	1 Constants in Aqueous and Nonaqueous Acet	onitrile
------------------	----------------------	--------------------------------------	--	----------

<sup>a</sup> Concentration of water determined by Karl Fischer method is 0.015 M. <sup>b</sup> Against Ag-AgCl (satd KCl) reference electrode. <sup>c</sup> Against Ag-0.01 M AgNO<sub>3</sub> + 0.1 TBATFB reference electrode.

the second oxidation step. However, the mechanism of its action is not explicitly obvious from measurements at a RDE.

Both oxidation steps were found to be reversible under our experimental conditions. The difference between  $E^{1/4}$  and  $E^{1/4}$  of both waves was between 55.0 and 57.0 mV as predicted in theory for reversible processes. The heterogeneous rate constant determined by cyclic voltammetry<sup>6</sup> was  $2.8 \times 10^{-2}$  cm sec<sup>-1</sup> for both waves in nonaqueous acetonitrile. The diffusion coefficient needed for this calculation was determined chronoamperometrically<sup>7</sup> as  $D = 3.3 \times 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup>. The cyclic voltammogram of the system is shown in Figure 3. Apart from the two pairs of peaks corresponding to the two main oxidation steps no other oxidation-reduction processes due to the presence of electroactive intermediates were detected by this method.

Constant Potential Electrolysis and Characterization of Products. The plot of electrolytic current against charge during constant potential electrolysis at the first wave was linear and had a slope corresponding to one electron as expected. On the other hand, the electrolysis at the second wave yielded a plot which was not linear, the slope increasing steadily as the electrolysis proceeded. The blue radical cation II formed during the electrolysis at the first wave was stable while the red dication III (or V) produced during electrolysis at the second wave decayed fairly rapidly. This behavior, together with observations made at the RDE, indicates that the second oxidation step is complicated by chemical reactions involving the dication. The first oxidation seems to be free of any such associated chemical reactions apart from the equilibrium I-III. As our studies were made under conditions where both kinematic viscosity of the medium and the liquid junction potential of the reference electrode were liable to change, relating the parameters of the second wave to the first one seems to be more appropriate than expressing them separately. For this reason data given in Figure 2 are expressed as ratios of the two currents even though the variable of interest is the limiting current of the second wave.

The only product of constant potential electrolysis at the first wave was the radical cation II. Its solution

![](_page_95_Figure_8.jpeg)

Figure 3. Cyclic voltammogram of I in nonaqueous acetonitrile. Concentration of I is  $9.26 \times 10^{-4} M_{j}$  the scan rate is 37 mV sec<sup>-1</sup>.

gave a strong esr signal, but the spectrum was not sufficiently well resolved for further interpretation. The ultraviolet and visible spectra of the II were identical with the ones described in the literature.<sup>1</sup> The solution after electrolysis at the second wave was initially red and gave a visible spectrum corresponding to the dication.<sup>1</sup> This solution gradually turned blue and the visible and uv spectrum showed increasing concentration of the radical cation. Besides that, there were characteristic absorption peaks at 287, 279, and 240– 260 nm gradually increasing in intensity as the dication spectrum faded away. A number of relevant species, namely 3-methyl-2-benzthiazolone<sup>3</sup> (VI), the protonated form of 3-methyl-2-benzothiazolinone imine (VII), and the protonated form of 3-methyl-2-benzo-

- (6) R. S. Nicholson, Anal. Chem., 37, 1351 (1965).
- (7) I. Shain and K. J. Martin, J. Phys. Chem., 65, 254 (1961).
- (8) G. De Stevens, A. Frutchey, A. Halamandaris, and H. A. Luts,
- J. Amer. Chem. Soc., 79, 5263 (1957).

thiazolinone hydrazone<sup>9</sup> (VIII) have this type of spectrum. As the dissociation constants of VII and VIII

![](_page_96_Figure_2.jpeg)

were determined spectrophotometrically as pK = 8.38 and 5.93, respectively, these two species were present in their protonized form in most of our experiments. Another conceivable intermediate or a final product could be 3-methyl-benzothiazolium ion (IX).

![](_page_96_Figure_4.jpeg)

There was, however, no evidence in the uv spectrum<sup>10</sup> for the presence of this species in any significant concentration. Neither were there lines present in the mass spectrum of the mixture of final products which would indicate its formation.

Attempts to isolate and characterize reaction intermediates failed. The separation after electrolysis by paper or thin-layer chromatography or by electrophoresis always resulted in formation of a diffused zone. The major constituents of this zone have been characterized as the radical cation II, ketone VI, and imine VII. On a large scale, using  $Ce(SO_4)_2$  to produce V, VI and VII (unprotonized) were extracted as final products and characterized by ir, mass spectroscopy, and nmr spectroscopy. In addition an appreciable amount of nitrogen was also produced in these experiments.

The decay of the dication was found to be dependent on the acidity of the medium, strongly acid solutions being more stable. It is evident that the dication decomposes to intermediates which can, under certain circumstances, cause a further reduction of the dication into the radical cation. The overall stability of the dication would then depend both on its rate of decomposition and on the oxidation-reduction properties of the intermediates. No oxidation of VI and VII has been observed at potentials below +1.200 V. It has been shown by Huenig and Balli<sup>11</sup> that the oxidation potential of hydrazone VIII depends on the acidity of the solution and that VIII can participate<sup>12</sup> in the oxidation mechanism of I. We have, therefore, investigated the electrochemical behavior of VIII.

Oxidation of 3-Methyl-2-benzothiazolinone Hydrazone at RDE. It has been shown<sup>11</sup> that the hydrazone can be oxidized at a platinum electrode in a single two-electron step to an unstable intermediate XI. Any further oxidation of XI could not be followed in phosphate-

![](_page_96_Figure_9.jpeg)

citrate buffers used by these authors because of the oxidation of the background electrolyte at potentials above +800 mV. The first half-wave potential in aqueous acetonitrile was identical with the one measured by Huenig, *et al.*,<sup>11</sup> and also shifted to more positive potentials with increasing acidity of the medium (Figure 4, curve a). It was followed by further oxidation barely distinguishable on a poorly developed dc voltammogram (Figure 5, curve a). However, it can be seen quite clearly on the derivative voltammogram (Figure 5, curve b). The dependence of the second peak potential on the acidity is shown in Figure 4, curve b. The overall appearance of the two waves and corresponding cyclic voltammograms indicate that both oxidation steps are completely irreversible. No de-

![](_page_96_Figure_11.jpeg)

Figure 4. Dependence of peak potentials (from derivative voltammograms) of oxidation of 3-methylbenzothiazolinone hydrazone on concentration of  $H_2SO_4$ .

(9) K. Soda, Agr. Biol. Chem., 31, 1054 (1967).

(10) J. Metzger, H. Larive, R. Dennilauer, R. Boralle, and C. Gaurat, Bull. Soc. Chim. Fr., 2857 (1964).

(11) S. Huenig and H. Balli, Justus Liebigs Ann. Chem., 628, 56 (1959).

(12) R. A. Bartsch, S. Huenig, and H. Quast, J. Amer. Chem. Soc., 92, 6007 (1970).

![](_page_97_Figure_1.jpeg)

Figure 5. Dc voltammogram (a) and derivative voltammogram (b) of 3-methylbenzothiazolinone hydrazone in 3:1 acetonitrile-water mixture, 0.5 M H<sub>2</sub>SO<sub>4</sub>. Concentration of VIII is  $4.1 \times 10^{-4} M$ .

finitive conclusions can be made about the nature of the product of the second oxidation step on the basis of these observations. Nevertheless, it could be an unstable diazonium cation XII, the idea, previously rejected<sup>11-14</sup> mainly on the grounds of the lack of any electrochemical evidence of further chemical oxidation of XI. Nonetheless, whatever this oxidation product

![](_page_97_Figure_4.jpeg)

is, it is quite important that the oxidation of VIII does occur in two steps and that these steps are electrochemically irreversible.

#### Discussion

The effect of acidity on the oxidation-reduction pattern of 2,2'-benzothiazolinone azines falls into two categories. The first one includes protonation equilibria I-IV  $(K_1)$  and III-V  $(K_2)$  and affects the stability of the radical cation II through the apparent semiquinone formation constant K'. The second one determines the rate of decomposition of the fully oxidized form III (or V) and has an effect on the overall chemical stability of the system.

Let us assume that, in the first approximation, all the oxidation steps are stable. The equilibrium concentrations of unprotonized forms are given by the semiquinone formation constant which is defined as

$$K = \frac{[\mathrm{II}]^2}{[\mathrm{I}][\mathrm{III}]} \tag{1}$$

Oxidation of I at a platinum RDE then gives two waves, separation of which depends on the value of K and on

the protonation equilibria I-IV and III-V. The electrode potential for the first one-electron oxidation step is given by the surface concentrations  $[I]_0$  and  $[II]_0$ 

$$E = E^{\circ}_{1/11} + \frac{RT}{F} \ln \frac{[\text{II}]_{0}}{[\text{I}]_{0}}$$
(2)

The dissociation constant of IV is

$$K_{1} = \frac{[I]_{0}[H^{+}]}{[IV]_{0}}$$
(3)

 $([H^+] = [H^+]_0)$  and the total surface concentration of the reduced form is

$$C_1 = [I]_0 + [IV]_0 \tag{4}$$

Combination of eq 2-4 and introduction of mass transport equations in the usual way<sup>15</sup> yields an expression for the half-wave potential

$$E^{1/*}_{I/II} = E^{\circ}_{I/II} + \frac{RT}{F} \ln \frac{K_1 + [H^+]}{K_1}$$
(5)

For  $H^+ \gg K_1$  the half-wave potential will shift towards more positive values with increasing concentration of hydrogen ions.

Similarly the expression for the half-wave potential of the second one-electron step is

$$E^{1/i}_{II/III} = E^{\circ}_{II/III} + \frac{RT}{F} \ln \frac{K_2}{K_2 + [\mathrm{H}^+]}$$
 (6)

For  $H^+ \gg K_2$  the half-wave potential will shift towards less positive potentials with increasing concentration of hydrogen ions.

Subtraction of eq 6 from eq 5 yields

$$\Delta E^{1/2} = E^{1/2}_{II/III} - E^{1/2}_{I/II} = E^{\circ}_{II/III} - E^{\circ}_{I/II} + \frac{RT}{F} \ln \frac{K_1 K_2}{(K_1 + [H^+])(K_2 + [H^+])}$$
(7)

In the absence of any protonation the constant K defined by eq 1 can be expressed as<sup>16</sup>

$$E^{\circ}_{II/III} - E^{\circ}_{I/II} = \frac{RT}{F} \ln K$$
 (8)

thus

$$\Delta E^{4/2} = \frac{2.303RT}{F} \log K + \frac{2.303RT}{F} \times \log \frac{K_1 K_2}{(K_1 + [\mathrm{H^+}])(K_2 + [\mathrm{H^+}])}$$
(9)

Defining K' as the apparent semiquinone formation constant the final expression for  $\Delta E^{1/2}$  is

- (13) S. Huenig, Angew. Chem., Int. Ed., 7, 335 (1968).
- (14) S. Huenig, J. Chem. Educ., 46, 734 (1969).
- (15) Reference 5, p 209.
- (16) R. Brdicka, Z. Elektrochem., 47, 314 (1941).

$$\Delta E^{1/2} = \frac{2.303RT}{F} \log K'$$
 (10)

where

$$K' = K \cdot \frac{K_1 K_2}{(K_1 + [H^+])(K_2 + [H^+])}$$
(11)

It follows from eq 11 that K' will decrease with increasing acidity of the solution, and in the limiting case when  $H^+ \gg K_1$ ,  $K_2$  the rate of change of log K' with the acidity should be twice that for  $E^{1/4}I_1II$  or  $E^{1/2}I_1IIII$ . In fact, slopes of linear extrapolations of curves in Figure 1 are  $\Delta E^{1/2} / \Delta [H_2SO_4] = 0.9$  and  $\Delta \Delta E^{1/2} / \Delta [H_2SO_4] = 1.8$ . In another limiting case when  $H^+ \ll K_1$ ,  $K_2$ , K' reduces to K.

It is evident that the decomposition of the dication occurs in two steps. In the first one a molecule of the dication decomposes to an intermediate which then reduces another molecule of the dication to the radical cation. This reducing species is most likely the intermediate XI. The observations made at the RDE demonstrate that water plays an important part at this

![](_page_98_Figure_7.jpeg)

stage. The intermediate XI can now, under certain conditions, reduce another molecule(s) of V to II giving possibly the diazonium cation XII. Hence the overall

 $\alpha V + XI \rightleftharpoons \alpha II + XII + (1 + 2\alpha)H^+$ 

decomposition assumes an autocatalytic character. Both intermediates XI and XII are expected to decompose to products which would give rise to the imine VII and nitrogen as final products.<sup>12</sup> The effect of acidity on the rate of disappearance of V from the solution is threefold. Firstly, hydrogen ions are produced in both reactions in which V decomposes. The increase in acidity will, therefore, tend to stabilize V. Secondly, the reduction potential of the dication  $(E^{1/2}_{II/III})$  shifts towards less positive potentials (Figure 1) while, thirdly, the second peak potential of the hydrazone (Figure 5) becomes more positive with increasing acidity of the solution. This means that the reduction of V to III in sufficiently acid solutions should not take place and V would decompose via the first route only. It has in fact been observed that the solution of V containing more than  $1.5 M H_2SO_4$  decomposes without formation of II although this decomposition takes a rather long time. Reduction of V to II depends ultimately on the relative value of the standard potential of the second oxidation step of azine with respect to the standard potential of the second oxidation step of the hydrazone in a given medium. While the first potential is represented by the half-wave potential  $E^{1/2}_{II/III}$ , the standard potential of the second hydrazone oxidation will be substantially more negative than the observed second peak potential due to the electrochemical irreversibility of this step. Bearing this in mind it is evident from Figure 1 and Figure 4 that in solutions of low acidity the reduction of V to II can occur. At the same time the electrochemical oxidation of XI can take place. The first decomposition route, *i.e.*, the reduction of V to II would cause the regeneration of electroactive species at the surface of the electrode by a purely chemical homogeneous reaction. The magnitude of the resulting catalytic current would then be governed solely by the rate of the second-order chemical reaction. This type of mechanism would fall into the category of ECE reactions. The second route taking place simultaneously is the direct oxidation of XI to XII (or other unstable intermediate). This is a typical ECE process in which the second electron transfer is irreversible. The electrolytic current due to this second oxidation would be, however, governed by the rate of the electrode reaction. Although theoretical treatments for a simple ECE mechanism are known for all common electrochemical techniques,<sup>17</sup> our case is much too complicated for them to be used quantitatively. At the same time all the techniques used support qualitatively the proposed mechanism. For this reason the quantitative evaluation of the decomposition of the dication has been followed by the means of homogeneous kinetics. Results of this work will be reported in the second part of this series.

Acknowledgment. We wish to express our thanks to Mr. R. Blacoe for supplying the samples of azines and related compounds. We are also much indebted to Dr. E. P. Goodings and Dr. R. A. N. Morris for helpful discussions and their interest in this work.

(17) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, p 247.

## Viscosity Effects on Ion-Recombination Kinetics. Bromocresol Green

## in Water-Glycerol Mixtures<sup>18</sup>

#### by P. Warrick, Jr.,<sup>1b</sup> J. J. Auborn,<sup>1c</sup> and Edward M. Eyring\*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (Received August 5, 1971) Publication costs assisted by the U. S. Air Force Office of Scientific Research

Acid-base recombination rate constants of bromocresol green have been determined by the electric field jump (E jump) relaxation method as a function of solvent viscosity in glycerol-water mixtures. These rate constants have been corrected for activity coefficient effects in these mixed-solvent systems. The recombination rate constant varies as the -0.6 power of the coefficient of bulk solvent viscosity. A mechanism involving diffusion of hydrogen ion and the indicator dianion together to form an ion pair, followed by reaction to form the monoanion, fits the data. If this mechanism is correct, the acid-base recombination of bromocresol green is limited by the second reaction in water, but is diffusion controlled in 70% glycerol. The Debye equation has been used to obtain diffusion coefficients which are in reasonably good agreement with those estimated from ionic mobilities in water at 25°.

#### Introduction

The fastest rate at which bimolecular chemical reactions can occur in liquids is the rate at which the reactants diffuse near enough to each other to react. For ions in solution, the Debye equation (1) predicts

$$k_{\text{DIFF}} = \frac{4\pi N_{\text{A}} Z_{\text{A}} Z_{\text{B}} e_0^2 (D_{\text{A}} + D_{\text{A}})}{1000\epsilon k T [\exp(Z_{\text{A}} Z_{\text{B}} e_0^2 / \sigma \epsilon k T) - 1]}$$
(1)

the rate constant of diffusion-controlled reactions.<sup>2</sup> Here  $N_A$  is Avogadro's number,  $Z_i$  is the charge on the ion, i,  $e_0$  is the electronic charge,  $D_i$  is the diffusion coefficient of ion i,  $\epsilon$  is the dielectric constant of the solvent, and  $\sigma$  is the interionic distance at which the ions react, typically of the order of about 7.5 Å in water. In recent years a large number of fast reactions have been studied and have been found to approach the rate predicted by eq 1.

Recently, the rates of ion recombination of several sulfonphthalein indicators have been determined in aqueous solution.<sup>3</sup> The general reaction studied is shown in eq 2. In each case, the recombination rate

$$HIn^{-} \underbrace{\underset{k_{r}}{\overset{k_{d}}{\longleftarrow}}}_{k_{r}} H^{+} + In^{2-} \qquad (2)$$

constant,  $k_r$ , has been found to be about one-half the value predicted by eq 1,  $1.4 \times 10^{11} M^{-1} \sec^{-1}$ .

A diffusion-limited rate constant should decrease as the viscosity of the solvent increases, in an approximately inverse manner. This behavior is described by the Stokes-Einstein equation (3) or some modification

$$D_i = kT/6\pi r_i \eta \tag{3}$$

of it.<sup>4</sup> Here  $\eta$  is the solvent viscosity and  $r_i$  is the radius of the ion i. Thus, one method of testing the applicability of these theoretical equations to these reactions is to examine the dependence of the recombination rate constant on the viscosity of the solvent. Any significant deviation from this inverse relationship may be interpreted as a contribution from nondiffusive processes.

The viscosity of aqueous solutions can be increased conveniently with only a small change in the dielectric constant by adding glycerol. An aqueous solution of 70% glycerol by weight has a viscosity 20 times as great as that of water, while the dielectric constant is about three-quarters that of pure water (see Table I). Such small changes in the dielectric constant make corrections in the Debye equation and activity coefficient calculations reasonably reliable. The mole fraction of water in a 70% glycerol solution is about 0.66, and glycerol should participate effectively in hydrogen bonding. Thus, the hydrogen-bonding properties of the solvent should not be drastically changed by the addition of glycerol. It is reasonable to expect that the only property of the solvent that changes very much is the viscosity. The present study was undertaken to investigate the viscosity dependence of the presumably diffusion-controlled bromocresol green (3',3'',5',5''tetrabromo-m-cresolsulfonphthalein) ion-recombination rate.

#### **Experimental Section**

The E-jump apparatus used in the kinetic experi-

(4) H. G. Hertz, Ber. Bunsenges. Phys. Chem., 75, 183 (1971).

<sup>(1) (</sup>a) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR-69-1717-F; (b) on sabbatical leave from Westminster College, New Wilmington, Pa., during the 1970-1971 academic year; (c) NDEA Title IV Fellow.

<sup>(2)</sup> P. Debye, Trans. Electrochem. Soc., 82, 265 (1942).

<sup>(3) (</sup>a) G. Ilgenfritz, Doctoral Dissertation, Georg-August University, Göttingen, 1966; (b) J. J. Auborn, P. Warrick, Jr., and E. M. Eyring, J. Phys. Chem., 75, 2488 (1971).

Table I: Properties in Glycerol-Water Mixtures

Wt % glycerol	$X_2^a$	ε <sup>b</sup>	$\eta$ , cP <sup>c</sup>	$A, M^{-1/2} d$	$a_{\rm In} \times 10^4$ $M^{-1} { m cm}^{-1}$
0.00	0.0000	78.48	0.893	0.509	4.22
19.98	0.0466	73.98	1.542	0.5519	4.27
49.99	0.1636	65.78	5.041	0.7042	4.35
55.00	0.1930	64.09	6.582	0.7411	4.15
69.97	0.3373	58.50	17.96	0.8778	3.97

<sup>a</sup> Mole fraction of glycerol. <sup>b</sup> Dielectric constant calculated from the data of P. S. Albright, J. Amer. Chem. Soc., **59**, 2098 (1937), by the interpolation formula  $\epsilon = 77.65 - 14.75W - 18.00W^2$ , where W is weight fraction of glycerol. The standard deviation of the calculated dielectric constant from the measured value from 9.88% glycerol to 70.00% is 0.075. <sup>c</sup> Viscosity from viscosity tables of Sheely.<sup>6a</sup> <sup>d</sup> Coefficient of the Debye-Hückel limiting law. <sup>c</sup> Molar absorptivity of the bromocresol green dianion at 617 nm.

ments has already been described.<sup>3b,5</sup> A new reaction cell was constructed of high-density polyethylene with larger electrodes, 25 mm in diameter. The windows were constructed of glass and had a 25  $\times$  4 mm cross section. The windows were press fitted into the cell to prevent leakage and to make glue unnecessary. The optical path length inside the cell was 25 mm. An interference filter passing light of 620  $\pm$  5 nm replaced the monochromator previously used.<sup>3b</sup>

Bromocresol green and water were purified as before.<sup>3b</sup> Glycerol (Matheson Coleman and Bell, USP grade) was used without further purification. A Karl Fisher titration showed  $3.73 \pm 0.03\%$  water present. All weight calculations of glycerol included this correction. Glycerol-water solutions were made up by weight on a Mettler P1200 balance and are reported in weight per cent glycerol.

Reference solutions for standardizing the pH meter were prepared in the following manner. A hydrochloric acid solution was titrated with certified primary standard THAM (tris(hydroxymethyl)aminomethane) from Fisher Scientific Co. and was found to be  $0.0211 \pm$  $0.0001 \ M$ . This solution was diluted by weight with glycerol and water to make accurately known concentrations of HCl. The densities of glycerol solutions at 25° were calculated from the relative density tables of Sheely.<sup>6a</sup> Values of  $pa_{\rm H}$  were calculated for each reference solution<sup>6b</sup> using the Debye-Hückel limiting law to correct for ionic strength. Concentrations of HCl were always less than  $10^{-3} M$ , so the limiting law is a good approximation. At least two and usually three different reference solutions that gave  $pa_{H}$  readings agreeing to within  $\pm 0.03$  pa<sub>H</sub> unit were used to standardize the pH meter for each solvent composition.

Measurements of  $pa_{\rm H}$  were made on a Beckman Model 1019 pH meter equipped with a Broadley-James 9007 combination electrode. The  $pa_{\rm H}$  of the indicator solution was adjusted with either a dilute acidic or basic solution of the indicator. Adjustments of  $pa_{H}$  were made in one direction only on each solution, so no unnecessary sodium or chloride ions were added. The  $pa_{\rm H}$  was measured in the E-jump cell immediately before and after each kinetic experiment and was constant to  $\pm 0.03$  pa<sub>H</sub> unit. These two readings were averaged to obtain the  $pa_{\rm H}$  of the solution during the E-jump experiment. An aliquot of this same sample solution was placed in a 1-cm cuvette and its  $pa_{H}$  measured. Immediately afterward, the optical absorbance of this solution was measured in a Beckman DB spectrophotometer at 617 nm, the wavelength of maximum absorbance of the bromocresol green dianion. The acid form, HIn-, does not absorb measurably at this wavelength. The concentration of the indicator dianion was calculated from this absorbance and the molar absorptivity, a, at this wavelength. The concentration of indicator dianion in the E-jump cell was calculated by correcting the spectrophotometrically determined concentration of the dianion in the cuvette by the difference in  $pa_{\rm H}$  between the two solutions. In most cases, the concentration of dianion,  $\bar{C}_{In2-}$ , was much less than the total concentration of indicator,  $\bar{C}_0$ , so the equilibrium expression may be modified to  $\bar{C}_0 K_{a} \gamma_{HIn} / I_{In^{2-}} = a_{H^8} \bar{C}_{In^{2-8}} = a_{H^k} \bar{C}_{In^{2-k}}$ , where superscript s refers to the solution used for the spectrophotometric experiment and superscript k refers to the solution used for the kinetic studies. The expression may be rearranged to solve for  $\overline{C}_{In^{2-k}} = \overline{C}_{In^{2-s}} \log^{-1} (pa_{H^s}$  $pa_{H^k}$ ). In other cases,  $\overline{C}_{In^{2-s}}$  and  $pa_{H^s}$  were used to calculate a value of  $K_a$  which was then used to calculate  $\bar{C}_{In^{2}}$  from the equilibrium constant expression. Usually the difference in  $pa_{H}$  was less than 0.05  $pa_{H}$  unit. The molar absorptivity was determined from the absorbance of a sample of the indicator solution that had been made basic by adding a small drop of concentrated NaOH solution to the sample. Several indicator concentrations were used to determine the average molar absorptivity. These data are listed in Table I.

At least two relaxation curves were analyzed for each set of reaction conditions. Between 9 and 12 different sample solutions were prepared for each solvent mixture. Equilibrium concentrations thus varied over a wide range of conditions: for example, a  $pa_{\rm H}$  range of more than 1.5 units. Uncertainties are about  $\pm 0.05$  in  $pa_{\rm H}$ ,  $\pm 3\%$  in dianion concentration, and  $\pm 10\%$  in inverse relaxation times.

#### Results

The experimental data for glycerol-water mixtures are listed in Table II. The data for the relaxation in pure water have already been reported,<sup>3b</sup> but are in-

<sup>(5)</sup> S. L. Olsen, R. L. Silver, L. P. Holmes, J. J. Auborn, P. Warrick, Jr., and E. M. Eyring, *Rev. Sci. Instrum.*, 42, 1247 (1971).

<sup>(6) (</sup>a) M. L. Sheely, *Ind. Eng. Chem.*, 24, 1060 (1932); (b) R. G. Bates, "Determination of pH, Theory and Practice," Wiley, New York, N. Y., 1964, p 23.

Table II: Concentrations and Relaxation Times

Wt % glycerol	Co, µMª	paH	$\bar{C}_{\mathrm{In}^{2}}$ , $\mu M^{b}$	$\tau^{-1}$ , 10 <sup>6</sup> sec <sup>-1</sup> c	Corr concn, µM <sup>d</sup>
0.00	2.02	5.53	1.64	1.16	4.30
	2.02	5.26	1.41	1.01	6.91
	50.55	4.40	12.51	3.13	50.24
	50.55	4.09	7.08	5.56	85.70
	101.1	4.02	12.53	7.87	100.5
	101.1	3.90	9.82	6.62	129.1
	101.1	3.75	7.20	11.24	176.0
	101.1	3.52	4.48	17.2	286.5
19.98	9.61	4.92	5.02	0.94	17.53
10.00	9.61	4.87	4.83	1.38	17.98
	9.61	4.57	3.05	1.58	29.32
	9.61	4.23	1.63	2.54	60.72
	9 61	3 95	0.99	4.67	109.2
	52 85	4 11	6.89	4.23	82.17
	52.85	3 83	3 74	5.65	146.0
	52.85	3.59	2 39	8 53	246.5
	52.85	3 40	1.52	15 1	369 3
	105.7	3 75	6 59	7 71	176 6
	105.7	3 48	3.67	12.31	326 0
40.00	0.07	5 46	4 72	0 303	7 98
49.00	9.97	5 34	4.60	0.380	8.96
	9.97	5 17	2 01	0.330	10.37
	9.97	5.04	3.91	0.468	12.08
	9.97 0.07	1 92	2.20	0.680	16.81
	9.97	4.60	1.61	0.009	24 22
	9.97	4.04	1.01	0.852	36 75
	9.91 10.95	4.44	8 20	0.55	20.50
	49.00	4.05	5.84	1 20	25.00
	49.80	4.47	2 22	1.29	65 22
	49.00	4.19	2 20	2 20	87 32
	49.00	4.00	2.39	2.20	145 5
55 00	16 50	5.90	7 20	0.359	19.0
55.00	16.59	0.20	1.20	0.338	14.42
	16.59	4.94	4.02	1 07	22 61
	16.59	4.49	1.02	1.07	55 55
	16.59	4.20	1.21	1.30	04.25
	10.09	4.01	6 65	0.08	25 79
	49.10	4.90	0.00	0.90	59 57
	49.70	9.09	0.70 1.67	1.32	115 5
	49.70	2 20	1.07	2.09	110.0
	49.10	3.80	1.20	3.31 2.61	100.0
	99.00	0.71	2.07	5.01	101.0 971.5
	99.00	2.00	1.7.5	0.25	467 0
60 07	99.00	5 90	1.09	9.33	407.9
09.97	9.14	5 20	3.97	0.0001	0.99
	9.14 0.14	5.00	3.00 1.70	0.099	1.14
	9.14	J.UU 1/79	1.19	0.120	11.44
	9.14 0.14	1 90	0.98	0.200	19.00
	50.29	1 70	6.45	0.407	00.91 00.01
	50.20	4.13 1 16	2 65	0.312	40.00 26 24
	50.20	1.40 1 00	0.00 177	0.440	00.04 01.00
	50.20	12.00 2.04	1.11	0.900	01.00
	JU. 40	J. 94	1.00	1.00	113.4

<sup>a</sup> Total concentration of bromocresol green in all forms. <sup>b</sup> Determined spectrophotometrically for glycerol-water mixtures; calculated from equilibrium constant data in water. <sup>c</sup> Inverse relaxation time, average of at least two relaxations. <sup>d</sup> All of the terms multiplying  $k_r^0$  in eq 5.

cluded with activity coefficient corrections which were not made previously. The relaxation time for the reaction, omitting activity coefficient corrections, is shown in eq 4, where

$$r^{-1} = k_{\rm r}(\bar{C}_{\rm H^+} + \bar{C}_{\rm In^{2-}}) + k_{\rm d}$$
 (4)

 $\tau^{-1}$  is the inverse relaxation time and  $\bar{C}_i$  is the concentration of reactant i at equilibrium. When the ionic strength changes significantly during the reaction and activity coefficient corrections are included, the expression given by Eigen<sup>7</sup> (eq 5) must be used. Since

$$\tau^{-1} = \frac{k_{\rm r}^{0} \gamma_{\rm H} \cdot \gamma_{\rm In^{2-}}}{\gamma^{\pm}} \left[ \bar{C}_{\rm H} \cdot \left( 1 + \frac{\partial \ln (\gamma_{\rm H} \cdot \gamma_{\rm In^{2-}}/\gamma^{\pm})}{\partial \ln \bar{C}_{\rm In^{2-}}} \right) + \bar{C}_{\rm In^{2-}} \left( 1 + \frac{\partial \ln (\gamma_{\rm H} \cdot \gamma_{\rm In^{2-}}/\gamma^{\pm})}{\partial \ln \bar{C}_{\rm H}} \right) \right] + k_{\rm d}^{0} \quad (5)$$

the maximum ionic strength was about 500  $\mu M$ , the Debye-Hückel limiting law is a good approximation. In this treatment the activity coefficient of a species is determined by the magnitude of its electrical charge. Since the transition state has a single negative charge,  $\gamma_{H^+} = \gamma^{\mp}$ . This reduces the activity coefficient correction to a contribution from only the indicator dianion. The Debye-Hückel limiting law may be expressed as  $\ln \gamma_{In^{2-}} = -2.303A(z_{In^{2-}})^2 I^{1/2}$ , so the partial differentials can be taken on the limiting law as in (6),

$$\frac{\partial \ln \gamma_{\text{In}^{2-}}}{\partial \ln \bar{C}_{i}} = \bar{C}_{i} \left[ -2.303A(-2)^{2} \frac{\partial I^{1/2}}{\partial \bar{C}_{i}} \right]$$
(6)

where A is the Debye-Hückel constant and I is the ionic strength. The Debye-Hückel coefficient was calculated from eq 7,<sup>8</sup> where  $\rho$  is the density and all

$$A^{2} = \frac{2\pi N_{A}\rho}{1000(2.303)^{2}} \left(\frac{e_{0}^{2}}{\epsilon kT}\right)^{3}$$
(7)

other terms are as defined previously. The values of A used are listed in Table I.

