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Thermal and Photochemical Decomposition of Methyldiimide in the Gas Phase¹

S. K. Vidyarthi,² C. Willis,* and R. A. Back

Chemistry Division, National Research Council of Canada, Ottawa, Canada (Received September 11, 1975) Publication costs assisted by the National Research Council of Canada

The thermal and photochemical decomposition of methyldiimide have been studied in the gas phase at pressures from 10 to 500 Torr and temperatures from 23 to 110 °C. Both decompositions yield CH_4 and N_2 in equal amounts and proceed by a radical chain mechanism with 3/2-order kinetics, propagated by the reactions $CH_3 + CH_3N_2H \rightarrow CH_4 + CH_3N_2$ and $CH_3N_2 \rightarrow CH_3 + N_2$. The rate constant for the former, which is rate controlling, was found to be $1.31 \pm 0.17 \times 10^7 M^{-1} s^{-1}$. Chain lengths are large ranging from 10^2 to 10^6 depending on the rate of initiation. The thermal initiation reaction has a low activation energy which suggests a surface process. The photochemical initiation was found to have a quantum yield of 0.74 based on the yield of ethane, the main chain termination product, although the quantum yield of the primary dissociation was probably close to unity.

Introduction

Methyldiimide (methyldiazene) is the simplest of a number of monoalkyl diimides that have been prepared in recent years,³ and which, like diimide itself, was found to be considerably more stable than had been supposed. Ackermann, Hallmark, Hammond, and Roe⁴ studied the properties of methyldiimide in the gas phase, and reported a moderately fast thermal decomposition at room temperature which followed 3/2-order kinetics, yielding CH₄ and N₂ in equal quantities, and showing characteristics of a longchain free-radical reaction. This behavior is in marked contrast to that of azomethane (dimethyldiimide) and of diimide itself; the former decomposes by a short-chain process at much higher temperature,⁵ and the latter by a nonradical mechanism.⁶ The present study was undertaken to examine the kinetics of the thermal decomposition more thoroughly and to investigate the photochemical decomposition which has not been studied before. It will be seen that the two processes are closely related.

Experimental Section

Methyldiimide was prepared in a vacuum line as described by Ackermann et al.⁴ and was collected in a U-trap at -196 °C. The pale yellowish white solid was vaporized into a second trap by warming with hot water, and was further purified by prolonged pumping at -196 °C. Very minor impurities were NH₃ and C₂H₆; passage through a

trap containing P_2O_5 removed most of the former and distillation the latter. The last traces of ethane were difficult to remove and caused scme difficulty in measurement of ethane produced in the reaction.

The thermal decomposition was initiated by vaporizing the purified sample into a cylindrical quartz reaction vessel, 20 cm long, 5 cm i.d., and 150 ml volume, mounted in a temperature-regulated furnace. The pressure in the reaction vessel was measured with a sensitive quartz spiral gauge. Preliminary experiments revealed that the system was highly sensitive to light, and in all subsequent work light was excluded from the reaction vessel, connecting tubing, and the preparation line.

After an experiment, products noncondensible at -196 °C were measured in a gas buret and analyzed for N₂, CH₄, and H₂ by gas chromatography on a molecular sieve column.

The photolysis was studied at two wavelengths, 4047 and 3660 Å, using a medium-pressure BTH 250 W ME/D mercury lamp with Corning filter 5-62 and Hanovia filter 3660, respectively. The reaction vessel used for the thermal decomposition was also used for the photolysis at 4047 Å. The light intensity and consequently the reaction rate was much higher in the photolysis at 3660 Å, and to avoid selfheating the experiments were done in a small water-cooled vessel of about 14-ml volume. The disappearance of methyldiimide was followed by changes in the light adsorbed, measured by a photomultiplier, since even in the jacketed vessel self-heating was enough to affect the pressure measurement appreciably. Azomethane obtained from Merck Sharp and Dohme was used as an actinometer in the photolysis.

Results and Discussion

Products and Stoichiometry. The sole products of any importance in both the thermal and the photochemical decompositions were methane and nitrogen, formed in equal amounts, so that the stoichiometry was accurately described by the reaction $CH_3NNH \rightarrow CH_4 + N_2$. Ethane and hydrogen, in trace quantities, were the only other products detected; yields of ethane in the thermal decomposition were about 10^{-3} % of the original methyldiimide, while in the photolysis they ranged up to 0.5% at the highest light intensity. The simple stoichiometry was followed, within the accuracy of the analysis, during the entire course of the reaction, which permitted the use of pressure measurements to follow the kinetics of the decomposition.

Kinetics of the Thermal Decomposition. It was discovered in preliminary experiments that the decomposition was extremely sensitive to light. Experiments with light carefully excluded, however, showed that there was a genuine thermal reaction, although its rate was much reduced from that in the presence of normal room light. Figure 1 shows a plot of $P_{\infty} - P$ (= $P_{CH_3N_2H}$) for a typical thermal decomposition in the dark at 21 °C, together with data from the experiment in which the vessel was exposed to the room light. Shown for comparison also are some results obtained by Ackermann and his coworkers in his earlier study;⁴ it is clear that in those experiments the reaction was strongly photosensitized. An important consequence is that methyldiimide is considerably more stable thermally in the gas phase than reported by Ackermann et al., with a halflife of about 1 h at 21 °C with an initial pressure of 50 Torr.

The thermal decomposition of methyldiimide was found for the most part to obey 3/2-order kinetics as reported by Ackermann et al.⁴ Figure 2 shows plots of $(P_{\infty} - P)^{-1/2}$ vs. time, which for a 3/2-order reaction should be linear, for several initial pressures of methyldiimide and for one case in which CO_2 was added. The data in Figure 2 show two distinct kinds of deviation for simple 3/2-order kinetics. The most obvious is the initial curvature, which corresponds to an enhanced initial rate of decomposition; 3/2order behavior is typically attained only after 20 or 30% of the methyldiimide has decomposed. The second deviation from simple kinetics is a variation with pressure of the 3/ 2-order rate constants, obtained from the linear portions of the plots in Figure 2, at average pressures below about 50 Torr. This is evident in the slopes of the plots in Figure 2, which should all be the same; in fact they rise sharply with decreasing pressure at the two lowest pressures. Addition of 100 Torr of CO_2 in one experiment reduced the slope to approximately the high-pressure value. The causes of these two deviations from simple 3/2-order kinetics are not obvious, and will be considered later in discussion of the reaction mechanism.

The temperature dependence of the thermal decomposition of methyldiimide is shown in Figure 3 as an Arrhenius plot of the 3/2-order rate constant, $k_{3/2}$, which gives an activation energy of 7.3 (±1.2) kcal/mol. These data were taken from the linear portions of plots similar to those in Figure 2 for pressures above 50 Torr where the rate constant was independent of pressure.



Figure 1. Pressure change in the thermal decomposition of methyldiimide at 21 °C: (O) in the dark; (Δ) in room light; (\Box) Ackermann et al.



Figure 2. 3/2-order plot of pressure change in thermal decomposition of methyldiimide at 22 °C: initial pressures, (I) 70.0 Torr; (II) 40.2 Torr; (III) 108 Torr, 8 Torr methyldiimide plus 100 Torr CO_2 ; (IV) 8.2 Torr; (V) 6.5 Torr.

Kinetics of the Photochemical Decomposition. Kinetic studies of the photolysis were done at 4047 Å, which lies out on the long-wavelength shoulder of the $\pi^* \leftarrow n^+$ absorption band of methyldiimide (Figure 4). This wavelength was chosen to ensure fairly homogeneous absorption of light; the absorption in fact was always less than 20%. The system again followed 3/2-order kinetics, shown in Figure 5 for three different incident light intensities; a thermal decomposition is shown for comparison. Little or no initial curvature is evident and the slope was not pressure dependent. The square of the overall 3/2-order rate constant, $k_{3/2}$, showed a linear dependence of the incident light intensity, illustrated in Figure 6, in which the intercept corresponds to the thermal reaction. The temperature dependence of $k_{3/2}$ for the photochemical reaction (corrected for the small thermal contribution) is shown in Figure 7 which yields an activation energy of 5.2 (± 1.0) kcal/mol.



Figure 3. Arrhenius plot of $k_{3/2}$ for the thermal decomposition of methyldiimide.



Figure 4. Near-uv absorption spectrum of methyldiimide vapor. (ϵ in decadic molar units.)



Figure 5. 3/2-order plot of pressure change in the photochemical decomposition of methyldiimide at 22 °C.

Overall quantum yields¹³ for methyldiimide disappearance were measured at 4047 and 3660 Å under a variety of conditions (Table I). Azomethane was used as an actinome-

TABLE I: Overall Quantum Yield for the Photochemical Decomposition of CH_3NNH at 21 \pm 2 $^{\circ}C$

Initial CH ₃ NNH concn, Torr	Incident light intensity, einstein 1. s ⁻¹	Wave- length, Å	ф	
43.7	9.3 × 10 ⁻¹¹	4047	2.74×10^{4}	
54.1	9.3×10^{-11}	4047	2.60×10^{4}	
26.0	1.86×10^{-10}	4047	1.55×10^{4}	
39.3	3.06×10^{-10}	4047	1.44×10^{4}	
26.2	2.60×10^{-10}	4047	1.25×10^{4}	
26.1	5.32×10^{-10}	4047	0.73×10^{4}	
235.0	2.0×10^{-6}	3660	478	
158.3	2.47×10^{-6}	3660	308	
109.4	2.72×10^{-6}	3660	222	
99 .5	1.17×10^{-6}	3660	213	
101.7	2.43×10^{-6}	3660	192	
69.6	2.31×10^{-6}	3660	170	
76.8	2.69×10^{-6}	3660	166	



Figure 6. Dependence of $k_{3/2}^2$ on absorbed light intensity.



Figure 7. Arrhenius plot of $k_{3/2}$ for the photochemical decomposition of methyldiimide.

ter, assuming a quantum yield of N_2 of one;⁷ the light absorbed by the methyldiimide was integrated over the course of the decomposition.

The Mechanism of the Decomposition. The large quantum yields (Table I), the 3/2-order kinetics, the low activation energy, and the dependence on the square root of the light intensity all strongly indicate a radical chain mechanism for the photodecomposition, and the similarities in the kinetics suggest that the thermal decomposition proceeds by a similar mechanism. The following common mechanism will be seen to account for most of the observed features of both decompositions:

$$CH_3NNH \rightarrow CH_3 + N_2H$$
 (1)
thermal initiation

$$CH_3NNH + h\nu \rightarrow CH_3 + N_2H$$
(2)
photoinitiation

$$N_2 H \to N_2 + H \tag{3}$$

$$N_2H + CH_3NNH \rightarrow N_2H_2 + CH_3NN \tag{4}$$

$$H + CH_3NNH \rightarrow CH_3NN + H_2$$
 (5)

$$H + CH_3NNH \rightarrow CH_3NNH_2$$
 (6)

$$CH_3NNH_2 + CH_3NNH \rightarrow CH_3NHNH_2 + CH_3N_2 \quad (7)$$

$$CH_3 + CH_3NNH \rightarrow CH_4 + CH_3NN$$
(8)
$$CH_3NN \rightarrow CH_3 + N_2$$
(9)

chain propagation

$$2CH_3 \rightarrow C_2H_6$$
 (10)

$$2CH_3 = C_2H_6$$

chain termination

This is essentially the mechanism suggested by Ackermann et al.⁴ for the thermal decomposition, with the addition of reactions 4, 6, and 7; a straightforward Rice-Herzfeld chain propagated by reactions 8 and 9. If every N₂H radical formed in reaction 1 or 2 initiates a chain via reactions 3 + 5, 3 + 6 + 7, or 4, then the rate of initiation R_i will be given by

$$R_{i} = 2(k_{1}[CH_{3}NNH] + I_{0}A\phi_{2})$$
(11)

where I_0 = incident light intensity per unit volume, A = fraction of light absorbed, and ϕ_2 = quantum yield of reaction 2. For the present experiments in which A was always less than 0.2 (usually much less), R_i is given to a good approximation by the relation

$$R_{i} = 2(k_{1} + k_{2}I_{0})[CH_{3}NNH]$$
(12)

where $k_2 = 2.303\epsilon L\phi_2$, $\epsilon =$ molar decadic extinction coefficient, and L = length of photolysis cell.

If now reaction 9 is much faster than reaction 8, the latter will be the rate-controlling propagation step, $[CH_3]$ will be \gg [CH₃NN], and reaction 10 will be the only important chain termination. The steady-state concentration of methyl radicals will then be

$$[CH_3] = (R_i/k_{10})^{1/2}$$
(13)

and, assuming long chains, the overall rate of the reaction will be

$$R = k_8[CH_3][CH_3NNH] = k_8(2(k_1 + k_2I_0)/k_{10})^{1/2}[CH_3NNH]^{3/2}$$
(14)

Equation 14 can be seen to predict the observed 3/2 order of both the thermal and photochemical decompositions, and the dependence of $k_{3/2}^2$ on I_0 (Figure 5).

Determination of ϕ_2 , the Primary Quantum Yield of Dissociation into Radicals. The value of ϕ_2 is of interest in itself and is also needed to obtain values of k_1 and k_8 . If reaction 10 is the only termination step, it follows that the rate of formation of ethane may be equated to the total rate of initiation, and $\phi(ethane)$ to ϕ_2 . Attempts to measure ethane yields at the low absorbed light intensities attainable at 4047 Å employed in the kinetic studies were rendered inaccurate by traces of ethane impurity and by the fact that the very large overall quantum yields of decomposition meant that yields of ethane were an extremely small fraction of the total methyldiimide decomposed. Since ϕ_2 is a primary quantum yield it should be independent of I_0 and of the spatial distribution of the absorbed light. Measurements of ϕ (ethane) were therefore made at the much higher absorbed light intensities attainable at 3660 Å. Here the chain length was much shorter and the ethane yield, though still small, was a much larger fraction ($\sim 0.5\%$) of the methyldiimide decomposed. Values of ϕ (ethane) are shown in Table II, and, while scattered, are probably significantly less than one. It would be surprising, to judge from the behavior of azomethane and other simple azo compounds,⁷ if the total quantum yield of dissociation were appreciably less than unity, and the value of 0.74 can be most simply explained by the occurrence of a molecular dissociation process (yielding $CH_4 + N_2$ or possibly $H_2 + CH_2 = NN$) with a quantum yield of 0.26. This may in fact be the true explanation, although it seems unlikely, since molecular dissociation has been notably absent in the photolysis of simple azo compounds.⁷ A much more likely possibility is that reaction 10 is not the only termination step, so that ϕ (ethane) is less than ϕ_2 . This would require that another radical besides CH_3 be present at steady-state concentrations high enough to take part in 20% of the termination reactions. The other chain propagating radical, CH₃NN, is probably not responsible as it is thought to have little or no stability. There is, however, some evidence from a study⁸ of the photolysis of N₂H₂ and from recent theoretical calculations⁹ that the N₂H radical may be stable enough so that reaction with CH_3 (probably to give $CH_4 + N_2$) could compete successfully with reactions 3 and 4 at the very high light intensities and high radical concentrations employed in measuring $\phi(C_2H_6)$. To account for $\phi(C_2H_6) = 0.74$, it can be shown that about 25% of the N_2H radicals must have reacted with CH_3 , and this seems to be the most probable explanation of the observed value. At the very much lower intensities employed in the kinetic studies, this radical-radical reaction should be negligible compared to reactions 3 and 4. In the treatment of the kinetic data which follows, it will be assumed therefore that R_i is accurately given by eq 12, and because a molecular photodissociation seems unlikely, that $\phi_2 = 1$. Some experimental support for these assumptions is afforded by the persistence of 3/2-order kinetics over a wide range of absorbed intensity, CH₃N₂H pressure, and extent of reaction, in the photochemical decomposition. If however $\phi_2 = 0.74$, the reported values of k_1 should be decreased by a factor of 0.74, while the estimates of k_8 and k_9 should be increased by 15%. Hydrogen should also be produced in measurable quantities (by reaction 5) at high intensity, although it was undetectable in the low-intensity kinetic studies. Measurements in several high-intensity experiments showed a yield of H₂ about $\frac{1}{3}$ of that of ethane. This suggest some loss of H atoms in reaction 6, and loss of N₂H in reaction 4 or by combination with CH₃.

Evaluation of k_1 , and the Nature of the Thermal Initiation. From the right-hand side of eq 14 it can be seen that the overall 3/2-order rate constant, $k_{3/2}$, will be given by the expression

$$k_{3/2}^2 = (4k_8^2/k_{10})(k_1 + k_2I_0) \tag{15}$$

A plot of $k_{3/2}^2$ against k_2I_0 is shown in Figure 6. It can be seen from eq 15 that k_1 = intercept/slope of this plot, and a

Thermal and Photochemical Decomposition of Methyldiimide

TABLE II: Quantum Yield for the Formation of Ethane, ϕ_E , in the 3660-Å Photolysis of CH₃N=NH in the Pressure Region 70–530 Torr at 21 \pm 1 °C

Total initial pressure, Torr	Total absorbed light, (einstein l. ⁻¹) × 10 ⁵	Total ethane yiəld, M × 10 ⁵	φ _E 3660
69.6	2.22	1.59	0.72
76.7	2.50	1.91	0.76
99.5	2.66	2.02	0.76
101.6	2.87	2.00	0.70
109.5	2.67	1.68	0.63
158.3	2 .78	1.58	0.57
234.9	2.53	2.54	1.00
530.4	8.52	6.39	0.57
		Av $\phi_{\rm E}$	0.74 ± 0.13

value of $k_1 = 1.05 \times 10^{-9} \text{ s}^{-1}$ was determined at 22 °C and a methyldiimide pressure of 50 Torr.

From eq 15 it can be seen that in the absence of light, $k_{3/2}$ (thermal) = $2k_8(k_1/k_{10})^{1/2}$, from which it follows that the overall activation energy of the thermal decomposition will be given by

$$E_{\text{thermal}} = E_8 + \frac{1}{2}(E_1 - E_{10}) = 7.3 \text{ kcal/mol}$$
 (16)

(from Figure 3). Also from eq 15, it is clear that $k_{1/2}^2$ can be separated into two parts, thermal and photochemical. Values of $k_{3/2}^2$ (and thence of $k_{3/2}^2$) for the photochemical reaction alone were obtained by subtracting $k_{3/2}^2$ (thermal) from $k_{3/2}^2$ (thermal + photochemical), and it is these values that are plotted in Figure 7. From eq 15, $k_{3/2}$ (photochemical) = $2k_8(k_2I_0/k_{10})^{1/2}$, from which it follows, since k_2I_0 should be almost independent of temperature, that

$$E_{\rm photochemical} = E_8 - \frac{1}{2}E_{10} = 5.2 \, \rm kcal/mol$$
 (17)

(from Figure 7). Combining eq 16 and 17, a value of E_1 = 4.2 kcal/mol is obtained, and from the value of k_1 at 22 °C, a frequency factor $A_1 = 1.3 \times 10^{-6} \, \text{s}^{-1}$ can be calculated.

The bond dissociation energy $D(CH_3-NNH)$ should be similar to that of azomethane, i.e., 45–50 kcal/mo⁻,⁵ and the very much lower value found for E_1 is only compatible with a surface-catalyzed decomposition, not unusual in compounds with N-H groups (cf. NH₃ or N₂H₄). This conclusion is supported by a comparison of the thermal decomposition in the two reaction vessels, which had surface/volume ratios of 0.9 and 4.0 cm⁻¹, respectively. These showed values of $k_{3/2}$ under similar conditions of 3.9 and 7.3×10^{-3} $M^{-1/2}$ s⁻¹, respectively, close to the (S/V)^{1/2} dependence expected for chain initiation at the surface (eq 14).

As noted earlier, the thermal decomposition shows some deviation from simple 3/2-order kinetics, namely, a faster than normal rate in the initial stages of the reaction and at pressures below about 50 Torr. Since they are not observed in the photochemical reaction, and since the only difference between the two systems appears to be in the initiation step, it is reasonable to attribute these effects to something affecting the initiation rate in the thermal decomposition. The initial enhancement of the rate could be explained either by surface poisoning by a reaction product, or by enhanced initiation by a trace impurity which was consumed as the reaction progressed. To test these hypotheses a decomposition was allowed to proceed until 3/2order behavior was attained. Products and reagents were

TABLE III: Chain Lengths and Value for k_s at 21 ± 1 °C

Initiation	Initial CH ₃ NNH pressure, Torr	Av chain length ^a	$\frac{10^{-7} k_{B}}{M^{-1} s^{-1}}$
Thermal	69.7	8.1×10^{5}	1.40
	33.8	6.3×10^{5}	1.55
	40.2	7.4×10^{5}	1.66
	7.8 ^b	2.5×10^{5}	1.30
	37.1	6.6 × 10 ⁵	1.55
Photochemical			
4047 A	26.2	5.4×10^{3}	1.18
	26.2	9.3×10^{3}	1.18
	3 9 .3	1.1 × 10⁴	1.22
	26.0	1.2×10^4	2.24
	54.I	1.9×10^4	1.03
	43.7	2.0 × 10⁴	1.21
	36.9	1.1 × 10⁴	1.30
	53.7	1.2×10^4	1.20
	47.4	1.3×10^4	1.33
3660 Å	158.3	2.3×10^{2}	Average value
	69.6	1.3×10^{2}	from thermal
	76.8	1.2×10^2	and 4047 Å
	101.7	1.4×10^{2}	results *
	109.4	1.6×10^{2}	$k_{*} =$
			1.31 ± 0.17
			$\times 10^{7} M^{-1}$
			s ⁻¹





Figure 8. Pressure dependence of k_1 at 22 °C.

then condensed out at -196 °C, N₂ and CH₄ were pumped away, and the reaction vessel thoroughly evacuated. The condensate was then revaporized into the vessel and the reaction allowed to proceed once more. The reaction after revaporization showed no deviation from 3/2-order kinetics, picking up where it had left off with no change in rate. This observation points to enhanced initiation by a trace impurity, although surface poisoning by a minor condensible product cannot be completely ruled out. The two most likely trace impurities which might cause enhanced initiation are N₂H₂ and oxygen. There is some evidence that the former is produced in small amounts in the synthesis of methyldiimide; diimide decomposes much faster than methyldiimide and would probably be consumed in the early stages of the reaction. On the other hand, free radicals do not seem to be involved in the thermal decomposition of diimide, although this may reflect an inefficient propagation rather than a lack of initiation. Oxygen has a spectacular effect on the decomposition of methyldiimide¹⁴ and in trace amounts might well cause enhanced initiation.

The enhanced rate at low pressures is less easily explained. If this is attributed solely to an increase in the rate of initiation, values of k_1 can be calculated. These are shown as a function of pressure in Figure 8. At the lowest pressure employed k_1 is enhanced by a factor of 10 above its high-pressure value. One might invoke surface poisoning (by CO₂) or saturation of more active sites by CH₃NNH to account for the fall in k_1 with increasing pressure, but this cannot be reconciled easily with the first-order initiation required for the observed overall 3/2-order kinetics. Alternatively a pressure-dependent diffusion of initiating radicals away from the surface might be suggested, but this should probably result in a steady decrease in k_1 with increasing pressure, not a levelling out as observed, and it seems questionable if such a nonhomogeneous system could exhibit the relatively simple kinetics observed. No simple explanation of the pressure dependence of k_1 can be seen at the present time.

Evaluation of k₈ and k₉, Rate Constants for the Propagation Steps. It is evident from eq 15 that k_8 can be evaluated from the slope of Figure 6, knowing k_{10}^{10} and k_2 ; values determined in this way are shown in Table III, and are seen to be independent of methyldiimide pressure, added CO₂, and the kinetic chain length. From eq 17, taking $E_{10} = 0$, E_8 is 5.2 kcal/mol, which can be combined with a value of k_8 from Table III to give a frequency factor $A_8 =$ $7.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This is a very large value for a bimolecular reaction, approaching the collision rate. It is not clear why this frequency factor is so large even though the CH₃NN-H bond is expected to be weak (cf. D(HNN-H) \simeq 75 kcal/mol¹¹); the equivalent reaction with HI ($D(H-I) \simeq$ 70 kcal/mol) has¹² E = 2.3 kcal/mol and $A = 3.2 \times 10^9$ M⁻¹ s^{-1}

Values of k_8 can also be obtained from $k_{3/2}$ for the thermal decomposition via eq 15, having established k_1 as described earlier. Values are shown in Table III together with some other parameters of the thermal reaction. Chain lengths are very large, approaching 10⁶, much larger than in the photolysis because the rate of initiation is much lower.

Only a lower limit can be estimated for k_9 . In the steady state, $k_9[NNH] = k_8[CH_3][CH_3NNH]$. At the highest pressure at which the reaction was studied (500 Torr), 3/2order kinetics were still obeyed, and the approximate assumption may be made that $[CH_3]/[NNH] \ge 10$. It follows that $k_9 \ge 10k_8[CH_3NNH] \ge 3 \times 10^6 \text{ s}^{-1}$ at 22 °C. This corresponds to $E_9 = 5.9$ kcal/mol for $A_9 = 10^{11}$ s⁻¹, which might be compared with E = 15 and $A = 2 \times 10^{10}$ estimated for the decomposition of the isoelectronic acetyl radical,¹⁰ which is considerably more stable than CH₃NN. It should be emphasized that our estimate of k_9 is a lower limit and that it may be much larger than E_9 correspondingly smaller. It should also be noted that E_9 cannot be equated to the bond dissociation energy (which is probably negative) since the reverse reaction of CH_3 with N_2 would almost certainly have a sizeable activation energy.⁹

Concluding Remarks

The present study has shown that both the thermal and photochemical decompositions of methyldiimide in the gas phase proceed by an unusually efficient radical chain reaction which in the thermal reaction at room temperature may have a chain length greater than 10^5 . Methyldiimide owes its instability to this enormous chain length which makes the thermal decomposition at 22 °C moderately fast even with a very low rate of initiation, and renders the system very sensitive to light. The magnitude of the chain length depends on the high speed of the propagation step, reaction 8, which in turn depends partly on a low activation energy which reflects a rather weak CH₃NN-H bond, but more especially on an exceptionally high frequency factor.

In marked contrast to methyldiimide, diimide itself, though less stable at room temperature, appears to decompose by a very efficient bimolecular, nonradical process.⁶ Radical chains can be generated in the gas-phase photolysis of diimide,⁸ but these are shorter than those observed for CH₃NNH consequently diimide appears to be less light sensitive, although primary yields of radicals in the two systems are probably similar. The propagation step in diimide analogous to reaction 7 should be as fast or faster, and the inefficiency of the chain must be attributed either to a competing addition reaction which yields rather unreactive N₂H₃ radicals, or to the greater stability of N₂H compared to CH₃NN. It is curious that while both diimide and methyldiimide decompose fairly quickly at room temperature, each owes its instability to a quite different cause. Neither molecule is inherently unstable at room temperature, i.e., neither molecule undergoes appreciable unimolecular decomposition, and the H-N bond dissociation energies are probably higher than those of the C-N bonds in azomethane, which is completely stable below 200 °C. Azomethane does not support a radical chain reaction at low temperatures, and even in its high temperature decomposition only very short chains are observed.⁵ This is partly due to much slower abstraction of H from the methyl groups, but also to the high stability of the CH₃NNCH₂ radical which does not decompose appreciably below 200 °C. Thus while CH₃NNCH₃, CH₃NNH, and HNNH are superficially similar, they show markedly different behavior in their thermal decompositions and their free radical reactions.