The ionic strength of this system can be expressed as a function of the measured concentrations for two cases.

Case 1. If  $\bar{C}_{H+} > (\bar{C}_{HIn^-} + 2\bar{C}_{In^{2-}})$ , the system may be described as "acidic," *i.e.*, HCl has been added to the bromocresol green solution and the only other ion to be considered in addition to H<sup>+</sup>, HIn<sup>-</sup>, and In<sup>2-</sup> is Cl<sup>-</sup>. By the principle of electroneutrality,  $\bar{C}_{Cl^-} \approx \bar{C}_{H+}$  $- \bar{C}_{HIn^-} - 2\bar{C}_{In^{2-}}$ . In addition,  $\bar{C}_0$ , the total concentration of bromocresol green, is just the sum,  $\bar{C}_{In^{2-}} + \bar{C}_{HIn^-}$ . Substituting these relationships into the expression for ionic strength, we get (8).  $\bar{C}_{H+}$  and  $\bar{C}_{In^{2-}}$ 

$$I = \frac{1}{2} \sum_{i} \bar{C}_{i} z_{i}^{2} = \bar{C}_{H^{+}} + \bar{C}_{In^{2}}$$
(8)

are also related by the equilibrium expression 9, which can be rearranged to give either  $\bar{C}_{H^+}$  or  $\bar{C}_{In^{2-}}$  as a func-

<sup>(7)</sup> M. Eigen and L. DeMaeyer, Tech. Org. Chem., 8, 904 (1963).

<sup>(8)</sup> S. W. Benson, "The Foundation of Chemical Kinetics," Mc-Graw-Hill, New York, N. Y., 1960, p 524.

VISCOSITY EFFECTS ON ION-RECOMBINATION KINETICS

$$K_{\rm a} = \frac{\bar{C}_{\rm H} + \bar{C}_{\rm In^2} - \gamma_{\rm H^+} \gamma_{\rm In^2}}{\bar{C}_{\rm HIn} - \gamma_{\rm HIn}} = \frac{\bar{C}_{\rm H^+} \bar{C}_{\rm In^2} - \gamma_{\rm In^2}}{\bar{C}_0 - \bar{C}_{\rm In^2}} \qquad (9)$$

tion of the other and the total indicator concentration,  $\bar{C}_0$ . In several of our experiments a trace of a basic impurity was present, which contributes about 10-15  $\mu M$  to the ionic strength, but does not affect calculations of any variable except *I*, either in "acidic" or "basic" solution. This represents a small change, noticeable only in the more basic solutions.

Combining eq 6, 8, and 9 results in the expressions shown in eq 10 for the partial derivatives.

$$\frac{\partial \ln \gamma_{\mathrm{In}^{2-}}}{\partial \ln \overline{C}_{\mathrm{H}^{-}}} = -4.605A \frac{\overline{C}_{\mathrm{H}^{+}}}{I^{1/2}} \times \left[1 - \frac{\overline{C}_{0}\gamma_{\mathrm{In}^{2-}}}{K_{\mathrm{a}}\left(\frac{\overline{C}_{\mathrm{H}^{+}}\gamma_{\mathrm{In}^{2-}}}{K_{\mathrm{a}}} + 1\right)^{2}}\right]$$
(10a)

$$\frac{\partial \ln \gamma_{\text{In}^{2-}}}{\partial \ln C_{\text{In}^{2-}}} = -4.605A \frac{\bar{C}_{\text{In}}}{I^{1/2}} \left[ 1 - \frac{K_{\text{s}}\bar{C}_{0}}{\gamma_{\text{In}^{2-}}\bar{C}_{\text{In}^{2-}}} \right]$$
(10b)

Case 2. If  $\bar{C}_{H^+} < (\bar{C}_{HIn^-} + 2\bar{C}_{In^{2-}}$ , the solution may be described as being "basic," *i.e.*, NaOH may be considered to have been added to the solution. In this case the additional ion to be considered is Na<sup>+</sup>, the concentration of which may be calculated by the principle of electroneutrality to be  $\bar{C}_{Na^+} \approx \bar{C}_{HIn^-} + 2\bar{C}_{In^{2-}} - \bar{C}_{H^+}$ . The expression for the ionic strength may be simplified to eq 11. The same procedure as in case 1

$$I = \bar{C}_0 + 2\bar{C}_{In^{2-}} \tag{11}$$

may be followed to obtain the partial derivatives shown in eq 12. These corrections were calculated and sub-

$$\frac{\partial \ln \gamma_{\text{In}^{2-}}}{\partial \ln \bar{C}_{\text{H}^{+}}} = 9.210A \frac{\bar{C}_{0}\gamma_{\text{In}^{2-}}\bar{C}_{\text{H}^{+}}}{K_{a}I^{1/2} \left[\frac{\bar{C}_{\text{H}^{+}}\gamma_{\text{In}^{2-}}}{K_{a}} + 1\right]^{2}}$$
(12a)  
$$\frac{\partial \ln \gamma_{\text{In}^{2-}}}{\partial \ln \bar{C}_{\text{In}^{2-}}} = -9.210A \frac{\bar{C}_{\text{In}^{2-}}}{I^{1/2}}$$
(12b)

stituted back into eq 5. At most they did not exceed 5.4%.

The corrected concentrations, all the terms in eq 5 multiplying  $k_r^0$ , and  $\tau^{-1}$  are shown in Table II. For each solvent mixture these data were graphed as  $\tau^{-1}$  vs. the corrected concentrations, and linear least-squares best fits were obtained. The slope is  $k_r^0$  in liters per mole per second and the intercept is  $k_d^0$  in reciprocal seconds. These are listed in Table III. A typical graph, in 50% glycerol, is shown in Figure 1.

#### Discussion

One-Step Diffusion-Controlled Mechanism. If the bromocresol green ion recombination is diffusion controlled, the Debye equation (1) predicts that the rate constant should be directly proportional to the sum of the diffusion coefficients of the reactants. When the

 Table III:
 Observed Rate Constants of Bromocresol Green

 Recombination Kinetics
 Image: Constant Science Constant Scien

Wt % glycerol	$k_r^0, 10^{10} M^{-1}$ sec <sup>-1</sup>	kd <sup>0</sup> , 10 <sup>5</sup> sec <sup>-1</sup>	Correlation coefficient
0.00	5.77	6.75	0.9889
19.98	3.73	5.15	0.9925
49.99	2.38	2.29	0.9961
55.00	1.92	2.66	0.9977
<b>69.97</b>	0.903	0.573	0.9827

![](_page_102_Figure_16.jpeg)

Figure 1. Plot of E-jump reciprocal relaxation times,  $\tau^{-1}$ , vs. the corrected concentration for bromocresol green in 49.99% glycerol at 25°.

solvent composition is changed, corresponding changes occur in the dielectric constant, hydrogen-bonding properties of the solvent, and the viscosity. The Debye equation corrects for the dielectric constant change to the extent that the dielectric constant in the bulk of the solvent describes the dielectric constant between the ions. Since the ions probably diffuse together from a distance greater than two or three solvent molecular diameters,<sup>9</sup> this is probably not a serious source of error for such small changes in dielectric constant.

A decrease in hydrogen bonding of the solvent should produce a decrease in the diffusion coefficient of the hydrogen ion due to loss of hydrogen-bond bridges for migration. Since the hydrogen ion almost certainly migrates five to ten times faster than the dianion, the effect on the hydrogen ion diffusion should mask the changes on the diffusion of the dianion. The change in mobility should not be great because even in solutions of the highest glycerol concentration water molecules comprise two-thirds of the species present. Another factor minimizing the change is the large number of hydrogen-bonding sites on a glycerol molecule; about half of the molecular volume is made up of hydroxyl groups capable of effective hydrogen bonding.

<sup>(9)</sup> M. Eigen and L. DeMaeyer, Proc. Roy. Soc., Ser. A, 247, 505 (1958).

These two factors argue for a small decrease in the diffusion coefficient of the hydrogen ion in glycerol-water mixtures due to hydrogen-bonding effects.

The large viscosity increase for glycerol-water solvent mixtures should effectively decrease the ionic diffusion coefficients. The Stokes-Einstein equation (3) does not adequately describe the observed viscosity effects in this study; however, most empirical or semiempirical treatments use a correction factor to the viscosity which is nearly constant as the viscosity is changed.<sup>4</sup> This suggests that a relationship such as eq 13 should be a fair description of the change in a

$$k_{\text{DIFF}} = \frac{B}{\eta} = \frac{B_0}{\eta_{\epsilon} [\exp(z_A z_B e_0^2 / \sigma \epsilon kT) - 1]}$$
(13)

diffusion-controlled rate constant with viscosity.

Thus, if this reaction is diffusion controlled, the rate constant should be nearly inversely proportional to the viscosity. A test of this prediction is shown in Figures 2 and 3. Figure 2 shows a graph of the observed recombination rate constant,  $k_r^0$ , as an inverse function of viscosity. The nearly straight line is calculated from eq 13 using  $k_{\rm r}^0$  in water as the reference point. The open circles, the observed values of  $k_r^0$ , fall consistently above the calculated line. Figure 3 shows a plot of the ratio of the observed  $k_r^0$  for each solvent composition to  $k_{\text{DIFF}}$  from eq 13, calculated as for Figure 2 as a function of  $\eta^{-1}$  and shows that the disagreement is significant and regular. Since the rate constant decreases with increasing viscosity, a diffusioncontrolled process appears to be involved in the reaction. However, the nonlinearity suggests that it is not the only process occurring.

It may be possible to explain the data assuming a different viscosity dependence for the diffusion coeffi-

![](_page_103_Figure_7.jpeg)

Figure 2. Plot of bromocresol green ion-recombination rate constant,  $k_r^0$ , as a function of bulk solvent viscosity: (O) observed rate constants, (—) calculated from eq 13 using the rate constant in water as a reference value.

![](_page_103_Figure_9.jpeg)

Figure 3. Plot of the ratio of the observed recombination rate constant to the value calculated from eq 13: (O) observed ratios, (-) result calculated from eq 13.

cient. A log-log plot of the observed rate constant vs. solvent viscosity gives a slope of -0.6, far away from the expected value of -1.0. An analogous system is HCl in glycerol-water mixtures. Equivalent conductance measurements have been made on 0.1 *M* HCl solutions.<sup>10</sup> A log-log plot of equivalent conductance against viscosity gives a slope of -0.77, still not the expected value of -1.0 but closer to it. These are different processes, but the viscosity dependence should be similar. This disagreement in viscosity dependence does not exclude the one-step mechanism, but data to be presented later make the one-step mechanism appear unlikely.

Two-Step Mechanism. Another way of looking at the reaction is a two-step mechanism<sup>11</sup> similar to the one proposed by Eigen<sup>12</sup> for metal-ligand complexation: diffusion to an ion pair, IP, followed by a chemical reaction to form the protonated form,  $HIn^-$ . The reaction scheme is shown in eq 14. Standard kinetic

$$H^{+} + In^{2-} \underbrace{\underset{k-\text{DIFF}}{\overset{k_{\text{DIFF}}}{\longrightarrow}} IP^{-} \underbrace{\underset{k-\text{CH}}{\overset{k_{\text{CH}}}{\longrightarrow}} HIn^{-}}_{k-\text{CH}} (14)$$

treatment, including the steady-state approximation,  $dC_{IP}/dt = 0$ , leads to exactly the same form as eq 4, with the replacements shown in (15). Inversion of

$$k_r^0 = \frac{k_{\text{DIFF}}k_{\text{CH}}}{k_{-\text{DIFF}} + k_{\text{CH}}}$$
(15a)

$$k_{\rm d}^{0} = \frac{k_{\rm -DIFF}k_{\rm -CH}}{k_{\rm -DIFF} + k_{\rm CH}}$$
(15b)

(15a), substitution of  $K_{\rm IP} = k_{\rm DIFF}/k_{\rm -DIFF}$ , and rearrangement gives

(10) I. I. Schukow and G. F. Dueprov, Russ. J. Gen. Chem., 8, 1476 (1938); cited in Landolt-Bornstein, Band II, Teil 7, p 605.

(11) J. M. Schurr, Biophys. J., 10, 700 (1970).

(12) M. Eigen, Z. Elektrochem., 64, 115 (1960); M. Eigen and K. Tamm, *ibid.*, 66, 93 (1962).

$$\frac{K_{\rm IP}}{k_{\rm r}^{0}} = \frac{K_{\rm IP}}{k_{\rm DIFF}} + \frac{1}{k_{\rm CH}}$$
(16)

The Fuoss equation  $(17)^{13}$  may be used to calculate the

$$K_{\rm IP} = \frac{4\pi\sigma^3 N_A}{3000} \exp(-z_A z_B e_0^2 / \sigma \epsilon kT)$$
(17)

ion-pair equilibrium constant,  $K_{\rm IP}$ . Values of  $K_{\rm IP}$  for interaction distances of 5, 7.5, and 10 Å calculated from (17) are shown in Table IV. These values of the interaction distance cover the plausible range; *i.e.*, the radius of the bromocresol green dianion is estimated to be at least 4.8 Å. It is reassuring to see that these values of  $K_{\rm IP}$  fall in the same range as measured ion pair equilibrium constants for 1-2 electrolytes, *i.e.*, 4-25  $M.^{14}$ 

Table IV :	Equilibrium	Constants	from	$\mathbf{E}\mathbf{q}$	17	and	Rate
Constants f	from Eq 18						

	~~~~~	-Interaction distanc	e
Wt % glycerol	5 Å	7.5 Å	10 Å
	K	IP	
0.00	5.49	7.14	10.42
19.98	6.53	8.02	11.48
49.99	9.52	10.32	13.87
55.00	10.42	10.96	14.51
69.9 <b>7</b>	14.57	13.70	17.31
	$K_{1P}k_{CH}, 10^{1}$	$M^{-1} \sec^{-1}$	
0	4.98	5.47	5.57
20	5.92	6.14	6.14
50	8.63	7.91	7.41
55	9.45	8.40	7.76
<b>7</b> 0	13.21	10.50	9.15
	$k_{\text{DIFF}}, 10^{10}$	$M^{-1} \sec^{-1}$	
0	19.36	19.74	20.03
20	11.22	11.43	11.72
50	3.43	3.50	3.59
55	2.63	2.68	2.75
70	0.963	0.982	1.01
$k_{\rm CH}, 10^{10}$			
sec <sup>-1</sup>	0.9065	0.7661	0.5345
B, 10 <sup>10</sup>			
sec <sup>-1</sup> P	0.1729	0.1763	0.1807
Correlation			
coefficient	0.99883	0.99870	0.99840

If  $D = D_{H^+} + D_{In^2-}$ , the diffusion coefficient sum, is inversely proportional to the solvent viscosity, then eq 13 may be applied to the diffusion step. Equation 13 is substituted into eq 16 to give eq 18, which may be

$$\frac{K_{\rm IP}}{k_{\rm r}^0} = \frac{K_{\rm IP}\eta}{B} + \frac{1}{k_{\rm CH}} \tag{18}$$

plotted as  $K_{\rm IP}/k_r^0 vs. K_{\rm IP\eta}$ . The intercept is  $k_{\rm CH}^{-1}$  and the slope is  $B^{-1}$ , from which  $k_{\rm DIFF}$  may be calculated for each solvent composition. Values of  $k_{\rm CH}$  and B, assuming the same interaction distances as before, are

![](_page_104_Figure_10.jpeg)

Figure 4. Plot of bromocresol green recombination rate constant vs. bulk solvent viscosity using eq 18 with  $\sigma = 7.5$  Å.

listed in Table IV, along with the least-squares correlation coefficient. The data for  $\sigma = 7.5$  Å are plotted in Figure 4.

The rate constants for the diffusion-controlled process are calculated from  $B/\eta$  and are tabulated in Table IV. The rate constants for the second-order chemically controlled rate process, the product  $K_{\rm IP}k_{\rm CH}$ , are also included in Table IV. It is interesting to note that in water the diffusion process,  $k_{\rm DIFF}$ , is about four times larger than the second-order chemical process,  $K_{\rm IP}k_{\rm CH}$ , while in 70% glycerol the diffusion process is about ten times smaller.

If this analysis is correct, this reaction is not diffusion controlled in water, in contrast to the usual presumption. Normally any difference between the calculated diffusion-controlled rate constant and the observed one has been ascribed to "steric factors."<sup>15</sup> In fact, steric factors may contribute to the decrease in the rate of the chemical process but other factors seem to be required to explain the significantly larger rate constant of bromocresol purple ion recombination,<sup>2a</sup>  $k_r = 8 \times 10^{10}$  $M^{-1} \sec^{-1}$ . Steric factors and diffusion coefficients for bromocresol green and bromocresol purple should be closely similar since bromocresol purple differs from bromocresol green only by the absence of two bromine atoms and a difference in position of two methyl groups

- (13) R. M. Fuoss, J. Amer. Chem. Soc., 80, 5059 (1958).
- (14) E. C. Righellato and C. W. Davis, Trans. Faraday Soc., 26, 592 (1930).
- (15) M. Eigen, Angew. Chem., Int. Ed. Engl., 3, 1 (1964).

(Figure 5). More typically, chemical factors, such as the electron density at the phenolic oxygens or changes in bond lengths or angles during the proton transfer, affecting  $k_{\rm CH}$ , may explain the significant difference in observed recombination rates.

A check on the validity of this analysis can be made by rearranging the Debye equation to calculate the sum of the ionic diffusion coefficients using the results in Table IV for the diffusion rate constant,  $k_{\text{DIFF}}$ . These diffusion coefficients may then be compared to those calculated from hydrogen ion mobility data and a reasonable estimate for the dianion diffusion coefficient. The result of the calculation from the Debye equation is listed in Table V. The diffusion coefficient of hydrogen ion may be calculated by eq 19,<sup>16</sup> where F is the

$$D_{\rm i} = RT/Fu_{\rm i} \tag{19}$$

Faraday constant, and  $u_i$ , mobility of hydrogen ion in water at 25°, is  $3.63 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$ ;  $D_{\text{H}^+}$  is 0.93  $\times$  $10^{-4}$  cm<sup>2</sup> sec<sup>-1</sup>. A reasonable estimate of the diffusion coefficient for the bromocresol green dianion is  $0.2 \times$  $10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ .<sup>17</sup> The sum  $D = D_{\text{H}^+} + D_{\text{In}^{2-}} \approx 1.1 \times 10^{-4}$  $10^{-4}$  cm<sup>2</sup> sec<sup>-1</sup> is in reasonably good agreement with the kinetically obtained diffusion coefficients listed in Table V. The best agreement occurs with the data calculated using the largest interaction distance,  $\sigma =$ 10 Å, where the diffusion coefficient is only 30% higher than the estimate from mobility data. By contrast, the diffusion coefficient calculated from the kinetic data assuming the one-step diffusion mechanism is  $0.455 \times 10^{-4}$  cm<sup>2</sup> sec<sup>-1</sup> in water, more than a factor of 2 smaller than the estimate from electrochemical data. This is an additional reason for rejecting a one-step mechanism.

 Table V:
 Diffusion Coefficients Calculated from the Debye

 Equation and Diffusion Rate Constant

Wt %	D <sup>a</sup> at interaction distance				
glycerol	5 Å	7.5 Å	10 Å		
0	1.83	1.56	1.43		
20	0.931	0.865	0.797		
50	0.257	0.243	0.227		
55	0.193	0.183	0.171		
70	0.0650	0.0625	0.0592		

<sup>a</sup> Diffusion coefficient, 10<sup>4</sup> sec cm<sup>-2</sup>; calculated from  $k_{\text{DIFF}}$  from Table IV and the Debye equation.

After the above calculations had been completed, Kreevoy called to our attention a paper<sup>18</sup> that reports experimental hydrogen ion mobilities in water-glycerol mixtures that should, in principle, be used in preference to Stokes-Einstein values. In Table VI are shown the results of calculations analogous to those of Table IV, at a 7.5-Å interaction distance, using these experimental hydrogen ion mobilities. In this case, a direct cal-

Figure 5. Structure of sulforphthalein indicator dianions.

culation of  $k_{\text{DIFF}}$  was made from (1) to obtain  $k_{\text{CH}}^{-1}$ from a  $K_{\text{IP}}/k_{\text{r}}^{0}$  vs.  $K_{\text{IP}}/k_{\text{DIFF}}$  plot. This plot should have a slope of unity. From a least-squares treatment, the slope is, in fact, 1.1021 and the intercept  $k_{\text{CH}}^{-1} =$  $0.9187 \times 10^{-10}$  or  $k_{\text{CH}} = 1.089 \times 10^{10} \text{ sec}^{-1}$ . Since we have ignored the comparatively small diffusion coefficient of the anion, this treatment slightly overestimates the effect of the odd variation of hydrogen ion mobility with viscosity. More to the point, the use of these experimental hydrogen ion mobilities does not alter the argument, since  $k_{\text{DIFF}}$  is still greater than the overall chemical rate constant  $K_{\text{IP}}k_{\text{CH}}$  in pure water.

If the two-step mechanism is correct, it may be worthwhile to consider whether other processes besides sulfonphthalein indicator ion-recombination kinetics may be chemically rather than diffusion controlled. A calculation of the recombination rate constant from (1) for hydrogen ion and hydroxide ion in water at  $25^{\circ}$ , with 7.5 Å as the interaction distance,<sup>9</sup> is about 10%lower than the observed value of  $1.4 \times 10^{11} M^{-1} \sec^{-1}$ . Thus, this process certainly appears to be diffusion controlled. In this case the Debye equation gives a slightly low prediction for the diffusion-controlled rate constant. Using the two-step mechanism for recombination of hydrogen ion and bromocresol green dianion, the Debye equation again gives a low value of the diffusion rate constant. This consistency is further corroboration for the two-step mechanism, since for bromocresol green the one-step mechanism gives a calculated rate constant much faster than the observed one.19

As another case similar to the bromocresol green reaction, a reasonable estimate by the Debye equation for the diffusion controlled recombination rate constant for phenols, *e.g.*, *p*-nitrophenol, is about  $9.7 \times 10^{10}$  $M^{-1} \sec^{-1}$ , again assuming a 7.5-Å interaction distance. The observed rate constant,<sup>15</sup> assuming the one-step mechanism, is  $3.6 \times 10^{10} M^{-1} \sec^{-1}$ , almost a factor of

<sup>(16)</sup> W. Nernst, Z. Phys. Chem., 2, 613 (1888).

<sup>(17)</sup> H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, Princeton, N. J., 1958, p 700.

<sup>(18)</sup> T. Erdey-Grůz, L. Majthényi, and I. Nagy-Czakó, Acta Chim. Acad. Sci. Hung., 53, 29 (1967).

<sup>(19)</sup> The low values predicted by the Debye equation may arise from an overestimate of the dielectric constant between the ions. The dielectric constant of the bulk solvent was used for these calculations, and may be a little too high owing to orientation of solvent molecules between the ions, thus transmitting electrostatic effects more effectively than a continuous medium.

Wt % glycerol	u <sub>H</sub> , <sup>b</sup> 10 <sup>-6</sup> cm <sup>2</sup> / (sec V)	$D_{\rm H}$ , c 10 <sup>-6</sup> cm <sup>2</sup> /sec	kDIFF, <sup>d</sup> 10 <sup>10</sup> M <sup>-1</sup> sec <sup>-1</sup>	K <sub>IP</sub> /k <sub>DIFF</sub> , 10 <sup>10</sup> sec	$K_{\rm IP}/k_{\rm r}$ <sup>1</sup> , 10 <sup>-10</sup> sec	KIPkCH, 10 <sup>10</sup> M <sup>-1</sup> sec <sup>-1</sup>
0.00	340.2	87.4	11.10	0.643	1.238	7.77
19.98	227	58.3	7.70	1.040	2.15	8.73
49.99	91.5	23.5	3.38	3.05	4.34	11.28
55.00	72.5	18.6	2.73	4.02	5.71	11.93
69.97	26.0	6.68	1.05	13.05	15.19	14.91

Table VI: Equilibrium Constants from Eq 17 and Rate Constants from Eq 18<sup>a</sup>

<sup>a</sup> Calculated for a 7.5-Å interaction distance using the experimental hydrogen ion mobilities of T. Erdey-Gruz, L. Majthényi, and I. Nagy-Czakó, Acta Chim. Acad. Sci. Hung., 53, 29 (1967). <sup>b</sup> Hydrogen ion mobilities interpolated from the graph in Figure 2 of ref 18. <sup>c</sup> Hydrogen ion diffusion coefficients calculated from eq 19. <sup>d</sup> Debye rate constants calculated from eq 1 assuming a 7.5-Å interaction distance.

**Table VII:** Type of Mechanism Required for Proton-Recombination Reactions<sup>a,b</sup>

Reaction	$k_{ m r}  imes 10^{10}$ $M$ <sup>-1</sup> sec <sup>-1</sup>	Mechanism
$H^+ + OH^-$	14	One step
H + F -	10	One step
$H^{+} + SO_{4^{2}}$	$10 (I^e = 0.01)$	<b>One step</b>
	$M, 20^{\circ})$	
$H^+ + HCO_3^-$	4.7	Two step
$H^+ + p$ -nitrophenoxide	3.6	Two step
$H^+ + \beta$ -naphthoxide	5.1	Two step
$H^+ + HS^-$	7.5	Two step
$H^+ +$ uric acid anion	0.85	Two step
$H^+ +$ bromocresol purple		
dianion	$8.0^{d} (15^{\circ})$	Two step
$H^+ + phenol red dianion$	$7.2^{d} (15^{\circ})$	Two step
$H^+ + bromocresol green$		
dianion	5.8	Two step
$H^+ + chlorophenol red$		
dianion	2.3' (I =	Two step
	$0.15 \ M_{\star}$	
	15°)	

<sup>a</sup> All reactions from ref 15, except as noted. <sup>b</sup> All reactions at I = 0 M and 25°, except as noted. <sup>c</sup> I is ionic strength. <sup>d</sup> Reference 3a. <sup>e</sup> Reference 3b. <sup>f</sup>M. Eigen and G. G. Hammes, J. Amer. Chem. Soc., 82, 5951 (1960).

3 slower than the calculated  $k_{\text{DIFF}}$ . This reaction also seems to require a two-step mechanism to explain this large difference. This relative slowness is a common occurrence in fast proton-recombination kinetics (see Table VII). A few reactions can be explained by the one-step mechanism.

Other bimolecular reactions that approach but do not reach their diffusion-limited rates to within an order of magnitude are the comproportionation reactions between benzoquinone and hydroquinone to form the semiquinone radical ion,<sup>20</sup> and a similar bimolecular electron-transfer reaction recently observed in this laboratory between reduced and oxidized violene radical ions.<sup>21</sup> These might also be found to be chemically rather than diffusion limited under appropriate conditions.

Schurr<sup>22</sup> has remarked that he would prefer to call the "one-step" reactions of Table VII "completely diffusion controlled" and the "two-step" reactions "non diffusion controlled." Rather than two successive steps, diffusion and reaction, proceeding according to mass-action rate expressions, he prefers the view that "there is only a single *bimolecular intrinsic chemical* step that proceeds with a mass-action rate expression, and that is incorporated as a boundary condition for the diffusion equation, the solution of which gives overall rate constants for the steady-state. These two points of view are indistinguishable for the steady-state, but they do predict different transient behavior" as he has previously shown.<sup>11</sup>

Acknowledgments. The authors thank Professor M. M. Kreevoy for suggesting an investigation of viscosity effects on proton-transfer reactions and Professor J. M. Schurr for a helpful discussion regarding a possible two-step mechanism. The authors are also grateful to Professor Paul Hemmes for helpful discussions.

(22) J. M. Schurr, private communication.

<sup>(20)</sup> H. Diebler, M. Eigen, and P. Matthies, Z. Naturforsch. B, 16, 629 (1962).

<sup>(21)</sup> B. C. Bennion, J. J. Auborn, and E. M. Eyring, J. Phys. Chem., 76, 701 (1972).

# The Viscosity Dependence of a Putative Diffusion-Limited Reaction

#### by Charles Cerjan<sup>1</sup> and Ronald E. Barnett\*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455 (Received December 20, 1971)

Publication costs assisted by the National Science Foundation

Variation of viscosity using water-glycerol mixtures appears to be a useful method for studying diffusionlimited reactions in aqueous solution, especially for reactions in which the rate-determining diffusion-limited step is preceded by unfavorable equilibria. In one such reaction, the hydrolysis of 2-methyl- $\Delta^2$ -thiazoline to give S-acetylmercaptoethylamine and N-acetylmercaptoethylamine, the breakdown of a neutral intermediate to give the thiol ester is diffusion limited for pH values greater than 2. The diffusion-limited step is proportional to the reciprocal of the viscosity, while equilibria and nondiffusion-limited steps are relatively unaffected in going from water to 60% glycerol.

### Introduction

In the formulation of reaction mechanisms for carbonyl and acyl group reactions it is often assumed that simple diffusion-limited proton transfer steps are too fast to be rate determining, and that breaking or making of bonds to carbon is concerted with proton transfer for general acid and general base catalysis.<sup>2-4</sup> However, in recent years evidence has accumulated for several carbonyl and acyl group reactions that the rate-determining step may be diffusion-limited<sup>5-12</sup> or have intermediates which are not at equilibrium with respect to simple proton transfers.<sup>13,14</sup> It seems likely that many other carbonyl acyl group reactions may also for some reaction conditions be limited by a simple proton transfer step not involving making or breaking of bonds to carbon. It would be desirable to have a technique by which one could readily determine whether the ratedetermining step for a reaction is diffusion limited even if preceded by an unfavorable preequilibrium without having to resort to rather elaborate methods and arguments.<sup>5-9,12-14</sup> One property which should be characteristic of a diffusion-limited reaction is an inverse dependence on the viscosity of the medium. Equilibrium constants and nondiffusion-limited processes should be independent of viscosity. One way of increasing the viscosity of aqueous media is to add glycerol. Water and glycerol form relatively ideal mixtures,<sup>15,16</sup> glycerol has a relatively high dielectric constant (42.5), and water activity seems to be linearly correlated with water mole fraction,<sup>16</sup> so this system looks promising for continuous variation of viscosity. In this paper we apply the viscosity variation method using aqueous glycerol to a reaction for which there is indirect evidence that the rate-determining step for some conditions is diffusion-limited.<sup>5,6</sup>

### **Experimental Section**

Materials and Methods. Reagent grade glycerol was used for all experiments. 2-Methyl- $\Delta^2$ -thiazoline (Eastman) was redistilled before use. Carbon dioxide-

free glass distilled water was used throughout. Viscosity measurements were made with a Cannon-Fenske viscometer. The initial ratio of thiol ester to amide formed in the hydrolysis of 2-methyl- $\Delta^2$ -thiazoline was determined as previously described.<sup>6</sup> Spectroscopic measurements were made with a Beckman DU spectrophotometer with a thermostated cell compartment. The temperature was maintained at 25.0° with a circulating water bath.

#### **Results and Discussion**

The hydrolysis of 2-methyl- $\Delta^2$ -thiazoline proceeds by way of a neutral intermediate which partitions to give S-acetylmercaptoethylamine and N-acetylmercaptoethylamine. Below pH 2 approximately equal amounts of thiolester and amide are produced, with the ratio of products being independent of pH.<sup>17,18</sup> As the

- (2) M. L. Bender, Chem. Rev., 60, 53 (1960).
- (3) S. L. Johnson, Advan. Phys. Org. Chem., 5, 237 (1967).
- (4) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms,"
- Vol. 1 and 2, W. A. Benjamin, New York, N. Y., 1966.
- (5) R. E. Barnett and W. P. Jencks, J. Amer. Chem. Soc., 90, 4199 (1968).
- (6) R. E. Barnett and W. P. Jencks, *ibid.*, 91, 2358 (1969).
- (7) R. K. Chaturvedi and G. L. Schmir, ibid., 91, 737 (1969).
- (8) R. E. Barnett and W. P. Jencks, J. Org. Chem., 34, 2777 (1969).
- (9) R. J. Zygmunt and R. E. Barnett, J. Amer. Chem. Soc., in press.
- (10) R. E. Barnett and W. P. Jencks, ibid., 89, 5963 (1967).
- (11) R. E. Barnett and W. P. Jencks, *ibid.*, 91, 6758 (1969).
- (12) L. D. Kirshner and R. L. Schowen, ibid., 93, 2014 (1971).
- (13) D. G. Oakenfull and W. P. Jencks, *ibid.*, 93, 178 (1971).
- (14) W. P. Jencks and K. Salvesen, ibid., 93, 1419 (1971).
- (15) R. H. Stokes and R. A. Robinson, J. Phys. Chem., 70, 2126
  (1966); R. A. Robinson and R. A. Stokes, "Electrolytic Solutions," 2nd ed, 1959, pp 241-245.
- (16) L. L. Schaleger and C. N. Richards, J. Amer. Chem. Soc., 92, 5565 (1970).

(17) R. B. Martin, S. Lowey, E. L. Elson, and J. T. Edsall, *ibid.*, 81, 5089 (1959).

(18) R. B. Martin and A. Parcell, ibid., 83, 4830 (1961).

<sup>(1)</sup> National Science Foundation Undergraduate Trainee, Summer 1971.
pH is increased above 2, however, the fraction of thiolester drops to near zero. This drop is not a result of a conversion of initially formed thiol ester into amide,<sup>5,6</sup> and so must be a result of a change in rate-determining step in the partitioning of the intermediate formed in thiazoline hydrolysis. The S to N transfer reaction of S-acetylmercaptoethylamine has also been studied.<sup>5,6,19</sup> There is a neutral intermediate in this reaction, and a change in rate-determining step occurs at the same pH at which the fraction of thiol ester formed in thiazoline hydrolysis drops off.<sup>5,6</sup> The data for thiazoline hydrolysis and the S to N transfer reaction could not be fit into a single mechanism which excluded simple proton transfer steps from being rate determining.<sup>5,6,20</sup> The mechanism shown in eq 1 has been proposed to explain the data.<sup>5,6</sup> The crucial part of the mechanism is the interconversion of  $X^{\pm}$  and  $X^{+}$ , a process which is a simple proton transfer and presumably diffusionlimited in the thermodynamically favored direction.<sup>21</sup> By the mechanism of eq 1 the interconversion of  $X^{\pm}$ 

$$k_{\rm ab} = \frac{4\pi N z_{\rm a} z_{\rm b} e^2 (D_{\rm a} + D_{\rm b})}{10^3 \epsilon k T \left[ \exp\left(\frac{z_{\rm a} z_{\rm b} e^2}{\epsilon k T \sigma_{\rm ab}}\right) - 1 \right]}$$
(2)  
RT

$$D_{i} = \frac{n_{i}}{6\pi\eta N\sigma_{i}} \tag{3}$$

and  $\sigma_i$  the radius of the molecule.<sup>23</sup> By combining eq 2 and 3, eq 4 is obtained. For nonspherical molecules

$$k_{ab} = C/\eta \tag{4}$$

$$C = \frac{\frac{2}{3}z_{a}z_{b}e^{2}N(\sigma_{a} + \sigma_{b})}{1000\epsilon\sigma_{a}\sigma_{b}\left[\exp\left(\frac{z_{a}z_{b}e^{2}}{\epsilon kT\sigma_{ab}}\right) - 1\right]}$$

the expression should have the same general form.

Assuming the mechanism of eq 1 it can be shown that  $k_{-2}/k_{\rm Hs0^+}$  is given by eq 5 where  $k_{\rm Hs0^+}$  is the second-order rate constant for the protonation of X<sup>±</sup> to give X<sup>+</sup>, f<sup>°</sup> is fraction of products formed as the thiol ester



and  $X^+$  is the rate-determining step above pH 2 in the S to N transfer reaction and is responsible for the drop in thiol ester formation from thiazoline hydrolysis above pH 2. The evidence for this mechanism has been discussed elsewhere.<sup>5,6</sup> This mechanism ultimately depends on being able to show that there must be at least *three sequential* steps, all of which can be rate determining under appropriate conditions in the S to N acetyl transfer reaction. For most reactions such detailed kinetic information cannot be obtained. The arguments for rate-determining, diffusion-limited steps in thiol ester hydrolysis<sup>8,9</sup> and amide hydrolysis<sup>12</sup> are indirect and not completely definitive.

The rate of a diffusion-limited reaction should be inversely proportional to the viscosity of the medium. If  $k_{ab}$  is the second-order rate constant for an encountercontrolled reaction of a and b, then the rate constant is given by eq 2, where  $z_a e$  and  $z_b e$  are the charges of a and b,  $D_a$  and  $D_b$  are their respective diffusion coefficients, k is Boltzmann's constant,  $\epsilon$  the dielectric constant, and  $\sigma_{ab}$  the reaction distance.<sup>22</sup> If the reactants are approximated as spheres, their diffusion coefficients are given by eq 3, where  $\eta$  is the viscosity of the medium in strong acid, and K is the hydrogen ion concentration

$$\frac{k_{-2}}{k_{\rm HsO^+}} = \frac{K}{1 - f^{\circ}} \tag{5}$$

for which  $f = 0.5f^{\circ}$ .

In Figure 1 is shown the dependence of f on the hydrogen ion concentration as the concentration of glycerol is varied from 0 to 60%. In strong acid the rate-determining steps in partitioning of the intermediate in thiazoline to give thiol ester and amide are pH independent and not diffusion-limited according to the mechanism of eq 1. If varying the glycerol concentration has little effect on nondiffusion-limited steps and on equilibrium constants, then  $f^{\circ}$  should be independent of the glycerol concentration. The effect on glycerol on  $f^{\circ}$  is shown in Table I. As the glycerol concentra-

(19) R. B. Martin and R. I. Hedrick, J. Amer. Chem. Soc., 84, 106 (1962).

- (20) R. B. Martin, R. I. Hedrick, and A. Parcell, J. Org. Chem., 29, 3197 (1964).
- (21) M. Eigen, Angew. Chem. Int. Ed. Engl., 3, 1 (1964).
- (22) P. Debye, Trans. Electrochem. Soc., 82, 265 (1942).
- (23) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1961, p 271.



Figure 1. The effect of acidity on the fraction of thiol ester formed in thiazoline hydrolysis at 25° for water ( $\bullet$ ), 10% glycerol ( $\blacktriangle$ ), 20% glycerol ( $\blacksquare$ ), 30% glycerol ( $\blacktriangledown$ ), 40% glycerol ( $\bigcirc$ ), 50% glycerol ( $\bigtriangleup$ ), and 60% glycerol ( $\square$ ).

tion is increased from 0 to 60%,  $f^{\circ}$  varies from 0.480 to 0.325. This is a small change and can probably be largely accounted for by the effect of lowering the dielectric constant on the equilibrium constant from X to X<sup>±</sup>. The dielectric constant<sup>24</sup> of 60% glycerol is 60. However,  $K/(1 - f^{\circ})$  should be proportional to the viscosity, as can be seen by taking  $k_{\text{HA}} = k_{\text{HAO}^{-}}$  and combining eq 4 and 5 to obtain eq 6. Since  $k_{-2}$  is not

$$\frac{K}{1-f^{\circ}} = \frac{k_{-2}\eta}{C} \tag{6}$$

diffusion-limited, and so should be independent of viscosity, a plot of log  $[K/(1 - f^{\circ})]$  vs. log  $(\eta/\eta_0)$ , where  $\eta_0$ is the viscosity of pure water, should be a straight line with a slope of unity if in fact the mechanism of eq 1 is correct and interconversion of X<sup>±</sup> and X<sup>+</sup> is rate determining when the hydrogen ion concentration is less than about  $10^{-2} M$ . Such a plot is shown in Figure 2. The slope is 0.94, which is in good agreement with eq 6, and is further confirmatory evidence for the mechanism of eq 1.

It is highly unlikely that the observed effects of glycerol on the partitioning of the intermediate formed in thiazoline hydrolysis are due to medium effects on nondiffusion steps and equilibrium constants. In support of this it should be observed that (a) the effects of glycerol on  $f^{\circ}$ , which include both rate and equilibrium effects, are small and (b) the  $pK_{a}$  of  $\beta$ -cyanoethylpiperidine hydrochloride is virtually independent of the medium up to 70% glycerol.<sup>25</sup>

Variation of viscosity by addition of glycerol appears to be of considerable potential usefulness in distinguishing diffusion-limited processes from nondiffusion-



Figure 2. The viscosity dependence of  $K/(1 - f^{\circ})$ .

Table I:	Effect of Gly	cerol on	$\mathbf{the}$	Formation	of
S-Acetylm	ercaptoethyla	mine in	the	Hydrolysis	
of 2-Methy	yl-∆²-thiazolin	ne at 25°			

%		$K \times 10^{3}$
glycerol	f	М
0	0.480	2.32
10	0.420	3.01
20	0.388	4.64
30	0.383	6.92
40	0.371	8.20
50	0.352	14.8
60	0.325	24.2

limited ones in aqueous solution. Reactions of reactive carbonyl compounds with good nucleophiles to give zwitterionic intermediates, which must be converted into neutral intermediates before breakdown to products can occur, may very well behave as does the S to N transfer reaction of S-acetylmercaptoethylamine, with interconversion of the zwitterionic and neutral tetrahedral intermediates being rate determining, for some conditions. For this to be possible, expulsion of the nucleophile from the zwitterion to give reactants should be quite rapid. In the case of the S to N transfer of S-acetylmercaptoethylamine  $k_{-2}$  is 6.6  $\times$  10<sup>8</sup>  $sec^{-1}$ . In the hydrolysis of methyl S-trifluoroacetylmercaptoacetate, a reaction which is also probably diffusion limited,<sup>8,9</sup> the rate constant for the expulsion of water from a zwitterionic intermediate has been esti-

(25) M. M. Kreevoy and J. Dolmar, J. Phys. Chem., in press.

<sup>(24)</sup> A. A. Newman, "Glycerol," Morgan-Grampion, London, 1968, p 29.

mated to be greater than  $3.8 \times 10^{10}$  sec<sup>-1</sup>. Reactions such as oxime and Schiff base formation, ester aminolysis, and amide hydrolysis may quite likely be diffusion limited for appropriate reaction conditions. For example, a zwitterionic intermediate is probably formed in oxime formation. Reimann and Jencks<sup>26</sup> have estimated that the rate constant for the expulsion of hydroxylamine from the intermediate formed with *p*chlorobenzaldehyde is about 10<sup>9</sup> sec<sup>-1</sup>. Since elimination of water to give the oxime must occur from the neutral intermediate, conversion of the initially formed zwitterionic intermediate into the neutral one may be

rate determining for some conditions. In problems such as this kinetic methods quite often may not provide sufficient information to decide whether a reaction is diffusion-limited, while variation of the viscosity of the medium using water-glycerol mixtures should provide the answer quite readily.

Acknowledgment. I wish to thank Professor Maurice Kreevoy for many helpful discussions and Mr. John Dolmar for making the viscosity measurements.

(26) J. E. Reimann and W. P. Jencks, J. Amer. Chem. Soc., 88, 3973 (1966).

## Solubility and Partial Molar Properties of Helium in Water and Aqueous

# Sodium Chloride from 25 to 100° and 100 to 600 Atmospheres<sup>1</sup>

### by Gregory E. Gardiner and Norman O. Smith\*

Department of Chemistry, Fordham University, New York, New York 10458 (Received August 5, 1971) Publication costs assisted by the Office of Research Services, Fordham University

The solubility of helium in water was measured at 50 and 100° at pressures from 100 to 600 atm. The results differ systematically from the only previous data. An explanation for the discrepancy is offered in terms of meniscus corrections. The solubility of helium over the same pressure range in 1 and 4 m NaCl at 25, 50, and 100° was also measured. The applicability of Henry's law to the results is considered in detail. A pressure dependence of the partial molar volume of the dissolved gas is proposed. For solutions of helium in water and in 1 m NaCl, the compressibility of the dissolved gas, defined as  $(-1/\bar{V}_2^0)(\partial\bar{V}_2/\partial P)_{T,X_2}$ , passes through zero at 25–30°. The relevance of such a compressibility to the structure of the solution is discussed. A set of isobaric solubility measurements at 200 atm in water is reported and the solubility of the gas shown to pass through a minimum at 28.3°. The thermodynamic quantities related to the solution process are derived. Calculation of the partial molar volume of helium in water as  $\varepsilon$  function of temperature shows that it also passes through a minimum near room temperature. The variation of the temperature of minimum solubility with pressure is treated semiquantitatively. The effect of added NaCl on the temperature and pressure dependence of  $\bar{V}_2$  is discussed. Salting-out coefficients are reported for the NaCl solutions. Generally these decrease with increasing salt concentration and the Setschenow relation is not strictly valid.

The solubility of helium in water and sodium chloride solutions is a topic of special interest to the physical chemist. As a key to understanding the structure of water and aqueous solutions, the solubility of noble gases has found wide use.<sup>2</sup> Helium is ideal for this purpose since, because of its small polarizability, interactions with the solvent are expected to be virtually negligible and its effects on water structure almost purely those arising from excluded volume phenomena. In the fields of geochemistry and oceanography, interest in helium is widespread: special attention has been given to its solubility in water and the effects of added salt, temperature, and pressure on the solubility. Though many studies have been made of the solubility of helium in water and salt solutions at atmospheric pressure, data on its high pressure solubility in water have been reported only twice in the past.<sup>3,4</sup> The first of these is the more extensive, covering the

(3) R. Wiebe and V. L. Gaddy, J. Amer. Chem. Soc., 57, 847 (1935).

Taken in part from the Ph.D. dissertation of G. E. G. Portions of this paper were presented before the Metrochem 69 Regional Meeting, New York, N. Y., May 1969, and the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.
 See, for example, H. S. Frank and M. J. Evans, J. Chem. Phys., 13, 507 (1945); W. Kauzmann, Advan. Protein Chem., 14, 1 (1959).

<sup>(4)</sup> H. A. Pray, C. E. Schweikert, and B. H. Minnich, Ind. Eng.

<sup>(4) 11.</sup> A. Fray, C. E. Schweikert, and B. H. Minnich, Ind. Eng. Chem., 44, 1146 (1952).

temperature range from 0 to  $75^{\circ}$  and pressures from 25 to 1000 atm, but the work of Pray, *et al.*, is too limited in scope for comparison with this study. The precision of the data reported here is at least equal to that obtained by Wiebe and Gaddy. However, their work does appear to contain a systematic error to be discussed below. The solubility of helium in aqueous solutions of simple salts has not been reported in the past.

The principal source of information on the partial molar volume of helium in water has been the data of Wiebe and Gaddy. One other value for 25°, obtained by dilatometric techniques, has been reported,<sup>5</sup> but it does not agree with their measurements and is inconsistent with the results reported here. No partial molar volumes of helium in simple salt solutions appear to be available in the literature.