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- These were corrected for thermal initiation on the basis of eq 14.
- (14) We have confirmed the observation by Ackermann et al.⁴ that methyldiimide explodes with some violence on mixing with oxygen in the gas phase at room temperature

Rates of Reactions CIO + CIO \rightarrow CI₂ + O₂ and CIO + O \rightarrow CI + O₂ at Elevated Temperatures

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A mixture of ozone and chlorine, diluted by oxygen and argon, was heated by reflected shock waves in a shock tube to temperatures and pressures in the range 1000–1400 K and 3.5-9 atm. From the variations in the concentration of ClO, determined via attenuation of the 2537-Å radiation, the rate coefficient for the reaction $ClO + ClO \rightarrow Cl_2 + O_2$ was determined to be $(1.4 \pm 0.7) \times 10^{-12} \text{ cm}^3/\text{s}$ at 1250 K. Similarly, the ratios of the rate coefficients for $ClO + O \rightarrow Cl + O_2$ to those for $Cl_2 + O \rightarrow ClO + Cl$ were found to be 26 ± 6 at 1250 K. If the coefficient value for the latter is $9.3 \times 10^{-12} \exp(-1560/T)$ as obtained by Clyne and Coxon, then the coefficient for the former would be $(7 \pm 1.5) \times 10^{-11} \text{ cm}^3/\text{s}$ at 1250 K.

Introduction

The kinetics of reactions involving chlorine and oxygen have been studied fairly extensively in the past with purely academic interest (e.g., ref 1). In particular, atomic chlorine and chlorine oxide radicals are highly reactive and undergo many interesting reactions. The interest in the chlorineoxygen system has been recently renewed with the concern over the possible role of chlorine in the chemistry of the upper atmosphere.²⁻⁵ In addition to natural causes such as the evaporation of sea water and volcanic eruptions,^{2,3} human activities such as the launching of solid-fuel rockets⁴ or the release of chlorofluoromethanes in the form of refrigerants or aerosol propellants⁵ are now thought to inject chlorine into the atmosphere. Once released into the atmosphere, chlorine could react via several processes ultimately to remove atmospheric ozone. Because of the seriousness of the possible consequences, more research is needed on the chemical kinetics involving chlorine and oxygen. One question remaining presently unanswered is the reaction rates of the chlorine-oxygen system at the temperatures prevailing in the upper atmosphere, i.e., around 200 K. Experiments are hampered by the fact that chlorine and its compounds tend to condense at such low temperatures. To circumvent this problem the reaction rates can be measured at high temperatures. Knowledge of the rates at both room temperature and at a high temperature would be helpful in estimating the rate values at low temperatures.

In the present work, a shock tube was employed to measure the reaction rates of chlorine-oxygen systems at high temperatures. A shock tube is capable of producing a high temperature and a high pressure uniformly throughout the test sample without being affected by the heterogeneous chemical reactions at the wall. By passing a shock wave through a gas mixture, one can heat the gas suddenly and cause a thermal decomposition⁶ of a species, e.g., ozone in the present study, which then produces a series of reactions that can be studied. This process is comparable with photolysis experiments¹ employed in past studies of the chlorine-oxygen system, in which the reactions are initiated by photodissociation of a species by a high flux of photons. In comparison with the photolysis experiments, a shock tube has the following two advantages: (i) the products of thermal decomposition are electronically unexcited as opposed to those of photolysis, which tend to be a mixture of excited and unexcited species; and (ii) the temperature, pressure, and species concentration in the reacting gas is more uniform in the shock tube than in a photolysis test.

In the present experiment, a mixture of chlorine and ozone, diluted by oxygen and argon, was heated by two consecutive shock waves, i.e., a primary and a reflected wave, within a time span of the order of 10 μ s, to produce a temperature in the range 1000-1400 K and a pressure in the range 3.5-9 atm. The primary shock produces a temperature below 800 K and is considered to cause no chemical change within the time span allowed. The reflected shock decomposes ozone thermally within 2 μ s typically, and the resulting atomic oxygen reacts with molecular chlorine to produce ClO. The variation in the ClO concentration after the passage of the reflected shock is observed by monitoring the intensity of 2537-Å radiation passing through the test gas. From the variation pattern, the rates of two reactions, $ClO + ClO \rightarrow Cl_2 + O_2$ and $ClO + O \rightarrow Cl$ $+ O_2$, are deduced.

Experimental Section

The driven and the driver sections of the shock tube are 3.8 and 1.8 m long, respectively, and have a common internal diameter of 5.1 cm (see Figure 1). The driven section was constructed of Pyrex and stainless steel. Three fibrereinforced Pyrex tubings (Corgard, Corning Glass Works) with the lengths of 0.9, 0.9, and 1.8 m, respectively, formed most of the length of the driven section. Stainless steel cylinders 3.2 cm long were inserted between the Pyrex pieces so that pressure transducers, windows, and plumbing attachments could be mounted. The end-wall of the driven section was also made of stainless steel. Optical measurements were made near the end-wall of the driven section through four quartz windows 1.27 cm in diameter and placed at 90° to each other around the tube. The distance between the optical axis and the end-wall surface was varied between 0.3 and 1.5 cm by varying the thickness of a gasket. Three pressure transducers were employed, two along the tube on the stainless steel pieces and one on the end-wall. There was an interval of 94 cm between the first two transducers and an interval which varied between 93.8 and 95 cm between the second and the third transducers, depending on the thickness of the gasket. The velocity of 566



Figure 1. Schematic of shock tube setup.

the primary shock wave was determined from the pressure signals from the three transducers, using digital clocks accurate to 0.1 μ s.

The driven section was evacuated by a large rotary pump via a liquid nitrogen trap before charging the test gas. The vacuum system attained a vacuum of 2×10^{-3} Torr within 5 min of pumping and had an apparent leak (or outgassing) rate of less than 5×10^{-3} Torr/min. Using a mass spectrometer, the residual gas was found to contain 5–10% $\rm CH_4$ by volume (the rest consisted of N₂, O₂, CO₂, and H₂O, which could all be considered inert in the present test). The molecule CH₄ reacts with atomic chlorine¹ and hence could affect the measurements. The CH4 concentration attained was considered negligible in the present test, however, since at this level the rate of Cl removal by CH4 would be negligibly small compared with the rates of production¹ by the reactions under study. Diaphragms were made of Mylar with thicknesses in the range of 0.05-0.13 mm. They were ruptured passively, i.e., by the high pressure in the driver section. The driver gas was unheated helium at a pressure between 3-11 atm. Typically 2-3 min elapsed between the vacuum pump shutoff and the firing of the shock tube. No significant chemical reaction is expected to occur in the measuring region within this time period.

The attentuation of 2537-Å radiation passed through the test gas was measured. A microwave-excited mercury lamp provided the 2537-Å radiation. The beam was passed diametrically through the test gas via a combination of optical filters and aperture baffles and was received by a Hamamatsu R-106 photomultiplier tube. The aperture between the light source and the test gas limited the intensity of radiation incident on the test gas so that significant photodissociation of the species under observation did not occur. The aperture between the shock tube and the photomultiplier tube minimized the radiation emitted by the test gas reaching the phototube. The output from the photomultiplier tube was displayed on an oscilloscope via a logarithmic amplifier. The photoelectric system had a rise time of approximately 2 μ sec to reach 90% of a steady-state output. The attenuation data were used quantitatively in the determination of the reaction rate values.

In addition to the quantitative attenuation measurement, the shock tube was equipped with two additional means of spectral analysis, i.e., emission measurement and flash lamp-absorption spectroscopy. Through the windows offset 90° to the optical axis of the absorption measured described above, two wide-band monochromators could be placed simultaneously to measure the radiation emission from the test gas. The monochromators consisted of a photomultiplier housed behind a filter. Otherwise, a beam of



Figure 2. Typical oscillograph record of end-wall pressure and attenuation of 2537 Å; Cl₂ at a reflected zone condition of 1024 K and 10.9 atm, $p_1 = 0.200$ atm, $U_s = 621$ m/s.

radiation produced by a xenon flash lamp could be passed through the windows, to be received by a spectrograph. A $\frac{3}{4}$ -m Spex Czerney-Turner spectrograph was used for this purpose. The spectrograph had a linear dispersion of 11.1 Å/mm, and could record the absorption spectra over a range of approximately 400 Å at a time. The data from the monochromators and the absorption spectra were used qualitatively in verifying the chemical composition of the test gas.

Ozone was produced by passing oxygen of 99.99% purity through an ozonator, in which oxygen is converted into ozone by an electrodeless electric discharge to a concentration of approximately 6% by volume. The purity of chlorine and argon used was 99.99 and 99.999%, respectively. The test gas mixture was prepared by introducing chlorine, the ozone-oxygen mixture, and argon sequentially into the shock tube through a gas-dispersing tube (see Figure 1). The dispersing tube consisted of a stainless steel tube 6.3 mm in o.d. and 4.8 mm i.d. spanning the entire length of the driven section with 0.343-mm holes drilled at 38-mm intervals throughout. Mixing was virtually instantaneous with the use of the dispersing tube.

The conditions in the test gas behind the reflected shock wave were deduced from both the speed of the primary shock wave and the end-wall pressure (see Figure 2). The velocity of the primary shock wave was attenuated between the two observation intervals so that the shock velocity was decreased by about 4% in the last 100 cm. When the shock attenuation was accounted for in the velocity determination, the end-wall pressures predicted through the use of the Rankine-Hugoniot relation agreed with the measured end-wall pressures to within the reading resolution of the oscillogram. The solutions to the Rankine-Hugoniot relation were obtained numerically by a computer, allowing for the change in the chemical composition across a shock wave and assuming the attainment of chemical equilibrium. The equilibrium thermodynamic properties of the gases involved were obtained from the JANAF Thermochemical Tables⁷ with the exception of ClO, for which updated data supplied by D. D. Wagman of the National Bureau of Standards was used. The updated ClO data result typically in a 2% lower concentration of ClO in an equilibrium chlorine-oxygen system at 2000 K compared with the JANAF Table data, while virtually no difference can he seen below 1000 K. The errors in determining the conditions of the test gas behind the reflected shock can be



Figure 3. Absorption spectra of 6.3% Cl₂, 1.5% O₃, and 92.2% O₂ mixture reacting in a reflected zone at 1180 K and 5.1 atm; $p_1 = 75$ Torr, $U_s = 964$ m/s: light source, xenon flash tube. Equivalent spectrograph entrance slit width = 0.28 Å.

caused in the present procedure by (i) the instrument noise in the pressure transducer, amplifier, and digital clocks, (ii) the error in assessing the effect of shock attenuation accurately, (iii) the reading error of the oscillogram, and (iv) the numerical errors involved in solving the Rankine-Hugoniot relation. The largest of these errors would be the reading resolution of the oscillograph, which is typically of the order of 3%. The reading error results mainly from the electronic oscillation, referred to commonly as "ringing" in the pressure transducer-amplifier circuit (see Figure 2). The possible reading errors result in a temperature uncertainty of the order of ± 15 K in the present experiment. This uncertainty is the principal source of error when the reflected-shock region is used for a kinetic study. In the reflected-shock region, the gas under observation is at rest and therefore does not present any additional uncertainty caused by the motion of the test gas. This situation is in contrast to the measurement behind a primary shock wave, where the motion of the test gas presents an uncertainty due to possible spatial nonuniformity along the shock tube such as that caused by the growth of a boundary layer.

Test Procedures and Results

1. Absorption Spectra. Before undertaking quantitative measurements, the compositions of the gas samples behind the reflected shock wave were studied qualitatively by means of absorption spectroscopy. The light source used for this purpose consisted of a xenon flash tube 3 mm i.d. and 38 mm arc length, flashed typically with 70 J of electric energy stored in a 2- μ F capacitor charged approximately to 8.5 kV. The discharge was moderately underdamped; one cycle of excursion to the opposite polarity was observed. The zero current point was crossed typically at around 15 μ s after the initiation of the arc, while the extinction of the arc occurred at around 50 μ s.

Figure 3 shows the absorption spectra for the wavelength range of 2600-3050 Å taken under conditions qualitatively identical with those in the main tests, i.e., a mixture of chlorine, oxygen, and ozone undergoing reactions behind a reflected shock wave. For the test, the width of the entrance slit of the spectograph was set at 25 μ , which is equivalent to a spectral bandwidth of 0.28 Å. Tri-X Panchromatic film was used and developed by D-19 developer for 5 min at 30 °C. The flash tube discharge was initiated at the instant the reflected shock passed the optical axis. The gas under observation consisted therefore of a mixture of Cl₂, O₂, O₃, Cl, O, and ClO; ClO was the main product, in a transient nonequilibrium state, of the reactions between



Figure 4. Densitographs of absorption spectra: (B) $p_1 = 20$ Torr, 32% O₂, 68% Ar; $p_5 = 3.6$ atm, $T_5 = 3070$ K ($U_s = 1380$ m/s); (C) $p_1 = 20$ Torr, 39% Cl₂, 61% Ar; $p_5 = 3.2$ atm, $T_5 = 2110$ K ($U_s = 1270$ m/s); (D) $p_1 = 75$ Torr, 6.4% Cl₂, 1.5% O₃, 91.1% O₂; $p_5 = 4.8$ atm, $T_5 = 1190$ K ($U_s = 973$ m/s); (E) $p_1 = 18$ Torr, 14.4% Cl₂, 26.7% O₂, 58.9% Ar; $p_5 = 4.0$ atm, $T_5 = 2250$ K, (ClO)₅ = 2 X 10^{16} cm⁻³. Equivalent spectrograph entrance slit width = 0.58 Å.

chlorine and ozone. As seen in Figure 3, the only distinct structure is that of ClO, except for self-absorption by xenon (see below) at around 2880 Å. This result is expected: molecular chlorine and ozone absorb only in continuum in this wavelength range; oxygen has a band absorption but it is too weak to appear here; and atomic chlorine does not absorb in the present wavelength range.

Figure 4 is an overlay of densitographs of spectra taken under five different conditions. All five traces were obtained with a spectrograph slit width of 50 μ , which corresponds to a spectral bandwidth of 0.56 Å. The film and its development method were the same as for Figure 3. In the figure, trace A shows the spectra of the light source to be nearly a continuum except for a deep self-absorption at around 2880 Å. Trace B is for oxygen at 3070 K, and shows the absorption below 2800 Å by the Schumann-Runge band from the vibrationally excited oxygen molecules. The spectra are taken only for reference; the Schumann-Runge band was not observed below 2100 K where the quantitative measurements were undertaken.

Trace C confirms that the absorption by chlorine is totally continuous even at an elevated temperature. Trace D, taken under conditions nearly identical with those for Figure 3 but with a different slit width, shows the same ClO band structure. As noted in the figure, the ClO concentration observed here represents a transient, nonequilibrium value. In contrast, trace E was taken with an equilibrium mixture of Cl₂, Cl, O₂, and ClO. This result was obtained by shock processing a mixture of Cl_2 and O_2 , and flashing the xenon light source at 500 μ s after the passage of the reflected shock. A time period of 500 μ s is considered long enough for the gas mixture to attain equilibrium. The concentrations of the gas species involved in this run were lower than those for trace D, and hence the absorption is not as pronounced. Nevertheless, the similarity between traces D and E with regard to the ClO band system is clearly recognizable.

2. Absorption Cross Sections of Cl_2 and ClO. Since the concentration of ClO is determined in the present work from the attenuation of 2537-Å radiation, accurate knowledge of the absorption cross section at that wavelength is essential. An absorption cross section σ (in cm²) as used in



Figure 5. Absorption cross section of Cl_2 at 2537 Å over a range of temperature.

the present work refers to that associated with base e instead of base 10, i.e., with the relation $I/I_0 = \exp(-\sigma nL)$, where I_0 and I refer, respectively, to the intensities of radiation before and after the passage through the absorbing media, n is the concentration of the absorbing media in cm⁻³, and L is the optical pathlength in cm. Since the absorption cross section of ClO is known only at room temperature, it was necessary to determine the values at the required high temperatures before the rate measurements could be undertaken. In order to determine the cross sections for ClO, however, it was necessary first to determine the cross sections for Cl₂ in the same temperature range; Cl₂ would exist with ClO in an experimental environment designed to yield the ClO cross section.

The absorption cross sections of Cl₂ at room temperature have been measured by Seery and Britton⁸ over a wide wavelength range. At 2537 Å, their data give the cross section as 1.48×10^{-21} cm². In the present work, the cross section measurement was repeated using the shock tube as an absorption cell. The cross section was found to be (8.4 \pm 0.2) $\times 10^{-22}$ cm². This discrepancy is presently unexplained.

To measure the cross sections at elevated temperatures, the shock tube was operated with chlorine as the test gas in the driven section. The charging pressure in the driven section was varied between 0.02 and 1.5 atm, and the shock velocity was between 275 and 1270 m/s. A typical oscillogram trace is shown in Figure 2. As seen in the figure, the intensity I decreases each time a shock wave passes the optical path, as expected. The results of the measurement in terms of absorption cross section are shown in Figure 5; the cross section increases rapidly with temperature. This result is not unexpected; at high temperatures, the excited vibrational levels of the lower electronic state involved will be populated. Some of these levels may have Frank-Condon factors greater than those for the vibrational ground state from which an absorption occurs at room temperature. The measured data are fitted in the figure with a curve derived under the assumption that (i) the vibrational energy spacing is even, i.e., harmonic, and (ii) the cross sections for the vibrational levels vary by a second-order polynomial in the vibrational quantum number v. Assumption i leads to the expression for the net cross section for Cl₂

$$\sigma = (1 - \exp(-807/T)) \sum_{v} \sigma_{v} \exp(-807v/T) \text{ cm}^{2}$$

where σ_v is the absorption cross section for the vth vibrational level. The summation here is taken from v = 0 to v =19. A best fit is obtained by selecting the polynomial to be



Figure 6. Absorption cross section of CIO at 2537 Å as a function of temperature.

$$\sigma_{\nu} = (4.5 + 37\nu + 15\nu^2) \times 10^{-22} \,\mathrm{cm}^2$$

The scatter in the data indicates an uncertainty in the cross section value of the order of $\pm 15\%$ around the curve at temperatures above 1000 K. At lower temperatures, the uncertainty decreases, converging to approximately $\pm 4\%$ at room temperature.

In order to measure the absorption cross section of ClO, the shock tube was operated with a mixture of chlorine, oxygen, and argon. The concentration ratio between Cl₂ and O_2 was kept at around 1:10 while the fraction of argon was varied between 0 and 70%. The charging pressure and shock velocity were between 10 and 76 Torr and between 1020 and 1350 m/s, respectively. The temperature behind the reflected shock was between 1660 and 2120 K, while the pressure varied between 2.5 and 6.5 atm. The oscillogram records (not shown) indicated that a steady state, considered to be equilibrium state, was reached within around 20 μ s, and remained so for the first 500 μ s. Based on this test and from the equilibrium thermodynamic calculations, it was concluded that the test gas consisted of O₂, Cl₂, Cl, ClO, and argon in the reflected shock region. (The atomic oxygen concentration was negligible.) The ratio of ClO to Cl_2 concentrations were always greater than 0.01, while the absolute concentration of ClO varied from 6.3×10^{15} to 2.2 $\times 10^{16} \, \mathrm{cm}^{-3}$

The 2537-Å beam is expected to be absorbed only by Cl₂ and CIO in the equilibrium region; absorption by O_2 is confirmed to be negligible in the tested temperature range through separate absorption tests with oxygen only. Using the cross section data of Figure 5 for Cl₂, the contribution by Cl₂ to the overall absorption was subtracted from the total absorption in order to determine the portion of the absorption attributable to ClO. Under the operating conditions chosen, ClO was always the major absorber i.e., greater than 50%. This procedure results in the cross section data shown in Figure 6. As seen in the figure, the cross sections at the tested temperatures are nearly the same as at the room temperature. The observed results are not surprising. Unlike Cl₂, the cross section for ClO at room temperature is observed to be nearly the maximum possible value; excitation into higher vibrational levels does not raise the overall absorption cross section beyond the maximum. The measurement could not be extended to other temperature ranges because dissociation of O2 tends to complicate the measurement at higher temperatures, while the CIO concentration becomes too low at lower temperature regions. The measured data are fitted in Figure 6 with a curve based on the same assumption as for Cl₂, which is

$$\sigma = (1 - \exp(-1236/T)) \sum_{\nu=0}^{7} \sigma_{\nu} \exp(-1236\nu/T) \text{ cm}^2$$
$$\sigma_{\nu} = (4.35 - 0.55\nu) \times 10^{-18} \text{ cm}^2$$

The observed scatter in the data indicates an uncertainty of the order of $\pm 10\%$ around the mean. Combined with the uncertainty in the Cl₂ cross section, the estimated uncertainty in the cross section value for ClO for 2537-Å radiation in the tested tempeaature range is around $\pm 15\%$.

3. Kinetics of Ozone Decomposition in Cl_2-O_3 System. To measure the rate coefficients for the two reactions under study, i.e., $ClO + ClO \rightarrow Cl_2 + O_2$ and $ClO + O \rightarrow Cl$ + O_2 , the shock tube was operated with a mixture of ozone, chlorine, oxygen, and argon. The concentrations of these species were typically (O_3) : (Cl_2) : (O_2) : $(A) \simeq 1:5:25:500$. The charging pressure was varied between 0.2 and 1 atm, and the velocity of the primary shock wave was between 540 and 810 m/s. These operating conditions produced a temperature in the range of 1000-1400 K and pressure from 3.5 to 9 atm behind the reflected shock. Temperatures and pressures behind the primary shock were roughly half the reflected-shock values. The distance between the optical axis and the end-wall surface was kept at around 0.5 cm for these tests. Under these conditions, the bulk of the gas mixture being observed undergoes the two shock compression processes within an interval of the order of 10 μ s. During this period, no significant chemical change can occur since the prevailing temperature is too low to cause any change. Significant chemical changes occur only after the gas passes the reflected shock wave. Decomposition of ozone and formation of ClO and Cl can occur there by the following reactions

$$O_3 + M \rightarrow O_2 + O + M \qquad (k_1) \qquad (R_1)$$

$$Cl_2 + 0 \rightarrow ClO + Cl$$
 (k₂) (R₂)

$$O_3 + Cl \rightarrow ClO + O_2 \qquad (k_3) \qquad (R_3)$$

$$ClO + O \rightarrow Cl + O_2 \qquad (k_4) \qquad (R_4)$$

where M represents the third body which consists mainly of argon. Other possible reactions. including $O_3 + O \rightarrow O_2$ + O_2 which is usually significant, are much slower than R_1 through R_4 , and hence can be neglected within the time span of concern. Among these reactions, R_2 , R_3 , and R_4 are so fast that a quasi-steady-state condition exists for the atoms involved. That is, O and Cl concentrations satisfy the approximate relations

$$d(O)/dt = k_1(O_3)(M) - k_2(O)(Cl_2) - k_4(ClO)(O) \simeq 0$$

$$\frac{d(Cl)}{dt} = k_2(O)(Cl_2) - k_3(Cl)(O_3) + k_4(ClO)(O) \simeq 0$$

By solving the last two equations, one obtains

$$(0)_{s} \simeq \frac{k_{1}(O_{3})(M)}{k_{2}(Cl_{2}) + k_{4}(ClO)}$$
$$(Cl)_{s} \simeq (k_{1}/k_{3})(M)$$

in which the subscript s refers to the quasi-steady-state condition. Using the $(Cl)_s$ expression for (Cl), the rate of change of ozone can be expressed by

$$\dot{a}(O_3)/dt = -2k_1(O_3)(M)$$

Likewise, using both (O)s and (Cl)s, the rate of change in (ClO) becomes

$$\frac{d(ClO)}{dt} \simeq \frac{2k_1(O_3)(M)k_2(Cl_2)}{k_2(Cl_2) + k_4(ClO)}$$

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The last two differential equations are now integrated simultaneously from time t = 0 to $t = t_1$ where t_1 is such time that decomposition of ozone can be considered to be finished. The time is typically 2 μ s under the present operating conditions. For an approximate solution, the concentration of Cl₂ can be considered constant because only a small fraction (less than 20%) of Cl₂ is converted to ClO or Cl. The approximation leads to the expression

$$\frac{k_4}{k_2} \simeq 2 \frac{(\text{Cl}_2)}{(\text{ClO})_1} \frac{(\text{O}_3)_0}{(\text{ClO})_1} - 1$$

Since (ClO) will be much smaller than $(O_3)_0$, the last equation can be approximated further by

$$\frac{k_4}{k_2} \simeq 2 \frac{(\text{Cl}_2)(\text{O}_3)_0}{(\text{ClO})_1^2}$$

This expression shows approximately how the ratio k_4/k_2 is related to the ClO concentration at the end of ozone decomposition.

At $t = t_1$, the gas mixture consists of Cl, ClO, O₂, and argon. The dominant reaction in this region is the quadratic decomposition of ClO

$$ClO + ClO \rightarrow Cl_2 + O_2$$
 (k₅) (R₅)

$$ClO + ClO \rightarrow Cl + ClOO$$
 (k_5') (R_5')

The reverse of the reaction R_2 occurs also, but its rate is probably slower than R_5 . If the reverse of R_2 can be neglected, (ClO) satisfies the differential equation

$$d(ClO)/dt = -(k_5 + k_5')(ClO)^2$$

the solution of which is

$$\frac{(\text{ClO})}{(\text{ClO})_1} \simeq \frac{1}{1 + (k_5 + k_5')(\text{ClO})_1 t}$$

The formula shows the dependence of the shape of ClO concentration variation on the rate coefficient $k_5 + k_5'$.

The above-derived relationships for k_4/k_2 and (ClO)/(ClO)₁ are approximate to within ±20%. In determining the rate coefficients, a more accurate method was used involving a computer. A family of theoretical curves was generated with the computer by integrating the rate equations for (O₃) and (ClO) given above with k_4 and $k_5 + k_5'$ as variable parameters, allowing for the change in (Cl₂) and the reverse of R₂ to take place. The rate coefficient k_1 was taken from ref 9 for this purpose. The theoretical curves were then compared with the experimental trace, and the curve that most closely resembled the data was selected via a process of trial and error. The absolute rate coefficient values for k_4 were then deduced from the ratio k_4/k_2 , assuming k_2 to be given by the expression

$$k_2 = 9.3 \times 10^{-12} e^{-1560/T} \text{ cm}^3 \text{ s}^{-1}$$

obtained by Clyne and Coxon.¹⁰

The rate coefficient k_4 determined here can be regarded as pertaining to the oxygen atoms in their electronic ground state O(³P). In the thermal decomposition of ozone by R₁ at temperatures below 1500 K, the energies of colliding partners are too low to produce an excited atom O(¹D) which is at 2 eV above the ground state. This fact was confirmed in separate tests as follows. The shock tube was operated with a 5% O₃-95% O₂ mixture to a total pressure of around 100 Torr, and the radiation emitted from the gas behind the reflected shock was measured using two monochromators (see Experimental Section). The reflectedshock temperature attained was approximately 1000 K



Figure 7. Typical oscillograph record of a run with a mixture composed initially of 0.7% Cl₂, 0.17% O₃, 3.9% O₂, 95.2% Ar, at a reflected zone condition of 1366 K and 5.1 atm; $p_1 = 0.19$ atm.



Figure 8. Interpretation of experimental data on attenuation of 2537 Å shown in Figure 5.

while the pressure was approximately 4 atm. The pass wavelengths of the monochromators were varied from approximately 2200–7700 Å between each run. The results indicated that the radiation was emanating over a range from about 3000 Å to the longest wavelength measured, the intensity being stronger toward the longer wavelength. The radiation was considered to be that of the oxygen atmospheric band. The absence of emission below 3000 Å proves that $O(^{1}D)$ does not exist. If $O(^{1}D)$ atoms were present to any significant concentration, they would have formed the complex $B^{3}\Sigma_{u}^{-}$ through collision with the ground state O atoms, resulting in emission in the Schumann-Runge band with wavelengths below 3000 Å.