From a practical point of view, the measurement of the compressibility of the dissolved gas is important in the extrapolation of solubility data to the high pressures encountered in geochemical and oceanographic studies. From a theoretical point of view, such measurements appear to be capable of shedding much light on the structure of aqueous solutions. In the past, the compressibility of dissolved gases has never been discussed in any quantitative sense nor have any measurements been reported. The temperature dependence of gas solubility at high pressures also does not appear to have been a subject of discussion. The minimum in the isobaric solubility, though frequently reported both at high and atmospheric pressures, has otherwise been largely ignored.

### **Experimental Section**

The experimental procedure and apparatus employed in this study have been previously described in detail.<sup>6</sup> The helium used was obtained from the Matheson Co., Inc.; its purity was given as 99.995%. The water used was distilled and passed through an ion-exchange column and helium bubbled through it overnight. All salt solutions were made up by weight using Baker Analyzed reagent grade NaCl. The solubility of the helium was calculated from the volumes of gas and liquid measured at room temperature and pressure. After correcting for the vapor pressure of the liquid,<sup>7</sup> the number of moles of gas was calculated using the equation of state given by Wiebe, *et al.*<sup>8</sup>

The use of burets in high-precision gas solubility measurements requires the application of a meniscus correction before the solubility of the gas is calculated. The buret system is similar to that described by Wiebe, *et al.*,<sup>9</sup> and used by them<sup>3,10</sup> and by others<sup>4,11</sup> in the measurement of gas solubilities at high pressures. It comprises essentially two burets connected together, shown in part in Figure 1. One of these (I) contains only gas and the other (II) contains both gas and a liquid, usually water, confined over mercury. Standard 50-ml analytical burets with an internal diameter



Figure 1. Buret meniscus corrections.

of 1.18 cm were used. If any correction for meniscus curvature is ignored the volume of the gas is  $V_{a} + V_{b} +$  $V_{\rm u}$ , where  $V_{\rm a}$  and  $V_{\rm b}$  are the buret readings and  $V_{\rm u}$  is the volume of the ungraduated part of the system. The volume of the liquid is similarly  $V_{\rm c} - V_{\rm b}$ . However, an examination of Figure 1 shows that a volume of liquid lies above  $V_b$  equal to  $V_b'$  and below  $V_c$  equal to  $V_{c}'$ , so that the liquid volume is actually given by  $V_{\rm c} - V_{\rm b} + (V_{\rm b}' + V_{\rm c}')$ . Similarly, the correct gas volume is  $V_{a} + V_{b} + V_{u} + (V_{a}' - V_{b}')$ . The liquid meniscus correction was measured in two ways. In the first, both burets were filled partially with water over mercury and the sum of the two apparent volumes, each  $V_{\rm c} - V_{\rm b}$ , was recorded. The true volume is the apparent volume plus  $2(V_b' + V_c')$ . Then, all of the water in one buret was transferred into the other and the combined apparent volume recorded. Since the true volume is now the apparent volume plus  $V_{\rm b}'$  +  $V_{c'}$ , the difference between the two apparent volumes gave the required correction,  $V_{b}' + V_{c}' = 0.34 \pm 0.04$ ml. A second procedure was used in which a volume of water from a calibrated pipette was discharged into a buret partially filled with mercury and the apparent volume in the buret measured. The correction was thus found to be  $0.36 \pm 0.04$  ml. The correction to be applied to the gas volume,  $V_{a'} - V_{b'}$ , was considered to be negligible.

The solubility of helium in water between 100 and 600 atm was measured to check the performance of our

- (5) T. Enns, P. F. Scholander, and E. D. Bradstreet, J. Phys. Chem., 69, 389 (1965).
- (6) T. D. O'Sullivan and N. O. Smith, ibid., 74, 1460 (1970).
- (7) "International Critical Tables," Vol. 3, McGraw-Hill, New York, N. Y., 1928.
- (8) R. Wiebe, V. L. Gaddy, and C. Heins, Jr., J. Amer. Chem. Soc., 53, 1721 (1931).
- (9) R. Wiebe, V. L. Gaddy, and C. Heins, Jr., Ind. Eng. Chem., 24, 823 (1932).

 <sup>(10)</sup> R. Wiebe, V. L. Gaddy, and C. Heins, Jr., J. Amer. Chem. Soc., 55, 947 (1933); R. Wiebe and V. L. Gaddy, *ibid.*, 56, 76 (1934).

<sup>(11)</sup> O. L. Culberson and J. J. McKetta, Trans. Amer. Inst. Mech. Eng., 192, 223 (1951); R. Kobayashi and D. L. Katz, Ind. Eng. Chem., 44, 1146 (1952); W. Schroeder, Z. Naturforsch. B, 24, 500 (1969).

apparatus<sup>6</sup> and to study the effect of the meniscus correction. Gas volumes measured ranged from 35 to 80 ml and liquid volumes from 10 to 30 ml. A correction of .35 ml was added to the latter and the results compared with those of Wiebe and Gaddy.<sup>3</sup> The resulting solubilities, in milliliters (STP) of gas/grams water, are shown in Table I. It is seen that the data of this study agree excellently with those of Wiebe and Gaddy when no meniscus correction is applied. Discrepancies are quite apparent, however, when the correction is made. This led to the belief that Wiebe and Gaddy had not applied a meniscus correction, and the suspicion was subsequently confirmed.<sup>12</sup> It can be seen that the error caused by the omission rises to about 4% at 600 atm, since at higher pressures one is forced to take smaller samples of liquid. The effect of the meniscus correction on calculated Henry's law constants and gas partial molar volumes will be discussed below.

<b>Table 1:</b> Solubility of Helium in water at 50	Table I:	Solubility	of	Helium	in	Water	at	$50^{\circ}$	а
-----------------------------------------------------	----------	------------	----	--------	----	-------	----	--------------	---

P, atm	Lit. value <sup>b</sup>	No meniscus corr	Meniscus corr
100	$0.883 \pm 0.001$	$0.874 \pm 0.002$	$0.862 \pm 0.002$
200	$1.734\pm0.004$	$1.733 \pm 0.004$	$1.697 \pm 0.004$
300	$2.546\pm0.004^{\circ}$	$2.542 \pm 0.009$	$2.467 \pm 0.009$
400	$3.358\pm0.004$	$3.352 \pm 0.006$	$3.242~\pm~0.004$
500	$4.202 \pm 0.005$	$4.216 \pm 0.002$	$4.039 \pm 0.009$
600	$4.844\pm0.002$	$4.867 \pm 0.009$	$4.677 \pm 0.007$
<sup>a</sup> Cubi ence 3.	c centimeters of gas f Interpolated.	s (STP) per gram	of water. <sup>b</sup> Refer

After adding the liquid meniscus correction of 0.35 ml, the number of moles of liquid was calculated from its known volume, composition, and density.<sup>7</sup> In this calculation the NaCl was treated as if it were *completely dissociated:* every mole of dissolved NaCl was regarded as contributing 2 mol to the liquid phase. At each pressure, three or four samples were withdrawn and the results averaged. The average precision of all of the measurements is 0.2%. It is estimated that the accuracy of the measurements is at least 0.5% at the lower and 0.3% at the higher pressures. In an isobaric study the pressure was kept constant at 200 atm and the temperature varied. Measurements were made with approach from both higher and lower temperatures.

#### **Results and Discussion**

All of the solubilities measured in the isothermal studies can be represented by an equation of the form

$$X_2 = aP + bP^2 + cP^3$$

where  $X_2$  is the mole fraction of the helium dissolved in the liquid and P is the absolute pressure of the system. This equation represents all of the data with an average accuracy of 0.2%. In no instance is the difference between the observed and calculated mole fractions greater than 0.3%. A centering procedure was used in the least-squares analysis to ensure that the curve passed smoothly through the origin.<sup>13</sup> The coefficients of the equation are given in Table II for P in atmospheres.

Table II :	Coefficients of $X_2$	= aP + bP	$^{2} + cP^{3}$ <sup>a</sup>	
Temp, °C	Solvent	$a   imes  10^6$	$-b \times 10^9$	$c \times 10^{12}$
25.0	1.003 m NaCl	5.769	1.307	0.249
	4.067 m NaCl	3.326	1.219	0.837
50.0	$H_2O$	7.247	3.328	3.529
	1.003 m NaCl	5.702	1.925	2.046
	4.067 m NaCl	3.371	1.382	0.788
100.0	$H_2O$	6.852	2.576	2.500
	1.003 m NaCl	5.332	1.387	1.351
	4.067 m NaCl	4.110	2.982	2.307

Solubility data on gases in liquids are usually analyzed in terms of Henry's law

$$f_2 = KX_2 (T, P \text{ constant})$$
(1)

where  $f_2$  is the fugacity of the solute gas and  $X_2$  is its mole fraction; eq 1 is not directly applicable to the data on helium since they were not obtained under isobaric conditions. For use with non-isobaric data Krichevsky and Kasarnovsky<sup>14</sup> and others<sup>6</sup> have derived the integrated form of

$$[\partial \ln(f_2/X_2)/\partial P]_T = \bar{V}_2/RT \qquad (2)$$

namely

$$\ln (f_2/X_2) = \ln K^0 + (\bar{V}_2^0/RT)P$$
(3)

where  $\overline{V}_2^0$  is the partial molar volume of the dissolved gas and  $K^0$  is the Henry's law constant, both in the limit of zero pressure. Equation 3 assumes that  $\overline{V}_2$  is independent of P. However, a least-squares analysis of the present data showed that, as found earlier,<sup>6</sup> eq 3 does not give an adequate representation of the results.

The application of eq 3 to gas solubilities requires knowledge of the fugacity of the gas in the mixture with the water vapor. Since the solubility of water in compressed helium has never been measured it was decided to use the fugacity of the pure gas at the temperature and pressure of the experiment,  $f_2^{\circ}$ , rather than risk making an erroneous correction. It is certain that  $f_2$ is less than  $f_2^{\circ}$ . The correction decreases rapidly with increase in pressure from about 1% at 100 atm to 0.1% at 600 atm at 100°, and it is much smaller at lower temperatures. The fugacities of pure helium were calcu-

(12) R. Wiebe, personal communication.

<sup>(13)</sup> N. R. Draper and H. Smith, "Applied Regression Analysis," Wiley, New York, N. Y., 1966.

<sup>(14)</sup> I. R. Krichevsky and J. S. Kasarnovsky, J. Amer. Chem. Soc., 57, 2186 (1935).



Figure 2. Solubility of helium at  $25^{\circ}$ : (O) in 1.003 m NaCl, (+) in 4.067 m NaCl.

lated from the pressure-volume data of Wiebe, et al.,<sup>8</sup> whose study covered the whole range of the present measurements and gave coefficients for Pv = A + BP $+ CP^{2}$  at -70, -35, 0, 50, 100, and  $200^{\circ}$ . The values of all three coefficients appear to depend linearly on temperature except for B and C at -70 and  $100^{\circ}$ , which do not, therefore, seem to be consistent with the rest of the data. These particular values of B and C were excluded from a least-squares procedure that was employed to yield the coefficients as a function of absolute temperature, T. The following results were obtained for v in Amagat units (22,397 cm<sup>3</sup> mol<sup>-1</sup>) and P in atmospheres:  $A = (3.661 \times 10^{-3})T, B = 5.818 \times 10^{-4}$  $- (2.197 \times 10^{-7})T, C = -6.312 \times 10^{-8} + (8.621 \times 10^{-8})T, C = -6.312 \times 10^{-8} + (8.621 \times 10^{-8})T, C = -6.312 \times 10^{-8}$  $10^{-11}$ )T. These relations reproduce A, B, and C at all temperatures except -70 and  $100^{\circ}$  with an accuracy of 0.03, 0.06, and 0.15%, respectively. At both -70and  $100^{\circ} B$  differs from the least-squares value by 5%; C differs by 4% at  $-70^{\circ}$  and 10% at  $100^{\circ}$ . No trend was noted in the residuals. These coefficients were used to calculate  $f_2^{\circ}$ .

Figures 2, 3, and 4 show  $\ln (f_2^{\circ}/X_2)$  vs. P for all of the isothermal data. The curvature of these lines indicates that cq 3 will not represent the solubilities adequately, and statistical analysis shows that  $\ln (f_2^{\circ}/X_2)$  is best represented by a quadratic equation in pressure. There are three possible explanations for the failure of eq 3. First, the failure may be only apparent, and due to the use of incorrect fugacities. This argument is easily answered. At 50 and  $100^{\circ}$  the data points lie below the limiting tangent corresponding to eq 3. Since the true fugacity is certainly less than  $f_2^{\circ}$ , the use of the true fugacity would only make the curvature more pronounced. Also, the correction which must be applied to obtain the true fugacity decreases as the pressure increases whereas the deviations increase. At 25°, the data for the 1.003 m NaCl lie above the limiting tangent



Figure 3. Solubility of helium at 50°: (+) in H<sub>2</sub>O, (O) in 1.003 m NaCl,  $(\times)$  in 4.067 m NaCl.



Figure 4. Solubility of helium at  $100^{\circ}$ : (×) in H<sub>2</sub>O, (O) in 1.003 m NaCl, (+) in 4.067 m NaCl.

but those for the 4.067 m NaCl lie below. If the fugacities used were at fault, one would expect to observe the same kind of error in both sets of data. The fact that the deviations do not even have the same sign provides a strong answer against the argument for more exact fugacities. A second possible explanation is that Henry's law does not apply. In this event, negative deviations from Henry's law would be implied, and they would have to become more negative with rise in temperature—both unlikely possibilities. It has been suggested<sup>15</sup> that the curvature is caused by the dependence of  $V_2$  on  $X_2$ . Concentration dependence, however, can be found only when Henry's law does not hold<sup>16</sup> and does not seem to be an adequate explanation

<sup>(15)</sup> I. R. Kritshevsky and A. Il'nskaya, Acta Physicochim. URSS, 20, 327 (1945).

<sup>(16)</sup> G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, N. Y., 1961, p 211.

for the failure of eq 3. Glew<sup>17</sup> has suggested that Kritchevsky and Il'nskaya's apparent discovery is the result of their neglect of the difference between the true and apparent partial molar volume of the water in the solutions, and that  $\bar{V}_2$  is not really concentration dependent. However, if Henry's law holds for the dissolved gas, Raoult's law must hold for the water, so the true and apparent partial molar volumes of the water must be identical. A final explanation for the curvature is that  $V_2$  depends on P, as contended by O'Sullivan and Smith.<sup>6</sup> There is no reason to suspect that the dissolved gas will be incompressible. The possibility of pressure dependence has already been suggested,<sup>18</sup> but for lack of data the hypothesis was not pursued. It will thus be assumed in what follows that Henry's law applies throughout the work, and that the curvature in Figures 2-4 is the result of the pressure dependence of  $\overline{V}_2$ . If Henry's law does not apply, the effects of deviations therefrom, and of change in total pressure, are inextricable, and partial molar volumes cannot be derived from these data.

If it is assumed that the dissolved gas has a finite compressibility,  $\bar{\beta}^0$ , taken to be independent of P, and defined by  $\bar{V}_2 = \bar{V}_2^0 (1 - \bar{\beta}^0 P)$ , then eq 2 becomes, on integration

$$\ln (f_2/X_2) = \ln K^0 + (\bar{V}_2^0/RT)P - (\bar{\beta}^0 \bar{V}_2^0/2RT)P^2 \quad (4)$$

The possibility of a Tait-type dependence of  $\overline{\beta}^{0}$  was investigated but none was found. Equation 4 was used to represent all of the data. The constants  $K^0$  so calculated are shown in Table III and the corresponding values of  $\bar{\beta}^0$  and  $\bar{V}_{2^0}$  in Table IV. Included for comparison are  $K^0$  determined from the data of Wiebe and Gaddy<sup>3</sup> and representative results from room pressure studies.<sup>19-21</sup> The low-pressure values for the salt solutions were calculated under the assumption that the Setschenow equation is valid. It will be seen below that this is not true for the He-H<sub>2</sub>O system. The difference between the  $K^0$  values from high- and low-pressure data has been noted and discussed previously.<sup>6</sup> Those calculated from eq 3 are not shown, but they do agree within about 2% with those in Table III, except for  $H_2O$  and 1.003 m NaCl at 100°, where they are appreciably higher. In Table IV the agreement of the  $ar{V}_2$  values with those calculated from Wiebe and Gaddy<sup>3</sup> is only fair. This results from their failure to make the appropriate meniscus correction. The latter does have an appreciable effect on the slope of  $\ln (f_2/X_2)$  vs. P, and the effect is in the correct direction to explain the discrepancies. (It may be noted that the analogous plots for hydrogen and nitrogen<sup>14</sup> would also probably have been curved had the data<sup>3</sup> on which they were based been similarly corrected.) Enns, et al.,<sup>5</sup> report a partial molar volume for helium in water at 25° of 29.7 cm<sup>3</sup>  $mol^{-1}$ . This is in complete disagreement with Wiebe and Gaddy's value and inconsistent with the rest of the data reported here. From a qualitative point of view the behavior of He in H<sub>2</sub>O and 1.003 m NaCl at 25° is similar and also anomalous. The 4.067 m NaCl solutions appear normal in the sense that the helium compressibilities are of the order of those for normal pure liquids, and do not show the anomaly observed in H<sub>2</sub>O and  $1.003 \ m$  NaCl. The negative compressibilities at 25°, which imply that  $\bar{V}_2$  increases with P, are of great interest. One can explain them by assuming a twostate model for the dissolved gas.<sup>22</sup> Helium in the hydrogen-bonded network has a small partial molar volume; surrounded by randomly oriented solvent molecules it has a large one. The application of pressure causes the network to break down, and the number of sites available in the network for the helium is decreased. It appears that at 25° an increase in pressure has the net effect of moving helium from the network into regions of randomly oriented solvent, causing the observed  $\overline{V}_2$  to increase. This negative "structural" compressibility dominates the "normal" compressibility (which is probably close to that in the 4.067 mNaCl) and makes the measured values negative. There is apparently enough structure in the 1.003 m NaCl to observe the effect, but not enough in the  $4.067 \ m$  NaCl. As the temperature is raised, the structural compressibility disappears with the breakdown of the network.

The values of  $\bar{\beta}^0$  in Table IV have been used to calculate the partial molar volumes of dissolved helium at rounded pressures. These are shown in Table V and discussed below.

# **Table III:** Henry's Law Constants $(K^0 \times 10^{-5} \text{ atm})$ Based on Eq. 4

ίπ.	$\sim$	10	auni	Dascu	011	ъч	1

Temp, °C	Solvent	From high- pressure data	From low-pressure data
25.0	H <sub>2</sub> O	1.432°	$1.47^{b}$
	1.003 m NaCl	1.790	1.80°
	4.067 m NaCl	3.041	3.36 <sup>c</sup>
50.0	$H_2O$	1.337	$1.44,^{b}1.43^{d}$
	H <sub>2</sub> O	1.361ª	
	1.003 m NaCl	1.698	
	4.067 m NaCl	2.917	
100.0	H <sub>2</sub> O	1.197	$1.04^{b,e}_{,1.10^{d}}$
	1.003 m NaCl	1.390	
	4.067 m NaCl	2.495	
<sup>a</sup> Calculat	ted from ref 3.	<sup>b</sup> Reference 19	. 'Reference 20

<sup>d</sup> Calculated from ref 3. <sup>c</sup> Reference 19. <sup>c</sup> Reference 20. <sup>d</sup> Reference 21. <sup>e</sup> By extrapolation from lower temperatures.

(17) D. N. Glew, J. Phys. Chem., 66, 606 (1962).

(18) I. R. Kritchevsky, J. Amer. Chem. Soc., 59, 596 (1937).

- (20) T. J. Morrison and N. N. B. Johnstone, *ibid.*, 3655 (1955).
- (21) S. K. Shorr, R. D. Walker, Jr., and K. E. Gubbins, J. Phys. Chem., 73, 312 (1969).
- (22) H. S. Frank and A. S. Quist, J. Chem. Phys., 34, 604 (1961).

<sup>(19)</sup> T. J. Morrison and N. N. B. Johnstone, J. Chem. Soc., 3441 (1954).

Temp, °C	Solvent	$\overline{V}_{2^0}, \operatorname{cm}^{\mathfrak{s}}$ mol <sup>-1</sup>	$\bar{\beta}^{0}$ , atm <sup>-1</sup> × 10 <sup>3</sup>
25.0	$H_{2}O$	14.8ª	-0.3
	1.003 m NaCl	14.3	-0.2
	4.067 m NaCl	20.7	0.5
50.0	$H_2O$	26.9	1.2
	$H_2O$	$20.0^{a}$	0.6
	1.003 m NaCl	23.6	1.1
	4.067 m NaCl	24.5	0.7
100.0	H <sub>2</sub> O	43.6	1.5
	1.003 m NaCl	50.5	1.5
	4.067 m NaCl	30.8	0.8
<sup>a</sup> Calculated	from ref 3.		

Table IV:Partial Molar Volumes and Compressibilities ofDissolved Helium Based on Eq 4

Table V :	Partial Molar	Volumes of	Dissolved	Gas
(cm <sup>3</sup> mol <sup>-</sup>	1) Based on Eq	4		

P, atm	H <sub>2</sub> O	1 m NaCl	4 m NaCl
	2	5.0°	
200	15.7	14.9	18.6
400	16.5	15.6	16.4
600	17.4	16.3	14.2
	5	60.0°	
200	20.3	18.3	21.2
400	13.6	13.0	17.9
600	7.0	7.6	14.7
	1	00.0°	
200	30.7	34.9	25.9
400	17.8	19.4	20.9
600	4.9	3.8	15.9

It is implicit in the results that, for helium in water and in 1 *m* NaCl,  $\bar{\beta}^0$  is zero at some temperature between 25 and 50°. Graphical interpolation of the data for water in Table IV shows that this occurs near 30°. For all three solvents,  $\bar{\beta}^0$  appears to be approaching a maximum value with rising temperature.

The isobaric solubility data for P = 200 atm are given in Table VI and plotted in Figure 5. These results were fitted to

$$\ln (f_2/X_2) = A + BT^{-1} + C \ln T$$
 (5)

giving the parameters A = 127.150, B = 5173.0, C = -17.1619, which reproduce the experimental values of ln  $(f_2/X_2)$  with an average deviation of 0.0016. In terms of the equilibrium gas  $\rightleftharpoons$  dissolved gas, assuming Henry's law to be valid and  $\Delta C_p$  independent of  $T, B = \Delta H_1^0/R$ ,  $C = -\Delta C_p^0/R$ , and  $\Delta H_T^0 = \Delta H_1^0 + \Delta C_p^0 T$ . In this way one can calculate that, at 200 atm,  $\Delta H_1^0 = -10.28$  kcal mol<sup>-1</sup>,  $\Delta C_p^0 = 34.1$  cal mol<sup>-1</sup> deg<sup>-1</sup>,  $\Delta H^0_{298} = -112$  cal mol<sup>-1</sup>,  $\Delta G^0_{298} = 7.12$  kcal mol<sup>-1</sup>, and  $\Delta S^0_{298} = -24.3$  eu mol<sup>-1</sup>, where the superscripts zero refer to the transfer of a mole of helium from the



Figure 5. Isobaric solubility of helium in water at 200 atm.

hypothetical ideal gas at unit fugacity to the usual hypothetical dissolved state where Henry's law holds, both being under a total pressure of 200 atm.

Table VI:	Solubility of Helium in Water at 200 Atm				
Temp, °C	$X_2 \times 10^3$	<b>Temp</b> , °C	$X_2 \times 10^3$		
20.0	$1.336 \pm 0.003$	40.0	$1.331 \pm 0.003$		
25.0	$1.323 \pm 0.004$	<b>45.0</b>	$1.343 \pm 0.004$		
30.0	$1.324 \pm 0.003$	50.0	$1.363 \pm 0.003$		
35.0	$1.329\pm0.003$				

The existence of a 200-atm solubility minimum is evident from Table VI; equating  $\Delta H^0$  to zero in eq 5 locates it at 28.3°. Morrison and Johnstone<sup>20</sup> have used an equation identical with eq 5 to analyze their 1-atm helium solubility data. Combining their results with the present 200-atm data and expressing  $\bar{\beta}^0$  in Table IV as a function of T lead to an expression of the form of eq 4 from which it may be shown that  $d\bar{V}_2^0/dT$ is -0.017 cm<sup>3</sup> mol<sup>-1</sup> deg<sup>-1</sup> at 298°K, and that  $\bar{V}_2^0$ passes through a minimum value of 15.7 cm<sup>3</sup> mol<sup>-1</sup> at about 300°K. These calculated results are only approximate, however, because of the sensitivity to errors in  $\Delta C_p$  at both pressures.

A minimum in  $\overline{V}_2$  was first suggested by Michels, et al.,<sup>23</sup> who found it to be reasonably consistent with their data on the system CH<sub>4</sub>-H<sub>2</sub>O-NaCl. Eley<sup>24</sup> stated that the minimum was in accord with his theories on aqueous solutions of nonpolar gases. The data of Krichevsky and Il'nskaya<sup>15</sup> for temperatures well below the isobaric solubility minimum for the gases in question indicate that in several cases  $\overline{V}_2$  seems to be decreasing with rising temperature. Though no minimum was

(24) D. D. Eley, Trans. Faraday Soc., 35, 1421 (1939).

<sup>(23)</sup> A. Michels, J. Gerver, and A. Bijl, Physica, 3, 797 (1936).

noted by O'Sullivan and Smith<sup>6</sup> in their data on CH<sub>4</sub> and N<sub>2</sub>, the partial molar volumes they quote become more reasonable if one postulates the existence of a minimum in  $\overline{V}_2$  in the region of minimum solubility. The hard-sphere fluid theory of gas solubility<sup>25</sup> suggests that a minimum exists in the region of the isobaric solubility minimum. For helium in water at 0 and 200 atm, the closeness of the temperatures of minimum  $\overline{V}_2$ and minimum solubility appears to support this suggestion, but at higher pressures the two temperatures seem to be widely different.

The large increase in the calculated  $\vec{V}_2$  values between 50 and 100° is perhaps unexpected. Difficulty experienced in making solubility measurements at temperatures of 125° suggests that proximity to the critical point was responsible.

Thus far all of the thermal properties of the solutions quoted, including the temperature of the isobaric minimum, have referred to a pressure of 200 atm. It is of interest to estimate these quantities at 1 atm in order to compare the current results with those of other authors. This may be done by applying the thermodynamic equation of state,  $(\partial H/\partial P)_{\rm T} = V - T(\partial V/\partial T)_{\rm P}$ . For the transfer gas  $\rightleftharpoons$  dissolved gas this becomes  $(\partial \Delta H^0/\partial P)_{\rm T} = \bar{V}_2^0 - T(\partial \bar{V}_2^0/\partial T)_{\rm P}$  when Henry's law applies,  $\bar{V}_2^0$  being the partial molar volume at infinite dilution at the given total pressure, and assumed independent of  $X_2$ . Using the values of  $\overline{V}_2^0$  and  $(\partial \overline{V}_2^0/\partial V)$  $\partial T$ )<sub>P</sub> given above, and making the approximation that they are independent of P between 0 and 200 atm, one finds  $(\partial \Delta H^0 / \partial P)_{298} = 0.50$  cal mol<sup>-1</sup> atm<sup>-1</sup>. Since  $\Delta H^{0}_{298}$  was found to be -112 cal mol<sup>-1</sup> at 200 atm, it is estimated to be -210 cal mol<sup>-1</sup> at 1 atm, which may be compared with values of -400 calculated from Morrison and Johnstone, 20 - 200 quoted by Glew and Moelwyn-Hughes,<sup>26</sup> and -840 cal mol<sup>-1</sup> by Frank and Evans.27

The above expression for  $(\partial \Delta H^0 / \partial P)_T$  can be used to estimate the temperature of the isobaric minimum at 1 atm from that at 200 atm, and thus constitute a check on the internal consistency of the data. In the bivariant system under consideration,  $\Delta H = \Delta H(T, P)$  and  $(\partial \Delta H/\partial P)_{\rm T}(\partial T/\partial \Delta H)_{\rm P}(\partial P/\partial T)_{\Delta \rm H} = -1$ , where  $\Delta H$  is the equilibrium enthalpy of solution. Since  $(\partial \Delta H/$  $\partial T$ )<sub>P</sub> may be replaced by  $\Delta C_p$  we have  $(\partial T/\partial P)_{\Delta H} =$  $-(\partial \Delta H/\partial P)_{\rm T}/\Delta C_{\rm p}$ .  $(\partial \Delta H/\partial P)_{\rm T}$  may be found from  $(\partial \Delta H^0 / \partial P)_T$ , calculated as just described. Since  $\Delta H =$  $\Delta H^0 + (\bar{H}_2 - \bar{H}_2^0) - (H_{gas} - H^0_{gas})$ , and since  $\bar{H} - \bar{H}_2^0$  is zero if Henry's law is valid,  $(\partial \Delta H / \partial P)_T =$  $(\partial \Delta H^0 / \partial P)_{\rm T} - [\partial (H_{\rm gas} - H^0_{\rm gas}) / \partial P]_{\rm T}$ , where the last term is obtained from the virial equation of state with the coefficients as given above. Taking  $30^{\circ}$  as an average temperature  $(\partial \Delta H^0 / \partial P)_{303}$  and  $[\partial (H_{gas} - H^0_{gas}) / \partial P)_{gas}$  $\partial P$ ]<sub>303</sub> are found to be 0.42 and 0.32 cal atm<sup>-1</sup> mol<sup>-1</sup>, respectively. These quantities, and an average  $\Delta C_{\rm p} =$  $\Delta C_{\rm p}^{0}$  of 37.4 cal deg<sup>-1</sup> mol<sup>-1</sup>, give  $(\partial T/\partial P)_{\Delta \rm H} = -0.0027$ deg atm<sup>-1</sup>. Integrating along the isenthalp where

 $\Delta H = 0$  shows that if the temperature of the solubility minimum is 28.3° at 200 atm it is 28.8° at 1 atm. This may be compared with the experimental temperature<sup>20</sup> of 34°. (There is a considerable possible error in the estimates of  $(\partial \Delta H / \partial T)_P$  here and in the preceding paragraph because of the nearness to the temperature of minimum  $\overline{V}_2$ , where the value of  $(\partial \overline{V}_2 / \partial T)_P$  is subject to much uncertainty.) It will be seen that for any gas exhibiting a solubility minimum, the latter will move to lower temperatures with increasing pressure if both  $\Delta C_{\rm p}$  and  $(\partial \Delta H/\partial P)_{\rm T}$  have the same sign. It may be pointed out that if the gas is sufficiently ideal, and if the solubility minimum does coincide with the minimum in  $\bar{V}_2$ , then  $(\partial T/\partial P)_{\Delta H}$  reduces to  $-\bar{V}_2/\Delta C_n$ , so that the temperature of the minimum will be lowered with increase in P if both  $\bar{V}_2$  and  $\Delta C_p$  have the same sign. In all known instances both are positive. Finally, since, at 25°,  $\Delta C_{p}^{0}$  is 40.7<sup>20</sup> and 34.1 cal deg<sup>-1</sup> mol<sup>-1</sup>, respectively, at 1 and 200 atm,  $(\partial \Delta C_{p}^{0}/\partial P)_{T}$  is negative. However,  $(\partial C_p^0 / \partial P)_T$  for helium is zero, so  $(\partial \bar{C}_{p2}/\partial P)_{T}$  is also negative.

Recently, Hepler<sup>28</sup> has proposed that  $(\partial \bar{C}_p / \partial P)_T$  for an aqueous solute is negative if the latter is a structure maker. Since there was previously a complete lack of information on this quantity, Hepler employed the relation  $(\partial \bar{C}_p / \partial P)_T = -T (\partial^2 \bar{V}_2 / \partial T^2)_P$  and examined the coefficient of thermal expansion of a number of solutes. Application of this concept to the volumetric data of Masterton<sup>29</sup> suggested that  $CH_4$ ,  $C_2H_6$ , and  $C_3H_8$  are structure breakers, an unexpected conclusion. However, it has already been shown above that  $(\partial \bar{C}_{p}/\partial P)_{T}$ is negative for helium and, since  $\bar{V}_2$  goes through a minimum,  $(\partial^2 \bar{V}_2 / \partial T^2)_P$  is obviously positive in the region of that minimum. Similar conclusions can be drawn from the studies on  $N_2$ ,  $CH_4$ , and a number of other gases.<sup>6,15,24,25</sup> It is likely that every gas which exhibits an isobaric solubility minimum in water is a structure maker. Furthermore, since Hepler's thesis seems reasonable, one may conclude that Masterton's data can yield no information on the value of  $(\partial \vec{V}_2 / \partial T)_{\rm P}$ .

An examination of Table V reveals the following behavior of  $\overline{V}_2$ . (1) As discussed above, it may well pass through a minimum with rise in T for water and 1 mNaCl. For 4 m NaCl, however, it rises almost linearly with T at a rate that decreases with increase in P. Presumably such a large proportion of salt has destroyed much of the water structure and the behavior is more "normal." (2) The temperature of the aforesaid minimum appears to rise markedly with pressure. This result is surprising, since increase in P would be expected to break structure and so lower the temperature

- (25) R. A. Pierotti, J. Phys. Chem., 67, 1840 (1963); 69, 281 (1965).
- (26) D. N. Glew and E. A. Moelwyn-Hughes, *Discuss. Faraday Soc.*, No. 15, 150 (1953).
- (27) H.S. Frank and M.W. Evans, J. Chem. Phys., 13, 507 (1945).
- (28) L. G. Hepler, Can. J. Chem., 47, 4613 (1969).
- (29) W. L. Masterton, J. Chem. Phys., 22, 1830 (1954).

of minimum  $\vec{V}_2$ . (3) The minimum in  $\vec{V}_2$  with change in T for 1 m NaCl suggests, according to Hepler's hypothesis,<sup>28</sup> that helium is a structure maker even in solutions containing appreciable salt concentration. (4) At lower temperatures and pressures, it appears to pass through a minimum with rise in salt concentration. In this respect the behavior differs from that of nitrogen and methane,<sup>6</sup> where such minima are not evident.

The solubility results for the salt solutions are quoted in Table VII as salting-out coefficients,  $k_{\text{NaCl}} = \log (S/S')/m$ , where S and S' are the gas solubilities in water and salt solution of molality m. With increase in m the coefficient decreases. These and other variations in  $k_{\text{NaCl}}$  show that the Setschenow relation is not strictly applicable. This was found earlier for nitrogen and methane.<sup>6</sup> The coefficients for helium are 10 to 20% smaller than those for the other two gases. The value in the limit of zero salt concentration at 25°, 0.10, is in poor agreement with 0.081 quoted by Morrison and Johnstone.<sup>20</sup> If the theory of Long and Mc-Devit<sup>30</sup> is applied, in conjunction with the partial molar volumes determined here, the calculated values of  $k_{\text{NaCl}}$  agree with the limiting ones quoted below within experimental error. This result agrees with their expectation that the theory would work best for solutes with low polarizability.

Table VII:	Salting-Out	Coefficients	$(k_{NaCl})$
------------	-------------	--------------	--------------

Temp, °C	m	100	200	<i>P</i> , 300	atm 400	500	600
25.0	1.003	0.0928	0.0963	0.0928	0.0924	0.0931	0.0938
	4.067		0.0858	0.0874	0.0870	0.0867	0.0859
50.0	1.003	0.0983	0.0956	0.0914	0.0903	0.0903	0.0910
	4.067		0.0828	0.0833	0.0852	0.0867	0.0898
100.0	1.003	0.0709	0.0850	0.0843	0.0851	0.0882	0.0886
	4.067		0.0721	0.0688	0.0727	0.0746	0.0750

Acknowledgment. The authors wish to acknowledge with thanks the assistance of a grant from the Earth Sciences Section of the National Science Foundation.

(30) W. F. McDevit and F. A. Long, J. Amer. Chem. Soc., 74, 1773 (1952).

## Use of F Centers for the Investigation of Alloy Thermodynamics.

The Potassium-Lead System<sup>1</sup>

by J. S. Bookless and J. J. Egan\*

Brookhaven National Laboratory, Upton, New York 11973 (Received November 1, 1971) Publication costs assisted by Brookhaven National Laboratory

The free energies of mixing for the binary liquid alloy system K-Pb have been studied at  $600^{\circ}$ . By examining F centers in KCl and KBr single crystals which have been equilibrated with the vapor over the alloys, the thermodynamic activities have been obtained. Results for the partial and integral free energies for the entire composition range are given.

### Introduction

The thermodynamic properties of liquid K–Pb alloys have been studied over the entire composition range at  $600^{\circ}$  by the following technique. A single crystal of KCl or KBr is equilibrated with the vapor above the alloy, thus producing F centers in the crystal. The F centers have a characteristic absorption spectrum, and the absorption constant at the maximum of the characteristic band is directly proportional to the fugacity of potassium in the vapor, as shown by Mollwo and Rögener.<sup>2</sup> Thus

$$\alpha = cf_{\rm K} \tag{1}$$

where  $f_{\rm K}$  is the fugacity of potassium, c is a constant, and  $\alpha$  is the absorption constant in reciprocal centimeters. ( $\alpha = (2.303/l) \log (I_0/I)$ , where l is the thickness of the crystal and  $I_0$  and I are the intensities of the incident and transmitted light, respectively.) The ac-

<sup>(1)</sup> This work was performed under the auspices of the U.S. Atomic Energy Commission.

 <sup>(2) (</sup>a) E. Mollwo, Z. Phys., 85, 56 (1933); (b) H. Rögener, Ann. Phys. (Leipzig), 29 (5), 386 (1937).

tivity of potassium  $(a_{\mathbf{K}})$  in the alloy at equilibrium is given by

$$a_{\mathbf{K}}(\text{alloy}) = \frac{f_{\mathbf{K}}(\text{vapor})}{f_{\mathbf{K}^0}(\text{vapor})}$$
(2)

where  $f_{\rm K}^0$  is the fugacity of pure potassium (600° in this case). Fugacities are used here instead of partial pressures since K vapor is known to deviate from ideal gas behavior at pressures above 20 mm. The fugacity as a function of temperature is given in the compilation by Hultgren, *et al.*<sup>3</sup> It follows then that

$$a_{\rm K}({\rm alloy}) = \alpha/cf_{\rm K}^0$$
 (3)

$$a_{\rm K}({\rm alloy}) = \alpha/\alpha_0$$
 (4)

By measuring the absorption constant of F centers, the thermodynamic properties are obtained. In the case of K alloys at 600°,  $\alpha_0$  cannot be measured, since the crystal is too opaque, so that eq 3 is used in conjunction with the fugacity data. In this technique the thermo-dynamic results do not depend upon the composition of the vapor above the alloy as in vapor pressure methods.

In the region of high potassium activity,  $x_{\rm K} > 0.65$  ( $x_{\rm K}$  is the mole fraction of potassium in the alloy), the crystals were too opaque to measure the absorption constant so that chemical analysis was used to obtain the excess potassium in the crystal. In this case

### $a_{\rm K}({\rm alloy}) = ({\rm concentration of excess K})/$

(concentration of excess K for pure potassium)

#### **Experimental Details**

The experimental arrangement used for the additive coloration of the crystals is shown in Figure 1. The container is made of stainless steel and is 16 in. high and 0.625 in. in diameter. The cover is sealed vacuum tight by melting a silver wire in an induction furnace under vacuum. Only the top of the tube becomes hot in this operation, the crystals and alloy remaining cold. The crystals (approximately  $1 \times 1 \times 0.1$  cm) are hung by stainless steel wire from a stainless steel tube. The entire container is cleaned prior to an experiment by degassing under high vacuum at 1000° for 6 hr.

The alloy is prepared by filtering fresh liquid potassium through a Pyrex frit directly into the previously weighed container. The container is then covered and weighed and then the appropriate amount of lead added, care being taken not to oxidize the potassium metal. The tube is then sealed under vacuum as described above.

The container is then placed in a two-zone wirewound resistance furnace so that the crystals and alloy can be held at different temperatures. Close temperature control is maintained by several thermocouples attached at various points along the outside of the container as well as another thermocouple that fits inside



Figure 1. Apparatus used for additive coloration of crystals.

of the tube holding the crystals. The crystals are generally heated for approximately 20 hr. The entire container is then immersed in a large basin of water to prevent colloidal K forming in place of the quenched color center. The container is opened in the induction furnace and the crystals are polished under kerosene on 600 soft-grit paper.

The optical measurements were made using a Cary Model 14 spectrophotometer modified by the addition of two 1-in. focal length silica lenses to accommodate the small crystals.

The chemical analyses were performed by dissolving the weighed crystals of KCl containing excess potassium in water freed of  $CO_2$  and  $O_2$ . These solutions were then titrated with standard HCl. A Gran plot<sup>4</sup> showing the appearance of hydrogen ion was used to determine the end point, and from this the excess potassium was calculated.

#### **Experimental Results**

Experiments were performed to confirm eq 1. Although Rögener<sup>2b</sup> had previously made these measurements, they were performed in a glass apparatus so that they were repeated here in the stainless-steel containers. Figure 2 shows results for KCl, where the crystal is held at a temperature of 550°. Comparison is made with results of Rögener, who held the crystals

(4) G. Gran, Analyst (London), 77, 661 (1952).

<sup>(3)</sup> R. Hultgren, R. Orr, P. Anderson, and K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," Wiley, New York, N. Y., 1963.

$x_{ m K}$	Crystal material	Crystal temp, °C	Alloy temp, °C	$\alpha$ , cm <sup>-1</sup>	¢fK⁰	٥K
0.10	KBr	550	600	2.07	2124	0.00098
0.20	KBr	550	600	6.0	2124	0.0028
0.294	KCl	550	600	10.8	944	0.011
0.299	KCl	600	600	9.0	$\sim$ 795	0.011
0.30	KCl	550	595	9.3	920	0.010
0.328	KCl	700	600	6.3	495	0.0127
0.397	KCl	550	598	37.2	934	0.04
0.401	KCl	550	600	36.5	944	0.039
0.50	KCl	550	595	120	920	0.13
0.59	KCl	700	603	139-165	503	0.276-0.328
0.60	KCl	700	600	173	495	0.36
0.63	KCl	700	600	198	495	0.40
0.70	KCl	700	600			0,69
0.80	KCl	700	600	Chemical		0.83
0.90	KCl	700	600	analysis		0.94
0.70	<b>K</b> C1	550	447	59	85.6	0.69
0.80	KCl	550	446	75	84.8	0.88
0.90	KCl	550	446	83	84.8	0.97

Table I: Experimental Results on K-Pb Alloys



Figure 2. Absorption constant in reciprocal centimeters vs. fugacity of potassium for KCl.

at 530° (shown with  $\times$ ). Results are also shown with the crystal held at 700°. Equation 1 was also confirmed for KBr with the crystal held at 550 and  $600^{\circ}$ :  $\alpha = 8f_{\rm K}$  for KCl at 550°,  $\alpha = 4.2f_{\rm K}$  for KCl at 700°,  $\alpha = 18f_{\rm K}$  for KBr at 550°, and  $\alpha = 8.5f_{\rm K}$  for KBr at 600°. Since the activity of K in K-Pb alloys extends over a range of several orders of magnitude (see Table II), different crystals as well as different temperatures were needed. For  $x_{\rm K} < 0.25$ , KBr crystals at 550° were used since they were most sensitive to coloration. For  $0.25 < x_{\rm K} < 0.55$ , KCl crystals at 550° were used. At  $0.55 < x_{\rm K} < 0.65$ , KCl crystals at 700° were used, since it was believed that the solubility limit of K in KCl was exceeded at 550°. For  $x_{\rm K} > 0.65$ , chemical analysis was used. The results are shown in Table I for all of these methods. Shown also are results for alloys at 447° and  $x_{\rm K} > 0.65$ , where optical measurements could be used.

Equations 1-4 are strictly valid only under isothermal conditions, whereas experiments were run with the crystal and alloy at different temperatures. Such a temperature gradient could cause a difference in the composition of the vapor phase at the two temperatures, *i.e.*, a difference in the ratio of monomer to dimer. Although it was believed that this would have a negligible effect on the derived thermodynamic measurements, a run was made under isothermal conditions and is shown in Table I. The value of the constant c was interpolated as 6.73 for the calculation, and this result is also listed in Table I.

It can be seen that the effect is a small one for the conditions needed to study K-Pb alloys and falls within the experimental error of the method.

Table II lists the derived thermodynamic quantities for alloys at  $600^{\circ}$  and all compositions.

The partial molar free energy of mixing for potassium is given by

$$G_{\mathbf{K}}^{\mathbf{M}} = RT \ln a_{\mathbf{K}}$$

The excess partial molar free energy of mixing is

$$G_{\mathbf{K}}^{\mathbf{E}} = G_{\mathbf{K}}^{\mathbf{M}} - G_{\text{ideal}}^{\mathbf{M}} = RT \ln a_{\mathbf{K}} - RT \ln x_{\mathbf{K}} = RT \ln \gamma_{\mathbf{K}}$$

where  $\gamma_{\mathbf{K}}$  is the activity coefficient.

The corresponding quantities for Pb were obtained by graphical integration with the help of the Gibbs-Duhem equation.

$$G_{\mathbf{Pb}}^{\mathbf{E}} = \int_{0}^{x_{\mathrm{K}}} \frac{G_{\mathrm{K}}^{\mathbf{E}}}{(1-x_{\mathrm{K}})^{2}} \mathrm{d}x - \frac{x_{\mathrm{K}}G_{\mathrm{K}}^{\mathbf{E}}}{1-x_{\mathrm{K}}}$$

The integral free energy of mixing is also tabulated

$$G^{\mathbf{E}} = (1 - x_{\mathbf{K}}) \int_0^{x_{\mathbf{K}}} \frac{G_{\mathbf{K}}^{\mathbf{E}}}{(1 - x_{\mathbf{K}})^2} \mathrm{d}x_{\mathbf{E}}$$

x <sub>K</sub>	aĸ	a <u>k</u> (Lantratov)	G <sub>K</sub> ™	$G_{\mathbf{K}}^{\mathbf{E}}$	G₽b <sup>M</sup>	$G_{Pb}{}^{\mathrm{E}}$	$a_{ m K}$	$G^{\mathbf{E}}$
0.10	0.00098	0.00087	-12,017	-8,023	-221	- 39	0.88	-837
0.20	0.0028	0.0027	-10,178	-7,386	- 549	-162	0.728	-1,606
0.294	0.011		-7,823	-5,699				,
0.30	0.010	0.0087	-7,988	-5,899	-1,314	-696	0.468	-2,226
0.328	0.0127		-7,573	-5,639				,
0.397	0.04		-5,583	-3,980				
0.401	0.039	0.028	-5,627	-4,041	-2,561	-1,675	0.228	-2,604
0.50	0.13	0.104	-3,539	-2,336	-4,232	-3,030	0.087	-2,683
0.59	0.328		-1,933	-1,017				
0.60	0.36	0.279	-1,772	- 886	-6,379	-4,790	0.025	-2,447
0.63	0.40		-1,589	-787				•
0.70	0.69	0.562	-643	-24	-8,434	-6,346	0.0077	-1,920
0.80	0.83	0.753	-323	+64	-9,375	-6,584	0.0045	-1,265
0.90	0.94	0.879	-107	+75	-10,597	-6,603	0.0022	- 592

Table II: Thermodynamic Quantities at 600°



Figure 3. Activity of K at all compositions for K-Pb alloys.

The activity of K is plotted in Figure 3 as a function of mole fraction of K, and the excess partial molar free energy is plotted in Figure 4 for all compositions.

The results of Lantratov<sup>5</sup> are also given in Table II for the K-Pb system at 600°. He performed his measurements by an emf technique using a potassium glass electrolyte. The agreement with these measurements is quite good for alloys dilute in K ( $x_{\rm K} < 0.50$ ). For alloys of high potassium content, the agreement is not as good. Perhaps some potassium in the alloy reacted with the glass electrolyte at 600°, thus changing the composition in the experiments of Lantratov.

It is believed that the large deviations from ideality



Figure 4. Partial excess free energy of mixing for K in K-Pb alloys.

in this binary system are due to changes in the quasifree electron concentration with composition as in the Mg-Bi system,<sup>6</sup> but no quantitative correlations could be made at this time.

Acknowledgment. The authors wish to thank Dr. Keith Rowley for performing the chemical analysis of excess potassium in the KCl crystals and Mr. R. J. Heus for design of the silver seal on the coloration apparatus.

- (5) M. Lantratov, Russ. J. Phys. Chem., 34, 372 (1960).
- (6) R. J. Heus and J. J. Egan, Z. Phys. Chem. (Frankfurt am Main), 74, 108 (1971).

## Pressure Effects in Polymer Solution Phase Equilibria. I. The Lower

## Critical Solution Temperature of Polyisobutylene and

**Polydimethylsiloxane in Lower Alkanes** 

by L. Zeman, J. Biros,<sup>1</sup> G. Delmas, and D. Patterson\*

Chemistry Department, McGill University, Montreal, Canada (Received August 6, 1971)

Publication costs borne completely by The Journal of Physical Chemistry

The effect of pressure on polymer solution phase equilibria has been investigated in the temperature range of  $0-200^{\circ}$  for various molecular weights of polyisobutylene in short-chain alkanes ( $C_3-C_6$ ) and of polydimethylsiloxane in  $C_2-C_4$ . Pressure displaces the phase boundary associated with the LCST to higher temperatures, *i.e.*, increases polymer solubility. A large difference in the solubility of the two polymers is associated with their widely different degrees of thermal expansion. The results are successfully correlated using a treatment based on the Prigogine and Flory theories of polymer solution thermodynamics. Although the absolute values for the LCST's are predicted too low, the variation between systems and the pressure effect on the LCST are reasonably predicted.

### Introduction

The most distinctive general feature of the phase behavior of high polymer solutions is the liquid-liquid phase separation reached by heating the solution under its equilibrium vapor pressure to the lower critical solution temperature (LCST). The application of hydrostatic pressure eliminates the vapor phase and displaces the LCST to higher temperatures. This positive pressure dependence has been measured for several polymer systems: polyethylene-pentane,<sup>2</sup> polyisobutylene-2-methylbutane,<sup>3</sup> and polystyrene-methyl acetate,<sup>4</sup> and may be viewed in terms of the general relation valid at a critical point<sup>5</sup>

$$\left(\frac{\partial T}{\partial P}\right)_{\rm c} = \frac{\left(\partial^2 \Delta V_{\rm M} / \partial w_2^2\right)_{\rm c}}{\left(\partial^2 \Delta S_{\rm M} / \partial w_2^2\right)_{\rm c}} \tag{1}$$

(Equation 1 is probably more correctly<sup>6</sup> written to correspond to the limit  $T \rightarrow T_c, w_2 \rightarrow w_{2c}$  since the numerator and denominator may vanish at the actual critical point.) Here  $w_2$  is the weight fraction of polymer (but this choice of composition variable is not essential);  $\Delta V_{\rm M}$  and  $\Delta S_{\rm M}$  are expressed per unit quantity of solution. The occurrence of an LCST requires the curvature of  $\Delta S_{\rm M}(w_2)$ , *i.e.*,  $(\partial^2 \Delta S_{\rm M}/\partial w_2)$ , to be positive.<sup>5</sup> The well-known combinatorial  $\Delta S_M$ , given, for instance by the Flory-Huggins theory is, however, a positive quantity of negative curvature. The LCST has its origin<sup>7</sup> in a negative, noncombinatorial contribution to  $\Delta S_{M}$  associated with the polymer having a much smaller "free volume" or degree of thermal expansion than the typical solvent. Since the polymer is also less compressible than the solvent, application of pressure decreases the free volume difference between

the components and increases the polymer-solvent compatibility. The LCST is recovered by raising the temperature, so that  $(dT/dP)_c$  should be positive at the LCST. This intuitive argument is consistent with eq 1. At sufficiently high temperatures,  $\Delta V_M$  has been observed to be negative for polymer-solvent mixtures, corresponding to a positive curvature of  $\Delta V_M(w_2)$ . Thus both numerator and denominator in eq 1 are positive at the LCST.

The LCST also occurs in the presence of a solute which is nonpolymeric if the difference of degrees of thermal expansion of the components is sufficiently large, e.g., methane-higher alkanes,<sup>6,8</sup> and these systems serve as models for the polymeric systems. It is then apparent that the LCST values as a function of pressure lie on a critical locus in (P, T, composition)space, the LCST under the saturated vapor pressure being a lower critical end point (LCEP). The critical locus rises to a maximum pressure and then decreases to finally reach the vapor-liquid critical point of the less volatile liquid. (This point would be unattainable in the case of a high polymer due to degradation.) Fig-

- (1) On leave of absence from the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague.
- (2) P. Ehrlich and J. J. Kurpen, J. Polym. Sci., Part A, 1, 3217 (1963).
- (3) G. Allen and C. H. Baker, Polymer, 6, 181 (1965).
- (4) C. D. Myrat and J. S. Rowlinson, *ibid.*, 6, 645 (1965).
- (5) I. Prigogine, R. Defay, and D. H. Everett, "Chemical Thermodynamics," Longmans, Green and Co., New York, N. Y., 1954, p 288.
- (6) G. M. Schneider, Advan. Chem. Phys., 17, 1 (1970).
- (7) D. Patterson, Macromolecules, 2, 672 (1969).

<sup>(8)</sup> J. S. Rowlinson, "Liquids and Liquid Mixtures," 2nd ed, Butterworths, London, 1969, pp 211-214.



Figure 1. (P, T) projection of the phase diagram for a binary system which exhibits limited mutual solubility behavior. (UCEP, upper critical end point; LCEP, lower critical end point; CPI, CPII, liquid-vapor critical points of pure components; UCST, upper critical solution temperatures; LCST, lower critical solution temperatures. A three-phase line connects LCEP and UCEP.) The UCST line and the dashed line are discussed in part II.

ure 1 shows schematically the projection on the (P, T)plane of the critical locus. Portions of the critical locus have been studied for systems containing polyethylene (PE) and a compressed gas solvent near or above its vapor-liquid critical temperature: butane,<sup>2</sup> propane<sup>2</sup>, ethane,<sup>2</sup> and ethylene.<sup>2,9</sup>

The foregoing results in polymeric or small molecule systems may be predicted semiquantitatively.<sup>10,11</sup> The treatments take account of the difference in thermal expansions of the components, either being based on more recent solution theories<sup>12,13</sup> as in the case of ref 10 or the van der Waals equation in the case of ref 11.

The present goal is to obtain data and to test theory, with polymers other than PE, again with the lower alkane solvents. Polydimethylsiloxane (PDMS) and polyisobutylene (PIB) were chosen since they have, respectively, extremely large and small thermal expansion coefficients. Values of the LCST have been reported<sup>14</sup> for both polymers in the *n*-alkanes from pentane to decane. Experiments are facilitated since these polymers, unlike polyethylene, are liquid at ordinary temperatures.

### **Experimental Section**

Materials. Four PIB fractions were used,  $\overline{M}_{v} = 2160, 6030, 703,000, and 1,660,000$ . The gpc technique gave an  $\overline{M}_{w}/\overline{M}_{n}$  value of 1.14 for the two low-molecular-weight fractions. Two fractions of Dow-

Corning PDMS were used of  $\overline{M}_{v} = 203,000$  and 626,000. In addition, three Dow-Corning PDMS samples were used of 10-, 50-, and 292-cSt viscosity, corresponding to  $\overline{M}_{n}$  values of 1170, 3200, and 14,200.

The ethane, propane, and butane solvents were Matheson "instrument grade" products; the 99.5%purity cited by the supplier was confirmed by gas chromatography. The 2-methylbutane was Phillips pure grade (99% pure), the *n*-pentane was Matheson Coleman and Bell "spectroquality grade" (99.0% pure), while the *n*-hexane from the same company was a "chromatoquality reagent," 99.0% pure. None was further purified.

Reduction Parameters of the Materials. Reduction parameters are required for application of theory. They have been calculated from equation of state quantities following the prescription of Flory<sup>13</sup> and are shown in Table I.<sup>15–17</sup> The references give the sources of the equation of state data, except for ethane where the reduction parameters were obtained<sup>10</sup> by extrapolation of higher alkane data. Values of the parameters depend somewhat on the temperature (given in Table I) at which the equation of state data were obtained. This variation apparently indicates an inadequacy of

<b>I abic I</b> . <b>I</b> Coulon I anameters for the component	Table I:	Reduction	Parameters	for the	Components
-----------------------------------------------------------------	----------	-----------	------------	---------	------------

	<i>T*</i> ,	P*,	v <sub>sp</sub> *,
	K	cal/cm <sup>3</sup>	cm³/g
$C_{2^{a}}$ (40°)	2674	78.9	1.43
$C_{3^{b}}(-30^{\circ})$	3278	81.0	1.18
$C_{4^{b}}(-30^{\circ})$	3772	104.8	1.14
C5° (25°)	4158	97.2	1.18
$2\text{Me-C}_{4^{d}}(20^{\circ})$	4098	100.5	1.19
$C_{6^{\circ}}(25^{\circ})$	4439	101.3	1.16
$PDMS^{e}$ (20°)	5600	82.7	0.84
PIB <sup>c</sup> (25°)	7580	106.8	0.95
<sup>a</sup> Reference 10. <sup>b</sup> F nce 17a. <sup>e</sup> Reference	Reference 15. 17b.	e Reference 16.	<sup>d</sup> Refer-

(9) R. Koningsveld, G. A. M. Diepen, and H. A. G. Chermin, Recl. Trav. Chim. Pays-Bas, 85, 514 (1966).

(10) D. Patterson and G. Delmas, Trans. Faraday Soc., 65, 708 (1969).

(11) P. H. van Konynenburg, "Critical Lines and Phase Equilibria in Binary Mixtures," (Ph.D. Dissertation, U.C.L.A.), 1968; R. L. Scott and P. H. van Konynenburg, *Discuss. Faraday Soc.*, 49, 87 (1970).

(12) I. Prigogine (with the collaboration of V. Mathot and A. Bellemans), "The Molecular Theory of Solutions," North-Holland Publishing Co., Amsterdam, 1957.

(13) P. J. Flory, Discuss. Faraday Soc., 49, 7 (1970).

(14) (a) D. Patterson, G. Delmas, and T. Somcynsky, *Polymer*, 8, 503 (1967); (b) J. M. Bardin and D. Patterson, *ibid.*, 10, 247 (1969).
(15) D. Patterson and J. M. Bardin, *Trans. Faraday Soc.*, 66, 321 (1970).

(16) P. J. Flory, J. L. Ellenson, and B. E. Eichinger, Macromolecules, 1, 279 (1968).

(17) (a) G. Allen, G. Gee, and G. J. Wilson, *Polymer*, 1, 456 (1960);
(b) G. Allen, G. Gee, G. J. Wilson, D. Sims and D. Mangaraj, *ibid.*, 1, 467 (1960).

the theoretical equation of state, and we ignore it here. The most important of the parameters is  $T^*$ , since the reduced temperature,  $\tilde{T} = T/T^*$ , is directly related to the thermal expansion coefficient and may be taken as a measure of the free volume of the liquid.

Apparatus. The stainless steel optical cell had two glass windows (0.36-in. thickness, 0.5-in. diameter) sealed with Teflon O-rings. The total volume of the cell was 4.50 ml, and the volume of the outlet tubing (0.19 ml) was neglected in concentration calculations. The solution was agitated using a magnetic stirrer. The circuit of the pressure generator (High Pressure Equipment Co., Model 37-6-30) was filled with oil and connected to the solution in the cell via a mercuryfilled steel U-tube. The cell was heated by a tape with autotransformer control. The volume of metal in the cell relative to that of the solution was such that uniform temperatures were attained in the cell, and a constant temperature bath was unnecessary. A thermocouple, in direct contact with the liquid, was used to measure the temperature. The pressure was measured on a factory calibrated Heise solid-front gauge. Thorough bleeding freed the Bourdon tube from air bubbles. The zero position was set against the vapor pressure of propane and butane.

*Procedure.* The cell containing a weighed amount of polymer was evacuated and kept under vacuum for a short time. The solvent was then distilled in, the magnetic stirrer switched on and sufficient time allowed for complete dissolution of the polymer (up to 1 day in the case of high-molecular-weight PIB in poor solvents). The solvent reservoir was usually closed off and pressure applied to facilitate dissolution. When the change of temperature brought the system to the cloud point, the pressure was raised slightly to cause the turbidity to disappear, the temperature was carefully equilibrated, and the pressure was lowered. Usually the transition from a clear to a cloudy solution took place within a change of 1 bar. Several readings were taken for each point to ascertain reproducibility. The pressure and temperature were then raised, and another cloud point was obtained. The values of Pand T are believed to be accurate to, respectively,  $\pm 0.5$  bar and  $\pm 0.25^{\circ}$ .

The experiments give the (P, T) coordinates at constant composition of points on the cloud point surface or phase boundary surface separating the two-phase region from the one-phase region. These points are joined in a "(P, T) cloud point curve." Ehrlich and Kurpen<sup>2</sup> have shown that the critical composition remains virtually constant along the critical locus in  $(P, T, w_2)$  space throughout a wide variation of P and T. Thus the (P, T) cloud point curve (CPC) at constant composition is essentially the (P, T) projection of the critical locus. This particular curve may be picked from the family of curves corresponding to different compositions since it should lie at the lowest tempera-

This follows since at constant P, an LCST lies ture. at the minimum of the  $(T, w_2)$  curve. However, as Koningsveld<sup>18</sup> has emphasized, any polymer is necessarily polydisperse and in multicomponent systems the critical temperature does not lie at the minimum of the  $(T, w_2)$  curve. For most of the systems in the present work, there is almost no variation of temperature along the  $(T, w_2)$  curve for small values of  $w_2$ , *i.e.*, from 0.01 to 0.05. The critical temperature should lie within  $\sim 1^{\circ}$  of the minimum of the CPC. Furthermore, the pressure dependence of any of the points along the CPC is virtually the same. Thus, the (P, T) cloud point curves at different values of  $w_2$  are very similar and essentially the same as the (P, T) projection of the critical locus which is directly obtainable from theory.

### Results

PIB-Alkanes. The (P, T) cloud point curves at constant composition were obtained for the PIB fractions in a series of lower alkanes: propane, butane, pentane, 2-methylbutane, and hexane. Typical curves are shown in Figure 2 for different molecular weights of PIB in butane, and in Figure 3 for the 1.66  $\times$  10<sup>6</sup> molecular weight fraction in four of the alkane solvents. (This fraction was found to be insoluble in propane at pressures up to 400 bar.) For these and other systems, the curves were fitted by a second-degree polynomial and values of the LCST extrapolated to zero pressure were determined, together with the slope  $(dT/dP)_{P=0}$ . The results are shown in Table II. The limited quantities of the fractions restricted the measurements to rather few concentrations for each system. However,



Figure 2. (P, T) cloud point curves for PIB fractions in butane (PIB mol wt 1.66  $\times$  10<sup>6</sup>:  $\triangle$ , 0.61 wt %;  $\Box$ , 1.12 wt %; O, 4.66 wt %; PIB mol wt 7.0  $\times$  10<sup>5</sup>:  $\times$ , 1.14 wt %; PIB mol wt 6  $\times$  10<sup>3</sup>: +, 0.79 wt %;  $\Diamond$ , 2.72 wt %;  $\nabla$ , 4.66 wt %).

(18) R. Koningsveld, Discuss. Faraday Soc., 49, 144, 180



Figure 3. (P, T) cloud point curves for PIB:  $1.66 \times 10^6$  mol wt in butane (a); 2-methylbutane (b); pentane (c); and hexane (d). Concentrations: (a), 0.61-4.66 wt %; (b), 2.20 wt %; (c), 2.43 wt %; (d), 2.04 wt %. Dotted line: calculated from eq 3 with  $\nu^2 = \pi = 0$ . Dashed line: calculated from eq 3 with  $\nu^2$  fitted as described in the text and  $\pi$  from P\* parameters in Table I.

the concentrations used were in the region of the minimum of the  $(T, w_2)$  curves. For the high-molecularweight fractions, the curves showed almost no variation of temperature in the concentration region studied, whereas for the low-molecular-weight fractions there is a very noticeable concentration dependence. Values extrapolated to zero pressure of the LCST and its temperature dependence have been given for the PIB-

#### Table II: LCST Data for PIB

Solvent	Polymer mol wt	Concn, wt %	(LCST) <sub>P=0</sub> , °C	LCST/ Tc,1	$(dT/dP)_{P=0}$ deg/bar
Propane	2160	1.30	18.4	0.788	0.33
	2160	3.74	6.7	0.720	0.48
	$7.03 imes10^{5}$	Ir	soluble belo	ow 400 b	oars
Butane	6030	0.79	71.2	0.808	0.47
	6030	2.72	64.7	0.792	0.50
	6030	4.66	48.7	0.755	0.58
	$7.03 imes10^{5}$	1.14	-8.4	0.621	0.37
	$1.66 imes10^{5}$	0.61	-19.3	0.595	0.37
	$1.66 imes10^6$	1.12	-19.3	0.595	0.37
	$1.66 imes10^{6}$	4.66	-19.3	0.595	0.37
Pentane	6030	2.26	130.4	0.858	0.57
	$7.03 imes10^{5}$	2.47	80.4	0.752	0.42
	$1.66 imes10^6$	2.43	74.2	0.739	0.45
2-Methyl-	6030	2.35	114.7	0.841	0.55
butane	$7.03  imes 10^5$	2.20	57.4	0.717	0.45
	$1.66 imes10^6$	2.20	50.2	0.702	0.44
Hexane	$1.66 imes10^{6}$	2.04	136.5	0.806	0.61

2-methylbutane system by Allen and Baker;<sup>19</sup> they are, respectively, 50.5° and 0.454°/bar for a 2.25  $\times$  10<sup>6</sup> molecular weight fraction and 69.0° and 0.393°/bar for a fraction of 6.2  $\times$  10<sup>4</sup> molecular weight. These values of the LCST agree very well with our results, as does the first value of the pressure dependence. The value of (dT/dP) for the low molecular weight appears to be ~30% too small.

PDMS-Alkanes. The results for high-molecularweight PDMS-alkanes (ethane, propane, and butane) were treated similarly to those with PIB and are presented in Table III and Figure 4. The cloud point curves were again not obtained over an extensive concentration range. It was observed that the difference between the curves for PDMS-ethane run at 2.67 and 6.57 wt % was only  $1.5^{\circ}$  and in the PDMS-propane case the curves obtained for 1.17, 4.02, and 11.30 wt %all fell within a 2° range, which is only slightly beyond the experimental error. The variation with concentration is probably more pronounced for the lowmolecular-weight samples of PDMS. As our 292-, 50-, and 10-cSt samples were not sharp fractions, but rather polydisperse cuts, no systematic study was made. The results obtained are included only as an illustration of the effect of polymer molecular weight. Higher concentrations were chosen since, from eq 2 the critical concentration is expected to lie at higher values. The LCST's in these systems lie close to the vaporliquid critical temperatures of the solvents, and hence the extrapolation to zero pressure is made over a wide interval of pressure (20-40 bars). Vogel and Kinsinger<sup>20</sup> have obtained LCST values at the saturated vapor pressure for a series of PDMS fractions in propane and butane. Figure 4 shows points interpolated to correspond to the molecular weights used in our work, and excellent agreement is obtained. The measurements of these authors agree with our finding that the  $(T, w_2)$  cloud point curves at constant pressure are only slightly dependent on concentration. A variation of  $0.5^{\circ}$  over 10 wt % was observed for PDMS-butane and even less for PDMS-propane.

### Discussion

A number of qualitative differences may be noted between the phase behavior of the three polymers, PIB, PDMS, and PE, in the alkanes. The results of Ehrlich and Kurpen<sup>2</sup> suggested that the (P, T) projections of the critical loci should reach a maximum pressure at a temperature close to the vapor-liquid critical temperature of the pure solvent. The present results for PDMS and PIB show a distinct negative curvature of the (P, T) cloud point curves, but a maximum was never reached, although temperatures con-

(19) G. Allen and C. H. Baker, Polymer, 6, 181 (1965).

(20) G. E. Vogel, "Lower Critical Solution Temperatures for Polydimethylsiloxanes," (M.Sc. Thesis, Michigan State University, E. Lansing, Mich., 1965).