4. Rate Data. A typical oscillogram obtained from the experiment is shown in Figure 7. The top photograph in Figure 7 shows the variation in the end-wall pressure and the intensity of the 2537-Å radiation attenuated by the test gas over the duration of the available test time. As seen in the figure, the change in intensity occurs within a small fraction of the total available time. The lower photograph shows the details of the intensity variation within the first 100 μ s. The two reference traces in the figure were recorded prior to the measurement. Figure 8 compares the oscillograph trace with the theoretical curves calculated assuming



Figure 9. Arrhenius plot for the rate of bimolecular removal of CIO. The present data represent the high-pressure limiting case corresponding to the first branch. The dotted line connects the present data to the high-pressure limit value at 300 K recommended by Watson. At low pressures, the second branch becomes important.



Figure 10. Arrhenius plot for the CIO + O reaction. The dotted curve extends the present data to lower temperature assuming constant reaction cross section and zero barrier. The rate coefficient for the reaction $CI_2 + O \rightarrow CI + CIO$ was assumed as $k_2 = 9.3 \times 10^{-12} exp(-1560/7) cm^3/s$.

different combinations of the constants k_4 and $k_5 + k_5'$. As shown in the figure, the noise in the trace is equivalent to an uncertainty of about $\pm 25\%$ in k_4 but a factor of about 1.5 for $k_5 + k_5'$.

Figures 9 and 10 summarize the rate coefficient values obtained, and compare them with available data.¹¹⁻¹⁵ The present data shown in Figure 9 indicate a median of around $1.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 1250 K. The measured rate coefficient value is linearly affected by the absorption cross section of ClO used. Considering the ±15% uncertainty in the cross section and the observed scatter of the data, the uncertainty factor in the rate data was judged to be $10^{\pm 0.3}$. Data shown in Figure 9 represent the total second-order rate coefficient and do not distinguish between the two possible branches of the quadratic reaction R_5 and R_5 ; in most tests, including the present work, the branching ratio was not measured independently. The low values such as those by Clyne and Coxon¹¹ were taken at low pressures (below 10 Torr). The present data and the data by Basco and Dogra¹³ were obtained at high pressures (above 100 Torr). The figure thus confirms the trend pointed out earlier (see, e.g., Watson¹) that the net rate of removal is faster at high pressures. This phenomenon had been attributed¹ to the difference in the degree of contribution of the second branch; the second branch becomes significant only at low pressures. To be consistent with this explanation, the

present data were interpreted as pertaining to the first branch R5 only. The dotted curve, expressed by

$$k_5 = 4.2 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ s}^{-1}$$

connects the median of the present data with the existing high pressure limit value at the room temperature.

In Figure 10, the present results on the ClO + O reaction are compared with the available data^{13,16,17} at room temperature. The median of the present data is $k_4 = 7 \times 10^{-11}$ $cm^3 s^{-1}$ at 1250 K. Since the rate coefficient is quadratically dependent on the ClO absorption coefficient used, the uncertainty in the rate value obtained is caused mainly by the uncertainty in the cross section, and was considered to be approximately $\pm 20\%$. Because the existing data are at a totally different temperature, comparison is not meaningful. However, if one assumes a zero barrier and a constant reaction cross section, assumptions considered appropriate to the fast exchange reaction concerned, the observed result can be extended into the low temperature region by

$$k_4 = 3.5 \times 10^{-11} \sqrt{T/300} \text{ cm}^3 \text{ s}^-$$

as indicated by the dotted curve. At 300 K, the dotted curve passes between the room temperature data points, showing the compatibility of the present results with the existing low temperature data. It is noted here again that the present experiment measures the ratio of the coefficients k_4/k_2 and that the absolute values shown in Figure 10 were derived by taking an existing set of values for k_2 .

Conclusions

At pressures in the range 3.5-9 atm and temperatures between 1000 and 1400 K, the rate coefficients of the sec-

ond-order decomposition of ClO, attributed mostly to ClO + ClO \rightarrow Cl₂ + O₂, are found to be in the range $k_5 = (4.2 \pm$ 2) \times 10⁻¹²exp(-1350/T) cm³ s⁻¹, the median value being 1.4×10^{-12} at 1250 K. In the same range of pressure and temperature, the ratio of the rate coefficient k_4 for the reaction ClO + O \rightarrow Cl + O₂ to k_2 for Cl₂ + O \rightarrow ClO + Cl is such that if $k_2 = 9.3 \times 10^{-12} \exp(-1560/T)$, then $k_4 = (7 \pm 10^{-12})$ 1.5) \times 10⁻¹¹ cm³ s⁻¹, the oxygen atom involved here being in the electronic ground state. The rate coefficient values are compatible with the existing data obtained in the lower pressure and temperature ranges.

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Reaction of Ozone with 1,1-Difluoroethane and 1,1,1-Trifluoroethane

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The reaction of ozonized-oxygen with 1,1-difluoroethane and 1,1,1-trifluoroethane was studied in thermostated, infrared gas cells, in the temperature range 34-86 °C. The products observed in the case of the latter were carbon dioxide. carbonyl fluoride, formic acid, and water, while the ozonation of 1,1-difluoroethane yielded, in addition to the above, carbon monoxide, acetyl fluoride, and acetic acid. The overall activation energy, calculated on the basis of the equation $-d[O_3]/dt = k[O_3][hydrocarbon]$, was found to be 15.8 ± 0.4 kcal mol⁻¹ for 1,1-difluoroethane and 17.5 ± 0.5 kcal mol⁻¹ for 1,1,1-trifluoroethane. The preexponential terms were $2.61 \pm 0.07 \times 10^8$ and $6.34 \pm 0.24 \times 10^8$ M⁻¹ s⁻¹, respectively.

Introduction

While substantial work has been done on the reaction of ozone with the paraffin hydrocarbons,¹⁻⁶ its reaction with the fluorine-substituted members of this series has not been studied, although Heicklen⁷ has reported the results of his investigations on the ozonation of perfluoroolefins. As a continuation of our program of hydrocarbon oxidation studies, we have investigated the reaction of ozone with several fluorine-substituted paraffins in order to determine whether the reaction kinetics are affected by the presence of a strong electron-withdrawing atom in the molecule. Reported here are the results of studies on the reaction of ozonized oxygen with 1,1-difluoroethane and 1,1,1-trifluoroethane.

Experimental Section

Ozone enriched oxygen was prepared by passing pure, dried oxygen through a Welsbach ozonizer which yielded a mixture ca. 3 mole percent in ozone. Higher concentrations of ozone were obtained by allowing this mixture to pass through a silica gel trap cooled to -78 °C with acetone and dry ice. Subsequent desorption at higher temperatures in a stream of dried oxygen yielded enriched ozone concentrations in which the ratio $[O_3]/[O_2]$ was = 0.122. Matheson Co. 1,1-difluoroethane and 1,1,1-trifluoroethane obtained from Hynes Chemical Research Corp. were used without further purification. Analysis by gas chromatography showed no significant impurities. The hydrocarbon and the ozone-enriched oxygen, after passing through Bernouillitype flowmeters, were mixed in a capillary mixer and passed into a previously evacuated 10-cm infrared gas absorption cell to a total pressure of 1 atm. The reaction vessel and contents were then warmed to run temperature. Any reaction which might have occurred between filling the cell and the time the desired temperature was reached was found to be negligible.

The reaction was followed by in situ infrared analysis of the reacting gases.² A balancing cell which was filled with hydrocarbon at the same partial pressure as in the reaction cell allowed only those absorptions due to reaction products and ozone to be recorded. The cells were used in conjunction with a Perkin-Elmer Model 21 recording spectrophotometer. Ozone was measured at 1055 cm⁻¹, carbon monoxide at 2183 cm⁻¹, carbon dioxide at 2344 cm⁻¹, carbonyl fluoride at 1931 cm⁻¹, acetyl fluoride at 1880 cm⁻¹, formic acid at 1754 cm⁻¹, and acetic acid at 1715 cm⁻¹. The concentrations of ozone and products were calculated from calibration curves constructed from reference spectra run on pure compounds at various known partial pressures under conditions as similar as possible to those prevailing during the oxidations. Initial hydrocarbon concentrations were determined from the flow rates employed in making up the reaction mixtures.

The reaction cell was Pyrex with end windows of sodium chloride. A water jacket allowed temperature control to ± 0.2 °C. All stopcocks were lubricated with Kel-F grease which is ozone resistant and has a vapor pressure of less than 1×10^{-3} mm of mercury. Time zero was recorded from the moment the reaction cell was brought up to temperature.

Reaction of Ozone with 1,1-Difluoroethane

(a) Experimental Results. The major products of the ozone-1,1-difluoroethane reaction as determined by infrared analysis were found to be carbon dioxide, carbon monoxide, carbonyl fluoride, acetyl fluoride, formic acid, acetic acid, and water. Formaldehyde was never observed in any of the experiments though conceivably it might be present in trace quantities. A moderately strong band appeared at 1026 cm⁻¹ superimposed on the ozone absorption. This was most likely silicon tetrafluoride resulting from fluorine attack on the glass walls of the reaction vessel. A plot of the concentrations of ozone and products vs. time is shown in Figure 1. It can be noted that the curves for carbonyl fluoride and carbon dioxide show the typical



Figure 1. Concentration of ozone and reaction products at 39.9 °C.

behavior of consecutive reactions. At higher temperatures $(55-65 \, ^{\circ}C)$, the carbonyl fluoride formed disappeared rapidly, due to the hydrolysis of this compound to carbon dioxide and hydrogen fluoride.

A slight amount of unreacted ozone could usually be detected in the reaction vessel even when the reaction was virtually complete. The ozone concentration at this point, however, was of the order of 10^{-4} M or less.

The concentration of fluorinated hydrocarbon in this series of experiments was on the average 2.9×10^{-2} M. In no case was the initial ozone concentration in excess of 1.6×10^{-3} M.

On the basis of product yields it was possible to determine the ratio of the number of gram atoms of oxygen fixed in products to the number of moles of ozone consumed. It was found that on the average 1.8 gram atoms of oxygen were fixed for each mole of ozone consumed.

(b) The Effect of Surface. In order to determine whether or not a heterogeneous reaction was occurring together with the homogeneous gas phase oxidation, it was decided to investigate the effect of changing the surface to volume ratio of the infrared cell. This was effected by inserting either Pyrex tubing or regular sodium chloride crystals into the reaction vessel. The salt surface to volume ratio was increased from 0.2 to 1.0 cm^{-1} , and the Pyrex surface to volume ratio from 2.2 to 5.8 cm^{-1} . In neither case was any significant change in the rate of the reaction observed. Plots of the logarithm of ozone concentration vs. time for reactions of ozonized oxygen with 1,1-difluoroethane conducted in the packed and unpacked reaction cells at 55 °C are shown in Figure 2.

(c) *Kinetics*. Plots of the logarithm of ozone partial pressure vs. time, e.g., Figure 2, were found to be linear in every case. This indicated that the reaction was first order with respect to ozone. Points obtained after the partial pressure of ozone fell below 2 mm of mercury were considered unre-

Ozone Reaction with Fluorinated Ethane

4 TABLE I



Figure 2. Effect of added surface on react on rate.

liable since at these low values product absorption often interfered with the ozone peak at 1055 cm^{-1} .

Previous work with unsubstituted hydrocarbons^{2,5,6} indicates that the rate expression for the ozone-1,1-difluoroethane reaction is best given by

$$-d[O_3]/dt = k[O_3][CH_3CF_2H]$$

Since in these experiments the isolation technique was employed by making up the reaction mixtures with the hydrocarbon in large excess, its concentration was effectively constant during the course of each run. The activation energy was determined from Arrhenius-type plots of the logarithm of the reaction rate constant vs. the reciprocal of absolute temperature, e.g., Figure 3. The activation energy, the preexponential term A, calculated from the equation

$$k = A \exp(-E_a/RT)$$

the rate constant at 25 °C, and the entropy of activation are given in Table I.

Reaction of Ozone with 1,1,1-Trifluoroethane

(a) Experimental Results. Ozone was found to react approximately ten times more slowly with 1,1,1-trifluoroethane than with 1,1-difluoroethane. The only reaction products observed were carbon dioxide, carbonyl fluoride, and formic acid. No carbon monoxide, formaldehyde, or trifluoroacetic acid was observed in any of the experiments. In all cases the concentration of carbon dioxide was equal to or greater than that of carbonyl fluoride. A typical plot of the concentration of ozone and reaction products vs.

573

1/T °K X 103

Figure 3. Logarithm of reaction rate constant vs. reciprocal of absolute temperature for ozone-1,1-difluoroethane

time is shown in Figure 4. The initial concentration of 1,1,1-trifluoroethane was on the average 3.1×10^{-2} M while that of ozone was 1.4×10^{-3} M.

Product balances for the reaction of ozone with 1,1.1-trifluoroethane calculated on the basis of 30 independent runs showed that on the average 0.9 gram atoms of oxygen were fixed per mole of ozone consumed.

(b) Effect of Surface. Since the reaction of ozone with 1,1-difluoroethane and with other hydrocarbons^{3,5,6} was shown to be independent of surface, it was not thought necessary to investigate the possibility of surface effects in this case

(c) Kinetics. The kinetic parameters of the ozone-1,1,1trifluoroethane oxidation are given in Table I. They were calculated in the same manner as was reported for the previous reaction.

Discussion

The products observed in this work suggest that the preferred site of initial ozone attack on 1,1-difluoroethane is the hydrogen attached to the fluorine-substituted carbon atom rather than the hydrogen of the methyl group. The resulting radical, CH₃CF₂, can easily sustain the odd electron because of the high electronegativity of the adjacent fluorine atoms. With 1,1,1-trifluoroethane, the radical ·CH₂CF₃ cannot be easily stabilized and consequently is more difficult to form. The finding that the reaction rate is approximately ten times slower in this latter instance seems to support this view. The initial step in ozone attack



Figure 4. Concentration of ozone and reaction products at 75.6 °C.

on saturated hydrocarbons has been proposed^{2,3,8} as

$$RH + O_3 \rightarrow R \cdot + O_2 + \cdot OH$$

There appears to be no reason for postulating a different mode of attack in the case of fluorine-substituted hydrocarbons.

In the case of 1,1-difluoroethane, for example, the following tentative sequence most easily accounts for the products observed:

$$CH_3CF_2H + O_3 \rightarrow CH_3CF_2 + O_2 + OH$$
(1)

$$CH_3CF_2 + O_3 \rightarrow CH_3CF_2O + O_2$$
 (2)

$$CH_3CF_2O \rightarrow CF_2O + \cdot CH_3$$
 (3)

$$\cdot CH_3 + O_2 \rightarrow CO, CO_2, H_2O, HCOOH$$
(4)

Ethoxy-type radicals are known to decompose by a reaction such as (3).⁹ The large amount of carbonyl fluoride observed among the reaction products appears to justify including a step such as (3) in the reaction scheme. The reaction sequence indicated by step 4 for the oxidation of the methyl radical has been outlined by others.¹⁰⁻¹² Since the methyl radical would most likely react preferentially with oxygen rather than with ozone in the presence of an excess of the former, step 4 employs oxygen as the oxidizing agent rather than ozone.

The kinetic equations for the relevant intermediate species are:

$$-d[CH_{3}CF_{2} \cdot]/dt = k_{1}[CH_{3}CF_{2}H][O_{3}] - k_{2}[CH_{3}CF_{2} \cdot][O_{3}] -d[CH_{3}CF_{2}O \cdot]/dt = k_{2}[CH_{3}CF_{2} \cdot][O_{3}] - k_{3}[CH_{3}CF_{2}O \cdot]$$

Making use of the stationary-state approximation, one finds

$$[\mathrm{CH}_3\mathrm{CF}_2\cdot] = (k_1/k_2)[\mathrm{CH}_3\mathrm{CF}_2\mathrm{H}]$$

and



Figure 5. Logarithm of reaction rate constant vs. reciprocal of absolute temperature for ozone-1,1,1-trifluoroethane.

$$[CH_3CF_2O \cdot] = (k_1/k_3)[CH_3CF_2H][O_3]$$

When these values are substituted into

$$-d[O_3]/dt = k_1[CH_3CF_2H][O_3] + k_2[CH_3CF_2 \cdot][O_3]$$

one obtains

$$-d[O_3]/dt = 2k_1[CH_3CF_2H][O_3]$$

The order of the disappearance conforms to that postulated by Schubert and Pease.² The overall reaction rate k_0 is related to k_1 by the equation:

$$k_0 = 2k_1$$

Taking the logarithm of both sides of the equality while substituting in the Arrhenius form gives:

$$\ln A_0 - \frac{E_0}{RT} = \ln 2A_1 - \frac{E_1}{RT}$$

Whence, at high temperature extreme

$$A_0 = 2A_1$$

and at low temperatures

$$-E_0 = -E_1$$

Hence E_1 should equal ca. 15 kcal mol⁻¹ to conform to experimental observations and which is not inconsistent with our understanding of this elementary step. It is, furthermore, in agreement with the findings of Schubert and Pease¹³ who postulate a similar activation energy for the analogous first step in the paraffin-ozone reaction.

The ratio $[CO]/([COF_2] + [CO_2])$ was found to be approximately one during most of the reaction. This finding could be taken as an indication that the oxidation of the methyl radical primarily yields carbon monoxide, and that the hydrolysis of carbonyl fluoride is responsible for the

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carbon dioxide observed. This, however, is open to several objections, the most serious of which is that it seems to imply that the methyl radical is being oxidized to carbon monoxide and water almost as rapidly as carbonyl fluoride is being formed. No completely satisfying explanation has yet been advanced for the rapid rate of carbon monoxide production, especially since the principal reaction product of methane ozonolysis is carbon dioxide.14

The reaction of O_3 with 1,1,1-trifluoroethane suggests the following step

$$CF_3CH_2O \rightarrow CF_3 + CH_2O$$
 (5)

However, since no formaldehyce was observed among the reaction products, a subsequent rapid reaction with ozone to yield carbon dioxide is indicated. The production of large amounts of carbonyl fluoride is explained in a manner analogous to the oxidation of the trifluoromethyl radi $cal.^{15}$

The observations that H is more readily abstracted from the 1 rather than the 2 position of 1,1-difluoroethane and that 1,1,1-trifluoroethane is even less susceptible to H abstraction are supported by the work of Whittle et al.^{16,17} who used Br and CF₃ to remove hydrogen atoms. Fluorine was shown to deactivate hydrogen atom abstraction on adjacent carbon atoms.

The formation of CH₃CFO and SiF₄ might be explained by a sequence:

$$CH_3CF_2 + O_2 \rightarrow CH_3CFO + OF$$
 (6)

$$\mathbf{OF} \rightarrow \frac{1}{2}\mathbf{O}_2 + \frac{1}{2}\mathbf{F}_2 \tag{7}$$

$$\frac{1}{2}F_2 + \text{wall} \rightarrow \text{Si}F_4$$
 (8)

The activation energy calculated for the reaction of

ozone with the fluorine-substituted saturated hydrocarbons is somewhat higher (ca. 2 kcal mol^{-1}) than those reported for the first three members of the paraffin series.^{5,6} Nonetheless, we feel that there is no significant difference in the values for these compounds. The similarity in the energies of activation suggests that the reaction processes involved are essentially the same in both cases. The calculated product yield shows an approximate 1:1 ratio of gram atoms of oxygen fixed to moles of ozone disappearing in the case of the 1,1,1-trifluoroethane reaction. It would be reasonable, therefore, to exclude a chain mechanism involving oxygen molecules. With 1,1-difluoroethane, the ratio was approximately 1.8:1 and the above conclusion is probably not valid in this case.

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Gas Phase Ion Chemistry of 2-Fluoropropane by Ion Cyclotron Resonance Spectroscopy

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The gas phase ion chemistry of 2-fluoropropane is reported. The parent ion fragments to yield (CH₃)₂CF⁺, CH_3CHF^+ , and CH_2CHF^+ as the abundant primary ions, all of which react with the parent neutral by Ftransfer to yield $(CH_3)_2CH^+$. $(CH_3)_2CH^+$ in turn reacts with the parent neutral by H⁻ transfer to regenerate $(CH_3)_2CF^+$, thus completing a chain reaction which leads to the conversion of 2-fluoropropane to a mixture of propane and 2,2-difluoropropane via ionic intermediates. This chain reaction is terminated by a slow condensation reaction of $C_3H_7^+$ with 2-fluoropropane to yield $C_6H_{13}^+$. A variety of trapped ion cyclotron resonance techniques, including in particular cyclotron resonance ion ejection methods, permits all of the rate constants for this reasonably complex reaction scheme to be extracted.

Introduction

We have recently reported the gas phase ion chemistry of the methyl and ethyl halides RX ($R = CH_3$, C_2H_5 and X =F, Cl, Br, I).² The chemistry of CH_3F and C_2H_5F proved to be of considerable interest, prompting us to investigate ionmolecule reactions of the variously substituted fluoromethanes $CH_{4-n}F_n$ (n = 1-4),^{3,4} fluoroethanes $C_2H_{6-n}F_n$ (n = 1-6),⁵ and fluoroalkenes.⁶ These studies in turn led to the development of methodology for the determination of carbonium ion stabilities, 3,7,8 using either H⁻ or halide ions as reference bases and interpreting the heterolytic bond dissociation energies (e.g., the enthalpy changes for reaction 1 and 2) as measures of ion stability. Of particular in-

$$\mathbf{RF} \to \mathbf{R}^+ + \mathbf{F}^- \qquad \Delta H = D(\mathbf{R}^+ - \mathbf{F}^-) \tag{1}$$

$$\mathbf{R}\mathbf{H} \to \mathbf{R}^+ + \mathbf{H}^- \qquad \Delta H = D(\mathbf{R}^+ - \mathbf{H}^-) \tag{2}$$

terest are cases where the relative heterolytic bond dissociation energies for F⁻ and H⁻ are reversed for a pair of carbonium ions R₁⁻ and R₂⁺. If reactions 3 and 4 are both exothermic (requiring that $D(R_1^+-F^-) \ge D(R_2^+-F^-)$ and $D(R_1^+-H^-) \le D(R_2^+-H^-)$, respectively) then the overall process 5 will be exothermic and may occur as a chain reac-

$$R_1^+ + R_2F \to R_2^+ + R_1F$$
 (3)

$$R_2^+ + R_1 H \to R_2 H + R_1^+$$
 (4)

$$R_1H + R_2F \rightarrow R_1F + R_2H \tag{5}$$

tion proceeding through ionic intermediates.⁴ The chain length will be determined by competing reactions as well as reactions with impurities. Thus far only one example of such a process has been observed, where $R_1^+ = CHF_2^+$ and $R_2^+ = CH_2F^+$, the overall reaction involving the conversion of CH_2F_2 to a mixture of CH_3F and CHF_3^{-4} We report in this paper the gas phase ion chemistry of 2-fluoropropane, where another chain reaction analogous to that described above is observed, and results in the overall conversion of 2-fluoropropane to a mixture of 2,2-difluoropropane and propane via ionic intermediates. Trapped ion cyclotron resonance techniques⁹ are used in the present study to follow the sequential bimolecular reactions occurring at relatively low pressures following ionization with a pulsed electron beam. Ion ejection techniques facilitate determination of the thermal rate constants for the complex sequence of reactions occurring in 2-fluoropropane.

Previous studies of the gas phase ion chemistry of fluoroalkanes have not included 2-fluoropropane. Studies of the decomposition of thermally and chemically activated 2-fluoropropane have been reported.¹⁰⁻¹²

Experimental Section

Instrumentation for ion cyclotron resonance spectroscopy has previously been described in detail.^{4,9,13} Two spectrometers were utilized in the present study, a Varian V-5900 spectrometer equipped with a 9-in. magnet and a spectrometer built in Caltech shops with a 15-in. magnet. Both spectrometers are equipped for ion trapping. All cyclotron resonance ion ejection experiments were performed with an irradiating oscillator applied to the source region of the ICR cell during the ion storage portion of the trapping sequence. Experiments were performed at ambient temperature (approximately 25 °C as determined by a thermistor attached to the cell mount).

The sample of 2-fluoropropane was prepared by treating 2-iodopropane with AgF. The products were distilled under vacuum and finally purified by gas chromatography to remove traces of propylene.

Results

Fragmentation of 2-Fluoropropane. The parent ion is observed only as a minor ion at the lowest electron energies. The major ions at all electron energies are those formed by fragmentation of the parent ion (reactions 6-8). The relative abundances at 15.0-eV electron energy are indicated.



Figure 1. Variation of ion abundance with time for 2-fluoropropane at 6.2×10^{-7} Torr ionized with a 6-ms electron beam pulse at 15.0 eV.

$$\stackrel{0.25}{\longrightarrow} \text{CH}_2\text{CHF}^+ (m/e\ 46) + \text{CH}_4 \qquad (6)$$

$$(CH_{a})_{2}CHF^{*+} = 0.59 - CH_{3}CHF^{*-} (m/e \ 47) + CH_{a}^{*-} (7)$$

0.16 $(CH_{a})_{a}CF^{*-} (m/e \ 61) + H^{*-} (8)$

Positive Ion Chemistry. The variation of ion abundance with time is illustrated in Figure 1 at an electron energy of 15.0 eV. The two primary ions at m/e 46 (CH₂CHF·⁺) and m/e 47 (CH₃CHF⁺) are observed to decay exponentially with time, leading to the rapid buildup of m/e 43 [(CH₃)₂CH⁺]. Double resonance experiments identify the fluoride transfer reactions 9 and 10 as accounting for the disappearance of m/e 46 and m/e 47.

$$CH_2CHF.^+ + (CH_3)_2CHF \xrightarrow{k_1} (CH_3)_2CH^+ + CH_2CHF_2.$$
(9)

$$CH_{3}CHF^{+} + (CH_{3})_{2}CHF \xrightarrow{k_{2}} (CH_{3})_{2}CH^{+} + CH_{3}CHF_{2}$$
(10)

$$(CH_3)_2CF^+ + (CH_3)_2CHF \xrightarrow{\pi_3} (CH_3)_2CH^+ + (CH_3)_2CF_2$$
(11)

The decay of m/e 61 [(CH₃)₂CF⁺] is somewhat more complicated, exhibiting an upward curvature at short times. Double resonance experiments identify m/e 61 as also contributing to m/e 43 (fluoride transfer reaction 11), with the latter ionic species regenerating the former in the hydride transfer reaction 12. Reactions 11 and 12 taken to-

$$(CH_3)_2CH^+ + (CH_3)CHF \xrightarrow{\kappa_4} (CH_3)_2CF^+ + (CH_3)_2CH_2$$
(12)

gether comprise a chain reaction in which the overall process 13 results in the conversion of 2-fluoropropane to a

Process	Thermal rate constant, 10^{-10} cm ³ molecule ⁻¹ s ⁻¹	ک $H,^b$ kcal/mol
$CH_2CHF^+ + (CH_3)_2CHF \xrightarrow{k_1} (CH_3)_2CH^- + CH_2CHF_2$	13.0 ± 2.0	-20
$\mathrm{CH}_{2}\mathrm{CHF}^{+} + (\mathrm{CH}_{3})_{2}\mathrm{CHF} \xrightarrow{k_{2}} (\mathrm{CH}_{3})_{2}\mathrm{CH}^{+} + \mathrm{CH}_{3}\mathrm{CHF}_{2}$	14.0 ± 2.0	-23
$(CH_3)_2CF^+ + (CH_3)_2CHF \xrightarrow{k_3} (CH_3)_2CH^+ + (CH_3)_2CF_2$	4.4 ± 0.6	-7
$(CH_2)_2CH^+ + (CH_3)_2CHF \xrightarrow{k_4} (CH_3)_2CF^+ + (CH_3)_2CH_2$	1.0 ± 0.2	-7
$(CH_3)_2CH^+ + (CH_3)_2CHF \xrightarrow{k_5} C_6H_{13}^+ + HF$	3.6 ± 0.5	-35°

^a Measured at 15.0 eV. Reported rate constants are the average of four determinations. ^b Calculated using thermochemical data in Table III for fluorocarbon species; other data are from standard sources. ^c $C_6H_{13}^+$ assumed to be a tertiary carbonium ion whose heat of formation is estimated to be ~154 kcal/mol using group equivalents.