### Table III: LCST Data for PDMS

Solvent	Polymer mol wt	Concn, wt %	(LCST) <i>P</i> =0, °C	LCST/ T <sub>c,1</sub>	$(dT/dP)_{P=0}, deg/bar$
Ethane	1,170	36.6	7.5	0.46	0.92
	3,200	26.2	0.0	0.40	0.90
	14,200	6.34	-1.0	0.31	0.89
	$6.26 imes10^{5}$	6.51	-13.5	0.35	0.85
Propane	$2.03 imes10^{5}$	4.00	67.0	0.40	0.92
	$6.26 imes10^{5}$	4.02	64.6	0.38	0.91
Butane	$6.26 imes10^{5}$	3.69	119.8	0.49	0.92

siderably above the solvent critical temperatures were attained  $(1.7 T_{\rm c} \text{ in the case of PDMS-ethane})$ . As expected, the extremely large expansion coefficient and low value of  $T^*$  (see Table I) leads to a much greater solubility of PDMS in all the solvents than of PIB or PE. In butane, for example, at 110°, Ehrlich and Kurpen report a minimum pressure (upper critical solution pressure, UCSP) of 210 bars necessary to dissolve PE of 261,000 molecular weight. For PIB of 1.6  $\times$ 10<sup>6</sup> molecular weight the UCSP is 260 bars but PDMS of  $6.26 \times 10^5$  molecular weight is completely miscible with butane at this temperature. This fraction of PDMS shows an LCST in ethane at  $-6^{\circ}$  at saturated vapor pressure and at 110° the UCSP is only 270 bars whereas for PE of comparable molecular weight in ethane at this temperature, the UCSP is 1300 bars. While the PDMS behaves as expected the similarity of the PE and PIB solubilities is not in accord with the large difference of  $T^*$  values for these two polymers. The detailed comparison with theory shows that the PIB and PDMS data correlate very well while the PE behavior is somewhat anomalous.

Comparison with Theory. The Flory-Huggins theory of polymer solution thermodynamics gives the critical value of the free energy parameter  $\chi$  to be

$$\chi_{c}(P,T) = \frac{1}{2}(1 + r^{-1/2})^{2}$$
 (2a)

Here r is the ratio of the molar volumes of the two components, or as has been recently suggested,<sup>13</sup> the ratio of the molar volume reduction parameters. In the theory, the  $\chi$  parameter was assumed independent of concentration leading to a single critical value of the volume fraction

$$\phi_{2c} = 1/(1 + r^{1/2}) \tag{2b}$$

Experimentally,<sup>21</sup> the critical composition of systems at saturation pressure has been found to differ considerably from that given in eq 2b. Part of this discrepancy may be due to polydispersity effects<sup>18</sup> as discussed above. Tompa<sup>21</sup> was the first to point out a similar effect arising from a concentration dependence of  $\chi$ . With a linear dependence of  $\chi$  on volume frac-



Figure 4. (P, T) cloud point curves for PDMS in different alkane solvents. Ethane: PDMS mol wt 626,000: +, 2.67 wt %;  $\diamond$ , 6.57 wt %; PDMS mol wt 14,200:  $\bigcirc$ , 6.34 wt %; PDMS mol wt 3200:  $\triangle$ , 26.18 wt %; PDMS mol wt '1170: •, 36.64 wt %. Propane: PDMS mol wt 626,000:  $\bigcirc$ , 1.17 wt %;  $\bigtriangledown$ , 4.02 wt %;  $\bigtriangledown$ , 11.30 wt %. Butane: PDMS mol wt 626,000:  $\square$ , 3.69 wt %;  $\diamondsuit$ , liquid-vapor critical points of corresponding solvents;  $\square$ , data of Vogel and Kinsinger.<sup>20</sup>

tion, the critical value of  $\chi$  is only slightly different from the Flory-Huggins value given by eq 2a. The newer theories of polymer solution thermodynamics predict<sup>13,22</sup> a concentration-dependent  $\chi$ . For solutions under pressure, the theory<sup>10</sup> indicates a continuum of critical concentrations as the pressure varies along the critical locus. In the case of a high polymer component, it is predicted<sup>10</sup> that the LCST at saturated vapor pressure should occur at a low concentration within a factor of about 2 of that given by eq 2b, and at a critical value of  $\chi$  given essentially by eq 2a. This is consistent with the conclusions of Tompa for the UCST. Furthermore, the critical locus up to high values of T and P is predicted to remain characterized by these same values. This is in agreement with experiment<sup>2</sup> for PE-alkane systems. Thus, the (P, T) projection of a large part of the critical locus may be calculated from eq 2 once the pressure and temperature dependence of  $\chi$  is known at very low polymer concentration.

The following equation has been used<sup>10</sup> to predict the critical loci of polymer solutions occurring at low polymer concentration

$$\chi_{c}(\tilde{P},\tilde{T}) = c_{l} \left[ -\frac{\tilde{U}_{1}}{\tilde{T}_{1}}^{\nu^{2}} + \frac{1}{2} \tilde{C}_{p,1}(\tilde{P}_{1},\tilde{T}_{1}) \times \left\{ \tau + \frac{\tilde{P}_{1}\tilde{V}_{1}^{2}}{\tilde{P}_{1}\tilde{V}_{1}^{2} + 1} \pi \right\}^{2} \right] = \frac{1}{2} (1 + r^{-1/2})^{2} \quad (3)$$

(21) H. Tompa, "Polymer Solutions," Butterworths, London, 1956, p 176.

(22) D. Patterson, J. Polym. Sci., Part C, 16, 3379 (1968).

The  $\tau$  parameter is a measure of the difference in degrees of thermal expansion or free volumes of the two components

$$\tau = 1 - T_1^* / T_2^* \tag{4}$$

and the  $\nu^2$  parameter expresses the difference of chemical nature of the components which results in a weakness of the energy of the (1-2) contacts relative to the (1-1) and (2-2) contacts. It is identical with the ratio  $X_{12}/P_1^*$  of the Flory theory; the  $\pi$  parameter expresses a difference in  $P^*$  reduction parameters, similar to eq (4):  $\pi = P_1^*/P_2^* - 1$ . The parameter  $3c_1$  is the number of external, volume-dependent degrees of freedom of the solvent molecule,  $\tilde{U}_1$  is the reduced configurational energy of the solvent, and  $\tilde{C}_{p,1}$  its temperature derivative, *i.e.*, the reduced configurational heat capacity. The Flory theory<sup>13</sup> essentially predicts  $\tilde{U}_1$ and  $\tilde{C}_{p,1}$  using a van der Waals model of the liquid state and the Hirschfelder-Eyring cell partition function. Using this model

$$\tilde{C}_{p,1}^{-1} = (1 - \frac{2}{3}\tilde{V}_1^{-1/3}) - \frac{2(1 - \tilde{V}_1^{-1/3})}{(1 - \tilde{V}_1^{-1/3})} - \frac{2(1 - \tilde{V}_1^{-1/3})}{(1 - \tilde{V}_1^{-1/3})}$$
(5a)

$$\tilde{T}_1 = (\tilde{P}_1 \tilde{V}_1 + \tilde{V}_1^{-1})(1 - \tilde{V}_1^{-1/s})$$
(5b)

According to the theory, the vapor-liquid critical temperature of the solvent,  $T_{\rm c,1}$  (or of any liquid) takes place at a universal reduced value, given in the case of the Flory model by  $\tilde{T}_{\rm c,1} = 0.1183$ . Thus, the reduced temperature  $\tilde{T}_1$  is proportional to  $T/T_{\rm c,1}$ 

$$\tilde{T}_1 = T/T_1^* = 0.1183(T/T_{c,1}) \tag{6}$$

The simplest case puts  $\nu^2 = \pi = 0$ , *i.e.*, the difference of chemical nature between the component is neglected as well as that of  $P^*$ . Equation 3 then states that the critical locus corresponds to a line of constant  $\tilde{C}_p$  or  $C_p$  of the solvent, *i.e.* 

$$\tilde{C}_{p,1}^{-1}(\tilde{P}_1,\tilde{T}_1) = c_1 \tau^2 / (1 + r^{-1/2})^2$$
(7)

Equations 5a, 5b, and 7 then give a prediction of the locus in  $(\tilde{P}, \tilde{T})$  coordinates which may be transformed into the (P, T) curve.

It may be noted that when the Flory model equations 5a and 5b are used in the expression for  $\chi$ , eq 3, and then the pressure is set to zero, one obtains essentially the  $\chi$  expression given by the Flory theory.<sup>23</sup> The treatment of ref 10, parts of which are applied here, may be considered as an extension of the Prigogine theory and the basically similar Flory theory to include pressure effects. The explanation of the LCST in polymer solutions at saturation pressure was first made<sup>24</sup> in terms of the Prigogine theory, and subsequently Flory and collaborators<sup>25</sup> have also used their theory to treat zero-pressure LCST data.

Slope of the (P, T) Cloud Point Curve at Zero Pressure. It is possible to calculate the slope of the critical locus at zero pressure from the above equations, giving<sup>10</sup>

$$(\mathrm{d}T/\mathrm{d}P)/(T_1^*/P_1^*) = (\mathrm{d}\tilde{T}/\mathrm{d}\tilde{P})_{\bar{P}=0} = \\ \tilde{V}_1(1 - \tilde{V}_1^{-1/s})(7 - {}^{9}/_2\tilde{V}_1^{1/s})$$
(8)

This equation predicts that  $\mathrm{d}\tilde{T}/\mathrm{d}\tilde{P}$  is independent of the polymer and should increase with increase of the value of  $\tilde{V}_1$  or  $\tilde{T}_1$  at which the LCST occurs, *i.e.*, according to eq 6, the ratio  $LCST/T_{c.I}$ . Table II shows that as the polymer molecular weight in a system is decreased and  $LCST/T_{c,1}$  increases, the value of (dT/dP) and hence  $(d\tilde{T}/d\bar{P})$  is indeed increased. Again as the chain length of the solvent is increased for a particular molecular weight of the polymer,  $(d\bar{T}/d\bar{P})$ increases, but of course the ratio of reduction parameters  $T_1^*/P_1^*$  also increases with the solvent chain length. The data are correlated by plotting  $(d\tilde{T}/d\tilde{P})$ against  $LCST/T_{c,1}$  (Figure 5). The theory gives a very good prediction of the magnitude of  $(d\tilde{T}/d\tilde{P})$ . Close inspection shows that  $(d\tilde{T}/d\tilde{P})$  values increase as the polymer molecular weight in a particular system is decreased, but the results for different systems do not superimpose. This slight failure of the theory is probably due to lack of precision in the reduction parameters for the different solvents.

Values of the LCST Extrapolated to Zero Pressure. Equation 3 may be used to correlate the data of Table II for the LCST's of different systems, extrapolated to zero pressure. The right hand side of the equation may be calculated for each system using the reduction parameters of Table I, giving values of  $\tilde{C}_{p,1}^{-1}$  at zero pres-



Figure 5. The reduced values of the P,T line slopes (extrapolated to zero pressure) plotted as a function of the LCST/ $T_{\rm c}$  ratio, where  $T_{\rm c.1}$  is the vapor-liquid critical temperature of the solvent. Full points are for the PIB systems, open points for the PDMS systems ( $\Delta$ , ethane;  $\nabla$ , propane;  $\Diamond$ , butane;  $\Box$ , 2-methylbutane; O, pentane;  $\bigcirc$ , hexane). Points for fractions of different molecular weight are included. Theoretical curve calculated according to eq 8 is also shown.

(25) (a) R. A. Orwoll and P. J. Flory, J. Amer. Chem. Soc., 89, 6822
(1967); (b) P. J. Flory, R. A. Orwoll, and A. Vrij, *ibid.*, 86, 3515
(1964).

<sup>(23)</sup> B. E. Eichinger and P. J. Flory, Trans. Faraday Soc., 64, 2035 (1968).

<sup>(24)</sup> G. Delmas, D. Patterson, and T. Somcynsky, J. Polym. Sci., 57, 79 (1962).

sure and at the reduced value of the LCST. These values should form a single curve against  $\tilde{T}_1$  or LCST/ $T_{c,1}$ . Figure 6 shows that all of the data of Table I can be correlated in this way.

Values of the LCST are available for infinite molecular weight PIB<sup>14b</sup> and PDMS<sup>14a</sup> at saturated vapor pressure in C<sub>5</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>, C<sub>10</sub>, and C<sub>12</sub>. We have used the theoretical value of (dT/dP) to extrapolate these values to zero pressure, and Figure 6 shows that they correlate perfectly with the values for the lower alkanes. The value of LCST/ $T_{c,1}$  increases as the polymer and the solvent become more similar in any one of three ways: by decreasing the molecular weight of the polymer, by increasing the chain index of the alkane solvent, or by changing from PIB to the more thermally expanded PDMS. Variation of the LCST/ $T_{c,1}$  ratio arising from these three changes gives overlapping sections of the curve.

It is of interest to investigate the generality of the curve shown in Figure 6 for predicting values of the LCST in other systems. We have calculated  $c_1\tau^2$  for the following systems containing polymers of effectively infinite molecular weight: PE-n-alkanes<sup>14a</sup> from C<sub>5</sub> to C<sub>8</sub>, PDMS-oligomers<sup>14a</sup> of dimethylsiloxane, polystyrene-benzene, polystyrene-toluene. The LCST data for PE-n-alkanes appear to fall on a different curve in Figure 6, and thus use of the correlation established for the PIB and PDMS systems will lead to uniformly incorrect predictions, about 0.1  $T_{c,1}$  too high. On the other hand, correct predictions would be made for the siloxane mixtures, polystyrene-benzene and -toluene.

A reasonable correlation is again obtained in Figure 6 using values of the LCST/ $T_{c,1}$  ratio obtained for the present systems at a constant value  $\tilde{P}_1 = 0.025$ , corresponding to pressures of  $\sim 100$  atm. The increased scatter could be due to the imprecision of the  $P^*$  values. The  $\tilde{C}_{p,1}^{-1}$  curve lies above the previous one for  $\tilde{P} = 0$ , as expected, since  $(\partial C_p / \partial P)_T = -(\partial^2 V / \partial T^2)_P$  and V(T) has positive curvature for all liquids.

Figure 6 also shows  $\tilde{C}_{p,1}^{-1}$  vs. LCST/ $T_{c,1}$  as given by the Flory model, *i.e.*, eq 5a and b. The shape of the empirical  $\tilde{C}_{p,1}^{-1}$  curve is reproduced by the model which also gives the correct displacement of the  $\tilde{C}_{p,1}^{-1}$  curve on increasing the pressure, as would be expected since (dT/dP) is well predicted by the model. However, the absolute magnitudes of  $C_{p,1}^{-1}$  are too small; values of the LCST calculated from the model would therefore lie at values which are too low or pressures which are too high.

The assumption of a nonzero value of the  $\nu^2$  parameter would increase the value of the calculated  $\chi$  parameter, further decreasing the predicted LCST, and so cannot explain the discrepancy between theory and experiment. The reduction parameters in Table I were obtained at temperatures much below the LCST's, and these parameters are somewhat temperature de-



Figure 6. The value of  $C_{p,1}^{-1}$  obtained from eq 7 plotted against the LCST/ $T_{c,1}$  ratio at two values of reduced pressure: full points, PIB-alkane systems; open points, PDMS-alkane systems;  $\times$ , PDMS-dimethylsiloxane<sup>14a</sup> oligomers; +, PE-alkane<sup>14a</sup> systems; O PS-benzene; O, PS-toluene. Full lines are those given by the theory according to eq 5.

pendent. However, the value of  $c_1\tau^2$  varies much less with temperature than the individual parameters. Calculation of  $c_1\tau^2$  at the LCST itself would not improve agreement significantly. On the other hand, the disagreement could be explained by the use of the Flory-Huggins approximation for the combinatorial entropy of the solution in calculating the critical value of  $\chi$ , *i.e.*, eq 2a. This assumes a random mixture (Bragg-Williams approximation) which may not be appropriate at temperatures approaching a critical solution point. An approximation such as the Guggenheim quasichemical which allows for nonrandomness would give a higher critical value for  $\chi$  than given by eq 2a. By using this value the empirical  $\tilde{C}_{p,1}^{-1}$  curve would be displaced downward in better agreement with that given by the model.

Calculation of the (P, T) Cloud Point Curves. As noted in the preceding section, use of eq 3 to 5a gives an unsatisfactory prediction of the positions of the (P, T) cloud point curves. Thus at 110° the UCSP is predicted to lie at 600 bars for high-molecular-weight PIB-n-butane and 26 bars for high-molecular weight PDMS-n-butane. The experimental value for the first system is 262 bars while the second system is completely miscible. The predictions of the UCSP are thus too high, although the theory does give the qualitative difference between the two systems. To test the prediction of the shape of the (P, T) cloud point curve, we have fitted eq 3 to one experimental point for a high polymer molecular weight adjusting the critical value of  $\chi$  upwards from the value of 0.5 given by the Flory-Huggins approximation. The calculated curves for the PIB-alkanes and PDMS-alkanes systems are shown in Figures 3 and 7. The slope of the curve is satisfactorily predicted at low temperatures, but the shape for the PDMS-alkanes systems is not correct in the supercritical region. The theory predicts a maxi-



Figure 7. Pressure-temperature cloud point curves for PDMS (mol wt 626,000) in ethane, propane, and butane (concentrations same as in Figure 4) compared with the theoretical curves: solid thin lines, critical curves calculated without the  $\nu^2$  and  $\pi$  terms; dashed lines, calculation retaining all terms of eq 3. Dotted line corresponds to constant  $C_{p,1} = 11.12$  cal/(deg mol) for ethane.<sup>26</sup>

mum in the cloud point curve at  $\sim 1.2 T_{\rm c}$ , whereas experimentally in the PDMS-ethane case the maximum must lie above 1.7  $T_{\rm c}$ .

Values of the configuration  $C_{p,1}$  of ethane have been taken from tables<sup>26</sup> and a (P, T) curve corresponding to  $C_{p,1} = 11.2$  cal/(deg mol) has been drawn in Figure 7. It has the same shape as the theoretical (P, T) curves indicating that they do correspond to constant  $C_{p,1}$ . It seems therefore that the theory is incorrect in identifying the critical locus with a curve of constant  $C_{p,1}$ . It is perhaps not surprising that the theory breaks down with the PDMS-alkanes systems where the cloud point curves pass close to the critical point of the solvent. The reduced volume of the solution is large in this region and increases rapidly as the predicted cloud point curve moves to higher P and T. The theory may well be in error in assuming that the numbers of external, *i.e.*, volume-dependent degrees of freedom of the components are the same as in the high density liquids.

The shape of the calculated (P, T) cloud point curves may be marginally improved in the PIB systems by allowing nonzero values of the  $\nu^2$  parameter. We have taken the value of this parameter (=  $X_{12}/P_1^*$  for the PIB-n-pentane case obtained by Flory, et al.,<sup>16</sup> who fitted their theory to heat of solution data. A new critical value of  $\chi$  was calculated by fitting the theory to the cloud point curve at a single point, and the curve for PIB-n-pentane was calculated. Similar calculations were performed for the other PIB-alkane and PDMS-alkane systems by keeping the same critical value of  $\chi$  and fitting  $X_{12}$  whence the cloud point curves were obtained. In all cases reasonable values of the  $X_{12}$  parameters were obtained. The curves are shown in Figures 3 and 7, but there is no substantial change in the calculated curves, particularly in the case of the PDMS systems.

Acknowledgment. We are grateful to the National Research Council of Canada for their support of our research, a fellowship to J. B., and a scholarship to L. Z.

(26) H. E. Tester in "Thermodynamic Functions of Gases," Vol. III, F. Din, Ed., Butterworths, London, 1961.

## Pressure Effects in Polymer Solution Phase Equilibria. II. Systems

## Showing Upper and Lower Critical Solution Temperatures

### by L. Zeman and D. Patterson\*

Chemistry Department, McGill University, Montreal, Canada (Received August 6, 1971) Publication costs assisted by the National Research Council of Canada

The effect of pressure on phase equilibria in polymer-solvent systems has been investigated for various molecular weights of polystyrene in methyl acetate and acetone and for two fractions of polypropylene oxide in propane. Both an upper and a lower critical solution temperature are found at the saturated vapor pressure for all molecular weights of polystyrene in methyl acetate. Pressure increases the polymer-solvent miscibility, decreasing the UCST and increasing the LCST. The effect on the LCST is ca. ten times greater than on the UCST. Polystyrene fractions of molecular weight greater than 19,000 are partially miscible with acetone at saturated vapor pressure. Complete miscibility is attained on raising the pressure; *i.e.*, the critical locus has a minimum in pressure lying above saturated vapor pressure. The minimum is displaced to higher pressure and temperature with increasing molecular weight of the polymer. The polypropylene oxide-propane system shows less miscibility, but is qualitatively similar to polystyrene-acetone. The phase behavior of these systems is predicted semiquantitatively using a treatment based on the Prigogine and Flory theories of polymer solution thermodynamics.

### Introduction

Part I<sup>1</sup> of this work dealt with systems showing only a lower critical solution temperature (LCST). The phase behavior could be treated semiguantitatively by taking account of the differing degrees of thermal expansion of the components, but ignoring any difference in intermolecular force fields. We now consider systems which show an upper critical solution temperature (UCST) at low temperatures as well as the LCST at high temperatures (cf. Figure 1, part I). This corresponds to a second contribution in the free energy of mixing arising from a difference of chemical nature and of intermolecular force fields between the components. Experimentally, it is found that while pressure apparently always increases the LCST, the UCST may be either decreased, as in Figure 1, part I, or increased, corresponding to, respectively, negative and positive values of the volume of mixing. In eq 1 of part I, the denominator is necessarily negative at the UCST, but the numerator may be of either sign. Many nonpolymeric systems show<sup>2</sup> the UCST and LCST. With increasing difference of intermolecular forces between the two components, the critical locus moves higher in pressure and corresponds to the dashed curve in Figure 1, part I. The critical locus no longer cuts the three-phase line, and the components are only partially miscible at the saturated vapor pressure. A further increase in the disparity of intermolecular forces causes the minimum in the critical locus to move to higher temperature and pressure, as illustrated in Figures 16.23, b-f of ref 2a. So far there has been no study of the corresponding effects of pressure on phase diagrams of polymer-solvent systems.

We have investigated the following systems, listed in order of decreasing miscibility of the components: polystyrene (PS)-methyl acetate, PS-acetone, and polypropylene oxide (PPO)-propane. The effect of pressure on all three systems is to greatly increase the miscibility, corresponding to negative volumes of mixing. In the PS-methyl acetate system both the UCST and LCST are found at the saturated vapor pressure of the solution for all molecular weights of the polymer. The pressure dependence of the LCST has been studied by Myrat and Rowlinson.<sup>3</sup> The (T,composition) cloud point curves (CPC) at the saturated vapor pressure have been obtained recently for polystyrene fractions in acetone.<sup>4</sup> With low-molecularweight fractions, both the UCST and LCST are found, and with increasing molecular weight, the two critical solution temperatures approach one another. For the 19,800 and higher molecular weight fractions, the two critical solution temperatures and their associated regions of limited miscibility have merged so that there is no temperature region in which polymer and solvent are completely miscible. (Acetone is usually considered a nonsolvent for PS.) These results are confirmed in the present work. For a 20,400 molecular weight fraction the minimum of the critical locus lies within 10 bars of saturated vapor pressure. With in-

<sup>(1)</sup> L. Zeman, J. Biros, G. Delmas, and D. Patterson. J. Phys. Chem., 76, 1206 (1972).

<sup>(2) (</sup>a) J. S. Rowlinson, "Liquids and Liquid Mixtures," 2nd ed, Butterworths, London, 1969, p 211; (b) G. M. Schneider, Advan. Chem. Phys., 16, 1 (1970).

<sup>(3)</sup> C. D. Myrat and J. S. Rowlinson, Polymer, 6, 645 (1965).

<sup>(4)</sup> K. S. Siow, G. Delmas, and D. Patterson, Macromolecules, 5, 29 (1972).

creasing molecular weight the minimum moves to higher pressure and temperature in a manner similar to that caused by increasing the disparity of intermolecular forces between components. The behavior of the PPO-propane system is similar except for smaller miscibility of the components.

### **Experimental Section**

Materials. The PS fractions were obtained from the Pressure Chemical Co., Pittsburgh, Pa., who cite  $\overline{M}_{\rm w}/\overline{M}_{\rm n}$  ratios not exceeding 1.20, and for most of the fractions less than 1.10. The two PPO fractions came from Waters Associates, Framingham, Mass., and had molecular weights 790 and 3900. The acetone was Fisher Certified reagent (99 mol % pure), the methyl acetate a British Drug Houses reagent of purity exceeding 98%, and the propane a Matheson instrument grade product of 99.5% purity. None of the solvents was further purified.

Reduction Parameters of the Materials. These have been calculated as in part I from equation of state data following the prescription of Flory and are listed in Table  $I_{,5^{-7}}$  together with the temperatures at which the data were obtained. The  $c_1$  parameter is found through  $c_1 = P_1^*/V_1^*/RT_1^*$ .

	<i>Т.</i> * К	P,* cal/cm <sup>3</sup>	v <sub>sp</sub> ,* cm³/g
Propane <sup>a</sup> $(-30^{\circ})$	3278	81	1.18
Methyl acetate <sup>b</sup> (20°)	4406	156	0.81
Acetone <sup>b</sup> (20°)	4349	141	0.96
Polystyrene <sup>c</sup> ( $\sim 50^{\circ}$ )	7500	125	0.80
Polypropylene oxide <sup>b</sup> (20°)	6010	120	0.84

Apparatus and Procedure. These are described in part I.

### **Results and Discussion**

Polystyrene-Methyl Acetate. For high-molecularweight fractions, the cloud point temperatures around both the UCST and LCST were found to be remarkably independent of the concentration. For example, in the case of a  $1.8 \times 10^6$  molecular weight fraction in methyl acetate under pressures of 0, 100, and 150 bars the cloud point temperatures around the LCST were found to vary by only 1° for a change of concentration from 1 to 5%. The corresponding variation at the UCST was less than 4°. At these concentrations, the cloud point temperatures must be very close to the critical temperatures. The flatness of the CPC with sharp fractions was also noted by Myrat and Rowlinson.<sup>3</sup> Figure 1 shows the effect of pressure on the



Figure 1. (P,T) cloud point curves for fractions of polystyrene in methyl acetate. All concentrations are between 2.3 and 2.4 wt % molecular weights: •, 51,000; □, 97,200; O, 160,000;  $\nabla$ , 498,000;  $\Delta$ , 670,000;  $\Diamond$ , 860,000; +, 1,800,000; •, UCST and LCST extrapolated to infinite molecular weight.

cloud point temperatures corresponding to UCST and LCST at low polymer concentration and for fractions of various molecular weight of PS. An increase of molecular weight raises the UCST and lowers the LCST. Pressure increases polymer-solvent miscibility throughout,  $(dT/dP)_c$  being negative at the UCST and positive at the LCST. The volume of mixing is therefore negative in both temperature regions. However, the magnitudes of  $(dT/dP)_c$  are quite different, ca.  $-0.06^{\circ}$ /bar at the UCST and  $0.46^{\circ}$ /bar at the LCST.

Polynomials were fitted to the (P,T) curves; in most cases a second-degree polynomial was sufficient. Values of the UCST and LCST at zero pressure were then obtained by extrapolation. Figure 2 shows the Shultz-Flory plot of  $T_c^{-1}$  against  $r^{-1/2}$ , where r is the ratio of the molar volumes of the components, or, as employed here, the closely related ratio of molar volume reduction parameters,  $V_2^*/V_1^*$ . Negligibly different results are obtained by plotting against the more exact expression,  $r^{-1/2} + (2r)^{-1}$ . Figure 2 includes data of Myrat and Rowlinson<sup>3</sup> on LCST of various fractions. These data are completely consistent with the present work. Other data<sup>8</sup> for the UCST and LCST are also in reasonable agreement. In the Shultz-Flory plot, based on the Flory-Huggins theory, the slope of  $T_{c}^{-1}$  against  $r^{-1/2}$  is  $(\psi_{1}\theta)^{-1}$  where  $\theta$  is the  $\theta$ temperature corresponding to the critical temperature for a fraction of infinite molecular weight and  $\psi_1$  is the dimensionless parameter proportional to the en-

<sup>(5)</sup> D. Patterson and J. M. Bardin, Trans. Faraday Soc., 66, 321 (1970).

<sup>(6)</sup> G. Allen, G. Gee, D. Mangaraj, D. Sims, and G. J. Wilson, *Polymer*, 1, 456, 467 (1960).

<sup>(7)</sup> T. G. Fox and S. Loshaek, J. Polym. Sci., 15, 379 (1955); G. Gee, Polymer, 7, 373 (1966).

<sup>(8)</sup> G. Delmas and D. Patterson, J. Polym. Sci., Part C, 30, 1 (1970).



Figure 2. Polystyrene-methyl acetate system: the Shultz-Flory plot of inverse critical solution temperatures vs.  $r^{-1/2}$  where r is the ratio of the molar volume reduction parameters, *i.e.*,  $V^*$ , for the components: O, experimental points of this work;  $\nabla$ , points of ref 3;  $\Box$ , points of ref 8.

tropy of dilution. The  $\theta$  temperatures found by an extrapolation of  $T_{c}^{-1}$  to infinite molecular weight are 47 (UCST) and 109° (LCST). Figure 2 shows that  $\psi_1$ and  $\Delta S_1$  are positive at the UCST but negative at the LCST. This is consistent with the thermodynamic conditions for the occurrence of the two types of critical point. However, the lines of  $T_{c}^{-1}$  are in fact slightly curved indicating that  $\psi_1$  is a continuous function of temperature which decreases through the range of increasing UCST values, changes sign, and then becomes increasingly negative with increasing LCST values. The values of  $\psi_1$  shown in Figure 3 have been obtained by fitting a polynomial to the curves in Figure 2 and obtaining the slope by differentiation. It is of interest that  $\psi_1 < 0.5$  throughout the temperature range. The difference  $\psi_1 - \frac{1}{2}$  represents the noncombinatorial contribution to the entropy of dilution analogous to the excess entropy in mixtures of quasispherical molecules. This contribution is therefore negative even at low temperatures as is typical of polymer-solvent systems. Flory<sup>9</sup> lists values of  $\chi_s \equiv 1/2$  $-\psi_1$  for a number of systems at 25° and  $\psi_1 - \frac{1}{2}$  is typically of order -0.3 or larger.

As discussed in part I, the  $\chi$  parameter is often found to be concentration dependent and may be taken to be of form  $\chi = \chi_1 + \chi_2 \phi_2$ , the  $\chi_2$  parameter contributing to the third virial coefficient. Phase relationships are sensitive to the higher coefficients, and hence the Shultz-Flory plot leads to apparent values of the  $\psi_1$ parameter which differ<sup>10</sup> from those found from os-



Figure 3. The entropic dimensionless parameter  $\psi_1$  obtained from the slopes of Figure 2 (as described in the text) plotted as a function of temperature (dashed line). The full line has been calculated from the theory, using  $X_{12} = 4.0$  ( $\nu^2 = X_{12}/P_1^*$ ).

motically determined values of the second virial coefficient. Values of  $\chi_2$  at lower temperatures are usually positive<sup>9</sup> and may be as large as 0.3. According to an examination we have made, a temperature-independent  $\chi_2 = 0.3$  would lead to an apparent  $\psi_1$  double the real value. After correction, the noncombinatorial contribution to the entropy of dilution, proportional to  $\psi_1 - \frac{1}{2}$ , would be negative as indicated above and, indeed, of larger magnitude.

Inspection of Figure 1 and Table II shows that the pressure dependence of the UCST,  $(dT/dP)_{\rm o}$ , at zero pressure is negative and decreases in absolute magnitude as the temperature decreases, *i.e.*, from  $-0.08^{\circ}/$  bar at 31° corresponding to a molecular weight of  $+1.80 \times 10^6$  to  $-0.02^{\circ}/{\rm bar}$  at 2° corresponding to a molecular weight of  $9.72 \times 10^4$ . This decrease of magnitude is associated with a fall in the magnitude of the negative  $\Delta V_{\rm M}$  as the temperature is decreased. (It may be assumed that the change of molecular weight would have little effect on the value of  $\Delta V_{\rm M}$ .) The results suggest that a further decrease of temperature could bring about a change of sign of  $\Delta V_{\rm M}$  and hence of  $(dT/dP)_{\rm c}$ .

The pressure dependence of the LCST is positive and very large,  $+0.45^{\circ}$ /bar corresponding to large negative values of  $\Delta V_{\rm M}$  at high temperatures. This seems to be a universal feature of the LCST in polymer-solvent systems.