Figure 2. Decrease in abundance of m/e 85 (C₆H₁₃⁺) at 600 ms resulting from the ejection of various precursor ions. The amplitude of the radiofrequency electric field is 0.08 V zero to peak. Higher levels lead to the appearance of flat bottom peaks, but result in no further decrease in the abundance of m/e 85. Other conditions are the same as for Figure 1.

$$2(CH_3)_2 CHF \rightarrow (CH_3)_3 CH_2 + (CH_3)_2 CF_2 \qquad (13)$$

mixture of propane and 2,2-difluoropropane. The chain reaction is interrupted by the condensation reaction 14 of

$$(CH_3)_2CH^+ + (CH_3)_2CHF \xrightarrow{s_5} C_6H_{13}^+ + HF \qquad (14)$$

m/e 43 with 2-fluoropropane which results in the production of a hexyl cation which does not react further. When m/e 43 is continuously ejected in a time short compared to the time between collisions, the product ion at m/e 85 (C₆H₁₃⁺) is not observed. When m/e 61 is continuously ejected a product ion at m/e 85 still appears, although reduced in abundance. These observations indicate that m/e43 is the sole precursor to m/e 85. The postulated reaction sequence accounts for the behavior of m/e 43 and m/e 61 shown in Figure 1. The initial buildup of m/e 61 is due to reaction 12. At long times m/e 43 and m/e 61 appear to decay together the two ions being interconverted by reactions 11 and 12 while m/e 43 reacts slowly in the condensation process 14.

Determination of Rate Constants. The rate constants k_1 and k_2 (summarized in Table I) for reactions 9 and 10 can be extracted in a straightforward fashion from the slopes for the decay of m/e 46 and m/e 47 shown in Figure 1. An ion ejection experiment yields a useful relationship between the rate constants k_4 and k_5 . Figure 2 illustrates the

TABLE II: Results of Ion Ejection Experiments to Determine Reaction Pathways Leading to m/e 85 (C₆H₁₃⁺) in 2-Fluoropropane^a

<i>m/e</i> ejected	Fractional decrease in intensity of m/e 85	Fractional abundance of m/e ejected at $t = 0$
43	1.00	0.00
46	0.25	0.25
47	0.60	0.59
61	0.34	0.16

^a Measured at 15.0 eV. Data from Figure 2.

decrease in the abundance of m/e 85 observed at 600 ms at 6×10^{-7} Torr, where this species is ~96% of the total ion abundance and the reaction sequence is nearly complete when various precursor ions are ejected. A comparison of the fractional decrease observed in m/e 85 (Figure 2) with the fractional abundance of the ejected ion at t = 0 is presented in Table II. These data have several implications. First, as noted above, m/e 43 is the sole precursor to m/e85. Second, since m/e 46 and m/e 47 contribute directly to m/e 43 and in turn to m/e 85, the observed fractional decrease in m/e 85 is equal to the fractional abundance of these ions at t = 0. Finally, it is expected from the proposed reaction scheme that the fractional decrease in m/e85 when m/e 61 is ejected will be larger than the abundance of this species at t = 0. The difference in these quantities is the fraction of m/e 43 produced by m/e 46 and m/e47 which reacts to produce m/e 61. This gives the relationship $0.34 - 0.16 = (0.25 + 0.60) k_4/(k_4 + k_5)$, which reduces to the rate constant ratio $k_4/k_5 = 0.27$. With this constraint, the kinetic equations describing the variation of ion abundance with time were solved and compared with the experimental results. The best fit obtained is indicated by the solid lines in Figure 1 and the rate constants are summarized in Table I.

Variation of Ion Abundance with Pressure. The variation of ion abundance with time illustrated for 2-fluoropropane in Figure 1 is examined under conditions which permit the decay of reaction intermediates formed in bimolecular processes. At higher pressures such intermediates may be intercepted and collisionally stabilized. The operation of the ICR spectrometer in the continuous drift mode permits the variation of ion abundance with pressure to be examined up to 10^{-3} Torr with a reaction time of ~1 ms.¹⁴ Such experiments were carried out, with results very similar to those shown in Figure 1. Thus at 10^{-3} Torr C₆H₁₃⁺ is the only remaining ionic species, and there is no evidence for collisional stabilization of intermediates in the proposed scheme of reactions deciphered from trapped ion experiments.

Discussion

Reactions Observed. Reactions of fragment ions are dominated by fluoride transfer processes. The interaction of carbonium ions with alkyl fluorides has been postulated to involve fluoronium ion intermediates which fragment to yield a new carbonium ion. This is generally illustrated for 2-fluoropropane in reaction $15.^{2-4}$ Only in the formation of

$$R^+ + (CH_3)_2CHF \rightarrow [R-F^+-CH(CH_3)_2]^* \rightarrow RF + (CH_3)_2CH^+ \quad (15)$$

the symmetrical disopropyl fluoronium ion do other fragmentation pathways compete with the bond cleavage indicated in reaction 15. Mechanisms for the observed processes are proposed which involve a fluoronium ion intermediate which decomposes either by disproportionation (equivalent to hydride transfer, eq 16) or by the more complex rearrangement elimination reaction in which HF is

$$CH_{a} \xrightarrow{CH_{a}} H \xrightarrow{C} H \xrightarrow{H} (CH_{a})_{2}CH_{2} + (CH_{a})_{2}CF^{+} \quad (16)$$

$$F \xrightarrow{C} CH_{a} \xrightarrow{CH_{a}} CH_{a}$$

$$CH_{a} \xrightarrow{CH_{a}} CH \xrightarrow{F} CH_{a}$$

$$CH_{a} \xrightarrow{CH_{a}} CH \xrightarrow{F} H^{+} \xrightarrow{CH_{a}} Ce_{6}H_{13}^{+} + HF \quad (17)$$

lost (eq 17). Although the proposed mechanisms are speculative, and isotopic labeling experiments were not performed, processes analogous to reaction 14 have been observed in the reaction of $C_2H_5^+$ with C_2H_5F and $C_2H_5Cl^2$ and $(CH_3)_3C^+$ with $(CH_3)_3CF$,¹⁵ (CH₃)₃COH,¹⁴ and a range of t- $C_5H_{11}X$ species (X = Cl, Br, OH, and SH).¹⁶ In each case a symmetrical "onium" ion of the type R_2X^+ can be inferred as a reaction intermediate.

The two reactions 12 and 14 make it difficult to use isopropyl fluoride as a reference species for the determination of unknown fluoride affinities (and thus carbonium ion stabilities) from F^- transfer equilibria. This has been the case for all monofluoroalkanes thus far investigated.¹⁵ Double resonance techniques are useful for identifying the preferred direction of fluoride transfer reactions, however, and ion ejection techniques such as described in the previous section can be used to extract forward and reverse rate constants even when other processes compete with the reactions of interest.

Thermochemistry. The heats of formation of many of the fluorinated ions and neutrals encountered in this study are not well characterized. The available data are summarized in Table III and have been used to calculate ΔH for each of the reactions summarized in Table I. The overall chain reaction 13 is exothermic by 14 kcal/mol, the exothermicity being determined by the special stability of geminal difluorides. It is known that C-F bond energies increase when a second fluorine atom is bonded to the same

TABLE III: Summary of Thermochemical Data

	$\Delta H_{\rm f}^{298}$, kcal/mol	Ref	
(CH ₃) ₂ CHF	-68		
$(CH_3)_2 CF_2$	-125	Ь	
CH ₃ CH ₂ F	-63	с	
$CH_{3}CHF_{2}$	-120	с	
CH_2CHF_2	-74	d	
$(CH_3)_2CH^+$	192	е	
CH ₂ CHF ⁺	206	f	
CH ₃ CHF ⁺	163	, g	
$(CH_3)_2 CF^+$	142	ň	

^a Reference 12. ^b Calculated assuming $D(CH_3CF_2-CH_3) \simeq D(C_2H_5-CH_3)$. ^c S. S. Chen, A. S. Rodgers, J. Chao, R. S. Wilhoit, and B. J. Zwolinski, J. Phys. Chem. Ref. Data, 4, 441 (1975). ^d Calculated assuming that $D(CF_2HCH_2-H) \simeq 98$ kcal/mol. ^e F. P. Lossing and G. P. Semeluk, Can. J. Chem., 48, 955 (1970). ^f Calculated using IP(CH_2CHF) = 10.31 eV and $\Delta H_f(CH_2CHF) = 31.6$ kcal/mol; S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968, Table A.11. ^g Calculated from AP(CH_3CHF⁺) = 12.04 eV from C_2H_5F (A. D. Williamson, P. R. LeBreton, and J. L. Beauchamp, unpublished photoionization experiments). ^h ± 7 kcal/mol, see text for discussion.

carbon. The effect has been attributed to the importance of bond-no-bond resonance structures of the type



Since reactions 11 and 12 are observed to proceed to the right it can be inferred, respectively, that $D[(CH_3)_2CF^+-F^-] \ge D[(CH_3)_2CH^+-F^-]$ and $D[(CH_3)_2CH^+-H^-] \ge D[(CH_3)_2CF^+-H^-]$. These relationships give $\Delta H_f[(CH_3)_2CF^+] = 142 \pm 7 \text{ kcal/mol. The pair of carbonium ions (CH_3)_2CF^+ and (CH_3)_2CH^+ correspond to R_1^+ and R_2^+ in the general sequence of reactions 3-5 discussed in the Introduction.$

Comparison to Solution Chemistry. The 2-fluoropropyl cation was the first fluorine substituted aliphatic carbonium ion directly observed in solution, produced either by the ionization of 2,2-difluoropropane in SbF_5-SO_2 solution at -60 °C or by protonation of 2-fluoropropene in FSO₃H-SbF₅SO₂ solution at -60 °C.^{17,18} Ionization of 2-fluoropropane with excess SbF₅ yields the propyl cation which is stable at room temperature.¹⁹ Possible further reactions of propyl cations with 2-fluoropropane [e.g., reactions 12 and 14] have not to our knowledge been characterized. It has been reported that the BF3 complex of 2-fluoropropane yields unidentified polymer products upon warming.²⁰ It is of further interest to note that ionization of 2-chloropropane in SbF_5-SO_2 solution leads to the formation of the isopropyl cation which, upon warming, reacts with the parent compound to generate hexyl cation products.²¹ This may suggest a process in solution analogous to the condensation reaction 14.

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Photoredox Chemistry of Iron(III) Chloride and Iron(III) Perchlorate in Aqueous Media. A Comparative Study¹

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Photoredox chemistry of iron(III) chloride and iron(III) perchlorate in aqueous media was investigated in the wavelength range 250-425 nm. The effects of incident intensity, iron(III) and iron(II) concentrations, wavelength of irradiation, chloride concentration, radical scavengers, pH, time of irradiation, and temperature on product quantum yields were investigated. The primary photoreaction is postulated to be Fe³⁺. $OH^- \rightarrow Fe^{2+} + OH$ in iron(III) chloride and iron(III) perchlorate solutions; secondary reactions of OH affect the product quantum yields. From the variation of quantum yields with the wavelength of irradiation the $OH^- \rightarrow Fe(III)$ charge-transfer excited state is concluded to be the one responsible for photoreduction. Under identical conditions, the product quantum yield (Φ_{Fe^2} -) for the photoreduction of iron(III) chloride is less than that of iron(III) perchlorate.

Introduction

Iron(III) ions in aqueous solutions containing inorganic anionic ligands show a tendency to form ion pairs of the type $Fe^{3+} \cdot X^-$ (where X = Cl, Br, OH, NCS, N₃, etc.).²⁻⁸ In aqueous solutions containing weak anionic ligands, such as NO_3^- and ClO_4^- , the principal ion pair is $Fe^{3+}OH^$ formed by hydrolysis,³ while in the presence of Cl⁻ the ion pairs Fe³⁺·OH⁻ and Fe³⁺·Cl⁻ coexist. The ion pair formation of Fe^{3+} with OH^- and Cl^- in aqueous media has been investigated.3,8-15

Even though the photochemistry of aqueous iron(III) chloride solutions dates back to 1949,16-18 hitherto no general agreement regarding the photochemical mechanism has been reached.¹⁹ While it was generally accepted that the primary photoreaction in aqueous solutions of iron(III) perchlorate was $Fe^{3+} \cdot OH^- \rightarrow Fe^{2+} + \cdot OH^{20-24}$ the primary photoprocess in aqueous iron(III) chloride was reported to be $Fe^{3+} \cdot Cl^- \rightarrow Fe^{2+} + \cdot Cl^{.16-18,22}$ However this latter mechanism has been contradicted by Saha et al.¹⁹ Saha et al. did not detect any appreciable concentration of a Cl end group in the poly(methyl)methacrylate obtained from aqueous solutions containing iron(III) chloride as photoinitiator of polymerization. Instead they detected an OH end group in the polymer. Hence, it was believed that a comparative investigation of the photochemistry of iron(III) chloride and iron(III) perchlorate in aqueous media would be informative with respect to correlations of both electronic spectra and structural features with photodecomposition modes.

Experimental Section

Materials. Iron(III) chloride (BDH) was purified by the published procedure.²⁵ Iron(III) perchlorate was prepared following the method of Mulay and Selwood.13 Potassium ferrioxalate for chemical actinometry was prepared and purified by the literature procedure.^{26,27} Purification of methylmethacrylate and sodium benzoate, used for chemical scavenging, has been described.²⁸ Water was distilled over alkaline permanganate, then over EDTA, and stored in polyethylene containers. All other materials used in this study were reagent grade and were used without further purification.

Methods. Gross irradiations, from which no quantum yield data were desired, were carried out either by means of a medium-pressure AH-4 mercury source or in a Royonet photochemical reactor; RPR-3500 Å lamps, which have a maximum intensity at 350 nm with a band width of approximately 40 nm, were used.

Photochemical irradiations, from which quantum yields were to be determined, were performed with a Hanovia 901C-1 150-W xenon lamp dispersed through a Bausch and Lomb 33-86-40 monochromator. Intensity changes were accomplished by Baird-Atomic neutral density filters. Samples were irradiated in a 1-cm rectangular cell (volume 4.5 ml) fitted with ground joint and teflon stopper. The cell was thermostated at the desired temperature by circulating water through the cell holder from a constant-temperature water bath. In determination of the product quantum yields, conversion of iron(III) to iron(II) never exceeded 5% of the initial iron(III) concentration. Since iron(III) solutions show great tendency to undergo hydrolysis, all solutions were prepared just before use.

Source intensities were measured by ferrioxalate actinometry.^{27,28} Iron(II) was determined spectrophotometrically as the $[Fe(phen)_3]^{2+}$ complex (phen = 1,10-phenanthroline).^{27,29} Calculations of the quantum yield have been described.²⁷ pH measurements were effected using a Corning Model 7 pH meter and a combination glass-calomel electrode (Beckman No. 39142 A8). Electronic absorption spectra and absorbance measurements were obtained using a Zeiss RPQ 20A recording spectrophotometer.

Results³⁰

Chemical Scavenging Experiments. Degassed solutions of iron(III) chloride and iron(III) perchlorate $(1.0 \times 10^{-3} \text{ M})$ and pH 2.0) were photolyzed at 350 nm in the presence of varying concentrations of methylmethacrylate (0.5-1.0 M). The polymers formed were recovered, purified, and analyzed for Cl and OH end groups.^{28,31-35} The test for the Cl end group was always negative, while that for the OH end group was strongly positive.

Benzoic acid was also employed as a radical scavenger. When aqueous solutions of iron(III) chloride or iron(III) perchlorate (0.001 M and pH 2.0) were irradiated in the presence of sodium benzoate (0.002 M), a deep purple color developed showing the formation of salicylic acid and, hence, OH radicals in the solution. In order to verify whether any chlorobenzoic acids were formed in iron(III) chloride, the irradiated solution was acidified with HCl and extracted with ether; the ether extract, after washing with water, was evaporated to dryness and the residue subjected to elemental analysis for chlorine. No chlorine was detected, thus showing the absence of any detectable amount of chlorobenzoic acid in the irradiated solution.

Effect of Added Concentration of Chloride on Quantum Yield. Addition of sodium chloride to iron(III) chloride or iron(III) perchlorate had a decelerating effect on the photoreduction (Figure 1). The quantum yield for the photoreduction of iron(III) chloride decreased by a factor of 5 on increasing the added [Cl⁻] to 1.0 M. For iron(III) perchlorate this factor was ca. 10. It should be noted that 0.005 M iron(III) perchlorate containing 0.015 M chloride gave nearly the same quantum yield as that of 0.005 M iron(III) chloride which contained 0.015 M chloride in the absence of any added Cl⁻.

Variation of Quantum Yield with Wavelength. As shown in Figures 2 and 3 the variation of quantum yields with excitation wavelength in the region 250-425 nm for iron(III) chloride and iron(III) perchlorate was dependent on the absorbance of the solutions at the respective wave-



Figure 1. Effect of [NaCI] on the product quantum yields for the photoreduction of iron(III) chloride (\bullet), and iron(III) perchlorate (O). Initial concentration of iron(III) chloride and iron(III) perchlorate was 5.0×10^{-3} M.



Figure 2. Product quantum yields for the photoreduction of iron(III) chloride as a function of wavelength of irradiation: (1) wavelength dependence on quantum yield at constant iron(III) concentration of 3.5×10^{-3} M; (2) wavelength dependence on quantum yield at constant absorbance of 0.55 ± 0.03 ; (3) absorbances of the 3.5×10^{-3} M solution as a function of wavelength.



Figure 3. Product quantum yields for the photoreduction of iron(III) perchlorate as a function of wavelength of irradiation: (1) wavelength dependence on quantum yield at constant iron(III) concentration of 7.0×10^{-3} M; (2) wavelength dependence on quantum yield at constant absorbance of 0.55 ± 0.03 ; (3) absorbances of the 7.0 $\times 10^{-3}$ M solution as a function of wavelength.

lengths. When a solution of the same iron(III) concentration was used at different wavelengths (the absorbances of this solution were different at different wavelengths), the quantum yields showed maxima at 300 and 400 nm. When the quantum yields were determined using solutions whose absorbances were nearly constant (ca. 0.5) at the desired wavelengths (this was achieved by using different iron(III) concentrations at different wavelengths), the quantum



Figure 4. Product quantum yields for the photoreduction of iron(III) chloride (1), and iron(III) perchlorate (2), as a function of concentration. (3) and (4) represent the absorbances of iron(III) perchlorate and iron(III) chloride, respectively, as a function of concentration.



Figure 5. Effect of pH on the product quantum yields for the photoreduction of iron(III) chloride (1), and iron(III) perchlorate (2). (3) and (4) represent the absorbances of iron(III) chloride and iron(III) perchlorate, respectively, as a function of pH.

yield values exhibited a single maximum at 300 nm; the quantum yields decreased on increasing or decreasing the wavelength from 300 nm.

Effect of Initial Iron(III) Concentration on Quantum Yield. The dependence of quantum yield on initial concentration of iron(III) is depicted in Figure 4 along with the absorbances of the solutions. The change in quantum yield was more pronounced at iron(III) concentrations below 0.002 M. When the concentration is decreased from 0.01 to 0.0005 M, the quantum yield increased by a factor of 4 for iron(III) chloride and by a factor of 7 for iron(III) perchlorate.

Variation of Quantum Yield with Incident Intensity. The quantum yields for iron(III) chloride and iron(III) perchlorate decreased with increase in incident intensity. For iron(III) chloride the quantum yields at incident intensity values ($\times 10^{-14}$ quanta s⁻¹) of 5.0. 2.6, 1.0, 0.50, and 0.23 were, respectively, 0.011, 0.015, 0.025, 0.035, and 0.068. For iron(III) perchlorate the quantum yields at identical incident intensity values were respectively 0.035, 0.045, 0.055, 0.110, and 0.300. The variation of quantum yields was more significant at incident intensity values less than 1.0×10^{14} quanta s⁻¹. For higher incident intensities the quantum yields showed a tendency to reach a limiting value.

pH and the Quantum Yield Values. The quantum yield



Figure 6. Product quantum yields and the concentrations of iron(II) formed in the photoreduction of iron(III) chloride (1 and 3, respectively), and iron(III) perchlorate (2 and 4, respectively) as a function of time of irradiation.



Figure 7. Product quantum yields for the photoreduction of iron(III) chloride ($\blacksquare -- \blacksquare$), and iron(III) perchlorate ($\blacksquare -- - \blacksquare$) as a function of added concentration of iron(III) perchlorate. A and B are the plots of $1/\Phi_{net}$ vs. [Fe²⁺]_{av} for iron(III) perchlorate and iron(III) chloride, respectively. Time of irradiation for iron(III) perchlorate solutions was 2.5 h.

values at various pH (adjusted with $HClO_4$) along with the absorbances of the solutions are displayed in Figure 5. For the iron(III) chloride, the quantum yields showed a maximum at pH 2.0. Iron(III) perchlorate exhibited the quantum yield maximum at pH 1.2. In comparison, the change in quantum yield was more pronounced for iron(III) perchlorate (a factor of 3.5 between the highest value at pH 1.2 and the lowest value at pH 2.8) than for iron(III) chloride (a factor of 1.7 between the highest value at pH 2.0 and the lowest value at pH 2.8).

Time of Irradiation and Quantum Yield Values. As shown in Figure 6, the quantum yields for the photoreduction of iron(III) chloride and iron(III) perchlorate decreased with the time of irradiation. The plot of $[Fe^{2+}]$ formed vs. time of irradiation showed that the iron(II) concentration reached a limiting value of ca. 1.4×10^{-4} M. The extrapolated quantum yield values to zero time of irradiation were 0.077 and 0.033, respectively, for iron(III) perchlorate and iron(III) chloride.

Variation of Quantum Yield with Added Concentration of Iron(II). Added concentrations of iron(II) (as iron(II) perchlorate) decelerated the photoreduction (Figure 7), the quantum yields dropping nearly to zero for iron(II) values ca. 1.4×10^{-4} M and higher. It is interesting to note that this concentration was nearly same as the limiting iron(II) concentration in the plot of $[Fe^{2+}]$ vs. time of irradiation (Figure 6). The plots of $1/\Phi$ vs. $[Fe^{2+}]_{av}$ (where $[Fe^{2+}]_{av} = [Fe^{2+}]_0 + \frac{1}{2}[Fe^{2+}]_f$; $[Fe^{2+}]_0$ is the concentration of iron(II) present initially and $[Fe^{2+}]_f$ is the concentration of iron(II) formed photochemically) gave straight lines (Figure 7) with slopes of 6.5×10^6 and 2.5×10^5 , and intercepts of 26 and 9.5, respectively, for iron(III) chloride and iron(III) perchlorate.

Dependence of Quantum Yields on Temperature. Quantum yield for the photoreduction of iron(III) chloride increased with increase in temperature of the irradiated solution, the quantum yields being 0.015, 0.017, 0.020, 0.025, and 0.032, respectively, at temperatures 5, 10, 20, 30, and 40 °C. The variation of quantum yields for iron(III) perchlorate was negligible (the quantum yield decreased ca. 5% as the temperature was raised from 5 to 40 °C).

Discussion

The experimental results presented herein are in agreement with the hypothesis that, in aqueous solutions of iron(III) chloride as well as iron(III) perchlorate, the primary photoprocess is the homolytic cleavage of the Fe(III)-OH bond.¹ The primary photoreaction may be represented as

$$Fe^{3+} OH^- \xrightarrow{h\nu} Fe^{2+} + OH$$

Radical scavenging experiments employing benzoate and methylmethacrylate clearly indicated that OH radicals were produced during the irradiation. There was no indication for the production of Cl radicals as was formulated earlier.¹⁶⁻¹⁸

Further evidence in support of formulating $Fe^{3+} \cdot OH^-$ as the photoactive species is the variation of quantum yield with added concentration of Cl^- (Figure 1). The concentration of $Fe^{3+} \cdot Cl^-$ increases with increase in $[Cl^-]^{.15}$ Hence, at constant pH, the molar fraction of $Fe^{3+} \cdot Cl^-$ increases in comparison to $Fe^{3+} \cdot OH^-$. Consequently, an increase in quantum yield for the photoreduction is expected if $Fe^{3+} \cdot$ Cl^- is the photoactive species. However the results, contrary to this prediction, indicate that $Fe^{3+} \cdot OH^-$, rather than $Fe^{3+} \cdot Cl^-$, is the photoactive species. A decrease in molar fraction of $Fe^{3+} \cdot OH^-$ with the consequent decrease in the fraction of light absorbed by it might account for the decrease in quantum yield with increase in $[Cl^-]$.

The dependence of quantum yield on excitation wavelength might prove to be another strong point in identifying $Fe^{3+}OH^-$ as the photoactive species. $Fe^{3+}OI^-$ has a charge-transfer maximum at 340 nm¹⁵ while Fe³⁺·OH⁻ has this charge-transfer absorption maximum at 300 nm.8-10 Both iron(III) chloride and iron(III) perchlorate showed quantum yield maxima at 300 nm (Figures 2 and 3) indicating the photoactive charge-transfer band centered at 300 nm. The slight decrease in quantum yield values at wavelengths lower than 300 nm might arise from the partial absorption of incident light by Fe_{aq}³⁺ which is photochemically less active than $Fe^{3+}OH^-$. The appearance of a second maximum at 400 nm on employing solutions of constant initial iron(III) concentration might be a manifestation of extremely low light absorption (<2%) in this region (see below).

Quantum yields for the photoreduction of iron(III) chlo-

- ... with it. -

ride as well as iron(III) perchlorate decreased with increasing iron(III) concentration. A sharp increase in quantum yield was observed in solutions absorbing less than 10% of the incident light intensity. Low absorbed intensity signifies a homogeneous absorption of light, a homogeneous distribution of the reduction products, and a lower rate of reduction. Assuming a steady-state concentration for OH, the recombination reaction $Fe^{2+} + OH \rightarrow Fe^{3+}OH^-$ depends on the effective concentration of Fe²⁺. Increase in concentration of iron(III) increases the absorbed light intensity and/or decreases the pathlength of the solution absorbing light. This amounts to the increase in photoreduction and/or restriction of the photoreduction to a narrower and narrower region of the solution with the consequent increase in the effective concentration of Fe²⁺. Similar effects were observed on decreasing the incident light intensity. Since a decrease in incident intensity reduces the rate of production of Fe²⁺, we may reasonably assume a parallelism between the variation of quantum yields with incident intensity and initial iron(III) concentrations (Figure 4). In the absence of its recombination with Fe^{2+} , OH radicals react with the impurities in distilled water.²²

Iron(III) chloride and iron(III) perchlorate showed slightly different behavior with variation in pH of the solutions (Figure 5). Under the conditions of the present study, the quantum yields for the photoreduction of iron(III) perchlorate increased until pH 1.3 and then decreased. As is depicted in Figure 5, the absorbance of the iron(III) perchlorate solution at 340 nm decreased with increase in pH, evidently due to the conversion of $Fe^{3+}OH^-$ to Fe_{aq}^{3+} . If we assume that $Fe^{3+}OH^-$ is the only light absorbing species at 340 nm in the pH range 2.8-1.3, the increase in quantum yield is a consequence of the fall in absorbed intensity and more homogeneous light absorption with the concomitant decrease in reoxidation of iron(II) (see above). The fall in quantum yield below pH 1.3 may arise from the increase in light absorption by Fe_{aq}^{3+} , which is photochemically less active than Fe³⁺·OH⁻. Iron(III) chloride showed a quantum vield maximum at pH 2.0. Since Fe³⁺·Cl⁻ and $Fe^{3+}OH^{-}$ are the two predominant light absorbing species, the quantum yield maximum at pH 2.0 signifies that the molar fraction of the photoactive Fe³⁺·OH⁻ is at a maximum at this pH. A decrease in pH decreases the molar fraction of Fe³⁺·OH⁻ with the consequent decrease in quantum yield. The decrease in quantum yield at pH higher than 2.0 results from the increase in light absorption and/or decrease in pathlength of the solution absorbing light, or formation of higher association species of Fe^{3+} and OH^- , namely, $Fe(OH)_2^+$ or $Fe_2(OH)_2^{4+}$, which might be photochemically less active.¹²⁻¹⁴

The variation of quantum yields for the photoreduction of iron(III) chloride and iron(III) perchlorate with time of irradiation (Figure 6) gives the best evidence of the importance of the reoxidation of Fe²⁺ by the radicals generated during the photoreduction. As is shown in Figure 6, the iron(II) concentration reached a limiting value; when $[Fe^{2+}]$ reached ca. 1.4×10^{-4} M reoxidation or recombination was 100% efficient so as to render the rate of production of Fe²⁺ zero. This conclusion is substantiated by the variation of quantum yield with added concentrations of iron(II) (Figure 7). The quantum yield decreased almost to zero when the added concentration of iron(II) was ca. 1.4×10^{-4} M, in good agreement with the limiting iron(II) concentration observed in the photoreduction as a function of time of irradiation.

If we assume that the termination of OH takes place entirely by reaction with Fe²⁺ and impurities in the distilled water,²² the following reactions may be written for the primary photoprocess and the ensuing thermal reactions:

$$Fe^{3+} \cdot OH^{-} \xrightarrow{\phi I_a} Fe^{2+} + OH$$
 (1)

$$Fe^{2+} + OH \xrightarrow{k_1} Fe^{3+} \cdot OH^-$$
 (2)

$$OH + IM \xrightarrow{k_2} products \tag{3}$$

IM represents the impurities in distilled water. Treating the above reactions by steady-state methods we have

$$\frac{1}{\Phi_{\text{net}}} = \frac{k_1}{\phi k_2 [\text{IM}]} [\text{Fe}^{2+}] + \frac{1}{\phi}$$
(4)

The plot of $1/\Phi_{net}$ vs. $[Fe^{2+}]_{av}$ gave a straight line (Figure 7). The primary quantum yield values (reaction 1) derived from the intercepts are 0.038 and 0.105, respectively, for iron(III) chloride and iron(III) perchlorate photoreductions. This low quantum yield value for iron(III) chloride evidently results from the partial absorption of the incident light by the photochemically inert Fe³⁺·Cl⁻. The slopes of the straight line plots, which are equal to $k_1/$ ϕk_2 [IM], enable us evaluate k_1/k_2 [IM]; this ratio is calculated as 2.5×10^4 in the system iron(III) chloride and $2.6 \times$ 10⁴ in the system iron(III) perchlorate. This high value shows that reoxidation of Fe²⁺ by OH is highly efficient in comparison to the termination of OH by reaction with impurities in distilled water.

The increase in quantum yield for iron(III) chloride with increase in temperature is evidently due to the increase in hydrolysis.^{3,8–10} If we assume $[Fe^{3+}\cdot Cl^{-}]$ constant, the concentration of Fe³⁺·OH⁻ increases with increase in temperature. Thus, an increase in molar fraction of $Fe^{3+}OH^-$, with the consequent increase in the fraction of light absorbed by $Fe^{3+}OH^-$, occurs and, hence, the increase in quantum yield.

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Photochemistry of Benzene in Aerated Aqueous Solutions in the Range of 214 to 265 nm

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Benzene in aerated aqueous solution irradiated at 214 nm (causing transition to the second excited singlet state) gives a similar major photoproduct, with similar yield, as irradiation at 229, 254, or 265 nm. The yield is nearly independent of temperature between 20 and 60 °C. The results in correlation with the wavelength dependence of fluorescence support the view that this photochemistry originates in nonrelaxed states prior to the formation of the thermalized fluorescent level.

We report our results on the photochemistry of aerated aqueous solutions of benzene irradiated with λ 214 nm and compare these with those of irradiations with λ 229, 254, or 265 nm. Absorption of light at 214 nm causes transition to the second, probably ${}^{1}B_{1u}$, excited singlet state of benzene, while the absorption at the three longer wavelengths results in excitation to the first, ${}^{1}B_{2u}$, singlet state (Figure 1).

Symmetry considerations make either electronic transition unallowed from vibrational levels of the planar ${}^{1}A_{1g}$ ground state to levels of either of the planar excited states, ${}^{1}B_{2u}$ or ${}^{1}B_{1u}$, unless the transition is such that at least one nontotally symmetrical vibrational mode is aroused or eliminated in the process. In our case transitions originate in a symmetrical ground state and result in excited states in which one quantum of nontotally symmetrical vibration evolves, accompanied by one or more quanta of symmetrical vibrations.

In the gas phase¹ as well as in nonpolar solvents^{2,3} deaerated benzene yields on illumination at 254 nm one major initial photoproduct only, benzvalene:



The reaction necessitates out-of-plane distortion for the formation of the valence-bond isomer. Recent detailed investigation^{3,4} supported the suggestion^{1,5} that such photochemistry originates in very short times, before vibrational relaxation to the fluorescent level.

This photochemistry in nonpolar solvent was shown to be nearly independent of temperature³ while fluorescence⁴ depends on it. Fluorescence was also shown to be wavelength dependent: in the gas phase on excitation by $\lambda < 250$ nm,⁶ and in solution by $\lambda < 230$ nm⁷ the yield of fluorescence decreases. At longer wavelengths the yield is constant up to ~265 nm. We have now reinvestigated these points in aqueous solution.

The wavelength dependence of photochemistry is difficult to determine in many organic solvents with sufficient accuracy since the solvents absorb at shorter wavelengths, e.g., at 214 nm too strongly. In the gas phase quantitative results on this system proved hard to obtain. In our experiments hitherto we too have not obtained satisfactory photochemical results at shorter wavelengths in solvents such as cyclohexane. However in aqueous solution it is possible to obtain reliable results at shorter wavelengths.

Aerated aqueous solutions of benzene give on illumina-

tion with λ 254 nm only one major photoproduct.⁸⁻¹² Its formation is readily and accurately determined by spectrophotometry. Once formed, the product is stable in solution for long periods. In aqueous solution the accessible wavelength range is readily extended to 214 nm. From the comparison of the results at various wavelengths and between the effects of temperature on the photochemical and fluorescence yields in water we shall argue on the pathway of the photochemical process. There is some disagreement⁸⁻¹³ on the exact nature of the product and the role of O₂ in the photochemistry. These points will also be discussed.

Experimental Section

Solutions of benzene (Fluka, puriss, 99.93%, thiophene free) in triple distilled water were freed of dissolved gases by repeated freeze-thaw cycles until the pressure of gases, noncondensable at liquid air temperature, was $<10^{-4}$ Torr in equilibrium with the solution at room temperature. The solutions were then equilibrated with the appropriate pressure of O₂. Alternatively, air saturated solutions were used directly. Benzene concentrations in the solutions before irradiation were determined by the method of Marketos.¹⁴ Solutions of 10^{-4} to 10^{-2} M were used, to avoid involvement of excimers. In this range we found that the results were independent of initial benzene concentration.

Irradiations were carried out on 4 ml of solution in 1-cm optical path length Spectrosil cells (Thermal Syndicate Ltd.). At 265 nm a 100-W Hanovia-SH high-pressure Hg lamp was used in conjunction with an American Optical Co. interference filter, with cutoffs at 260 and 280 nm and transmitting at 265 nm $\sim 2\%$ of the light. At 254 nm we used the emission line from a Thermal Syndicate flat spiral low-pressure resonance Hg lamp, in conjunction with a 1 M KCl filter of 1-cm optical path length to remove light at 185 nm. Emission lines from 25-W Phillips Cd or Zn lamps were used at 229 and 214 nm, respectively. These lamps give no other line which would be absorbed by the benzene solution.

Light intensity was determined using the Forbes-Heidt uranyl oxalate actinometer,¹⁵ taking its quantum yield as 0.50 at 214 nm; 0.55 at 228 nm; 0.60 at 254 nm; 0.60 at 265 nm. In a previous investigation the use of these light sources and of the actinometer over this wavelength range was discussed in some detail.¹⁶ Dose rates were $\sim 10^{-6}$ einstein l.⁻¹ s⁻¹ for the lamps at the shorter wavelengths and $\sim 10^{-7}$ einstein l.⁻¹ s⁻¹ at 265 nm. Light absorbed in the benzene solution was calculated from the actinometry and



Figure 1. Absorption spectrum of benzene in water.

absorption spectrum, and determined accurately at least twice daily. Spectra and yields of products were determined using a Cary 14 instrument.

For fluorescence measurements we used the apparatus described by Feitelson¹⁷ with a high-pressure Xe-Hg lamp as the light source in the excitation range of 225-265 nm. At 214 nm a Phillips Zn lamp, as in the photochemical experiments, served as the excitation light source. The fluorescence output was measured always at 280 nm.

Results

As Figure 1 shows, the molar extinction coefficients in aqueous benzene solution are similar and relatively high at 254 and 214 nm; similar and relatively low at 265 and 229 nm. At 254 and 214 nm solutions were adjusted to OD \sim 2 for the photochemical experiments, and at 265 and 229 nm to OD \sim 0.2.

All photochemical experiments were carried out in unbuffered solutions at pH ~6. On illumination, as discussed in detail previously,¹⁰ one major photochemical product is formed in aerated solutions, with an absorption spectrum in near neutral solutions showing a single maximum at 294 nm. In alkaline solution this peak shifts to 308 nm (Figure 2). We followed the formation of the photoproduct by measuring absorption changes at 294 nm and calculated the quantitative yield from the acid-base titration of the product.

We have to correct here an error in our calculation reported previously¹⁰ where we used the titration value at the point where pH = pK and only half the acid is neutralized. Thus our previous calculated value of ϵ has to be divided by a factor of 2. Hence, for the photochemical product $\epsilon_{\text{PH 6.5}}^{294}$ nm = 4815 M⁻¹ cm⁻¹ and $\epsilon_{\text{pH 10}}^{308}$ nm = 7820 M⁻¹ cm⁻¹.

Figure 3 shows, in air saturated and O_2 free solutions, the formation of the photoproduct. In air saturated solutions initially at 254 and at 214 nm the rate of formation of the product is equal and high; the rate of formation at 214 nm decreases at higher doses, while at 254 nm it is still constant. This we attribute to the fact that the product itself absorbs light appreciably more at 214 nm than at 254 nm, and is thus itself attacked at 214 nm.

From the initial slopes of some 10 experiments at every wavelength we obtained the quantum yield in *aerated* solutions at room temperature, as shown in Figure 4. Within our experimental error the initial quantum yield appears to be nearly constant over the wavelength region.



Figure 2. Absorption spectrum of photoproduct at pH 6 and 10.



Figure 3. Formation of photoproduct as a function of dose (O) in aerated solution illuminated with λ 214 nm and in deaerated solutions illuminated with λ (\bullet) 214 and (Δ) 254 nm.



Figure 4. Initial quantum yield as a function of wavelength of illumination.

In view of the contradictions in the literature^{10–13} on the requirement for oxygen in the formation of the photoproduct and the claim that the same photoproduct is formed in yields of exactly one-half of that in presence of oxygen even in its absence, we reinvestigated this point. Figure 3 shows that in the absence of oxygen in thoroughly deaerated solutions the yield of the photoproduct rapidly reaches a low residual level, beyond which the rate of formation becomes very low. The results are consistent with the assumption that oxygen is required for the formation of appreciable yields of this photoproduct.

Figure 5 shows the dependence of photoproduct yield at 254 nm on oxygen pressure. A limiting quantum yield of $\sim 18\%$ is obtained at 1 atm pressure of O₂ in equilibrium



Figure 5. Quantum yield as a function of O_2 concentration in solutions illuminated with λ 254 nm.



Figure 6. Quantum yield as a function of temperature.

with the solution. Similar results were obtained at 214 nm, except that the limiting yield was achieved at lower O_2 pressures and appeared to be some 15% lower than at 254 nm.

We investigated at 214 nm and at 254 nm the effect of temperature on the quantum yield. Figure 6 shows at 214 nm that ϕ is nearly independent of temperature between 20 and 60 °C. Similar results were obtained at 254 nm now and previously.¹⁰

We also examined the wavelength dependence of fluorescence yield. Previously results were obtained on this in the gas phase⁶ and in nonpolar solvents.⁷ We used solutions of sodium salicylate, as the reference standard, as did Braun et al. for this purpose.⁷ We obtained relative to salicylate a constant fluorescence yield from H₂O solutions of benzene on excitation from 260 nm to ~230 nm; and a decrease to ~0.4 of that at 258 nm at 214 nm (Figure 7). The fluorescence of benzene in H₂O solution is not affected by the presence or absence of O₂ within our experimental error,⁴ in view of the short lifetime.

Discussion

The photoproduct at 214 nm appears from the spectroscopic evidence now reported to be indistinguishable from that obtained at 254 nm. We have not established whether the precursors are identical and indeed the detailed mechanism of formation of the photoproduct in aerated water from the primary excited benzene is still to be established though our previous flash photolysis results¹⁰ give some indications of it. The reproducible formation of the product, however, allows us to follow the effect of experimental parameters on the photochemistry.

Chemical evidence shows that the photoproduct from benzene in aerated aqueous solution illuminated with λ 254



Figure 7. Fluorescence in aqueous solution of benzene relative to that of salicylate as a function of wavelength.

nm is a cyclopentadienylaldehyde, I, where $R = OH^{9,10}$ or, as proposed by Wilzbach and Kaplan, $R = H.^{11,12}$



The resolution of this difference (on which we continue to work) does not affect the conclusions of the present work, though it is of considerable importance for the detailed mechanism of reactions leading from the primary photochemical step to the final stable product.

So is the second point on which there is disagreement in the literature, i.e., the role of oxygen in the formation of the product. In previous work we have shown in steady (254 nm) and in flash irradiation¹⁰ that oxygen is required for the efficient formation of photoproduct I. In contrast, it was stated that the presence or absence of O_2 makes no difference to, or affects only little,^{11,12} the yield of the photoproduct. Quantitatively it was claimed¹³ that the yield of I is exactly double in the presence of that in the absence of O_2 . The present work at 254 and 214 nm shows that the yield of I in the presence of O_2 follows regular kinetics while in its absence (which we are not certain we achieved completely) it is difficult to establish whether any I is formed at all and if so in what yield.

In the presence of O_2 I is formed in quantitatively reproducible yields. In aerated solutions the initial yield is constant within the experimental error between 214 and 265 nm. In solutions saturated with O_2 at 1 atm pressure the quantum yield of I approaches a limiting value of ~18% at 254 and ~16% at 214 nm. This limiting yield is achieved at somewhat lower O_2 pressures at 214 nm than at 254 nm. The yield is nearly independent of temperature.

The fluorescence yield from such solutions shows a sharp decline on excitation by wavelengths shorter than ~ 230 nm. It also decreases appreciably with increasing temperature.⁴ These results make it very unlikely that the photochemistry passes through the same state which is responsible for the fluorescence, i.e., the thermalized lowest vibrational level(s) of the first excited singlet ¹B_{2u} state.

The results are consistent with the assumption¹⁰ that in aqueous solutions, as also in nonpolar solvents,³ this photochemical pathway arises from and its extent is decided in very short times in the spectroscopically prepared higher levels, prior to interaction with the environment and thermalization. This would be in agreement with the original proposal by Kaplan and Wilzbach to this effect, deduced from their experiments in the gas phase.

Indeed the limiting yields now determined, $\sim 18\%$ and ~16%, are similar to the extrapolated value ~18% derived for the formation of the photoproduct, benzvalene,³ in a nonpolar solvent, cyclohexane, in the absence of O_2 . The quantitative reproducibility is much better in the present work. The extrapolation to initial yields in nonpolar solvents is based on an analytical method subject to considerable error at low doses. The similarity of initial yields is consistent with the assumption that a common precursor arising from the spectroscopically prepared state is responsible for the ultimate photochemical product in both cases.

Support for these views was obtained from experiments showing¹⁸ that the effect of the heavy atom Xe is to decrease fluorescence in nonpolar solvents appreciably, without affecting the photochemical yield.

Various mechanistic hypotheses may be proposed to account for these observations. We pointed out^{3,4,10,18} that transition from the lowest vibrational levels of the totally symmetrical, planar, ¹A_{1g} ground state to either the first excited singlet ${}^{1}B_{2u}$ or the second excited singlet ${}^{1}B_{1u}$ is forbidden unless the transition is coupled with the evolution of at least one nontotally symmetrical vibrational quantum in the excited level. Indeed spectroscopic study showed that the detailed structure of these two electronic transitions consists of one such nontotally symmetrical vibrational mode and one or more symmetrical vibrations. There exists the possibility that the formation of the present photoproduct may proceed through out-of-plane distortion, as does the formation of benzvalene,³ and that this is connected with the asymmetric component induced selectively by the optical transition.

We would then argue that the component leading to photochemistry is induced to a similar extent over the range of 265 to 214 nm, the division of pathways between that leading to the photochemical product on the one hand, and to radiationless conversion resulting, inter-alia, in the formation of the fluorescent level occurs before thermalization, from the spectroscopically prepared state rich in nontotally symmetrical vibration.

Our results leave open the possibility that the difference between the ${}^{1}B_{2u}$ and ${}^{1}B_{1u}$ states may lead to some difference in the structure of the primary valence-bond isomer which¹⁹ eventually yields I. The similarity of the yields at 214 and at 254 nm show, however, that the decisive photophysical factors are closely related.

Previously we discussed in some detail^{3,4} how the fluorescent level of benzene may be depopulated through thermally promoted pathways, which, in the case of the highly symmetrical benzene, do not lead efficiently to the present photoproduct, since thermally accessible higher vibrational levels do not preferentially include asymmetric vibrations, while the levels prepared by light absorption require this mandatorily. The results in the present paper showing the feeble effect of temperature on the photochemical yield agree with these previous views, and compare with the considerable temperature effect, $E \sim 5$ kcal/mol; we reported⁴ on the fluorescence of benzene in water.

By contrast the less symmetric molecules of fluorobenzene and toluene do yield in aerated aqueous solution a related photoproduct²⁰ but their formation shows, as does the fluorescence of the parent molecules, an appreciable temperature effect.

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Pulse Radiolytic Studies on Reactions of Aqueous Superoxide Radicals with Copper(II) Complexes

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The reactivities of Cu(II) complexes, including formate, ammonia, Cl⁻, SO₄²⁻, and some amino acids, toward O_2^- were investigated in the presence of excess of the complex forming additives. The reactivity of the Cu(II) complexes is substantially smaller than that of free Cu²⁺ ions, when several ligand molecules are attached.

Introduction

The dismutation of superoxide radicals recently became a subject for research by several groups.²⁻¹⁰ Enzymatic catalysis of superoxide dismutation has been a matter for investigation since the work of McCord and Fridovich.⁵ The rate of catalysis by bovine superoxide dismutase and its mechanism received particular attention.⁵⁻⁸ The mechanism for catalysis was shown to involve alternate reduction and oxidation of the copper atoms in the enzyme.⁷ A similar mechanism was proposed for free Cu²⁺ ions.⁹ In this manuscript we extend the previous work⁹ to include the catalysis of O₂⁻ dismutation by various copper complexes. As before, we use pulse irradiated O₂ saturated aqueous solutions containing formate as a source of O₂⁻ radical ions. The following reactions take place in the irradiated solutions:

$$H_2O \longrightarrow e_{aq}^-$$
, H, OH, H_3O^+ , OH^- , H_2O_2 , H_2 (1)

$$e_{aq}^{-} + O_2 \rightarrow O_2^{-}$$
 $k_2^{11} = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (2)

$$H + O_2 \rightarrow HO_2$$
 $k_3^{12} = 2 \times 10^{10} M^{-1} s^{-1}$ (3)

$$H + HCO_2^- \rightarrow H_2 + CO_2^ k_4^{13} = 5 \times 10^8 M^{-1} s^{-1}$$
 (4)

$$OH + HCO_2^- \rightarrow H_2O + CO_2^ k_5^{14} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$
(5)

$$CO_2^- + O_2 \rightarrow CO_2 + O_2^ k_6^{15} = 2.4 \times 10^9 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$$
 (6)

$$HO_2 = H^+ + O_2^ K^{3,4} = 1.6 \times 10^{-5} M$$
 (7)

At sufficiently high [formate], O2- radical ions (in equilibrium with HO_2) are produced within a short time after the electron pulse. No other radical species are present under such conditions. In the absence of other additives, O_2^- radical ions decay away to form O_2 and H_2O_2 , according to a pH dependent mechanism.^{3,4} In the presence of a catalyst, the decay of O_2^- becomes enhanced. The catalysts which are described in the present manuscript include Cu(II) complexes with various inorganic and organic ligands. In principal, both Cu(II) complexes and the free ligand molecules are capable of reaction with e_{aq}^- , H, and OH in competition with reactions 2, 3, 4, and 5.¹⁶ However, in most of our experiments, conditions were chosen so that such competition was not important. In some cases relatively high concentrations of amino acids were employed while formate ions were excluded. Under such conditions, peroxy radicals of the type RHO₂ might have formed (RH is an amino acid of which a hydrogen atom was abstracted), together with O_2^- . Despite the more complex nature of such systems, we found these experiments useful to test the effect of reducing the free [Cu²⁺] (in equilibrium with Cu(II) complexes).

Experimental Section

The pulse radiolysis apparatus and the optical detection system have been described previously.⁴ Control experiments were always carried out before injection of $Cu(ClO_4)_2$. The lifetimes of O_2^- absorption in the absence of Cu(II) indicated a fairly low level of impurities.³ The pH was adjusted with the aid of phosphate buffer, or NaOH (when an amino acid was present). All solutions were saturated O_2 (Matheson' ultrapure). Appropriate light filters were used in order to minimize unnecessary light. With these, scattered light was less than 5% and was ignored. Unless otherwise stated, a 4 cm long cell, with a single light pass was employed. A 150-W Xe-Hg lamp was used as a light source. Oscilloscopes (Tektronix, 556 dual beam and 549 memory), 1P28 photomultiplier, and B and L monochromator were used. The time resolution was better than $2 \mu s$. The temperature was $23^{\circ} \pm 2 {}^{\circ}C$.

Materials. Water was triply distillated. Other materials were used as received: $Cu(ClO_4)_2$ (Fluka purum), NaCl (Baker analyzed), Na₂SO₄ (BDH analar), mono sodium and disodium phosphates (Malinckrodt analytical), ammonium hydroxide (Frutarom analytical), sodium formate (B and A). L-valine (Merck for biochemistry), L-proline and Lhydroxyproline (NBC), L-glutamate (Merck pure), DL-alanine, glycine, L-methionine, and glycylglycine (Fluka puriss), hemocyanine (from Marine-Invertebrabe (keyholelimtet), product of Pacific Biomarine Supply Co.), and plastocyanine (from Chlamidomonas Reinhardi).

Results

Complexes of Cu(II) with Formate Ions. Formate ions are known to form complexes with Cu(II), the stability constants being 37, 4.5, 0.7, and 2.5 M^{-1} for Cu(HCO₂)⁺, Cu(HCO₂)₂, Cu(HCO₂⁻)₃, and Cu(HCO₂)₄²⁻, respectively, at ionic strength 2.¹⁷ We tested the ability of the various formate-Cu(II) complexes formed at different [HCO₂⁻] to react with O₂⁻ presumably according to the general eq 8. Cu(II) represents here all the forms of bivalent copper which are present in the solution. At a given formate concentration

or

$$O_2^- + Cu(\Pi) \rightarrow O_2 + Cu(I) \tag{8}$$

$$O_2^- + Cu(II) \xrightarrow{2H^+} H_2O_2 + Cu(III)$$

several Cu(II) complexes may participate in the reaction, therefore k_8 is an apparent reaction rate constant of $O_2^$ with the various Cu(II) complexes, which are present under the experimental conditions. The apparent reaction rate



Figure 1. The reactivity of Cu(II)-formate complexes toward O_2^{-1} : (a) calculated using $k_{8a} = 1.7 \times 10^9$, $k_{8b} = 3.0 \times 10^8$, $k_{8c} = 8.0 \times 10^8$, $k_{8d} = 4.0 \times 10^8$, $k_{8f} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; (b) as (a) except that $k_{8b} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was chosen; (c) as (a) except that $k_{8a} = 2.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was chosen; (d) as (a) except that $k_{8a} = 2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was chosen.

constant k_8 can be expressed according to

$$k_{8} = (k_{8f} + k_{8a}K_{a}[HCO_{2}^{-}] + k_{8b}K_{a}K_{b}[HCO_{2}^{-}]^{2} + k_{8c}K_{a}K_{b}K_{c}[HCO_{2}^{-}]^{3} + k_{8d}K_{a}K_{b}K_{c}K_{d}[HCO_{2}^{-}]^{4})/\alpha$$
(9)

 K_{a} , K_{b} , K_{c} , and K_{d} are the stability constants for the mono, di, tri, and tetra complexes, respectively, k_{8f} is k_{8} for the free Cu²⁺ ions, k_{8a} , k_{8b} , k_{8c} , and k_{8d} represent the reaction rate constants of O_{2}^{-} with the mono, di, tri, and tetra complexes, respectively, and α is defined by

$$\alpha = (1 + K_{a}[\text{HCO}_{2}^{-}] + K_{a}K_{b}[\text{HCO}_{2}^{-}]^{2} + K_{a}K_{b}K_{c}[\text{HCO}_{2}^{-}]^{3} + K_{a}K_{b}K_{c}K_{d}[\text{HCO}_{2}^{-}]^{4}) \quad (10)$$

Equation 9 is correct for $[HCO_2^{-}] \gg [Cu(II)]$, which suits our experimental conditions. We used about 10⁻⁴ M Cu(II), >10⁻³ M HCO₂⁻, and 1-2 μ M O₂⁻, for the measurements of k_8 . The light path was 12.3 cm; measurements were carried out at 248 nm. In Figure 1 we present k_8 values as a function of $[HCO_2^-]$, at constant ionic strength (2 M). Sodium perchlorate was added to keep the ionic strength at a constant level. The line (Figure 1) was calculated using eq 9, taking $k_{8f} = 1.9 \times 10^9$, $k_{8a} = 1.7 \times 10^9$, k_{8b} = 3.0×10^8 , $k_{8c} = 8.0 \times 10^8$, and $k_{8d} = 4.0 \times 10^8$ M⁻¹ s⁻¹. The value $k_{8f} = 1.9 \times 10^9$ M⁻¹ s⁻¹ is considerably lower than $k_{8f} = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ measured in 10^{-3} M formate.⁹ The difference is in agreement with an expected ionic strength effect on the reaction rate of O_2^- with the doubly charged Cu²⁺ ions. At 3×10^{-2} M formate, and at 0.1 M formate, $Cu(HCO_2)^+ + Cu^{2+}$ ions compose 93 and 72% of the total Cu(II) concentration. As these forms of copper formate are the most reactive, the increase of $[HCO_2^-]$ above 0.03 M is followed by a decrease in k_8 . The results make it possible to determine k_{8f} as equal to k_8 at [HCO₂⁻] $< 10^{-2}$ M. The value of k_{8a} is calculated with a lower accuracy, since the calculation of k_{8a} depends somewhat on the value used for k_{8f} and on K_a . Of the other rate constants, $k_{\rm 8d}$ can be obtained from the experiments at 2 M formate, where reaction 8 is mainly the reaction of $Cu(HCO_2)_4^{2-}$. The values of k_{8b} and k_{8c} are correct only to within a factor of 2. We estimate the error limits of k_{8f} , k_{8a} , and k_{8d} as $(\pm 0.3) \times 10^9$, $(\pm 0.6) \times 10^9$, and $(\pm 1.5) \times 10^8$ M⁻¹ s⁻¹, respectively.