In Figure 1 the shapes of the (P, T) cloud point curves at the LCST show an interesting variation as the molecular weight of the fraction is changed. For the lower fractions which give the (P, T) CPC at high temperatures the curves are concave downwards. This

(9) P. J. Flory, Discuss. Faraday Soc., 49, 7 (1970).

(10) W. H. Stockmayer, Makromol. Chem., 35, 54 (1960).

PS	UCST	(dT/	LCST	(dT/
molecular	(°C) at	$dP)_{P=0}$	(°C) at	$\mathrm{d}P)_{P=0}$
weight	P = 0	deg/bar	P = 0	deg/bar
51,000			150.2	0.47
97,200	2.0	-0.018	142.0	0.45
160,000	8.3	-0.041	135.9	0.44
498,000	21.0	-0.056	127.4	0.46
670,000	23.3	-0.060	124.7	0.47
860,000	26.1	-0.073	123.0	0.47
1,800,000	30.0	-0.082	119.6	0.48

Table II: Polystyrene-Methyl Acetate Data

curvature was seen in part I with systems which did not show a UCST. However, for the highest fraction and hence the (P, T) curve at lowest temperature, the curve is concave upward at low pressure. It seems evident, particularly after comparing with the polystyrene-acetone system below, that this behavior is due to the relative proximity of the UCST for this high molecular weight fraction. The pressure effect on the LCST at zero pressure shows a corresponding variation with the molecular weight and the value of the LCST. With decreasing molecular weight and hence increasing LCST, the value of  $(dT/dP)_c$  decreases, passes through a minimum, and then increase again. With the systems in part I, a uniform increase of  $(dT/dP)_c$  is observed with increasing LCST.

Polystyrene-Acetone. Figure 4 shows typical cloud point curves in a (T, composition) phase diagram for a polystyrene fraction of 20,400 molecular weight. It is seen that at zero pressure the UCST and LCST and their associated immiscibility regions have merged to give a single region of "hour-glass" shape. The CPC has been recently found<sup>4</sup> for a fraction of 19,800 molecular weight in acetone at saturated vapor pressure. When corrected to zero pressure it is in excellent agreement with the zero pressure CPC here (cf. Figure 4 where some of the points are included). Figure 4 shows that an increase of pressure to only 20 bars causes the UCST and LCST to be separated by an interval of  $40^{\circ}$  in which the polymer and solvent are miscible in all proportions. The CPC for increasing pressure are similar to those seen using fractions of decreasing molecular weight.<sup>4</sup> A 140° separation of the UCST and LCST is produced by lowering the molecular weight from 19,800 to 10,300 and keeping the system at saturated vapor pressure. Pressure decreases the size of the  $\chi$  parameter itself, whereas decreasing the molecular weight increases the critical value which must be reached by the  $\chi$  parameter for the critical solution temperature to occur.

Figure 5 shows the (P, T) CPC for a single concentration, 14.67 wt % of the 20,400 molecular weight fraction. This concentration gives the maxima or minima of the  $(T, w_2)$  CPC in Figure 4 and hence must be very close to the critical concentration. It is seen that the



Figure 4. (T,w) cloud point curves (w is wt %) for polystyrene of molecular weight 20,400 and  $M_w/M_n$  less than 1.06 in acetone:  $\bullet$ , 0 bar;  $\bigcirc$ , 20 bars;  $\bigtriangledown$ , 50 bars; +, 100 bars;  $\Box$ , results from ref 3 extrapolated from the solvent saturated vapor pressure to 0 bar.

minimum pressure required to separate the UCST and LCST is  $\sim 10$  bars. The (P, T) CPC were obtained at some ten other concentrations but for clarity are omitted from the figure. As indicated in Figure 4 those at high and low concentrations cut the zero pressure axis. Figure 5 also shows (P, T) CPC for fractions of molecular weight 51,000 and 97,200, demonstrating the decreasing miscibility of the polymer with the solvent and a movement of the minimum of the CPC to higher P and T. The curves are all concave upwards as in the PS-methyl acetate systems. Fractions lower than 20,400 molecular weight would have CPC which cut the zero pressure axis, and hence would resemble those in Figure 1 for the PS-methyl acetate systems.

The behavior shown in Figures 1, 4, and 5 is found<sup>2</sup> quite generally in systems with a large difference of degrees of thermal expansion between the components coupled with a difference of chemical nature, *i.e.*, difference in intermolecular force fields. For instance, the 1-hexene-methane system<sup>11</sup> shows both the UCST and LCST and a phase diagram similar to Figure 1 for PS-methyl acetate, while 1-heptene-methane has a phase diagram<sup>11</sup> similar to Figure 5 for higher molecular weight PS-acetone. The methylcyclopentane-methane system is analogous to 1-heptene-methane and

(11) D. Oeder and G. M. Schneider, Ber. Bunsenges. Phys. Chem., 73, 229 (1969).



Figure 5. (P,T) cloud point curves for different fractions of polystyrene in acetone. Experimental points: O, mol wt 20,400, 14.67 wt %;  $\Box$ , mol wt 51,000, 14.60 wt %;  $\Delta$ , mol wt 97,200, 14.66 wt %. Full lines are calculated from the theory with the  $X_{12} = 4.483$  ( $\nu^2 = X_{12}/P_1^*$ ). Thin line: saturated vapor pressure of acetone.

gives<sup>11</sup> (T, composition) CPC of the "hour-glass" type shown in Figure 4.

Polypropylene Oxide-Propane. The behavior of this system is similar to that of polystyrene-acetone. Figure 6 gives the (P, T) curves at various concentrations for a fraction of low molecular weight,  $\overline{M}_{n} = 3900$ , and at a single concentration for a fraction of  $\overline{M}_n = 790$ . Only the latter is ever completely miscible with the solvent at saturation vapor pressure. The 3900 molecular weight requires a pressure of about 150 bars to bring about complete miscibility. On the other hand, we find that PPO of  $M_n = 3900$  is completely miscible with butane under the vapor pressure of the solution and shows an LCST of 118°. Allen and Baker<sup>12</sup> have studied the phase behavior of higher molecular weights of polypropylene oxide in isobutane and in pentane. In the former system they have observed limited miscibility of the type shown in Figure 6.

Comparison of Theory with the Results. The theory<sup>13</sup> described in part I gives a semiquantitative prediction of the phase diagrams. Again assuming that the polymer concentration is small, eq 3, part I, is used to predict the  $\chi$  parameter as a function of P and T. Now because of the wide difference of chemical nature of the two components, of which the UCST is a consequence, the  $\nu^2$  parameter may not be neglected. ( $\nu^2 = X_{12}/P_1^*$  in the Flory nomenclature.) The reduced quantities  $\tilde{P}_1$  and  $\tilde{T}_1$  are given by the requirement that for each molecular weight fraction,  $\chi$  should have the critical value given by eq 3, part I. The actual (P, T) coordinates of the projection of the critical locus may then



Figure 6. (P,T) cloud point curves for polypropylene oxide in propane. PPO,  $M_n = 3900$ :  $\times$ , 3.45 wt %;  $\bullet$ , 10.92 wt %; +, 23.81 wt %;  $\bigcirc$ , 33.93 wt %. PPO,  $M_n = 790$ :  $\Box$ , 14.50 wt %. Dashed line: propane saturated vapor pressure.



Figure 7. Polystyrene-methyl acetate. Comparison of the experimental (P,T) cloud point curves and the (P,T) critical lines calculated from the theory according to eq 3, part I,  $X_{12} = 4.0 \ (\nu^2 = X_{12}/P_1^*)$ . Experimental points: O, mol wt 1,800,000;  $\triangle$ , 860,000;  $\Box$ , 160,000.

be calculated using the values of  $P^*$  and  $T^*$  listed in Table I for the solvents.

In the PS-acetone case the  $\nu^2$  parameter was obtained by fitting the theoretical (P, T) projection of the critical locus of the 20,400 molecular weight to the experimental minimum point. The value of  $X_{12} = 4.48$  cal/ cm<sup>3</sup> is in the range encountered in polymer and smallmolecule systems.<sup>9</sup> This is the only fitted parameter. Figure 5 shows that the theory gives the correct shape

- (12) G. Allen and C. H. Baker, Polymer, 6, 181 (1965).
- (13) D. Patterson and G. Delmas, Trans. Faraday Soc., 65, 708 (1969).

of the critical locus. It also predicts the displacement of the curves to higher P and T with fractions of increasing molecular weight. This is due to the reduction of the critical value of  $\chi$  (cf. eq 3, part I). A decrease of predicted polymer-solvent miscibility would also occur if the value of  $\nu^2$  were to be increased corresponding to an increase in the disparity of the intermolecular forces between components. We have calculated the (P, T) projections of the critical loci for the 20,400 molecular weight but with increasing values of  $\nu^2$  or  $X_{12}$ . The minimum of the curve is similarly displaced to higher P and T. It becomes shallower and finally disappears, the locus then being of negative slope throughout. This corresponds to the evolution of the critical locus projections for nonpolymeric systems shown in Figures 16.23, b-f, of ref 2a.

An approach similar to that used for PS-acetone gives the (P, T) projections of the critical loci for PSmethyl acetate, shown in Figure 7 for three representative fractions. Here, however, the shapes could not be reproduced keeping the Flory-Huggins critical value of  $\chi$ . This is similar to our experience in part I. We arbitrarily put  $\chi_c = a(1 + r^{-1/2})^2$  and adjusted the values of a and  $\nu^2$ . As in part I, the value of a was greater than 0.5, viz. a = 0.555, which is possibly justified by more exact treatments of the combinatorial entropy. The value of  $X_{12} = 4.0$  cal/cm<sup>3</sup> seems reasonable. Figures 5 and 7 show that the theory gives a satisfactory prediction of the main qualitative features of the phase diagrams.

We have also used the theory to predict the  $\psi_1$  parameter as a function of temperature for the PS-methyl acetate system, in order to compare with the experimental results in Figure 3. The difference  $\psi_1 - \frac{1}{2}$ , representing the noncombinatorial part of the entropy of dilution, is related to  $\chi_1$  by  $\psi_1 - \frac{1}{2} = -\partial(T\chi_1)/\partial T$ . By differentiation of eq 3, part I, one has, at zero or negligible pressure

$$\psi_1 - \frac{1}{2} = c_1 [\tilde{C}_{\mathrm{p},1}\nu^2 - (\tilde{C}_{\mathrm{p},1} + \tilde{T}\partial\tilde{C}_{\mathrm{p},1}/\partial\tilde{T}_1)\tau^2]$$

This relation, and the Flory model, *i.e.*, eq 5a and b of part I, were used, together with the same value of  $\nu^2$  as for the phase diagrams. Figure 3 shows that reasonable agreement is obtained. In the above equation for  $\psi_1 - 1/2$  the term in  $\nu^2$  is never large enough to outweigh that in  $\tau^2$  which is characteristic of polymer-solvent systems, so that  $\psi_1$  is always less than 0.5. At high temperatures  $\psi_1$  becomes rapidly more negative. This is in harmony with the very rapid change of heats and entropies of dilution found in polymer-solvent systems at temperatures approaching the vapor-liquid critical temperature of the solvent.

Acknowledgment. We thank the National Research Council of Canada for its support of this research and also for a scholarship to L. Z.

## Proton Mobility in Solids. IV. Study of Proton Motion in the

## **Decationated Y Zeolite by Nuclear Magnetic Resonance**

### by M. M. Mestdagh, W. E. Stone, and J. J. Fripiat\*

Laboratoire de Physico-Chimie Minerale, Institut des Sciences de la Terre, 3030 Heverlee, Belgium (Received July 19, 1971) Publication costs assisted by Musée Royal de l'Afrique Centrale, Tervuren (Belgium)

The second moment and the longitudinal and transverse relaxation times have been determined for a decationated Y zeolite between -180 and  $+400^{\circ}$ . At room temperature the second moment is mostly due to a proton-aluminum interaction and the structure model proposed by Olson and Dempsey is compatible with the observed value. Above 200° the longitudinal as well as the transverse relaxation time varies exponentially with respect to the inverse of the absolute temperature. This variation has been interpreted assuming an isotropic diffusion of the proton with respect to a paramagnetic continuum of Fe<sup>3+</sup> impurities. The proton jump frequency is represented by the following relationship:  $\nu = 3.3 \times 10^{10} \exp (-10^4/RT) \sec^{-1}$ . The jump distance calculated from the theory is of the order of 7.5 Å while from the structure model a distance of 4 Å may be calculated.

### Introduction

Decationation of a near-faujasite zeolite (Linde Y molecular sieve) is obtained by heating the ammoniumexchanged form at temperatures higher than 350° in order to remove NH<sub>3</sub>. The proton left in the structure forms an OH group bond to silicon. Proton motion in decationated zeolites has been an important question for several years but until recently, the evidences for these motions were mainly indirect. Ward,<sup>1-3</sup> for instance, has devoted great attention to the eventual relationships between the decrease in the intensity of OH stretching band and proton jumps. Uytterhoeven and Schoonheydt<sup>4</sup> have studied, on the electrical conductivity of HY sieves, the effect of temperature. On the other hand, O'Reilly and Hall<sup>5</sup> have recorded the proton magnetic resonance spectra of silica gel and silico-alumina at temperatures between 20 and 600°K and found no detectable narrowing of the nmr signal in this range. This, together with the sharp OH stretching band in the same temperature range were considered as evidence that proton hopping was negligible. However, in other structures such as, for instance, that of boehmite, the nmr line width evolution with respect to temperature clearly indicates that a proton delocalization process takes place. In this example, the decrease in intensity of the OH stretching infrared band was interpreted in the same way, so that some confusion presently exists in the recent literature concerning the significance of a decrease in intensity of ir bands.

Recently, Rouxhet and Fripiat,<sup>6</sup> in a theoretical study of a simple model, namely the linear  $OH \cdots O$  system, have shown (1) that the decrease in intensity of the OH stretching band was more apparent than real, as it was due mainly to the "melting" of the band in-

tensity into the background, *i.e.*, the true integrated intensity is not greatly reduced, and (2) that the apparent reduction in the intensity may be assigned either to an increase in the anharmonicity and/or to the real transfer of the proton between adjacent sites. In a sense, the reduction in the ir band intensity cannot be unambiguously attributed to the shortening of the residence time of a proton on a particular site.

In providing valuable information on lifetime of the order of magnitude of that being eventually expected, nmr is a method better adapted to the study of proton motions in solids. In this study two techniques were employed, namely, wide-line nmr and pulsed magnetic resonance. The experiments were performed in the temperature range above that used by O'Reilly and Hall,<sup>5</sup> namely up to 500° using decationated Y zeo-lites.

Gvakharia, et al.,<sup>7</sup> have also studied this problem by nmr. However, their results cannot be directly compared with those described in this paper for the following reason. Their ammonium Y zeolite was pretreated in the presence of air up to 550° and after that it was dehydrated under vacuum up to 400°. The first step partially destroys the lattice structure as shown by Kerr.<sup>8</sup> In fact, the signal observed at 90°K was com-

- (1) J. W. Ward, J. Catal., 9, 225 (1967).
- (2) J. W. Ward, *ibid.*, 9, 396 (1967).
- (3) J. W. Ward, *ibid.*, 16, 386 (1970).
- (4) J. B. Uytterhoeven and R. Schoonheydt, *ibid.*, 13, 425 (1969).

<sup>(5)</sup> D. E. O'Reilly and W. K. Hall, J. Chem. Phys., 29, 970 (1958).

<sup>(6)</sup> P. G. Rouxhet and J. J. Fripiat, Bull. Cl. Sci. Acad. Roy. Belg., 101 (1971).

<sup>(7)</sup> V. G. Gvakharia, V. I. Kulividze, A. A. Kubasov, B. V. Romanovskii, K. V. Topchieva, and G. W. Tsitsishvili, *Kinet. Katal.*, 6, 1392 (1969).

<sup>(8)</sup> G. Kerr, J. Catal., 15, 200 (1969).

posed of a narrow line, assigned to OH groups, and of a wide line assigned to immobile  $H_2O$ . As shown hereafter this line due to  $H_2O$  molecules has not been observed in our case.

Our pretreatment conditions were always carried out in order to preserve the zeolite structure. Stevenson<sup>9</sup> has analyzed in a way very similar to that described in the first part of this paper the room temperature second moment for a decationated sieve. He shows, as in this paper, that the main contribution to the second moment arises from an aluminum-proton dipolar interaction.

#### **Experimental Procedures**

(A) Sample Preparation. A sample of Na-Linde Y (Union Carbide) zeolite has been used for these experiments. It is characterized by an Si/Al ratio of 2.5 and an iron content of 1450 ppm. The ionic exchanges Na<sup>+</sup>-NH<sub>4</sub><sup>+</sup> were carried out by repeated contacts at room temperature with a 1 N NH<sub>4</sub>Cl solution. The exchange sample was washed by centrifugation until there was complete removal of Cl<sup>-</sup> and was dried for 24 hr at 40°. It was evacuated at 10<sup>-6</sup> Torr for 24 hr at room temperature and then pretreated under vacuum at increasing temperature. The rate of the temperature increase was 1.8 deg/min and the sample was maintained for 1 hr at the desired maximum temperature. The sample container was then sealed.

(B) Determinations. The wide-line spectra of the decationated samples were recorded with a Varian DP 60 spectrometer under the following conditions: resonance frequency, 60 MHz; modulation frequency, 40 Hz; field heterogeneity, 0.045 G. The rf power and the scanning speed have been chosen to avoid signal saturation.

The second-moment values were corrected for modulation broadening by the factor  $H_m^2/4$ . The relaxation times have been measured with a Bruker BKR 302 (60 MHz) pulse spectrometer. The longitudinal  $T_1$ relaxation was obtained by using a two-90° pulse sequence. The transverse  $T_2$  relaxation times were measured from the slope of the free induction decay signal according to the following relationship for a Gaussian line

$$M_{t} = M_{0} \exp(-t^{2}/2T_{2}^{2})$$

and also from a 90-180° pulse echo sequence.

### Model for the Second Moment $(S_2)$

(1) Results. Experimental results for the second moment  $S_2$  are shown in Figure 1 (open circles) together with a set of  $S_2$  measurements obtained by Dollish and Hall<sup>10</sup> for an HY sieve containing 290 ppm of Fe (closed circles). As can be seen, the two independent sets of results are quite similar and both show a very sharp decrease in the values of  $S_2$  for temperatures above 500°K. The curve was drawn by hand through the experimental points.



Figure 1. Variation of  $S_2 vs. T^{-1}$  (°K<sup>-1</sup>) for the decationated Y sieve. Extent of Na-NH<sub>4</sub><sup>+</sup> exchange: O, 72%;  $\bullet$ , 69%. Extent of decationation: O, 94%;  $\bullet$ , 83%. Closed circles are values obtained by Dollish and Hall<sup>10</sup> for a similar sample but with a lower Fe content (see text).

(2) Interpretation. In order to interpret these results, one has to take into account the various magnetic interactions between the proton and its environment. In the zeolite lattice, the second moment can result a priori from the joint contributions of the proton-proton, proton-sodium, proton-aluminum, and proton-paramagnetic interactions.

(a) Rigid Lattice Region. The second moment general relationship for a powder specimen is

$$S_{2} = \frac{3}{5} \frac{1}{N} I(I+1)g^{2}\mu_{0}^{2} \sum_{i} \sum_{j} r_{ij}^{-6} + \frac{4}{15} \frac{1}{N} \sum_{i} \sum_{k} I_{k}(I_{k}+1)g_{k}^{2}\mu_{0}^{2}r_{ik}^{-6} + \frac{4}{5} \frac{1}{N} \bar{\mu}_{p}^{2} \sum_{i} \left|\sum_{p} r_{ip}^{-3}\right|^{2} - \frac{4}{5} \frac{1}{N^{2}} \bar{\mu}_{p}^{2} \left(\sum_{i} \sum_{p} r_{ip}^{-3}\right)^{2}$$
(1)

The first term corresponds to the proton i-proton jinteraction, the second one to the proton i-diamagnetic nucleus k (sodium or aluminum) interaction,

<sup>(9)</sup> R. L. Stevenson, J. Catal., 21, 113 (1971).

<sup>(10)</sup> F. Dollish and W. K. Hall, personal communication. We wish to thank these authors for the permission to use some of their unpublished results.

whereas the third and the last terms are due to the proton-paramagnetic moment  $(\bar{\mu}_p^2)$  interaction. Nis the number of protons, g and  $g_k$  are the splitting factors of the proton and of nucleus k, respectively, and I and  $I_k$  are the corresponding spin quantum numbers. The proton-sodium interaction has been neglected because the proton-sodium distance is large ( $\sim 4$  Å). The last term may also be neglected because the absorption band is symmetric.<sup>11</sup> The third term, namely the proton-paramagnetic moment interaction, should be the most important because of the magnitude of the electronic moment  $\mu_p$ . In fact the resonance frequency of protons under the direct influence of Fe<sup>3+</sup> is strongly displaced and only those protons outside a sphere of radius  $R_c$  such as

$$R_c^3 = \frac{\bar{\mu}_p}{\delta H_{\max}} = \frac{\bar{\mu}_p}{\sqrt{S_2}}$$
(2)

will contribute to the absorption line.<sup>12,13</sup>  $\delta H_{\max}$  is the peak-to-peak width measured on the first derivative of the absorption line and  $\bar{\mu}_p$  is the paramagnetic moment averaged for the fast reorientation process experienced by the nucleus

$$\bar{\mu}_p = \frac{\mu_{\rm eff}^2 H_0}{3kT}$$

where, as usual<sup>14</sup>

$$\mu_{eff} = g_p \sqrt{I_p(I_p+1)}$$

 $H_0$  is the steady magnetic field. For a uniform distribution of the paramagnetic impurities around a specified proton the summation  $(\Sigma_p)$  on p in (1) may be approximated by an integration process on a sphere between  $r = R_c$  to  $r = \infty$  and the paramagnetic contribution becomes

$$S_{2p} = \frac{16}{15} \pi N_p \frac{\bar{\mu}_p^2}{R_c^3} = \frac{16\pi}{15} N_p \frac{\mu_{\rm eff}^2 H_0}{3kT} \delta H_{\rm max} \qquad (3)$$

where  $N_p$  is the number of Fe<sup>3+</sup> cations per volume unit.

The shifts of many nuclei will be such as to broaden only the wings of the resonance line. Therefore the second moment is more affected than the line width. This explains why  $\delta H_{\max}$  is preferably obtained from the square root of the experimental second moment.

For  $\mu_{eff} = 5.9$  BM,  $H_0 = 14 \times 10^3$  G,  $N_p = N_{Fe} = 2.3 \times 10^{19}$  Fe<sup>3+</sup> cations/cm<sup>3</sup>, and  $\delta H_{max} = 0.89$  G, it follows that  $S_{2p} = 0.02$  G<sup>2</sup> at 298° and  $R_c = 7.2$  Å.

In order to evaluate the first two terms of eq 1, we have used the structure proposed by Broussard and Shoemaker<sup>15</sup> and by Olson and Dempsey<sup>16</sup> (Figure 2). The average H-Al distance is 2.178 Å for an Al-O-H angle of 108°. The corresponding second moment contribution of Al-H is 1.18 G<sup>2</sup>. A change in this angle provokes an important variation of this value. For instance, for Al-O-H equal to 90°,  $S_2 = 2.43$  G<sup>2</sup>, while for Al-O-H equal to 180°,  $S_2 = 0.6$  G<sup>2</sup>. The position



Figure 2. Schematic structure of the Y sieve according to Broussard and Shoemaker.<sup>15</sup> The numbers in the oxygen network refer to their nomenclature: ▲, silicon or aluminum; O, oxygen. The average lattice parameters are as follows: Si-O: 1.664 Å; O-O: 2.683 Å; Si(Al)-O-Si(Al): 145.3°; O-Si(Al)-O: 109.5°, according to Olson and Dempsey.<sup>16</sup>

of the hydrogen nucleus being quite uncertain, the Al-H contribution may be considered as being between the above limits.

In the Olson and Dempsey model, the shortest H-H distance is 3.75 Å: the corresponding H-H contribution to  $S_2$  is 0.13 G<sup>2</sup>. This seems to be a maximum. The sum of the aluminum-proton and proton-proton contribution is roughly between 0.7 and 2.5 G<sup>2</sup>. The paramagnetic contribution has to be added to these values.

(b) Line Narrowing Region. The observed line narrowing when temperature is increased above  $500^{\circ}$ K is difficult to interpret. However, it could be suggested that the main contribution to  $S_2$ , in the range of temperature where it decreases, should arise from the Al-H interaction modulated by the motion. This seems reasonable considering that samples with large differences in iron content give similar results. Assuming a rotation of the Al-H vector around an Al-O axis, as shown in Figure 3, the corresponding contribution to  $S_2$  should be that shown in Table I and derived from the following relationship

(16) D. H. Olson and E. Dempsey, J. Catal., 13, 221 (1969).

<sup>(11)</sup> J. M. Dereppe, dissertation, University of Louvain, 1967, p 110.
(12) D. J. Kroon, *Philips Res. Rept.*, 15, 501 (1960).

<sup>(13)</sup> T. G. Stoebe, T. O. Ogurtani, and R. A. Huggins, *Phys. Rev.*, **A239**, 138 (1965).

<sup>(14)</sup> G. E. Pake, "Paramagnetic Resonance," W. A. Benjamin, New York, N. Y., 1962.

<sup>(15)</sup> L. Broussard and D. B. Shoemaker, J. Amer. Chem. Soc., 82, 1041 (1960).

$$S_{2(A1-H)} = \frac{1}{15} I_{A1} (I_{A1} + 1) g_{A1}^2 \mu_0^2 \times (3 \cos^2 \alpha - 1)^2 r_{H-A1}^{-4}$$

where  $\alpha$  is the angle between  $\overline{Al-H}$  and the rotation axis  $\overline{Al-O}$ . For the rotation around  $O_1$ -Al, with  $\alpha = 25^{\circ}$ , the proton remains on the same lattice site while the rotation with  $\alpha = 109^{\circ}$  involves 3 adjacent oxygens, namely  $O_2$ ,  $O_3$ , and  $O_4$ . The variation of the observed  $S_2$  might involve jumps of the proton on different oxygens but the uncertainty on the model and on the values of the various contributions to  $S_2$  does not allow a firmer conclusion. Moreover, it will be shown in the next section that this conclusion belies another aspect that will appear as being more founded.

Table I:	Contribution of the Al-H Interaction to $S_2$ in the
Hypothesi	is of a Rotation of the $\overline{\text{Al-H}}$ Vector around $\overline{\text{O}_1\text{-AL}}$

Motion	Angle between Al-O1 and Al-H, <i>a</i> , deg	S2, G2
<b>Rigid</b> lattice	25	1.18
Al-H rotation	25	0.57
Al-H rotation	109	0.11

### Model for the Proton Relaxation Mechanisms

(1) Results. Results for the spin-lattice relaxation time  $(T_1)$  and the spin-spin relaxation time  $(T_2)$  are shown in Figure 4. From 90°K up to 330°K the value of  $T_1$  remains constant: for higher temperatures, it abruptly decreases. In order to extract the exact slope followed by the decreasing  $T_1$  values as temperature is raised, the following relation was applied

$$T^{-1} = T^{-1}_{exp} - T^{-1}_{constant}$$

This is valid as obviously the two mechanisms ruling  $T_1$ 



Figure 3. Model used for the calculation of the second moment for the rigid lattice and for the Al-H interatomic vector rotations (Table I).

in the two regions are different. This procedure gives the solid lines drawn in Figure 4 while the dashed line represents the joint contributions of the two relaxation rates.



Figure 4. Variation of  $T_1$  and  $T_2$  vs.  $T^{-1}$  (°K<sup>-1</sup>) for HY (extent of the Na-NH<sub>4</sub><sup>+</sup> exchange 72%, extent of decationation 95%; thin bed calcination):  $\Box$ ,  $T_2$  obtained from the echo; O,  $T_2$  from  $S_2$  (assuming a gaussian line shape); •,  $T_2$  from the slope of the free induction decay signal.

Concerning  $T_2$ , an abrupt increase is observed above  $435^{\circ}$ K. The  $T_2$  values extracted from the echo experiments could not be pursued above  $500^{\circ}$ K because of poor signal to noise ratio. In the interpretation of the results we will consider separately the region where the values of  $T_1$  and  $T_2$  are temperature dependent and the region where the  $T_1$  and  $T_2$  values are constants.

(2) Interpretation. (a) Temperature-Dependent Relaxation Time Values. The longitudinal and transverse relaxation rates for unlike spins can be written as (see, e.g., Abragam<sup>17</sup>)

$$(T_{1}^{-1})_{II} = \gamma_{I}^{2} \gamma_{s}^{2} \hbar^{2} S(S+1) \left\{ \frac{1}{12} J^{(0)}(\omega_{1}-\omega_{s}) + \frac{3}{2} J^{(1)}(\omega_{I}) + \frac{3}{4} J^{(2)}(\omega_{I}+\omega_{s}) \right\}$$
(4)

(17) A. Abragam, "Principles of Nuclear Magnetism," Oxford 1961.

$$(T_{2}^{-1})_{I} = \gamma_{I}^{2} \gamma_{s}^{2} \hbar^{2} S(S+1) \left\{ \frac{1}{6} J^{0}(0) + \frac{1}{24} J^{0}(\omega_{I} - \omega_{s}) + \frac{3}{4} J^{(1)}(\omega_{I}) + \frac{3}{2} J^{(1)}(\omega_{s}) + \frac{3}{8} J^{(2)}(\omega_{I} + \omega_{s}) \right\}$$
(5)

 $\gamma_I$  and  $\gamma_s$  are the gyromagnetic ratios, S is the spin quantum number of spin "S," while the J functions are the usual spectral densities.  $\omega_I$  and  $\omega_s$  are the Larmor precession frequencies of spins I and S respectively. According to the usual assumption of the BPP theory

$$J_{(\omega)}{}^{(1)} = \frac{2}{15} \frac{1}{r^6} \frac{2\tau_o}{1 + \omega^2 \tau_o^2}$$
(6)

where  $\tau_c$  is the correlation time,  $\omega$  is the precession frequency, and r is the distance between spins I and S. It is shown also that  $J^{(2)} = 4J^{(1)}$  and that  $J^{(0)} = 6J^{(1)}$ . Let us assume an isotropic diffusion process and in the temperature domain where  $\omega \tau_1 \gg 1$ , the longitudinal and transverse relaxation rates are transformed into

$$(T_{1}^{-1})_{II} = \frac{48}{25} \pi N \gamma_{I}^{2} \gamma_{s}^{2} \hbar^{2} S(S+1) \frac{D}{l^{5}} \times \left\{ \frac{1}{3(\omega_{I}-\omega_{s})^{2}} + \frac{1}{\omega_{I}^{2}} + \frac{2}{(\omega_{1}+\omega_{s})^{2}} \right\}$$
(7)

$$(T_2^{-1})_{\rm I} = \frac{4\pi}{135} N \gamma_{\rm I}^2 \gamma_{\rm s}^2 \hbar^2 S(S+1) (lD)^{-1} \qquad (8)$$

Equations 7 and 8 derive from eq 4 and 5 by integrating from l to  $\infty$  over a sphere element  $4\pi r^2 dr$  and by assuming that  $\tau_c = r^2/6D$ . The factor 6 is introduced because only spin I diffuse. D is the diffusion coefficient and l is the closest approach distance between spins I and S. N is the number of spin S per cubic centimeter.

In eq 7 and 8, D and l are two unknown parameters. By combining (7) and (8) and introducing the experimental values for  $T_1$  and  $T_2$ , these parameters can be determined independently. Two cases will be considered, namely the diffusion motion with respect to Fe<sup>3+</sup> or to Al<sup>3+</sup>. This then gives rise to the two sets of values of  $D_0$  and l of Table II.  $D_0$  is defined by the equation

$$D = D_0 e^{-E/RT} \qquad (E = 10 \text{ kcal}) \tag{9}$$

These results were obtained by introducing the following parameters into relationships 7 and 8:  $\gamma I =$  $2.67 \times 10^4$  radians G<sup>-1</sup> sec<sup>-1</sup>;  $\gamma_{A1} = 0.69 \times 10^4$  radian G<sup>-1</sup> sec<sup>-1</sup>;  $\gamma_{Fe^{3+}} = 1.76 \times 10^7$  radians G<sup>-1</sup> sec<sup>-1</sup>;  $S_{A1} = S_{Fe} = \frac{5}{2}$ ;  $\omega_I = 376 \times 10^6$  radians sec<sup>-1</sup>;  $\omega_{A1} =$  $97.34 \times 10^6$  radians sec<sup>-1</sup>;  $\omega_{Fe} = 246.2 \times 10^9$  radians sec<sup>-1</sup>;  $N_{Fe} = 2.3 \times 10^{19}$  atoms/cm<sup>3</sup> and  $N_{A1} = 3.96 \times 10^{21}$  atoms/cm<sup>3</sup>. Obviously the distance obtained for the diffusion with respect to Al<sup>3+</sup> is too short. According to the model shown in Figure 2 distances between 2.2 and 3 Å are to be expected. The value of closest approach (l) obtained for the diffusion with respect to Fe<sup>3+</sup> is within a factor of 2-3 of these distances. Such a discrepancy is still acceptable taking into consideration the rough approximation of the theoretical model.

**Table II:**  $D_0$  and l Obtained for the Diffusion Motion ofProton (I) with Respect to Either  $Al^{3+}$  or to  $Fe^{3+}$  (spin "S")(Experimental Data Taken from Figure 4)

Spin S	D <sub>0</sub> , cm <sup>2</sup> sec <sup>-1</sup>	l, Å	a, Å
Fe <sup>3+</sup> Al <sup>3+</sup>	$2  imes 10^{-5}$ 1 $.5  imes 10^{-8}$	6 0.21	7.5