The catalysis of O_2^- dismutation by low Cu(II) concen-

trations in the presence of relatively high [HCO₂⁻] was also tested. In these experiments, 2×10^{-5} M O₂⁻ was allowed to react with (1-4) $\times 10^{-6}$ M Cu(II). Solutions containing 2 M formate showed a catalytic effect by the copper with an apparent reaction rate constant $k_{11} = 2.7 \times 10^8$ M⁻¹ s⁻¹. Cu represents the total copper ions, at all reactive valence states.

$$\operatorname{Cu} + 2\operatorname{O}_2^{-} \xrightarrow{2\operatorname{H}^+} \operatorname{Cu} + \operatorname{H}_2\operatorname{O}_2 + \operatorname{O}_2 \tag{11}$$

The catalytic reaction was found to be pseudo-first order in O_2^- , the rate being proportional to [Cu]. We assume that the mechanism of catalysis is similar to that suggested for free Cu²⁺ ions,⁹ namely, reaction 8 is followed by regeneration of Cu(II) according to

$$Cu(I) + O_2^{-} \xrightarrow{2H^+} Cu(II) + H_2O_2$$
(12)

The apparent reaction rate constant $k_{11} = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (or if reaction 8 involved the formation of Cu(III):

$$Cu(III) + O_2^- \rightarrow Cu(II) + O_2)$$

was measured in 0.2 M HCO₂⁻. (Note that at the relatively low Cu concentrations, the results had to be corrected since the control experiments showed that the non-copper-catalytic decay of O₂⁻ could not always be neglected.) These results show that the reactivity of Cu(I) toward O₂⁻ cannot be much lower from that of Cu(II), under the experimental conditions. In conclusion, there is a definite decrease in the reactivity of Cu(II) toward O₂⁻ as higher HCO₂⁻ complexes are formed. This becomes evident if the ionic strength effects are considered. At zero ionic strength, k_{8f} is about fourfolds higher than the value we measured at ionic strength of 2 M.⁹ Similarly, k_{8d} is probably about fourfold lower at zero ionic strength and thus the ratio $k_{8f}/k_{8d} \simeq$ 10^2 is obtained for zero ionic strength.

Ammonia Complexes. The stability constants for $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$, $Cu(NH_3)_4^{2+}$, and $Cu(NH_3)_5^{3+}$ have been determined to be 1.86×10^4 , $3.9 \times$ 10^3 , 1.0×10^3 , 1.55×10^2 , and 0.30 M^{-1} , respectively.¹⁸ Values of the apparent reaction rate constant k_8 , at various $[NH_3]$, are given in Table I, together with the distribution of Cu(II) among the various complexes. The reactivities of OH radicals with the free Cu²⁺ ions,^{16b} and with NH₃¹⁹ are known. Under the conditions of Table I, at least 50% of the OH radicals (usually >90%) react with HCO_2^- according to reaction 5. Both spectral and kinetic measurements show that the absorption observed several microseconds after the pulse can be attributed to O_2^- . This absorption decays away by a single process in both the absence and the presence of Cu(II) indicating that under our conditions, products other than O_2^- which might have formed, e.g., by the reaction of a small fraction of the OH radicals with NH₃, did not interfere with the measurements. From the results of Table I, it is possible to calculate $k_{8a} = (2.2 \pm 0.6) \times 10^9$, $k_{8b} = (2.2 \pm 0.8) \times 10^9$, $k_{8c} = (1.0 \pm 0.5) \times 10^9$, and $k_{8d} = (2.1 \pm 0.5) \times 10^9$ \pm 0.8) \times 10⁸ M⁻¹ s⁻¹ for the appropriate complexes between Cu(II) and NH₃. For these calculations we took k_{8f} = 2.2×10^9 M⁻¹ s⁻¹, and neglected the penta complex which is expected to account for 6% of the Cu(II) at the highest [NH₃] used. In addition, we assumed no formation of mixed complexes of $[HCO_2^-]$ and $[NH_3]$. This assumption is undoubtedly correct for $[HCO_2^-] < 2 \text{ mM}$, but is not certain for 100 mM formate (last two experiments of Table I). Therefore, the value of k_{8d} is doubtful. Nevertheless, it is clear that the reactivity of Cu(II) toward O₂ - remains rela-

TABLE I: Reactivity	of Copper	Ammonia	Complexes	toward O_{2}^{-a}
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рН	Total [Cu(II)], μΜ	Total [NH₃], mM ^b						e i e		$10^{-9} (k_{s})$ or k_{11} , $M^{-1} s^{-1}$
5.8	3-100 ^c		(1	0	0	0	0	0	0)	2.0 ^d -1.7 ^e
6.9	100 <i>c</i>	0.12	(0.51	0.42	0.07	0.003	<10-4	<10-9	4.4×10^{-5})	2.2 ^d
6.9	30 <i>c</i>	0.35	(0.0066	0.37	0.43	0.13	0.006	<10-6	3.0×10^{-4}	2.1 d
6.9	71 ^c	9.2×10^{-2}	(0.48	0.43	0.08	0.004	<10-4	<10-9	4.8×10^{-4}	1.9 ^d
7.0	100 <i>c</i>	1.0	(0.01	0.15	0.45	0.35	0.04	10-5	7.8 × 10-⁴)	2.2 ^d
7.0	3.0 <i>c</i>	1.0	(0.006	0.11	0.41	0.41	0.06	2×10^{-5}	1.0×10^{-3}	1.7 <i>°</i>
7.0	3.0 <i>c</i>	1.6	(0.002	0.051	0.32	0.51	0.12	6 × 10 ⁻⁵	1.6×10^{-3}	1.6 ^e
7.0	100 <i>c</i>	1.9	(0.002	0.051	0.32	0.51	0.12	6 × 10 ^{-s}	1.6×10^{-3}	2.2 ^d
7.4	300 <i>f</i>	6.0	(<10-⁴	0.005	0.10	0.51	0.38	6 × 10⁻⁴	4.9×10^{-3}	0.43 ^d
7.5	100 ^f	5.0	(<10-4	0.006	0.11	0.51	0.37	5 × 10⁻⁴	4.7×10^{-3}	0.61 <i>d</i>
7.4	100 ^f	1.0	(<10-5	0.001	0.04	0.38	0.58	2×10^{-3}	9.8×10^{-3}	0.49 <i>d</i>
7.7	300 <i>f</i>	2.0	(<10-6	1.7 × 10-⁴	0.013	0.25	0.73	4×10^{-3}	1.9×10^{-2}	0.37 <i>d</i>
8.2	100g	100	(<10-9	<10 ⁻⁵	6 x 10-⁴	0.06	0.91	0.03	0.1)	0.29 <i>d</i>
8.5	1008	200	(<10-10	<10-6	10-4	0.03	0.91	0.06	0.2)	0.20 <i>d</i>

^a Measurements carried out at 248 nm, using optical path 12.3 cm. Each value is an average of three to four determinations. ^b The numbers in parentheses represent the fractions of free Cu²⁺ ions, mono, di, tri, tetra, and penta ammonia complexes, and the concentration of free NH₃ (M) respectively. These were calculated from the appropriate stability constants (see text). ^c 2 mM formate present, ionic strength = 1 M (NH₄ClO₄ + NaClO₄) [O₂⁻]₀ = 2 × 10⁻⁶ M for the measurements of k_8 , and 2 × 10⁻⁵ M for the measurements of k_{11} . ^d k_8 . ^e k_{11} . ^f As c, but 1 mM formate present. ^g As c, but 100 mM formate present.

TABLE II: Reactions of O_2^- with Cu(II) Complexes in the Presence of NaCl or Na₂SO₄^{*a*}

TABLE III:	Reactivity of	f Cu(II)–Amin	o Acid
Complexes t	owards O,		

Cu(II), μM	[O ₂ ⁻] ₀ , μM	$10^{8} k_{8}, M^{-1} s^{-1}$	
1.0	15	4.7 ^b	
1.0	15	4.8 b,c	
100	3.5	4.1 b	
1.0	15	8.0 <i>d</i>	
100	3.5	6.0 <i>d</i>	
100	3.5	4.5 d,e	

^a 12.3-cm light path at 248 nm. Each value is an average of three experiments. ^b 1 mM formate, 0.95 M NaCl, pH 6.3. ^c 25th pulse on the same solution, with total $[O_2^{-}] = 380 \ \mu\text{M}$. ^d 1 mM formate, 0.33 M Na₂SO₄, pH 7.2. ^e 100th pulse on the same solution, with total $[O_2^{-}] = 350 \ \mu\text{M}$.

tively high when the first three NH_3 molecules add as ligands. The addition of the fourth NH_3 ligand has an effect on k_8 which is smaller than the effect of adding the fourth HCO_2^- ion. This may be due to a charge effect. Copper continues to act as a catalyst for O_2^- dismutation, even when complexed.

Complexes with Cl^- and with SO_4^{2-} . Experiments in 0.95 M NaCl show a considerable reactivity of Cu(II) both in excess over $[O_2^-]$, and as a catalyst for O_2^- dismutation. The same is correct for 0.33 M Na₂SO₄. The results are summarized in Table II.

Cu(II) Complexes with Amino Acids. In Table III we present data on the reactivity of Cu(II) in the presence of amino acids.

The initial absorption observed in the solutions which contained both formate and an amino acid was similar to that observed in formate solutions, in the absence of amino acids. In both cases the absorption was due to O_2^- , which formed according to reaction $6.^{15}$ HCO₂⁻ competed successfully with amino acids for OH, and O_2 succeeded to scavenge practically all the electrons.¹⁶ In the case of gly-cylglycine, about 10% of the initial absorption decayed away with $\tau_{1/2} \simeq 200 \ \mu s$ despite the presence of 5 mM formate. Glycylglycine reacted with a fraction of the OH radicals, eventually producing peroxy radicals which decayed away considerably faster than O_2^- . In the absence of formate.

	Amino acid				
	concn, mM		Cu(II),		
		pН	μM	$k_{B}, M^{-1} s^{-1}$	
Alanine ^{a-d}	10	7.4	100	2.8 × 10°	
Alanine ^{<i>a,b,d</i>}	10	7.4	300	3.5×10^{6}	
Glutamate ^{b,d,e}	100	7.1	100	$(1-2) \times 10^{6}$	
Glutamate ^{b,d,e}	100	7.1	300	$(1-2) \times 10^{6}$	
Glycine ^b f	1000	6.0	100	~1 x 10 ⁶	
Glycine ^{a,c,d}	20	7.9	100	2.1×10^{6}	
Glycine ^{a,c,d}	20	7.9	300	2.1×10^{6}	
Hydroxyproline ^{a,b,g}	2	8.1	50	1.2×10^{6}	
Hydroxyproline ^{4, b, g}	2	8.1	100	1.0×10^{6}	
Hydroxyproline ^{b,g,h}	10	7.7	100	9.0 × 10 ^s	
Methionine ^{<i>b,d,i</i>}	50	7.8	100	6.8 × 10 ⁶	
Methionine ^{b,d,i}	50	7.8	200	8.0 × 10°	
Methionine ^{b,d,h}	50	7.1	100	5.6 × 10°	
Methionine ^{b,d,h}	50	7.1	300	4.8×10^{6}	
Proline ^{a, b, g, j}	1	7.5	100	5 × 10 ^s	
Valine ^{b,d,k}	0.5	6.2	100	2.4×10^{8}	
Valine ^{b,d,h}	10	8.1	100	1.7 × 10°	
Glycylglycine ^{<i>a,d,j</i>}	10	6.7	100	1.9×10^{7}	
Glycylglycine ^{<i>a,d,j</i>}	10	6.7	200	2.0×10^{7}	

^a 5 mM formate present. ^b 3.5 μ M radicals produced per pulse. ^c 15 μ M radicals produced per pulse. ^d Measured at 280 nm, with 4-cm light path. ^e No formate present. In the absence of copper the optical absorption decayed away by two processes. The slower of these accounted for about 40% of the optical absorption and was attributed to the decay of O₂⁻. ^f Measured at 248 nm, light path 12.3 cm. ^g Measured at 270 nm, light path 4 cm. ^h No formate present. Two decay processes in the absence of copper. The slower accounted for 80% of the initial absorption and was attributed to the decay of O₂⁻. ⁱ 0.2 M formate present. ^jIn the absence of copper there were two decay processes. The slower of these accounted for 90% of the initial absorption and was attributed to O₂⁻. ^k 10 mM formate present.

mate, about 50% of the radicals are still expected to form O_2^- according to reaction 2. The reactivity of the amino acids used by us toward e_{aq}^- is generally low enough to neglect the possible reactions of amino acids with e_{aq}^- . 1 M glycine is an exception to this, as it is expected that about
25% of e_{aq}^{-} react with it in O_2 saturated solutions. However, in this solution still about 90% of the total radicals produce O_2^- , because the peroxy glycine radicals (which are formed as a result of the OH attack on glycine, followed by reaction with O_2) are converted to O_2^- , within about 50 μ s, under our experimental conditions.²⁰

In all other experiments where formate was absent eag formed O₂⁻ according to reaction 6. OH radicals reacted with the amino acids to produce amino acid radicals which were converted to the appropriate peroxy radicals upon reaction with O_2 . These radicals may have yielded additional O_2^- , the yield of which, if any, is still open for further research. Indeed, the initial absorbance in the absence of formate was not exactly the same as in the HCO_2^- solutions; variations up to 20% were observed. This is expected, if the peroxy radicals have absorptions which are somewhat different from the absorption of O_2^- . In all the cases except in glycine, where amino acids were irradiated in the absence of both formate and copper, the absorption decayed away by two processes. The first usually accounted for 10-20% of the initial absorption (except in the case of gluzamate, where it was 60%). The second process can be attributed to the decay of O_2^- , the source of which is reaction 2 plus $O_2^$ produced from the reactions of amino radicals with O_2 . This conclusion is supported by the fact that the absorption remaining at the end of the fast process was normally much higher than the absorption expected from O2formed by reaction 2 alone. The half-life of the fast process was of the order of 5×10^{-4} s, and varied from one amino acid to another.

The absorption which remained after this decay disappeared considerably slower (half-life 0.1-0.2 s), all in one process. This agrees with the assumption that this absorption belongs to O_2^- . Further work is needed to establish the fate of peroxy radicals derived from amino acids.

Copper Proteins. 1-2 µM of hemocyanine and of plastocyanine were tested for catalysis of O_2^- dismutation in O_2 saturated solutions containing 20 mM formate at pH 8.0 (3 \times 10⁻³ M phosphate buffer). No activity was observed at 290 nm (k_8 , $k_{11} < 10^6 \text{ M}^{-1} \text{ s}^{-1}$).

Conclusions

The reactivities of Cu(II) complexes toward O₂⁻ decrease when several ligand molecules become attached to the copper atoms. This effect may be connected with changes in the redox potential of the Cu(II). It is known that Cu(II) may be stabilized with respect to reduction, upon complexing. As the reaction of Cu^{2+} with O_2^{-} was suggested to involve the formation of Cu^+ , it is not surprising that $O_2^$ is less efficient in reactions with Cu(II) complexes. In fact, the possibility that O_2^- may tend to oxidize Cu(II) (as complexes) rather than reduce it to Cu(I) cannot be ruled out at present.

Our conclusions are in agreement with previous work, in which Cu(II) chelates were found, in some other cases, to have relatively low reactivities toward $O_2^{-.21-23}$

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On the Nature of the Radicals Produced by γ Radiolysis of 2-Methyltetrahydrofuran in Adamantane. A Variable Temperature Comparative Study via X-Band and Q-Band Electron Spin Resonance

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The effects of γ radiolysis on adamantane- d_{16} and adamantane- d_{16} containing 2-methyltetrahydrofuran solute molecules have been examined via X-band 9.5-GHz and Q-band 35-GHz electron spin resonance at temperatures down to 77 K. Adamantane- d_{16} appears to produce at least two radical species, a fact that cannot be deduced from X-band ESR alone. 2-Methyltetrahydrofuran produces two distinct radicals (II and IV) and hyperfine splitting constant values have been assigned to each species. A third radical is formed from 2-methyltetrahydrofuran at high temperature, but is presently unidentified. These two radicals are believed to be formed in γ radiolysis of 2-methyltetrahydrofuran glass, but they do not seem to suffice to entirely explain the observed spectrum in the glass.

Introduction

The radiolysis of 2-methyltetrahydrofuran (MTHF) glass at 77 K is of considerable interest because of the high yield of trapped electrons produced. However, the fate of the concomitant cation produced in the initial ionization process is not so clear. The radiolytic mechanism has been suggested to be as follows¹

MTHF
$$\xrightarrow{\gamma \text{ rays}} e_m^- + \text{MTHF}^+$$
 (1)
 $e_m^- \longrightarrow e_n^- (G = 2.6)$ (1a)

$$e_m^- \longrightarrow e_t$$
 (G = 2.6)
MTHF⁺ + MTHF \longrightarrow

 $MTHFH^+ + MTHF \cdot (G = 2.6)$ (1b)

MTHF
$$H + MTHF (G = 0.2)$$
 (2)

$$H + MTHF \longrightarrow H_2 + MTHF \cdot (G = 0.2)$$
 (2a)

where G represents the molecular yield per 100 eV of radiation energy absorbed and the subscripts m and t refer to mobile and trapped. This scheme gives $G(e_t^{-}) = 2.6$ and G(MTHF) = 3.0 as observed, but only reactions 1 and 1a have been clearly demonstrated. Electron spin resonance (ESR) studies¹ clearly identify a singlet at g = 2.002 with a 4.2-G peak-to-peak derivative line width (ΔH_{pp}) as due to e_t^{-} . In addition a seven-line spectrum at g = 2.003 with an average splitting of 20.1 ± 0.4 G, relative intensities of approximately 1/4/7/8/7/4/1, and $\Delta H_{pp} \simeq 10$ G has been assigned to either or both neutral radical A² or the protonated radical B.³ The proton on the oxygen of the protonated radical would not be expected to show hyperfine interaction with 10-G line widths, so the ESR spectra of A and B are expected to be the same. The seven-line spectrum is



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explained by assuming that the three methyl protons and one of the β -CH₂ protons are equivalent and have ~20-G splitting while the other β -CH₂ proton has a 40-G splitting.

If the above explanation is correct, γ radiolysis of MTHF- d_3 should show the same seven-line spectrum.



However, γ radiolysis of MTHF- d_3 glass gives a nine-line radical spectrum with an average splitting of 13.6 G and relative intensities of approximately 1/1/4/4/7/4/4/1/1; this is not readily interpretable as due to a single radical.⁴ This suggests that reaction 1b and perhaps reactions 2 and 2a do not give rise to a single radical as has been commonly assumed.

To help resolve the identity of the primary radicals produced in MTHF radiolysis we have investigated the radicals produced in the radiolysis of adamantane doped with MTHF. Previous studies have shown that adamantane is a useful matrix for obtaining well-resolved ESR spectra of solute radicals produced by radiolysis.⁵

Experimental Section

Adamantane (Ad, Aldrich Chemical Co.), adamantane d_{16} (Ad- d_{16} , Merck Sharp and Dohme (Canada)), and 2methyltetrahydrofuran (Matheson Coleman and Bell) were purchased in the highest purity available. Ad and Ad- d_{16} were purified by three to five sublimation procedures. Fresh samples of multiply resublimed Ad and Ad- d_{16} were used for each radiolysis experiment since previous experimental work has disclosed that reirradiation of a sample produces poorly resolved electron spin resonance spectra and generally irreproducible data.⁵ MTHF was purified by standard methods involving the following sequential operations: repetitive washing with 10% aqueous NaOH, vacuum distillation from CaH₂, repetitive passages through newly

activated (650 K) Al₂O₃ under N₂ or Ar atmospheres, refluxing over Na metal on a vacuum line, and storage on a vacuum line over an alloy of Na and K.6 Samples were prepared on the vacuum line by methods described previously for cyclopentadiene⁵ and sealed off in quartz ESR tubes at pressures of <10 Torr. Samples were irradiated in a Co-60 source with a γ ray flux of $\sim 2 \times 10^{17}$ eV g⁻¹ min⁻¹; doses were usually $\sim 5 \times 10^{18}$ eV g⁻¹ for each sample. To avoid complications from signals developed in ESR cells, samples were inverted prior to irradiation, the top of the cell flamed after irradiation and prior to ESR monitoring to reduce the population of color centers produced in the quartz tube, and then reinverted for ESR monitoring. The sample temperature was maintained at 77 K throughout these manipulations. The resonance cavity was maintained at 92 K prior to insertion of the sample; this was the coldest accessible temperature conveniently maintained by the N₂ gas flow system used for the variable temperature study in both spectrometers. Room temperature studies via Q-band ESR were carried out by compressing Ad or $Ad - d_{16}$ samples into a disk⁷ via a standard KBr die and press at $\sim 6 \times 10^3$ psi, and then mounting the sample directly in the resonance cavity. This obviated any possible interference from signals not originating from the Ad samples themselves. ESR spectra were recorded with a Varian E-4 X-band 9.5-GHz spectrometer and a Varian Associates E-9 Q-band 35-GHz spectrometer. Computer simulations⁸ were obtained via an IBM 360/75 computer and CalComp accessory plotter. The gauss baselines for each spectrometer was calibrated from a sample of Mn in MgO, a value of 86.8 G being taken for the separation of the two center lines of the sextet equal intensity spectrum resulting from ⁵⁵Mn²⁺ ions in the MgO matrix.9 The errors for both X-band and Q-band spectrometers did not exceed 1.5% as measured from the Fielddial scanning parameters of the instruments.

Results and Discussion

Usage of Ad and $Ad \cdot d_{16}$ as isolation matrices, and the superiority of $Ad \cdot d_{16}$ over Ad for this purpose, is now well established (cf. the spectrum of $C_6H_5CH_2$ shown in Ad and $Ad \cdot d_{16}$ matrices in ref 5e). There is still an element of controversy as to the exact identity of the primary radical produced from adamantane, and there is little published data at all concerning radiolysis of $Ad \cdot d_{16}$ or the temperature dependence of the observed data from the radiolysis of Ad itself. Since this latter is pertinent to this investigation of the temperature dependence of radiolysis data for MTHF, we have included a brief description of our date on this topic.

Radiolysis of Adamantane- d_{16} . Temperature Dependent Study. Since Ad, Ad- d_{16} , and diamantane^{5d} are all structurally similar, and since Ad and diamantane seem to produce structurally equivalent radicals (the bridgchead radical),^{5d} we assume that Ad- d_{16} will also produce a structurally equivalent radical, the 1-adamantyl radical.^{5c,d}

The ESR spectrum obtained at Q-band following γ irradiation of Ad- d_{16} at 77 K is shown in Figure 1a. The changes noted as the monitoring temperature rises from ~95 K to room temperature are detailed in Figure 1a-d. No qualitative or quantitative changes were noted in the spectrum until the temperature began to approach ~200 K. It is assumed that the spectrum that would be seen at 77 K is very similar to that shown in Figure 1a. The broad singlet envelope is similar to that seen previously for Ad at Xband. The ESR singlet envelope from Ad A_{16} in the Q-band



Figure 1. First-derivative ESR spectra taken at Q-band of purified adamantane- $d_{16} \gamma$ irradiated at 77 K. (a) Spectrum typical of the temperature range 92–180 K, this scan taken at 110 K; (b) spectrum taken at ~210 K; (c) spectrum at room temperature ~300 K; (d) spectrum at room temperature after more than 15 h at ~300 K. Spectrometer settings in this figure, and for subsequent Q-band spectra, are typically 12,150 G center at 34.782 GHz, ±50-G scan, 1.0 dB below 70-mW power, 100-kHz modulation frequency, and 2.0-4.0-G modulation amplitude.

spectrum at low temperature has a total width of ~42 G, a peak-to-peak line width of ~7 G, and does not exhibit any significant degree of microwave power saturation up to 70 mW. These data may be contrasted with those obtained previously^{5c,d} for adamantyl radicals at X-band at room temperature, where values of 50-G spectral width and 12-G peak-to-peak line width were obtained, and significant saturation was seen at ~35 mW.

As the temperature of the γ irradiated Ad- d_{16} is raised from ~180 K through the crystal transition temperature at 208 K to ~215 K, the singlet envelope changes slowly and a second peak at higher field develops (Figure 1b). As the temperature rises to ~300 K this second peak becomes somewhat better resolved (Figure 1c). This two line spectrum is qualitatively stable for more than 7 days, and is identical with the spectrum obtained if Ad- d_{16} is γ irradiated and observed at room temperature. The upfield peak decays slowly at room temperature with a first half-time for decay of >5 h. The kinetics fit a second-order plot over ~90 h.

These data suggest that at least two distinct radical species contribute to the observed ESR spectrum from γ irradiated $Ad-d_{16}$, and therefore by analogy to the ESR spectrum observed from Ad itself. The appearance of a second upfield line in the Q-band spectrum as the temperature rises implies that two radicals of different g factors are present at room temperature. This structure is not observed at X-band. The existence of two radicals is supported by the decay of the upfield line at room temperature independent of the other line without any concomitant growth elsewhere in the spectrum. By analogy with the Xband studies^{5c,d} we tentatively assign the dominant line at room temperature in Figure 1c to the 1-adamantyl radical. The identity of the other radical is presently unknown; it does not seem reasonable to assign the other line in Figure 1c to 2-adamantyl since its g factor is expected to be similar to that for 1-adamantyl. However, the spectral changes in Figure 1 are qualitatively important for understanding of the spectral features from a solute in the Ad- d_{16} matrix.



Figure 2. First-derivative Q-band and X-band ESR spectra for γ irradiated adamantane- d_{16} containing 2-methyltetrahydrofuran as a solute; γ irradiation temperature was 77 K. Q-band spectra at (a) 150, (b) 170, and (c) 200 K; (d) stick spectrum assignment and hyperfine values for Q-band ESR spectrum, (e) X-band ESR spectrum at 200 K. Spectrometer settings are typically those given in Figure 1. The field increases to the right.