As we have assumed implicity the same relaxation mechanisms for  $T_1$  and  $T_2$  by combining eq 7 and 8, the two exponential variations of  $T_1$  and  $T_2$  may be extrapolated toward their intercept where a value for the jump distance may be deduced (see Figure 4). For a single isotropic relaxation mechanism, this intercept should correspond approximately to the minimum value of  $T_1$  as function of 1/T. At this hypothetical minimum

$$\omega \tau_{\rm c} \simeq 1 \simeq \frac{\omega_{\rm I} a^2}{6D} \tag{10}$$

where *a* is the jump distance of the proton.

Introducing in relationship 10 the *D* value of eq 9 and the  $D_0$  of Table I obtained for the diffusion with respect to Fe<sup>3+</sup>, a value of 7.5 Å is obtained for *a*. From the model of Figure 2, a jump distance of approximately 4 Å can be estimated. Again this seems a reasonable agreement in view of the assumptions involved in these calculations.

The temperature at which the hypothetical  $T_1$  minimum should occur is far above the dehydroxylation temperature of the decationated sieve. It is a matter of fact that in the present work, no minimum of  $T_1$  has been observed.

The first part of this discussion may therefore be summarized as follows. By considering an isotropic diffusion of protons and by assuming that the main relaxation mechanism is contributed by the proton interaction with  $Fe^{3+}$  for  $T_1$  as well as for  $T_2$  in their exponential variations, a reasonable distance of closest approach  $Fe^{3+}$ -H is obtained. Moreover, the jump distance derived from the approximate position of the hypothetical  $T_1$  minimum is in reasonable agreement with that suggested by the proton site distribution in the lattice. Consequently, a proton diffusion coefficient can be written as

$$D = 2 \times 10^{-5} e^{-10^4/RT} \,\mathrm{cm}^2 \,\mathrm{sec}^{-1} \tag{11}$$

whereas the jump frequency is

$$\nu = \frac{6D}{a^2} = 3.3 \times 10^{+10} e^{-10^4/RT} \sec^{-1} \qquad (12)$$

(b) Temperature Independent Relaxation Time Values. In the model adopted in the preceding paragraph (originally introduced by Resing and Thompson<sup>18</sup>) a uniform distribution of  $Fe^{3+}$  is assumed and the proton is supposed to make jumps of length "a" in random directions in this paramagnetic environment.

However, this environment could not be considered any further as a continuum when the time spent by the proton under the influence of a specified  $Fe^{3+}$  paramagnetic moment is long as compared with the relaxation time  $T_2$ . At high temperature, the time "t" spent by a mobile proton inside the sphere defined previously (eq 2) may be approximated by the time required for moving within  $R_c$  or

$$t = \frac{R_c^2}{6D} = 6.3 \times 10^{-10} e^{+10^4/RT} \text{ sec}$$
 (13)

It may be expected that at decreasing temperature and for  $t \leq (T_2)_{I}$ , a break will occur in the variation of  $T_2$ .

The measured rigid lattice  $T_2$  being 42  $\mu$ sec (Figure 4), the temperature at which the discontinuity in the exponential variation of  $T_2$  must occur may be obtained from eq 13; it turns out to be  $1/T = 2.54 \times 10^{-3} \,^{\circ}\mathrm{K}^{-1}$ , in agreement with the observations. Therefore below this temperature, the free induction decay should show a two-component behavior: the first part of the signal decreasing very rapidly with time and caused by the proton Fe<sup>3+</sup> interaction and the second part, reflecting the proton-Al<sup>3+</sup> contribution. The first phase is hidden in the instrumental recovery time ( $\sim 12 \ \mu sec$ ), and therefore only the proton-Al interaction is observed, in agreement with the prediction made from the secondmoment calculation. Concerning the observed echo, the field inhomogeneity deduced from the comparison with the free induction decay signal was many orders of magnitude too large. The origin of this echo is still not clear; a possible explanation of this static homogeneous broadening can perhaps be found in the frequency shifts that occur for protons which lie somewhere at mid-distance between paramagnetic centers.

For another reason a discontinuity is also observed in the variation of  $T_1$  with respect to the temperature. It occurs when the longitudinal relaxation rate due to the diffusion motion (eq 1) becomes lower than the relaxation rate due to the proton-Fe<sup>3+</sup> direct interaction. The discontinuity in  $T_1$  occurs at the same temperature as for  $T_2$  but the two breaks are due to entirely different reasons. In fact, the observed  $T_1^{-1}$  is considered as the sum of two contributions

$$T_1^{-1} = (T_1^{-1})_{II} + T_{1p}^{-1}$$
(14)

The longitudinal relaxation time of spin I at a distance r of an electronic moment S may be approximated by

(see Abragam<sup>17</sup>)

$$T_{1p}^{-1} = \frac{2}{5} S(S+1) \gamma_{\rm I}^2 \gamma_{\rm s}^2 \hbar^2 \frac{\tau_p}{1+\omega_{\rm I}^2 \tau_p^2} (r^{-6}) \quad (15)$$

where  $\tau_p$  is the longitudinal electronic relaxation time.

In order to evaluate  $T_{1p}^{-1}$ ,  $\tau_p$  and  $\langle 1/r^6 \rangle$  should be known. As an example, let us tentatively calculate  $T_{1p}^{-1}$  by integrating eq 15, assuming that  $(\omega_1 \tau_p)^2 \gg 1$ 

$$T_{1p}^{-1} = \frac{2}{5} S(S+1) \gamma_{\rm I}^2 \gamma_{\rm S}^2 \hbar^2 \frac{4\pi N_{\rm Fe}}{\omega_{\rm I}^2 \tau_{\rm p}} \int_l^\infty \frac{\mathrm{d}r}{r^4} \quad (16)$$

or

$$T_{1p}^{-1} = \frac{8\pi}{15} S(S+1) \gamma_{I}^{2} \gamma_{S}^{2} \hbar^{2} \frac{N_{\text{Fe}}}{\omega_{I}^{2} \tau_{p} l^{3}}$$
(17)

Resing and Thompson<sup>18</sup> have suggested that  $\tau_p \simeq 1.2 \times 10^{-6}$  sec for the Linde X sieve. We will assume the same value. The experimental  $T_1$  at low temperature being 1.6 sec, it follows that  $\langle l^3 \rangle^{1/3} = 9.0$  Å. This result is appreciably higher than the distance of closest approach shown in Table II but is still acceptable in view of the uncertainty on the iron distribution, on  $\tau_p$  and on the exact value of  $\mu_p$ .

### Conclusions

The exponential decreases of the second moment  $(S_2)$ and of the spin-lattice relaxation time  $(T_1)$  of a decationated Y sieve when the temperature is increased above approximately 200° have been assigned to proton motions involving jumps on lattice oxygens.

For the catalytic properties of the decationated sieve, the frequency of these jumps may be an important factor since the lifetime of the proton on a surface site is a critical parameter for its acid character. This time parameter may be found in eq 12.

From eq 12, at 300°, the jump frequency should be approximately  $3.2 \times 10^{6} \sec^{-1}$  and at  $450^{\circ}$ , it should be  $1.96 \times 10^{7} \sec^{-1}$ . As suggested recently by Fripiat,<sup>19</sup> for a proton lifetime of the order of  $10^{-7}$  sec, the residence time of a molecule on the surface site occupied by the proton should be at least of the order of  $10^{-6}$  sec in order to have an appreciable chance to capture this proton.

The main ambiguity in these measurements arises from the fact that, unfortunately, the minimum that could be expected in the variation of  $T_1$  with respect to the temperature in the case of a single relaxation mechanism should occur far above the limit of the thermal stability of the decationated sieve.

For this reason, the deduction of the diffusion coefficient and of the jump distance from  $T_1$  is not possible and the two parameters cannot be determined independently unless (1) the experimental values of  $T_1$ 

(18) H. A. Resing and J. K. Thompson, J. Chem. Phys., 46, 2876 (1967).

(19) J. J. Fripiat, Catal. Rev., 5(2), 269 (1971).

and  $T_2$  are used simultaneously and (2) the same relaxation mechanism is supposed to control both relaxation times. It has been shown that under these conditions and at high temperature,  $T_1$  and  $T_2$  appear to be ruled by a pseudo-isotropic diffusion of protons with respect to paramagnetic centers (Fe<sup>3+</sup>).

Further work is in progress in order to try to answer various questions such as (1) the influence of paramagnetic impurities content, (2) the influence of sample conditioning, and finally (3) the influence of the extent of decationation and dehydroxylation.

Acknowledgment. We wish to thank Dr. H. Resing of the U. S. Naval Research Laboratory, Washington, D. C., for stimulating discussions and Mr. M. Bulens for determinations of the second moment.

## Paramagnetic Relaxation Study of Spatial Distribution of Trapped Radicals

### in $\gamma$ -Irradiated Alkaline Ice and Organic Glasses at 4.2°K

### by D. P. Lin, Peter Hamlet, and Larry Kevan\*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202 (Received January 3, 1972) Publication costs assisted by the U. S. Atomic Energy Commission

The spatial distribution of trapped radicals in  $\gamma$ -irradiated 10 *M* NaOH (alkaline ice), 2-methyltetrahydrofuran (MTHF), and triethylamine (TEA) has been studied at 4.2°K by measuring the characteristic paramagnetic relaxation time vs. radiation dose. Radical spur radii of <36 Å in alkaline ice, <34 Å in MTHF, and <37 Å in TEA are deduced from the data. These radii are smaller than the trapped electron spur radii measured previously in these same matrices.

The spatial distribution of trapped electrons, generated by  $\gamma$  irradiation in glassy alkaline ice (10 M NaOH)<sup>1</sup> and in organic glasses,<sup>2</sup> has been studied by electron paramagnetic resonance (epr) relaxation characteristics. The dose dependence of the characteristic relaxation time.  $(T_1T_2)^{1/2}$  where  $T_1$  is the spin-lattice relaxation time and  $T_2$  is the spin-spin relaxation time, shows that the trapped electron spatial distributions are nonuniform and that the degree of nonuniformity depends on matrix polarity. The trapped electron spatial distributions have been semiquantitatively characterized in terms of a spur radius in which a spur is a region of higher than average spin concentration. In addition to electrons, radicals are also trapped in these  $\gamma$ -irradiated matrices and for a more complete knowledge of the spatial nonuniformity of radiation-produced species it is necessary to obtain spatial distribution information about the trapped radicals as well. These radicals generally do not saturate sufficiently at 77°K to carry out relaxation studies of spatial distribution, as do trapped electrons. But, since  $(T_1T_2)^{1/2}$  generally increases as the temperature decreases, we find that the radicals do saturate sufficiently at 4.2°K to carry out relaxation studies of spatial distribution. The results show that

the radicals have smaller spur radii than the trapped electrons.

The experimental methods have been described.<sup>2</sup> The samples were sealed in spectrosil quartz tubes. Irradiations were done at 77°K at a nominal dose rate of 0.4 Mrad/hr. The samples were then transferred to a liquid helium dewar<sup>3</sup> designed with an 11-mm diameter tip for insertion into a standard Varian epr cavity. The ratio of liquid to vapor helium densities at 4.2°K is small (7.5) in comparison with that for nitrogen densities at 77°K (~180), so the noise due to helium bubbling is not a problem.  $(T_1T_2)^{1/2}$  was calculated from eq 1 in which  $H_{1/2}$  was determined from microwave

$$(T_1T_2)^{1/2} = 3^{1/2} / \gamma H_{1/2}$$
 (1)

power saturation curves and  $\gamma = 1.76 \times 10^7 \text{ sec}^{-1}$ G<sup>-1</sup>. For the O<sup>-</sup> radical in alkaline ice 100-kHz magnetic field modulation was used, and for the radicals in methyltetrahydrofuran (MTHF) and triethylamine (TEA) 400-Hz modulation was used. It does not mat-

- (1) J. Zimbrick and L. Kevan, J. Chem. Phys., 47, 2364 (1967).
- (2) D. P. Lin and L. Kevan, ibid., 55, 2629 (1971).
- (3) P. Hamlet and L. Kevan, J. Amer. Chem. Soc., 93, 1102 (1971).



Figure 1. Characteristic relaxation time  $(T_1T_2)^{1/2}$  vs.  $\gamma$  radiation dose at 4.2°K for O<sup>-</sup> in 10*M* NaOH glassy ice, for  $e_t^-$  in glassy MTHF, and for radicals (R) in MTHF and TEA.

ter that slow passage conditions were not achieved since we are only interested in relative values of  $(T_1T_2)^{1/2}$  vs. radiation dose for the analysis here.

Figure 1 shows the dose dependence of  $(T_1T_2)^{1/2}$  for both trapped electrons  $(e_t^-)$  and radicals in MTHF at 4.2°K. The result for  $e_t^-$  is exactly the same as previously found for  $e_t^-$  in MTHF at 77°K<sup>2</sup> except for a change in the absolute magnitude of  $(T_1T_2)^{1/2}$ . The initial region from 0 to 1.4 Mrads in which  $(T_1T_2)^{1/2}$  is constant indicates a nonuniform spatial distribution, and the dose (D) above which  $(T_1T_2)^{1/2}$  begins to decrease can be used in eq 2, where  $\rho$  is the matrix density,

$$r(\mathbf{\ddot{A}}) = (4.8 \times 10^{6}/4\pi D\rho)^{1/2}$$
(2)

to estimate an upper limit for the spur radius.<sup>2</sup> As described before,<sup>1,2</sup> the constancy cf  $(T_1T_2)^{1/2}$  with dose indicates that the magnetic exchange interaction occurs within the spur. The electron spur radius is 63 Å independent of whether the relaxation measurements are done at 77 or 4.2°K. This is as expected since the irradiation temperature was 77°K in both measurements. The MTHF radicals exhibit a  $(T_1T_2)^{1/2}$  which is constant with dose to beyond 8.5 Mrads. This indicates that the MTHF radicals have a significantly

smaller spur radius than the  $e_t^-$ . This finding is consistent with the expectation that the electrons initially produced by the irradiation will travel a short distance from their point of origin before being trapped. If we take 8.5 Mrads as D we find that the MTHF radical spur radius is less than 34 Å.

Figure 1 also shows the dose dependence for  $(T_1T_2)^{1/2}$ of TEA radicals and of O<sup>-</sup> from alkaline ice.  $(T_1T_2)^{1/2}$ for TEA radicals is constant to about 8 Mrads, which gives a TEA radical spur radius less than 37 Å. This is much less than the 101 Å spur radius for electrons in TEA.<sup>2</sup>  $(T_1T_2)^{1/2}$  for O<sup>-</sup> is constant to about 6 Mrads and then shows a definite decrease at higher doses. Here, the experiments were run to a sufficiently high dose to clearly show the break point in the  $(T_1T_2)^{1/2} vs$ . dose plot which corresponds to the onset of spur overlap. The spur radius of O<sup>-</sup> is less than 36 Å, which compares with an electron spur radius of 41 Å in the alkaline ice matrix.

In all matrices the radical spur radii are smaller than the  $e_i$  spur radii with the difference being greatest in the least polar matrix, TEA. It may also be significant that all the radical spur radii are similar ( $\sim$ 35 Å) even though no break point was observed in TEA or MTHF. This radius probably more truly represents the intrinsic average spur size characteristic of the radiation energy deposition process. However, this is still an upper limit since eq 2 gives an upper limit. It is clear, though, that the  $e_t$  – nonuniform spatial distributions represent an expanded spur. Finally, it is noteworthy that  $(T_1T_2)^{1/2}$  for radicals and  $e_t^-$  in MTHF approach the same value at high dose. This is shown in Figure 1 for MTHF and is also true in TEA but not in alkaline ice. This probably indicates that both  $e_t^-$  and radicals depend on the same relaxation mechanism at high dose in TEA and MTHF.

Acknowledgment. This research was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-2086.

### **Resolution of an Infrared Band of HDO into**

### Hydrogen-Bonded and Nonbonded Components

Publication costs borne completely by The Journal of Physical Chemistry

Sir: The important role of water structure in determining the properties of aqueous solutions has become increasingly clear in recent years. Numerous experimental approaches have been taken in an attempt to elucidate the "degree of association" of water, with infrared spectroscopy being one of the most successful. Although water molecules are known to be continuously making and breaking hydrogen bonds, infrared spectra represent an average structure in that species having lifetimes of  $10^{-13}$  sec may be detected. The conclusions reached from spectral investigations have, nevertheless, not always been in agreement since shifts in the positions of infrared bands have led some to represent water by a "continuum" model<sup>1</sup> while others have preferred to think of water in terms of a model in which the molecules have "varying degrees of polymerization."

Although there are many infrared and near-infrared (NIR) spectra of aqueous solutions and of liquid water as a function of temperature, they are limited<sup>2</sup> by the fact that the water bands are broad and shifts in the intensity and frequency are not pronounced. A rather complete set of spectra of this type is given by Gordon, et al.<sup>3</sup> A major improvement in the NIR spectra is obtained if one uses dilute solutions of  $H_2O$  in  $D_2O$  since the fundamental vibrational modes are uncoupled and the bands are much sharper. Worley and Klotz<sup>2</sup> observed a sharp band at 1416 nm which was assigned to an overtone of the free OH stretching mode on the basis of its temperature-intensity relationship and other broader bands between 1525 and 1666 nm which "were thought to arise from various overtone modes of vibration of different hydrogen bonded species." There was, however, no resolution of a single band into its hydrogen-bonded and nonbonded components. These workers used a 5% solution of  $H_2O$  in  $D_2O$  and absorption cells with a light path of 1 cm. The strong absorbance of  $H_2O$  limited their observations to the 1350-1750-nm region.

Our interest in the effect of water structure on the properties of aqueous solutions led us to repeat the above experiments, but the availability of a more sensitive 0-0.2-mV slidewire enabled us to use a shorter path length cell (0.5 mm) for the solutions, and slit openings could still be controlled on the Cary Model

14 M instrument at much longer wavelengths. In a typical experiment solutions containing 5% H<sub>2</sub>O-95% D<sub>2</sub>O were placed in the sample compartment and compared with 99.77% D<sub>2</sub>O in the reference compartment. The temperature of both samples was varied between 25 and 70° and also various solutes were added to the solutions at 25°. The sensitivity was sufficient to enable measurements on solutions containing as little as 1% H<sub>2</sub>O-99% D<sub>2</sub>O. The D<sub>2</sub>O concentration of the sample solution was calculated from the relation-ship

$$H_2O + D_2O = 2HDO$$
 (K = 3.80)

and the path length of the reference cell was adjusted so as to compensate exactly for  $D_2O$  absorbance. A spectrum similar to that reported by Worley and Klotz<sup>2</sup> was reproduced in detail to 1750 nm (Figure 1, curve A) but there was also a very sharp intense band at 2030 nm. A weak band at 1905 nm was also observed. Upon increasing solution temperatures to 70° spectrum B was obtained. Several interesting observations may be made about these spectra: (a) the intensity of the band at 1905 nm increases with increasing temperature while the effect of a change in temperature on the band at 2030 nm is just the opposite; (b) both bands are very sharp and have similar band widths when they are of similar intensity; (c) the sum of the band intensities over the 25-70° temperature range increases only slightly as the temperature is elevated.

It thus appears reasonably certain that the band at 2030 nm is due to hydrogen-bonded modes and the band at 1905 nm is due to free OH groups. The assignment of a band at this position to the  $\nu_2 + \nu_3$  combination has been made by Bayly, *et al.*<sup>4</sup> They, however, observed only one band at 2022 nm. The 1905-nm band was probably not observed since it is so weak at 25°. The shift of the 2022-nm band to our observed position of 2030 nm is probably caused by our use of D<sub>2</sub>O in the reference cell. The position of the  $\nu_2 + \nu_3$  combination band in the vapor state<sup>5</sup> is 5332 cm<sup>-1</sup>

- (1) M. Falk and T. A. Ford, Can. J. Chem., 44, 1699 (1966).
- (2) J. D. Worley and J. M. Klotz, J. Chem. Phys., 45, 2868 (1966).
- (3) H. Yamatera, B. Fitzpatrick, and G. Gordon, J. Mol. Spectrosc., 14, 268 (1964).
- (4) J. G. Bayly, V. B. Kartha, and W. H. Stevens, Infrared Phys., 3, 311 (1963).

<sup>(5)</sup> G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1959.
corresponding to 1875 nm. The shift of the nonbonded band to 1905 nm upon condensation is similar to that reported<sup>6</sup> for other combination bands. The shift in the position of the band upon hydrogen bonding is also reasonable. The greater intensity of this combination band when compared with others in the spectra (Figure 1) is not unexpected if one remembers that the  $\nu_2$  and  $\nu_3$  modes in the vapor state have much greater intensities than the  $\nu_1$  mode. These observations, together with the isosbestic point which occurs at 1960 nm when data at several temperatures are plotted in Figure 1, furnish substantial evidence that we are observing the resolution of a single band into its bonded and nonbonded components.



Figure 1. Absorbance spectrum of 5% H<sub>2</sub>O-95% D<sub>2</sub>O against a reference of 99.77% D<sub>2</sub>O: curve A, HDO solution at 25°; curve B, HDO solution at 70°.

Since this is the first instance in which a single band has been resolved into components due to both bonded and nonbonded OH groups, the effect of "structure making" and "structure breaking" solutes was also noted. A 3 M solution of NaClO<sub>4</sub> yields a spectrum intermediate between curves A and B in Figure 1, with the sum of the intensities of the two bands remaining approximately the same as that of pure water. Sodium perchlorate thus has the same effect as an increase in temperature. A solution of LiCl almost eliminates the band at 1905 nm while the intensity of the band at 2030 nm increases.

It is anticipated that spectra involving this band will be very useful in the study of the effects of various organic solutes on the structure of water. It should complement the data obtained from the 1416-nm band by the method of Worley and Klotz<sup>2</sup> and from the 958-nm band by the method of Bonner and Woolsey.<sup>6</sup> The availability of three useable bands for the estimation of the degree of hydrogen bonding in aqueous

(6) O. D. Bonner and G. B. Woolsey, J. Phys. Chem., 72, 899 (1968).

solutions will circumvent in many instances the interference of the C-H, N-H, or C-N bands of the solute.

Department of Chemistry O. D. Bonner University of South Carolina Columbia, South Carolina 29208

RECEIVED OCTOBER 26, 1971

#### **Comment on "Theories of the Primitive**

Model of Ionic Solutions"<sup>1</sup>

Publication costs borne completely by The Journal of Physical Chemistry

Sir: The theory of the thermodynamic properties of a quantal assembly of point ions given in this paper exhibits some features which are not consistent with earlier results in this area of physical chemistry.

The expression given<sup>1</sup> for fugacity

$$f = f_0 + f_{\rm DH} + f_{\rm A}$$
 (1)

with the terms as evaluated by Jones and Mohling<sup>1</sup> is regular in the classical limit, while according to a theorem of Kramers<sup>2</sup> an assembly of classical point charges is unstable; it tends to coalesce to a point. The singular behavior in the classical limit must be found in the higher terms which are omitted from eq 1 and have not been investigated by Jones and Mohling. Thus their claim of rapid convergence of the series, which is based upon the neglect of the higher terms, cannot be right when one is near the classical limit as in the example in the Appendix.<sup>1</sup> In that example the ratio of deBroglie thermal wavelength to mean particle separation is less than 0.02, so small that eq 1 gives practically the same result as for classical point charges. This observation is consistent with the well known result that  $f_{DH}$  and  $f_A$  (even the correct form, see below) are independent of the ion sizes in the classical primitive model. It confirms that one must look at the remaining terms when close to the classical limit.

The so-called Abe term  $f_A$  appears in place of a term having the same logarithmic concentration dependence first reported in 1928<sup>3</sup> and found in precisely the same form in other independent theories of the thermodynamic properties of assemblies of ions.<sup>4</sup> In all the earlier results the logarithmic term vanishes identically

(1) R. W. Jones and F. Mohling, J. Phys. Chem., 75, 3790 (1971).

(2) H. A. Kramers, Proc. Roy. Acad. Sci., Amsterdam, 30, 145 (1927);
 L. Onsager, J. Phys. Chem., 43, 189 (1939).

<sup>(3)</sup> T. H. Gronwall, V. K. La Mer, and K. Sandved, Phys. Z., 29, 588 (1928).

<sup>(4)</sup> H. L. Friedman, "Computed Thermodynamic Functions and Distribution Functions for Simple Models of Ionic Systems," in "Modern Aspects of Electrochemistry," No. 6, J. O. Bockris and B. E. Conway, Ed., Plenum Press, New York, N. Y., 1971.

in solutions of 1-1 electrolytes (this is merely a sufficient condition),<sup>4</sup> while the expression given for  $f_A$  by Jones and Mohling (eq 3.3<sup>1</sup>) does not vanish for 1-1 electrolytes in the classical limit.

The statement<sup>1</sup> that the corrections to McMillan-Mayer states are not significant on the scale of Figure 1 (of the Jones-Mohling paper<sup>1</sup>) is not consistent with the thermodynamic theory of these corrections.<sup>5</sup> Applying this theory one finds, for example, that the corrected CsI curve falls close to the given KCl curve in Figure 1.

Finally, it may be helpful to note that the characteristic lengths which appear in  $f_{DH}$  in the classical limit are  $\kappa^{-1}$ , the Debye length, and

$$b = \frac{1}{2} Z_{\alpha}^2 e^2 / \epsilon k T \tag{2}$$

which is the Bjerrum length. It happens that for 1-1 electrolytes in water  $b \simeq 3.5$  Å; thus it roughly equals so-called distance of closest approach *a* for all the electrolytes in Figure 1 of Jones and Mohling.<sup>1</sup> Finally their result for  $f_{\rm DH}$  leads to

$$\gamma_{\pm} = 1 - b\kappa + (b\kappa)^2 + \dots \qquad (3)$$

which is rather close to what one gets from the familiar form

$$\ln \gamma_{\pm} = -b\kappa/(1+a\kappa) \tag{4}$$

if he takes b = a, namely

$$\gamma_{\pm} = 1 - b\kappa + \frac{3}{2}(b\kappa)^2 + \dots$$
 (5)

So it is not surprising that the curve labeled DH in Figure 1 of Jones and Mohling is rather close to the familiar curves derived from eq 4 with ion-size parameters a in the usual range. On the other hand, this is obviously a rather special case and there is no assurance that eq 1 will give qualitative agreement with experiment in cases in which b is quite different from a realistic value for a.

(5) H. L. Friedman, "Ionic Solution Theory," Interscience-Wiley, New York, N. Y., 1962, eq 16.59; J. Chem. Phys., 32, 1351 (1960).

DEPARTMENT OF CHEMISTRY		HAROLD L. FRIEDMAN
STATE UNIVERSITY OF NEW	York	
at Stony Brook		
STONY BROOK, NEW YORK	11790	

**Received January 20, 1972** 

# what's happening

on the frontiers

ACCOUNTS OF CHEMICAL RESEARCH LETS YOU KNOW....

# of chemical research?

 Whether you are a practicing chemist, professor or student, you want to
 cha

 keep up with the latest developments. Yet few of you have the time
 to read thoroughly all the journals of primary publications.

 ACCOUNTS fills the gap.
 Written by investigators active in the fields reviewed, ACCOUNTS'

 concise, brief articles place recent developments in perspective—
 and relate them to earlier work and their probable future significance.

 Once you start relying on ACCOUNTS to keep you informed,
 Cov

you'll wonder how you got along without its monthly arrival.

in short, critical articles that cover all areas of chemical research.

Complete and mail back the form below. We'll prove how valuable this publication can be to you.

		incert at the following suc	oscription rates:
ACS members:	□ U.S. \$ 5.00	Canada, PUAS \$ 9.00	□ Other Nations \$10.0
Nonmembers:	□ U.S. \$15.00	Canada, PUAS \$19.00	□ Other Nations \$20.0
ame		Title	
Address: 🔲 Home 🔲 Business			<u>-</u>
Employer Address: 🗌 Home 🔲 Business Dity	State/	Country	Zip
Employer Address: 🗌 Home 🗌 Business City	State /	Country	Zip
Address:  Home Business City Nature of employer's business?	State/ Manufacturing or processi Other	Country ng	Zip Government

# Men & Molecules New CASSETTES

## NOBEL PRIZE WINNERS

- Dr. Linus Pauling The Committed Scientist Dr. Jacob Bronowski Science and Man
- Dr. Glenn Seaborg
   The Atomic World of Glenn Seaborg
   Dr. George Wald
   Vision, Night Blindness, & Professor Wald
- Dr. Melvin Calvin The Search for Significance—Parts I & II

## ENVIRONMENT

- Mercury: Another Look, Part I Dr. John Wood Mercury: Another Look, Part II Dr. John Wood & D. G. Langley
- The Troubles with Water Dr. Daniel Okun Pure Oxygen for Polluted Water Dr. Jack McWhirter
- Bubble Machines & Pollution Finders
   Dr. K. Patel & Dr. L. Kreuzer
   The Steam Engine: A Modern Approach
   Dr. W. Doerner & Dr. M. Bechtold
- Insects: The Elements of Change—Parts I & II Dr. Carroll M. Williams
- New Weapons Against Insects Dr. G. Staal & Dr. J. Siddall Moths, Drugs, & Pheromones Dr. Wendell Roelofs
- The Lead Issue H. Mayrsohn & M. H. Hyman Smog: An Environmental Dilemma Dr. James Pitts
- The Fusion Torch
   Dr. B. Eastlund & Dr. W. Gough
   The Impermanent Plastic Dr. James Guillet

#### ENERGY

Fusion and Fission: An Appraisal
 Dr. James L: Tuck
 The Prospects for Energy Dr. M. King Hubbert

Single ( Any Six

Any 18

## **BIO-MEDICAL**

- Birth Control: Problems & Prospects
   Dr. Carl Djerassi
   Hormones, Terpenes, & the German Air Force
   Dr. A. J. Birch
- Prospects for Implants Dr. Donald Lyman New Dimensions for Polymers Dr. Alan Michaels
- Fabricating Life An Essay Report New Ways to Better Food Dr. R. W. F. Hardy
- Chemistry of the Mind: Schizophrenia Dr. Larry Stein Chemistry of the Mind: Depression Dr. Joel Elkes
- The Molecules of Memory
   Dr. W. L. Byrne & Dr. A. M. Golub
   The Matter with Memory Dr. J. M. McGaugh
- Dissonant Harmony Dr. Denham Harman Why We Grow Old Dr. Howard Curtis
- New Materials for Spare Parts Dr. V. Gott & Dr. A. Rubin Against Individuality Dr. R. Reisfeld & Dr. B. Kahan
- A Richness of Lipids Dr. Roscoe O. Brady Life: Origins to Quality Dr. Stanley Miller
- The Nitrogen Fixer Dr. Eugene van Tamelen Prostaglandins: A Potent Future Dr. E. J. Corey & Dr. S. Bergstrom
- A Glass Revolution Dr. S. D. Stookey A View of Genes Dr. Norman Davidson
- Chemical Evolution Dr. Russell Doolittle An Evolving Engine Dr. R. E. Dickerson

#### **OUTER SPACE**

- Molecules in Space Dr. D. Buhl & Dr. L. Snyder Chemistry Among the Stars Dr. Bertram Donn
- Molecules Meeting Molecules
   Dr. John Richards
   The Neutrinos of the Sun Dr. Raymond Davis

# SCIENCE

- Probing Creation Dr. Myron A. Coler New Directions in U.S. Science Dr. William McElroy
- Aspirins, Enzymes, & Fragrant Redheads
   An Essay Report
   Vitamin D: A New Dimension Dr. Hector DeLuca
- Pica Dr. J. Julian Chisolm, Jr. Technology in the Nursery Dr. William J. Dorsor
- Engineering Microbes Dr. Elmer Gaden Liquid Crystals: A Bright Promise Dr. George Heilmeier
- Hot Brines in the Red Sea Dr. David Ross Complete Corn Dr. Edwin T. Mertz
- Lively Xenon Dr. Neil Bartlett The Repressor Hunt Dr. Mark Ptashne
- The New Prospectors Dr. William Prinz A Sober Look at Alcoholism Dr. Jack Mendelsohn
- Probing the Active Site Dr. David Pressman The Puzzle of Diversity Dr. Oliver Smithles
- Help for the Have Nots Dr. Harrison Brown The Closing Circle Dr. Preston Cloud

#### CANCER RESEARCH

- Cancer Research I—Perspective & Progress
  Dr. Frank Rauscher
  Cancer Research II—Viruses
  Dr. R. Gallo & Dr. G. Todaro
- Cancer Research III—Chemotherapy Dr. C. Gordon Zubrod Cancer Research IV—Immunology Dr. Paul Levine
- Cancer Research V—Environmental Agents
   Dr. Umberto Saffiotti
   Cancer Research VI—NCI Roundtable

	ACS Members	Nonmembers	Large Volume Orders Negotiable	
assette	\$4.49	\$5.49	For orders outside U.S.A. add 75 cents handling charge	
Cassettes	\$3.95/cassette	\$4.95/cassette	5% Discount if payment accompanies order	
or more cassettes to one Address \$3.75%cassette		3.75%cassette	Order From: American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036, ATTN: A. Poelos	