Radiolysis of MTHF in Ad-d₁₆. The nature of the changes observed, and the explanations proposed for these changes, when Ad-d₁₆ containing MTHF as a solute is γ irradiated at 77 K and then monitored via both Q-band and X-band ESR from ~95 to 300 K, are complicated, and in some cases unexpected. To simplify such descriptions we have broken the text up into sections devoted to specific temperature ranges. These regions are: temperatures below ~140 K, where signals from radicals derived from the matrix only are seen; ~140-240 K, where one specific solute radical is seen; ~240-270 K, where a second solute radical appears; and from 270 K to room temperature, where observed changes correlate with changes in matrix radical species and not primarily in solute species.

 $MTHF-Ad-d_{16}$ System below 140 K. When Ad- d_{16} containing MTHF as a solute is γ irradiated at 77 K and then monitored at 95-140 K, a singlet spectrum is observed at X-band and at Q-band which seems primarily due to the adamantane matrix radical.

MTHF-Ad-d₁₆ System at 140-240 K. Both the Q-band and X-band ESR spectra remain qualitatively similar and stable as the temperature is slowly raised from 95 K, until at \sim 140 K there begins to appear hyperfine structure over a span of approximately 70 G. These changes are detailed in Figure 2. There are three prominent lines to high and to low field of the center asymmetric line. An additional high field line shows up fairly clearly on the high field side of the center line above 170 K and we deduce that its symmetry partner lies under the center line. In total there is a new spectrum with a pattern of eight, equal intensity lines. This eight-line Q-band spectrum can be analyzed by the stick diagram in Figure 2d to give independent hyperfine values of 13.3 ± 0.5 , 21.7 ± 0.5 , and 32.0 ± 1.0 G. The peak-topeak line widths for the Q-band spectrum vary between 2.2 and 3.7 G, with an average value of 2.9 G for the clearly distinguishable outer six lines of the octet. A comparable X-

band spectrum at 200 K, shown in Figure 2e, displays three individual hyperfine values of 14.0 ± 0.5 , 22.1 ± 0.5 , and 34.4 ± 2 G. The average line width for the X-band spectrum is 2.1 G for the outer six lines of the octet.

We note that these line widths are typical of alkyl radicals with localized spin centers in $Ad-d_{16}$ matrices and are larger than the line widths found for delocalized spin centers such as aryl and allyl radicals (0.6-1.8 G) in Ad- d_{16} matrices.^{5d,11} The following empirical observations on these line width differences can be made. First, use of Ad d_{16} rather than Ad reduces the effects of unresolved proton hyperfine coupling from long-range matrix dipolar interactions, and thus significantly reduces the line width. This effect seems more pronounced for delocalized spin centers than it is for localized spin centers typical of alkyl radicals, and may reflect a difference in the matrix dipolar interactions exhibited by each system. Secondly, in a adamantane matrices delocalized radicals typically exhibit narrower line widths than a corresponding localized radical with apparently similar structure. This can be illustrated by comparison of cyclopentenyl radical

with the alkyl radical

derived from cyclopentane,^{5b,10} by comparison of aliphatic linear alkyl radicals with similar allylic radicals derived from alkenes,^{5a,11a,c} and by comparison of radicals derived from 2,5-dimethylthiophene by H abstraction (allylic) and H addition (alkyl).^{11b,c}

These three hyperfine values are clearly attributable to three independent hydrogen atoms in an alkyl radical derived from the MTHF solute, and are consistent with two possible structures, I and II. We find it difficult to rational-



ize the hyperfine values in terms of structure I from four viewpoints. First, this structure would imply that two of the observed hyperfine values are α -proton coupling constants (a_{α}^{H}) , and only one (22 G) resembles the typical values for a_{α}^{H} in alkyl radicals. Secondly, a_{α}^{H} values should be virtually temperature independent, and only one of these hyperfine values is found to be so (see X-band spectra in Figure 4). Thirdly, by analogy with other systems, it is difficult to see why two a_{α}^{H} values should differ by such a large amount for a -CH2 group that should be undergoing relatively free rotation about the single C-C bond at this temperature. If the $-\dot{C}H_2$ group is rendered immobile for some reason, then interaction with the tertiary H atom attached to the carbon atom at position 2 (C2) will certainly lead to nonequivalence, but even for systems involving $=\dot{C}H_2$ (such as a delocalized allyl radical)¹² where free rotation has been severely curtailed, the two a_{α}^{H} values for individual protons rarely differ by more than 2-3 G, and never by 8-10 G. Fourthly, by analogy with other systems subjected to radiolysis, it is most unusual for the

methyl group attached to a *saturated* ring or alkane moiety to undergo attack. Customarily in adamantane matrices, the methyl group will stay intact while radiation damage in the form of H-atom abstraction will occur from the main carbon skeleton of the molecule. This is particularly true when a tertiary H atom is available on the molecule, as exemplified by isopentane, 2-methylpentane, and 3-methylpentane,^{5a} and particularly by the structural equivalent to MTHF, methylcyclopentane.^{5b}

Another possible radical structure, III, caused by C-C



bond cleavage and methyl radical loss from the 2 position, can be rejected also because radical III would be expected to have equivalent β protons. This is a subtle point which will be discussed in the next section.

The assignment of individual hyperfine values to particular protons in II can be made relatively easily because II has a similar spin environment to III and the liquid phase ESR spectrum of III has been assigned with $a_{\alpha}^{H} = 12.3$ G and $a_{\beta}^{H} = 28.3$ G.¹³ Note that the a_{α}^{H} coupling is greatly reduced from the typical 22-G a_{α}^{H} values in alkyl radicals. In other liquid phase studies of radicals derived from alcohols, carboxylic acids, and ethers, Norman and co-workers¹⁴⁻¹⁶ also found that a_{α}^{H} values were typically less than 20 G in oxygen containing radicals. Thus we can assign the 14-G coupling to the α hydrogen of II.

If we assume that the 14-G hyperfine constant is that from the α hydrogen, then the 33-G coupling and the 22-G coupling are assigned to two distinct β -hydrogen atoms at C₄. The angular dependence of the a_{β}^{H} values in hydrocarbon radicals is well described by the Heller-McConnell equation¹⁷

$$a_{d}^{H} = (B_1 + B_2 \cos \theta)\rho$$

where B_1 is usually close to zero and $B_2 \simeq 50 \text{ G.}^{18}$ Thus the maximum coupling of ~50 G is found for a β -proton orientation at a projected angle on a plane perpendicular to the C-C axis of 0°. Hyperfine values of 33 and 22 G correspond to $\theta \sim 36^\circ$ and $\theta \sim 48^\circ$, respectively, and thus a projected angle between the two β protons at C₄ of ~96°. This is smaller than the angle of 120° expected by looking down the C-C bond of sp³-hybridized carbons. Some distortion is expected at each carbon atom in view of the constraints imposed by a five-membered ring configuration.

MTHF-Ad-d₁₆ System at 240-270 K. In this temperature range three distinct sequences of events can be distinquished. First, the center of the spectrum alters both in intensity and fundamental pattern. Secondly, a new set of lines begins to appear, seen easily by two lines more than 15-G downfield and upfield of lines 1 and 8 of the doublet pattern octet from II, and by two lines just inside lines 1 and 8 of the octet and separated from them by ~7 G. Other lines also show plainly in the interior of the octet. Thirdly, the relative intensities of the lines comprising the octet change at the same rate as the new lines appear indicating overlap of the octet with a new radical spectrum. Also the octet separation changes very slightly to give a new set of hyperfine values. The final Q-band spectrum obtained after these changes, which exhibits a qualitatively stable



Figure 3. First-derivative Q-band ESR spectrum from γ irradiated adamantane- d_{16} containing 2-methyltetrahydrofuran solute, the γ irradiation temperature was 77 K. (a) Spectrum observed at ~260 K; (b) stick spectrum assignment for radical II; (b) stick spectrum assignment to the new radical that grows into the doublet pattern octet contributed by II at temperatures of ~200 K. The field increases to the right.

ESR pattern with respect to temperature, is shown in Figure 3 at 260 K. The spectrum in Figure 3a remained stable up to temperatures of \sim 270 K.

The appearance of the new lines in the spectrum outside the main octet from II separated by ~102 G, the new lines that appeared at several points within the octet pattern, and the marked increase in intensity of lines that comprised the octet due to overlap with an underlying spectrum allow identification of a new radical spectrum. A welldefined set of 12 lines is found with a 1:2:1 triplet separation of 23.9 \pm 0.5 G and a 1:3:3:1 quartet pattern with a separation of 19.0 \pm 0.5 G. This radical spectrum can only be assigned to a structure such as IV. Although this assign-



ment of 19.0 G to the methyl group coupling is unusual with respect to typical $a_{CH_3}^{H}$ magnitudes of ~23 G (e.g., methylcyclopentyl has $a_{CH_3}^{H}$ = 23.0 G),^{5b} there are three factors that support this assignment. First, the 1:3:3:1 relative intensities in the pattern can only mean three equivalent protons. Secondly, it is expected that the α -carbon spin density would be reduced by the adjacent oxygen atom, as was seen for II. Thirdly, a structurally similar radical has been formed by γ radiolysis incuded H-atom addition to 2,5-dimethylthiophene in adamantane with structure V.^{11b,c}

Since radical IV is not seen until nearly 100 K after II has developed, and grows concomitantly with a spectral loss attributable to matrix radical decay, it seems reasonable to postulate formation of IV by radical attack on the solute from an adjacent matrix radical. A plausible reason for the late appearance of IV with respect to II is then attributed to steric hindrance produced by the shielding



Figure 4. First-derivative X-band ESR spectra obtained by γ radiolysis of adamantane- d_{16} containing 2-methyltetrahydrofuran; γ irradiation temperature was 77 K. (a) Spectrum taken after warming to 260 K; (b) spectrum obtained by recooling sample to 160 K; (c) spectrum obtained after sample has been rewarmed to ~270 K. The field increases to the right.

methyl group at C_2 relative to the unshielded and equally reactive 5 position of MTHF. The possibility that IV is formed from II by a unimolecular or bimolecular reaction can be discounted. First, the degree of migrational mobility accessible to a molecular species in adamantane is severely limited, thus bimolecular reactions are improbable. Secondly, no discernible loss of a spectrum attributable to II can be seen. Thirdly, unimolecular rearrangements involving this extent of bond making and breaking can be ruled out from conventional mechanistic arguments.

If the lines attributed to IV are subtracted from the observed spectrum, a set of equal intensity lines remain that can be fitted to an octet pattern with hyperfine values of 13.2, 24.4, and 30.1 G (Q-band). This pattern is obviously that from structure II with a small mixing of β -proton hyperfine values induced by motional averaging. A stick spectrum of this modified octet, and the stick spectrum of IV, are given in Figures 3b and 3c, respectively. The equivalent X-band spectrum to that in Figure 3 is shown in Figure 4, and exhibits considerable line broadening due partly to an unfortunate similarity of a major hyperfine coupling in each radical (23.9 and 24.4 G), but also to severe overlapping caused by nearly coincident, but not identical g values. There is a ~1.3-G separation of centers at Q-band, with the octet spectrum from II lying upfield of IV.

It is interesting and instructive at this point to consider the reasons for the equivalency of the β protons in IV, and the nonequivalency of the β protons in II, when they are both apparently similar radicals in the same matrix. This apparent anomaly is linked, not with molecular inversion vibrations, but to the reduced molecular symmetry of II relative to IV. Examination of molecular models clearly indicates a significant amount of diaxial interaction between the axial methyl at C_2 (the preferred conformer) and the axial proton at C₄; thus the β protons of II are not magnetically equivalent. On the other hand, in radical IV the methyl group is no longer axial and the β protons become equivalent. On this basis we may also reject the possibility that the low temperature octet pattern is assignable to radical III produced by methyl group loss at C₂. Although III is formally identical with II with respect to spin center environment, III would be expected to have two equivalent β protons and a sextet ESR spectrum.



Figure 5. First-derivative Q-band ESR spectra from γ irradiated adamantane- d_{16} containing 2-methyltetrahydrofuran; γ irradiation temperature was 77 K. (a) Spectrum taken at 280 K; (b) spectrum at 300 K; (c) spectrum after several hours at 300 K. The field increases to the right.

One final point should be added in denial of structure III formed by methyl group loss. If the methyl group is indeed cleaved, it will be trapped in the same matrix cage as the major radical (III), and if it cannot escape the cage it will undergo prompt geminate recombination. We have found no evidence for molecular migration of a species as large as CH₃, and can confirm that NH₃ does not appear to migrate freely through an adamantane lattice.^{5d} The only migration seen in adamantane matrices has been by H atoms (and presumably by D atoms) together with the ubiquitous electron; moreover, no traces have been found of free methyl radicals from MTHF or similar solutes trapped in adamantane. Thus, if methyl group cleavage does occur, prompt geminate recombination should remove the possibility of stabilizing radical III.

MTHF-Ad-d₁₆ System from 270 K to Room Temperature. The final changes noted as adamantane- d_{16} containing 2-methyltetrahydrofuran solute is warmed from ~ 270 K to room temperature following γ radiolysis at 77 K appear to mainly reflect changes in the radical or radicals derived from Ad_{16} itself. These changes are detailed in Figure 5. The first striking change is a growth, and then a rapid decay of a large central peak (Figure 5a), which then gives rise to the two-line Q-band spectrum seen in Figure 1, and shown overlaid with the solute spectrum in Figures 5b and 5c. More important than these adamantyl radical changes is the observation that the spectrum attributed to the tertiary radical IV has completely decayed. The octet pattern from II is still easily visible in Figure 5a, together with a rapidly decaying contribution from IV. In Figure 5b, IV has disappeared altogether, and the octet from II is becoming obscured by the ESR spectral pattern of another species. This new radical has vastly different power saturation characteristics from both II and the matrix radical contributions, since peaks can be selectively enhanced by increasing the Q-band microwave power from ~ 0.7 to 70 mW. However, the entire upfield portion of the spectrum is obscured by the two-line spectrum from adamantyl species, and we are unable to identify the major solute species contributing to the observed spectrum.

After several hours at room temperature the spectrum appears as in Figure 5c. It has narrowed in overall width 844.5

TABLE I: Hyperfine Splitting Constants Found from a Variable Temperature Study of 2-Methyltetrahydrofuran in Adamantane- d_{16} Matrices γ Irradiated at 77 K

Temp, K	Hyperfine values found, G	Structure . assigned
~140-240	Octet pattern Q-band: 13.3, ^a 21.8, ^a 32.0 ^b X-band: 14.0, ^a 22.1, ^a 34.4 ^b	(13) (13) (13) (13) (13) (13) (13) (13)
~240–270	Octet pattern Q-band: 13.2, ^a 24.4, ^a 30.1 ^b	(301 G) H H H (244G) H H H H CH ₃
~240–270	Triplet of quartets Q -band: 23.9, ^b 19.0 ^b	$H \xrightarrow{H} H^{(239G)}$ $H \xrightarrow{H} CH_{a}$ $(190G)$
^a ±0.5 G.	$b \pm 1 \text{G.}^{c} \pm 2 \text{G.}$	IV

from the original 71 G of the octet pattern from II alone shown in Figure 2, to a value of just over 50 G in Figure 5c. This indicates that a new unidentified species is formed from, or replaces, radicals II and IV.

Comparison of Data with MTHF Glass. It is of interest to compare the present results with the radicals produced in MTHF glass. The X-band ESR spectrum from the γ radiolysis of MTHF glass at 77 K shows an intense central singlet attributed to trapped electrons superimposed on a radical spectrum.¹ The radical spectrum alone is obtained after optical bleaching of the trapped electrons and it has seven lines with approximately pyramidal intensity ratios, an overall width of 120 G, and a peak-to-peak width of ~ 10 G. We have simulated⁸ the first-order spectra from radical species II and IV with line widths of 4-6 G which are typical of a glassy matrix. Neither spectrum agrees well with the glassy phase spectrum. Radical II degenerates to a seven-line spectrum with an intense line at the center and nearly equally intensity lines on either side. The spectrum has a total width of only ~70 G for a line width of 4 G. Radical IV produces a six-line spectrum with roughly pyramidal intensities and an overall width of 100 G for a 6-G line width. We have also tried various mixtures of spectra II and IV to simulate the glass spectrum to no avail. We conclude that the previous assignment of the radical spectrum in glassy MTHF to radical IV is quite doubtful. The radical spectrum in the glass may well be composed of radicals II and IV as well as radicals formed by loss of H at carbons 3 and 4. This suggests that there may be little specificity in ion-molecule reaction 1b.

It is possible that different dominant radicals are formed by γ radiolysis of the glass and of the doped adamantane. Willard and co-workers have demonstrated that 3-methylpentane glass at 77 K tends to form the secondary radical, $CH_3CHCH(CH_3)CH_2CH_3$, under radiolysis.¹⁹ However it appears that the only radical produced from 3-methylpentane in adamantane by radiolysis is the tertiary radical, CH₃CH₂Č(CH₃)CH₂CH₃.^{5a}

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Summary and Conclusions

A comparison of X- and Q-band ESR spectra of adamantane- $d_{16} \gamma$ irradiated at 77 K and studied upon warming -shows that at least two radical species are produced. When Ad - d_{16} is doped with MTHF, γ irradiated at 77 K, and warmed several identifiable radical species are formed as summarized in Table I. Below 140 K only the adamantane matrix radical is observed. From ~140 to 240 K MTHFsolute radical II is formed, presumably by H abstraction from MTHF by the matrix radical. From \sim 240 to 270 K a second solute radical IV is formed, while II also remains. When both radicals II and IV appear, the matrix radical partially decays. The initial preference for formation of II is rationalized on steric grounds. At temperatures above \sim 270 K, IV decays rapidly, II decays more slowly, and a new solute radical begins to dominate the spectrum. The parameters of neither radicals II and IV, nor their mixture, can be used to successfully simulate the radical spectrum found in irradiated MTHF glass.

NOTE ADDED IN PROOF: Recent work by Dismukes and Willard²⁰ confirms the production of radicals II and IV by γ -irradiation of MTHF in adamantane, but they indirectly conclude that the two equivalent β protons in radical IV at \sim 230 K and above become inequivalent with one coupling constant twice the other at 77 K so that radical IV can explain the spectrum in MTHF glass. Their conclusion remains inconsistent with our results on the irradiation of MTHF- d_3 glass at 77 K so methods of specifically producing solely radical IV at 77 K are being investigated.

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Cis-Trans Equilibria of 1-Chloropropene in Organic Solvents

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Ternary systems of the type isomer cis + isomer trans + solvent are considered. Preponderance of the cis form of 1-chloropropene in a series of organic solvents is discussed in terms of the configurational energies $U_{\rm ii}$ of the isomers; experimentally found independence of the cis/trans ratio of the solvent used is explained using the configurational energy formula for the ternary system and a simple combining rule. The equations obtained enable predictions of isomeric equilibria in solutions, provided the configurational energies of components are accessible. Limitations of the present method are related to strong specific interactions between molecules of isomers.

1. Introduction

This work is related to studies of the thermal decomposition of some substituted diazirines by one of us 1,2 The decomposition of 3-chloro-3-ethyldiazirine in various solvents produces nitrogen and *cis*- and *trans*-1-chloropropene. The dipole moments of the solvents used varied over a considerable range. In spite of this, the cis/trans concentration ratio in 1-chloropropene was about 5:1, changing only very slightly with the solvent used.² Analogous result has been obtained for *cis*- and *trans*-1-bromopropene, produced in various solvents by the thermal decomposition of 3-bromo-3-ethyldiazirine.²

Abell and $Adolf^3$ have studied the gas phase bond isomerizations of allyl fluoride, allyl chloride, and allyl bromide to the corresponding 1-halo-1-propenes. They have also found the cis/trans ratios of the olefins equal approximately to five, and this independently of the halogen in the halopropene. Abell and Adolf admit frankly that they are unable to explain such a result.

In the present paper we discuss the above results in terms of the configurational or interactional energy U^c . For a ternary system cis-olefin c + trans-olefin t + solvent s we thus write

$$U^{c} = x_{s}^{2}U_{ss} + x_{c}^{2}U_{cc} + x_{t}^{2}U_{tt} + 2x_{s}x_{c}U_{cs} + 2x_{s}x_{t}U_{ts} + 2x_{c}x_{t}U_{ct}$$
(1)

where x's denote mole fractions and double identical indices of the type ii refer to pure components. U^c is clearly a molar quantity. Terms of the U_{ii} or U_{ij} type necessarily contain ternary, quaternary, etc. interactions, and represent thus effective binary interactions. The state of equilibrium of the system may be characterized by x_s and by concentration of one of the isomers, say x_{cmin} , corresponding to the minimum of the configurational energy U^c .

2. Basic Relations

Given eq 1, the first task consists in calculating the pair interaction energies U_{ij} . There are at least two distinct methods of doing this. The first consists in summing up orientational, inductive, and dispersive contributions;⁴⁻⁶

we can write the interaction energy of a pair of molecules u_{ij} (cf. eq 3.71 in ref 4) as

$$\mu_{ij}(R) = \frac{1}{R^6} \left(\frac{2}{3} \frac{\mu_i^2 \mu_j^2}{kT} + \mu_i^2 \beta_j + \mu_j^2 \beta_i + 3II\hbar\beta_i \beta_j \frac{\nu_i \nu_j}{\nu_i + \nu_j} \right)$$
(2)

where R = intermolecular distance, μ = dipole moment, β = polarizability, k = Boltzmann constant, T = thermodynamic temperature, \hbar = reduced Planck constant, and ν = characteristic frequency. The last term in (2) may be approximately substituted⁴⁻⁶ by

$$\Pi \hbar \frac{\nu_{i} \nu_{j}}{\nu_{i} + \nu_{j}} = \frac{I_{i} I_{j}}{2(I_{i} + I_{j})}$$
(3)

where I = ionization potential. Values of U_{ij} featured in (1) are simply obtained from u_{ij} by summations over all ij pairs in the system; average intermolecular distances \bar{R} may be introduced into (2).

An alternative to eq 2 consists in assuming an explicit dependence of the configurational energy on the molar volume V. We consider the form proposed for pure liquids by Frank,⁷ namely

$$U_{\rm ii} = -E_{\rm ii}/V_{\rm ii}n_{\rm ii} \tag{4}$$

where E_{ii} and n_{ii} are constants for a given pure substance i. The beauty of eq 4 consists in the fact that differentiating it with respect to volume at constant temperature produces U_{ii} again, only multiplied by a factor, so that

$$U_{\rm ii} = \frac{-V_{\rm ii}}{n_{\rm ii}} \left(T \frac{\alpha_{\rm ii}}{\kappa_{\rm ii}} - P \right) \tag{5}$$

where α , κ , and P are, respectively, the isobaric expansivity, the isothermal compressibility, and the macroscopic pressure. Quantities featuring in eq 4 and 5 have been extensively used by Bagley and his collaborators.⁸⁻¹⁰ In particular the internal pressure, which is the term in braces on the right-hand side of eq 5, has been used for successful predictions of enthalpies and entropies of mixing in binary liquid mixtures.¹⁰

The parameter n is, e.g., for cyclohexane^{8a} equal to 1.15

Cis-Trans Equilibria of 1-Chloropropene in Organic Solvents

TABLE I: Concentrations of *cis*-1-Chloropropene in a Series of Organic Solvents, Enthalpies of Vaporization, and Configurational Energies of Solvents at 25 °C

Solvent	x _s	x _{cmin}	-10 ⁴ H ^{vap} , J mol ⁻¹	-10 ⁴ U _{ii} , J mol ⁻¹
Cucloherene	0.0708	0.0165	3 374	3 1 2 6
Anisole	0.9784	0.0105	4.854	4.607
tert-Butyl alcohol	0.9812	0.0144	4.661	4.413
Dimethyl sulfoxide	0.9858	0.0105	5.289	5.041

 \pm 0.01 when *n* is calculated as the ratio of internal pressure to cohesive energy density. Bagley et al. maintain that *n* becomes exactly unity when due account is taken of the effect of external modes of motion of the molecule in the liquid state. Denoting the molar volume of the vapor phase by $V_{\rm v}$, we write the equation of state of the vapor as

$$PV_{\rm vii} = NkT - B_{\rm ii}P \tag{6}$$

where N is the Avogadro constant and B the vapor second virial coefficient. By thermodynamics we now obtain the equation for $n as^{11}$

$$n_{\rm ii} = \frac{V_{\rm ii} \left(T \frac{\alpha_{\rm ii}}{\kappa_{\rm ii}} - P\right) - P\left(\frac{B_{\rm ii}P}{Nk} + T\right) \frac{\mathrm{d}B_{\rm ii}}{\mathrm{d}T}}{H_{\rm ii}^{\rm vap} - P\left(\frac{NkT}{P} - B_{\rm ii} - V_{\rm ii}\right)}$$
(7)

Here H^{vap} represents the enthalpy of vaporization; we remember that V, α , and κ refer to the liquid phase while B to the vapor. Given eq 5 and 7 we can readily eliminate n and write

$$U_{\rm ii} = \frac{-V_{\rm ii} \left(T \frac{\alpha_{\rm ii}}{\kappa_{\rm ii}} - P\right) \left[H_{\rm ii}^{\rm vap} - P\left(\frac{NkT}{P} - B_{\rm ii} - V_{\rm ii}\right)\right]}{V_{\rm ii} \left(T \frac{\alpha_{\rm ii}}{\kappa_{\rm ii}} - P\right) - P\left(\frac{B_{\rm ii}P}{Nk} + T\right) \frac{\mathrm{d}B_{\rm ii}}{\mathrm{d}T}}$$
(8)

The last result represents an alternative to eq 2 for interactions in pure components; for mixed interactions combining rules of the general form $U_{ij} = U_{ij}(U_{ii}, U_{jj})$ may be used.

3. Calculations

The experimental data we have considered are taken from Table 3 of Liu and Chien.² Since 1-bromopropene has been studied in a smaller number of solvents than 1-chloropropene, we have concentrated on the latter. Concentrations of isomers given in ref 2 are, within limits of the experimental error, independent of the temperature. For each solvent we have, therefore, performed averaging over data for various temperatures displayed in ref 2. Our present calculations have been made for 25 °C, taking into account that in each solvent the total concentration of the olefin (i.e., cis plus trans) was 0.2 M. The respective concentrations of the solvent x_s and the equilibrium concentrations of the cis isomer $x_{c_{min}}$ in all solutions are given in columns 2 and 3 of Table I. Experiments described in ref 2 involved one more solvent, namely, hexamethylphosphoramide; since its heat of vaporization was not available, we have excluded this compound from Table I.

We now return to eq 1. By differentiating (1) with respect to x_c , we find that at the state of equilibrium of the cis and trans forms in a given solvent, the corresponding concentration x_{cmin} is

$$x_{\rm c_{min}} = \frac{(1 - x_{\rm s})(U_{\rm tt} - U_{\rm ct}) + x_{\rm s}(U_{\rm ts} - U_{\rm cs})}{U_{\rm cc} + U_{\rm tt} - 2U_{\rm ct}}$$
(9)

 $x_{t_{min}}$ has been eliminated from eq 9 by simply putting $x_{t_{min}} = 1 - x_s - x_{c_{min}}$.

To determine various U_{ii} parameters, we turn first to eq 2. A fairly extensive search of the literature has revealed, however, that the polarizability β values for components of our systems are not available. We turn therefore to eq 8. We again encounter some difficulties, since there are no second virial coefficient B values in the standard source of data of this kind;¹² the literature published since the compilation of Dymond and Smith was made does not contain such data either. There are methods of predicting values of B, notably the correlation of Chang and Lu¹³, which has been successfully tested for about 20 compounds. The second virial coefficients are calculated by Chang and Lu from the values of vapor-liquid critical temperature $T_{\rm c}$, critical pressure $P_{\rm c}$, and the accentric factor as proposed by Pitzer. However, from the compilation of Kudchadker et al.¹⁴ it turns out that the critical constants of our compounds are not available! Even a very simple B(T) correlation used for some alcohols¹⁵ is in terms of the critical temperature, so it cannot be presently applied either.

We omit, therefore, the term containing the second virial coefficient in eq 8. Since at atmospheric pressure the term $-PV_{ii}$ in the numerator of (8) is of the order of -10 J mol⁻¹, and the PB_{ii} term typically of the order of -100 J mol⁻¹, there is little point in retaining PV_{ii} in (8) even if it can be calculated. We thus write

$$U_{\rm ii} = -H_{\rm ii}^{\rm vap} + NkT \tag{8a}$$

a simple equation which has been extensively used before.

The values of H^{vap} of our solvents have been obtained from the following sources. For cyclohexene the P(T) Antoine equation constants given by Forziati et al.¹⁶ and the Clausius-Clapeyron relation were used. Similar calculations were made for anisole, taking the Antoine equation constants recommended by Boublik et al.¹⁷ For *tert*-butyl alcohol a directly measured experimental value of Wadsö¹⁸ was accessible. For dimethyl sulfoxide the value of Douglas,¹⁹ obtained by him from the vapor pressure measurements, was used. The corresponding values of H^{vap} , as well as the values of the configurational energy calculated from them using eq 8a, are given in the last two columns of Table I. We notice that U_{ii} values change considerably from one solvent to another.

As for the isomeric olefins, no H^{vap} were accessible; vapor pressure P(T) equations have not been found either. The only data useful in this connection were the tonometric coefficients dT/dP listed in ref 20; these are 0.039 K/ Torr for the cis isomer and 0.040 K/Torr for trans-1-chloropropene. From these values, using the Clausius-Clapeyron relation at the atmospheric pressure and eq 8a, one obtains $U_{cc} = -2.246 \times 10^4 \text{ J mol}^{-1}$, $U_{tt} = -2.183 \times 10^4 \text{ J}$ mol⁻¹, and the ratio U_{cc}/U_{tt} = 1.029. These values appear reasonable enough, but clearly to better visualize small difference between the U_{ii} values for the isomers, we have obtained values with four significant figures from experimental measurements made within two significant figures. In view of the kind and accuracy of the available experimental data, the only acceptable conclusion from these values is the qualitative one, namely, that $(U_{cc}/U_{tt}) > 1$.

In general, when U_{ii} values are accessible, the next step consists in calculating mixed configurational energies of

the type U_{ij} . We have obtained the values of U_{ii} from the simplified eq 8a rather than from (8). If highly accurate U_{ii} values were accessible, the use of sophisticated combining rules would be desirable. Presently we write simply

$$U_{\rm cs} = \lambda_{\rm cs} (U_{\rm cc} + U_{\rm ss}) \tag{10a}$$

$$U_{\rm ts} = \lambda_{\rm ts} (U_{\rm tt} + U_{\rm ss}) \tag{10b}$$

$$U_{\rm ct} = \lambda_{\rm ct} (U_{\rm cc} + U_{\rm tt}) \tag{10c}$$

We then assume

$$\lambda_{\rm cs} = \lambda_{\rm ts} \equiv \lambda \tag{11}$$

as well as

$$\lambda_{\rm ct} = \lambda \tag{12}$$

Consider now carefully eq 10–12. Equations 10 are all true by definition. Equation 11 is quite plausible and easy to accept, since we are dealing here with two isomers of the same chemical compound, interacting with a liquid solvent. Equation 12 appears less obvious. We have to remember here that U_{cc} and U_{tt} are very close to one another; this can be expected on the general grounds and it has already been confirmed by the values of the tonometric coefficients, crude as they are. Under the circumstances, any combining rule which puts U_{ct} in the vicinity of the values of U_{cc} and U_{tt} cannot be far off the real value of U_{ct} . Provided λ is of the order of 0.5, eq 12 thus becomes acceptable also.

The equilibrium state between cis and trans isomers has been expressed by eq 9. Substituting (10-12) into (9) we obtain

$$x_{\rm cmin} = \frac{\lambda U_{\rm cc} - (1 - \lambda - x_{\rm s} + 2x_{\rm s}\lambda)U_{\rm tt}}{(2\lambda - 1)(U_{\rm cc} + U_{\rm tt})}$$
(13)

Equation 13 represents a very interesting result. We notice that $U_{\rm as}$ does not feature in it at all. Equation 13 predicts thus $x_{\rm cmin}$ independent of the kind of solvent used, in agreement with the experimental facts outlined in the beginning of this paper.

Since we expect λ to be of the order of 0.5, we can now determine whether λ is larger or smaller than one half. From (13) we obtain by pure algebra

$$\frac{U_{\rm cc}}{U_{\rm tt}} = \frac{1 - \lambda + (x_{\rm c} + x_{\rm s})(2\lambda - 1)}{\lambda - x_{\rm c}(2\lambda - 1)} \tag{14}$$

where the second index in x_c has been omitted. For large values of x_s , such as in the experiments under consideration, we have the last term in the numerator $(x_c + x_s)(2\lambda - 1) \approx 2\lambda - 1$. Then

$$\frac{U_{\rm cc}}{U_{\rm tt}} \approx \frac{1}{1 - x_{\rm c} \frac{2\lambda - 1}{\lambda}}$$
(15)

From the experimental data we have found that $(U_{cc}/U_{tt}) > 1$. According to eq 15 this is only possible if $\lambda > 0.5$.

4. Discussion

Inspection of the experimental concentrations in Table I demonstrates that x_c decreases by 0.070 when passing from anisole through cyclohexene and *tert*-butyl alcohol to dimethyl sulfoxide. At the same time the solvent concentration x_s increases by 0.074. Thus, for a given concentration of a solvent, the concentration of the cis form of the olefin is indeed virtually independent of the kind of the solvent. This takes place in spite of large differences between con-

figurational energies of solvents, as shown in the last column of Table I. The reason why this happens is explained by eq 13, in terms of the general equilibrium condition (9) and simple combining rules (10).

The second natural question to ask is, why the cis form of 1-chloropene appears always in preponderance as compared to the trans olefin? A simple answer to this results from the experimental values of the tonometric coefficients, namely, that the absolute value of the configurational energy is larger for the cis isomer. One would like this qualitative answer to become quantitative; but that will be possible only when all experimental parameters featured in eq 8 are available.

In principle at least, the $U_{cc} - U_{tt}$ difference may be found from quantum mechanical calculations, but this alternative presents some difficulties also. Electrolytic synthesis of difluorodiazine leads invariably to a mixture containing 85% of the cis isomer, something very similar to our case of 1-chloropropene. Kaufman et al.²¹ and Turner²² performed energy calculations for both isomers of N₂F₂. Kaufman and her colleagues have found that the cis form is favored energetically; their calculations were based on the extended Hückel method. Turner using the CNDO/2 method has found that the trans form is favored by about 1.2 kJ mol⁻¹, but he remarks that within the error of his calculations both forms have the same energy. There exists a distinct energy barrier when passing from the trans to the cis form of N_2F_2 ; this has been explained by Turner in terms of simple atom-atom repulsion, rather than any alterations in chemical bonding.

Our eq 1 has been written for any system of the general type isomer cis + isomer trans + solvent. For any such system, therefore, eq 9 is applicable also. Given configurational energies of all components and the solvent concentration, one can predict the concentration of the cis isomer according to (9). If the U_{cc} , U_{tt} , and U_{ss} values available were highly accurate, a more sophisticated combining rule such as

$$U_{ij} = 2 \left/ \left(\frac{1}{U_{ii}} + \frac{1}{U_{jj}} \right)$$
(16)

might become worth using. The harmonic mean rule (16) has been discussed by Kreglewski in his monograph.²³ Lin and Robinson²⁴ have demonstrated that this rule is superior to some other combining rules for rare-gas pairs, and the rule has been used extensively by Kreglewski and his colleagues.^{25,26} We have to remember, however, that all combining rules are of limited validity only for systems with strong interactions.²⁶ Kolbe²⁷ has studied cis and trans forms of 1-tert-butylcyclohexan-4-ol by infrared spectroscopy, with CCl₄ as the solvent. He has concluded, that the degree of hydrogen bond autoassociation of the cis compound is remarkably lower than that of the respective trans form. Clearly, for systems with strong specific interactions such as the one studied by Kolbe, finding parameters U_{ct} , $U_{\rm ts}$, and $U_{\rm cs}$ for our eq 9 would represent a formidable task. For other systems there is no fundamental difficulty; the practical difficulty is related to the accessibility of experimental parameters featuring either in eq 2 and 3 or else in eq 8.

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Thermodynamics of Mixed Electrolyte Solutions. V.¹ An Isopiestic Study of the Agueous Systems Tetra-n-propylammonium Bromide-Sodium Bromide and Tetramethylammonium Bromide–Sodium Bromide at 25 °C²

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Osmotic and activity coefficients were measured by the gravimetric isopiestic vapor pressure technique in the aqueous systems tetramethylammonium bromide-sodium bromide and tetra-n-propylammonium bromide-sodium bromide. The excess Gibbs free energy of mixing and Friedman's interaction coefficients were obtained and interpreted in terms of ion-ion interactions leading to self-salting-in in the case of the Pr₄NBr-NaBr-H₂O system and to salting-out in the case of the Me₄NBr-NaBr-H₂O system.

Introduction

Studies of the thermodynamic properties of aqueous mixed electrolyte solutions have been very useful in increasing our understanding of the nature of specific ion interactions in solution. The tetraalkylammonium electrolytes in particular have received considerable attention in recent years.⁴ Wen and co-workers⁵ have determined the excess free energy of mixing of some tetraalkylammonium halides with potassium halides and found them to be considerably smaller than heats of mixing.⁶ The difference between ΔG^{ex} and ΔH^{ex} is very large, indicating a large negative ΔS^{ex} , thereby confirming the predominantly structural effect of the large tetraalkylammonium ions. Similar conclusions may be drawn from the heats of mixing of Pr₄NCl with LiCl, KCl, and NaCl⁷ and excess free energy of mixing in the $Pr_4NCl-NaCl-H_2O$ system which indicate that ΔS^{ex}

is large and negative and consistent with the water structure-promoting effect of Pr_4N^+ .

The present research was designed to expand the knowledge of the nature of the tetraalkylammonium ions by comparing the interaction of a structure breaker, the Me_4N^+ ion, and a hydrophobic structure maker, the Pr_4N^+ ion, in mixtures with an electrostrictive structure maker, the Na⁺ ion, using osmotic coefficient measurements and excess free energy of mixing determinations.

Experimental Section

Materials. Sodium bromide (Baker analyzed chemical reagent) was recrystallized twice from conductivity water and dried carefully for 24 h at 180 °C before use. Tetramethylammonium bromide (Fluka purum certified reagent) was purified and recrystallized a few times from a 50% methanol-50% ethanol mixture,⁹ while tetra-*n*-propylammonium bromide (Eastman Kodak Co.) was recrystallized from acetone.⁹ The tetraalkylammonium bromides were subsequently dried at 80 °C for 3–4 days under vacuum (10^{-5} Torr) and then sealed in vials until msed.

Stock solutions were prepared by weight. The concentrations were determined by gravimetric analysis of the bromide and indicated a minimum purity of 99.9% for the bromide salts. The constant ratio mixtures were prepared by weight from the stock solutions and then diluted by the weight dilution method. All weights were corrected to vacuo.

Apparatus and Experimental Procedure. The osmotic coefficients were determined by the gravimetric isopiestic comparison method with an apparatus which has been described previously.¹⁰ No significant changes were made in the procedure. The measurements were carried out over a concentration range of 0.3-6 m at 25 °C in both systems. Activity coefficients of sodium bromide in mixed solutions were obtained from emf measurements. The procedure has already been described¹ and measurements were carried out at an ionic strength of 0.75 m at 25 °C using a Beckman sodium sensitive glass electrode and an Ag/AgBr electrode manufactured by Orion.

Results

Equilibrium isopiestic concentrations determined are presented¹¹ in Tables I and II together with the concentration of the bromide reference solutions, the ionic strength I which is identical with the total molality $m = m_{\rm B} + m_{\rm C}$ (B and C denoting the sodium and tetra-n-alkylammonium salts, respectively), $y_{\rm C}$ the molal fraction of the latter salt defined by $m_{\rm C}/(m_{\rm B} + m_{\rm C})$, and ϕ the osmotic coefficient. The values of the osmotic coefficients of the pure tetraalkylammonium salts determined in this work were plotted against the molality m in Figures 1 and 2 and compared with literature data.^{5,12-14} The agreement is generally good. For tetramethylammonium bromide our results are nearly identical with those obtained by Levien^{14b} which deviate slightly from those reported by Lindenbaum and Boyd¹² at concentrations higher than 5 m. On the other hand, our tetra-n-propylammonium bromide results generally agree best with the data of Lindenbaum and Boyd.¹²

Treatment of the Results

The excess free energy change ΔG^{ex} per kilogram of water during the mixing of $m_{\rm B}$ moles of NaBr and $m_{\rm C}$ moles of R₄NBr in aqueous solution may be written¹⁵

$$\Delta G^{\text{ex}}(y,I) = G^{\text{ex}}(y,I) - yG^{\text{ex}}(1,I) - (1-y)G^{\text{ex}}(0,I) \quad (1)$$

where $G^{ex}(1,I)$ applies to a solution of pure R₄NBr and $G^{ex}(0,I)$ applies to a solution of pure NaBr and the free energies all pertain to the same ionic strength *I*.

The excess free energy of mixing is usually expressed in terms of the Harned¹⁶ or Scatchard¹⁷ coefficients. The most direct way of determining $\Delta G^{\text{ex}}(y,I)$ makes use of eq 16.22 from ref 15 whereby

$$[\partial(\Delta G^{\mathbf{ex}}/I)/\partial(1/I)]_{p,T,y} = \Delta G_{\mathbf{w}}^{\mathbf{ex}}$$
(2)

where $\Delta G_{\mathbf{w}}^{\mathbf{ex}}$ is the solvent contribution to the excess free energy of mixing. Similarly to eq 1, $\Delta G_{\mathbf{w}}^{\mathbf{ex}}(\mathbf{y}, I)$ is defined as

$$\Delta G_{\mathbf{w}}^{\mathbf{ex}}(y,I) = G_{\mathbf{w}}^{\mathbf{ex}}(y,I) - yG_{\mathbf{w}}^{\mathbf{ex}}(1,I) - (1-y)G_{\mathbf{w}}^{\mathbf{ex}}(0,I)$$

The integration of eq 2 at constant y yields¹⁸



Figure 1. Plot of the osmotic coefficient ϕ vs. *m* for pure solutions of Pr_4NBr .



Figure 2. Plot of the osmotic coefficient ϕ vs. *m* for pure solutions of Me₄NBr.

$$\Delta G^{\mathbf{ex}}(\mathbf{y},I) = I \int_0^I \Delta G_{\mathbf{w}}^{\mathbf{ex}}(\mathbf{y},I') \,\mathrm{d}(1/I') \tag{3}$$

which can be shown to be equivalent to

$$\Delta G^{\text{ex}}(y,I) = -4RTI \left[\int_{0}^{I} \frac{1 - \phi(y,I')}{\sqrt{I'}} \, \mathrm{d}\sqrt{I'} - y \right]$$
$$\int_{0}^{I} \frac{1 - \phi(1,I')}{\sqrt{I'}} \, \mathrm{d}\sqrt{I'} - (1,y) \int_{0}^{I} \frac{1 - \phi(0,I')}{\sqrt{I'}} \, \mathrm{d}\sqrt{I'} \left]$$
(4)

A ccording to the Debye-Hückel limiting law for 1-1 elect-olytes at 25 °C, the expression $(1 - \phi)/\sqrt{I}$ tends to a finite limiting value of 0.3908 as I tends to zero. The integration may be carried out graphically or numerically within reasonable agreement. The values obtained for ΔG^{ex} of the tetrapropylammonium and tetramethylammonium bro-



Figure 3. Excess free energy of mixing $(\Delta G^{ox}/RT)$ aqueous Pr₄NBr and NaBr at constant ionic strength (*1*) plotted against *y*, the molal fraction of Pr₄NBr in the mixed electrolyte at 25 °C.



Figure 4. Excess free energy of mixing $(\Delta G^{ex}/RT)$ aqueous Me₄NBr at constant ionic strength (*I*) plotted against *y*, the molal fraction of Me₄NBr in the mixed electrolyte at 25 °C.

mide systems¹¹ were plotted against y_C at various ionic strengths in Figures 3 and 4, respectively.

A general expression for the excess free energy of mixing has been derived by Friedman's extension¹⁵ of Mayer's ionic solution theory¹⁹ which in the case of a 1-1 electrolyte yields the following expression

$$\Delta G^{\text{ex}}(y,I) = RTI^2 y(1-y) [g_0 + g_1(1-2y) + g_2(1-2y)^2 + \dots]$$
(5)

where the g_i are free energy interaction parameters. The excess free energy of mixing values ΔG^{ex} were fitted by a

TABLE III: Friedman's Interaction Parameters in the Pr₄NBr-NaBr System

Ι	g_0, m^{-1}	g_1, m^{-1}	g_2, m^{-1}
0.5	0.5146	0 1056	0 1231
1.0	0.3649	0.0850	0.1075
1.5	0.2750	0.0753	0.0996
2.0	0.2146	0.0695	0.0947
2.5	0.1699	0.0653	0.0924
3.0	0.1352	0.0618	0.0943
3.5	0.1075	0.0591	0.0918
4.0	0.0849	0.0570	0.0931
4.5	0.0661	0.0558	0.0954
5.0	0.0503	0.0554	0.0985

TABLE IV: Friedman's Interaction Parameters in the Pr4NBr-NaBr System

Ι	$g_{0},^{a} \mathrm{m}^{-1}$	$g_{0,}{}^{b} \mathrm{m}^{-1}$	$g_{1},^{a} m^{-1}$	$g_{2},^{b} m^{-2}$
		0.0000	0.0100	0.0100
0.5	0.0336	0.0368	0.0130	0.0138
1.0	0.0192	0.0216	0.0107	0.0120
1.5	0.0101	0.0107	0.0095	0.0105
2.0	0.0026	0.0019	0.0074	0.0088
2.5	-0.0043	-0.0053	0.0054	0.0068
3.0	-0.0107	-0.0115	0.0034	0.0048
3.5	-0.0171	-0.0170	0.0012	0.0029
4.0	-0.0233	-0.0222	-0.0008	0.0008
4.5	-0.0294	-0.0272	-0.0028	-0.0012

^a Values obtained from the McKay transform. ^b Values obtained from Friedman's equation (eq 5).

TABLE VII: Harned Coefficients in the Pr₄NBr-NaBr-H₂O System at 25 °C⁴

m	$\alpha_{\rm B}$	$\beta_{\mathbf{B}}$	δB	αc	β _C	δ _C
0.5	0.0083	-0.3555	0.5722	0.2761	-0.5594	1.2368
1.0	0.0074	-0.1374	0.1195	0.1743	-0.1930	0.2295
1.5	0.0092	-0.0813	0.0486	0.1215	-0.1029	0.0850
2.0	0.0104	-0.0573	0.0259	0.0908	-0.0689	0.0432
2.5	0.0106	-0.0443	0.0160	0.0722	-0.0533	0.0264
3.0	0.0103	-0.0365	0.0110	0.0609	-0.0449	0.0181
3.5	0.0100	-0.0316	0.0081	0.0541	-0.0397	0.0134
4.0	0.0100	-0.0287	0.0063	0.0500	-0.0359	0.0103
4.5	0.0109	-0.0271	0.0052	0.0476	-0.0327	0.0082
5.0	0.0130	-0.0267	0.0044	0.0461	-0.0296	0.0066

 $^{\alpha}$ The subscripts B and C correspond to NaBr and $Pr_{4}NBr,$ respectively.

method of least squares to eq 5 and the g_i parameter values are listed in Tables III and IV.

The activity coefficients were obtained from the change in ΔG^{ex} at constant ionic strength, since by definition

$$[\partial \Delta G^{\text{ex}}(y,I)/\partial I_i]_{P,T,I_i} = RT \ln \left(\gamma_i/\gamma_i^0\right) \tag{6}$$

Their values, listed in Tables V and VI¹¹ are plotted in Figures 5 and 6.

The classical method of Robinson,^{20a} which makes use of the McKay-Perring transform²¹ to determine the activity coefficients from the experimental osmotic coefficients, could be applied to the tetramethylammonium bromide system, but not to the tetrapropylammonium bromide mixtures. The experimental isopiestic data obtained in the latter case (Table I) would not be reproduced by less than a quartic equation in $y_{\rm C}$. Because of the inherent difficulties involved in the integration of the McKay transform²¹ in even simpler cases, as pointed out by Robinson and Co4.5

0.0585

 $\beta_{\rm C}$ m $-\alpha_{\rm B}$ $\beta_{\rm B}$ αc 0.0074 0.1057 0.0179 0.5 0.1000 0.0112 0.0020 0.0707 1.0 0.0732 0.0629 0.0017 0.0542 0.0078 1.5 0.0057 2.0 0.0583 0.0018 0.0449 0.05620.0020 0.0389 0.0042 2.53.0 0.0554 0.0022 0.0347 0.0032 0.0025 3.5 0.0556 0.0023 0.0316 0.0025 0.0020 0.0566 0.0291 4.0

TABLE VIII: Harned Coefficients in the Me₄NBr-NaBr-H₂O System at 25 °C^a

 a The subscripts B and C correspond to NaBr and Me_4NBr, respectively.

0.0271

0.0018

0.0027



Figure 7. Plot of the activity coefficients of sodium bromide γ_{NaBr} vs. y_{NaBr}

vington,^{20b} Robinson's method^{20a} was not used for the $Pr_4NBr-NaPr$ system. The results obtained¹¹ for Me_4NBr by this method, however, are expected to be slightly less reliable because of the uncertainty involved in the extrapolation to zero, and the indirect way of calculating the excess free energy of mixing ΔG^{ex} from the activity coefficients.

Calculated values of the activity coefficients for NaBr obtained from the isopiestic measurements are compared at an ionic strength of 0.75 m with those determined directly from emf measurements in Figure 7. The agreement could not be better taking into account the various extrapolations involved.

The results obtained for the activity coefficients can be reproduced within experimental error by the expression

$$\log (\gamma_i / \gamma_i^{0}) = \alpha_i m_i + \beta_i m_i^{2} + \delta_i m \gamma_i^{3}$$

where two Harned coefficients¹⁶ α_i and β_i are sufficient for the tetramethylammonium bromide system, but at least three, α_i , β_i , and δ_i , had to be used for the tetra-*n*-propylammonium bromide system. The coefficients are listed in Tables VII and VIII. It may be easily shown¹⁵ that the g_i of eq 5 and the Harned coefficients are related as follows:

$$g_0 = 2.303[(\alpha_{\rm B} + \alpha_{\rm C}) + I(\beta_{\rm B} + \beta_{\rm C}) + \frac{7}{8}I^2(\delta_{\rm B} + \delta_{\rm C}) + \dots]$$
(7a)

$$g_1 = 2.303 [\frac{1}{3}I(\beta_{\rm C} - \beta_{\rm B}) + \frac{1}{2}I^2(\delta_{\rm C} - \delta_{\rm B}) + \dots]$$
(7b)

$$g_2 = 2.303 [\frac{1}{8} J^2 (\delta_{\rm B} + \delta_{\rm C}) + \dots]$$
(7c)

where $g_i = \sum_l I^{l+l-2}g_{il}$ and l represents the order of interaction $(l \ge 2 + i)$.

Discussion

I. The $Pr_4NBr-NaBr$ System. As shown in Figure 3, the ΔG^{ex} values plotted against $y(Pr_4NBr)$ at constant ionic strength give parabolic curves similar to those obtained in the aqueous systems $Pr_4NBr-KBr^5$ and $Pr_4NCl-NaCl.^8$ The positive values of g_0 at low ionic strength I may be taken as evidence that two tetrapropylammonium ions can be separated only by doing a considerable amount of work.²² At larger I values the skewness of the curves toward the other component is even more pronounced than in similar cases,^{5,8} as displayed by the finite values of the g_i (i > 0) interaction coefficients which indicate the presence of ion triplets and larger aggregates in solution.

According to Friedman's formalism¹⁵ the multiple particle interactions present in the solution are significant. Since a g_2 term is required to fit the data, a contribution from interactions of four or more particles is indicated. The ion pair term g_{02} [identified with 2.303($\alpha_{\rm B} + \alpha_{\rm C}$)] is positive over the entire concentration range and points to likeion pairs $Pr_4N^+-Pr_4N^+$, Na^+-Na^+ being favored over mixed pairs Pr₄N⁺-Na⁺. The contribution of the triplet interaction term g_{03} to the value of g_0 is negative in sign (g_{03} = $2.303(\beta_{\rm B} + \beta_{\rm C})$) and this may explain the general decrease of g_0 with increasing I (Figure 8). The negative sign of g_{03} indicates that mixed charged ion triplets (Pr_4N^+ - $Br^{-}-Pr_4N^+$) are being favored over like-charged ion triplets $(Pr_4N^+ - Pr_4N^+ - Pr_4N^+)$ already present in the mixture. This is further confirmed by the relatively small values of g_{13} (I/3($\beta_{\rm C} - \beta_{\rm B}$)) which is the like-charged ion triplet contribution to g_1 . The large contribution of quadruplet interaction (g_{i4}) to the various parameters g_i is especially significant at higher concentrations and indicates a substantial salting-in of the tetrapropylammonium ion. The same picture is obtained by considering the values of ln $(\gamma_{\rm C}/\gamma_{\rm C}^0)$ in Figure 5. These values show that at y = 0.0 this ratio is positive and increases with I. This indicates most probably the removal of the self-salting-in effect of Pr_4N^+ by the increase in Na^+ concentration. At constant I the effect of Na⁺ on promoting the reduction in the overlap of the Pr_4N^+ hydration spheres is seen to decrease as expected. The values of ln $(\gamma_{\rm C}/\gamma_{\rm C}^0)$ go through a broad maxima in the range of I values between 1.0 and 2.0 pointing toward a relatively strong self-salting-in effect of Pr_4N^+ at high ionic strengths. This is in agreement with the interpretation^{6,7} of measurements of heats of mixing and heats of dilution of tetrapropylammonium salts²³ which suggests that the large effect of the Pr₄N⁺ self-interaction is due to the completion of hydration cospheres⁴ on dilution both with the solvent alone⁷ and with small cations⁵ at constant ionic strength.

II. The $Me_4NBr-NaBr-H_2O$ System. As shown in Figure 4, the values of ΔG^{ex} plotted against y_C at constant ionic strength I give parabolic curves at low concentrations similar to those obtained in the $Me_4NBr-KBr-H_2O$ system.⁵ At larger I the skewness of the curves, due to the nonzero value of the parameter, g_i , increases. The excess free energy of mixing changes its sign from positive to negative and at I

= 2 the ΔG^{ex} curve is similar to curve d presented by Wu in his study of Young's mixture rule.²⁴ At least one other system is known to present such a behavior,²⁵ which is rather common in mixtures of nonelectrolytes.²⁶ At still higher concentrations, the ΔG^{ex} values remain negative but the usual parabolic curves are again obtained with a minimum near $y_{\rm C} = 0.5$.

The concentration changes in ΔG^{ex} may be interpreted using Friedman's formalism.¹¹ Applying Reilly and Wood's expansion²⁷ it may be shown that when all classes of triplet interactions²⁸ are taken into consideration

$$g_0 = B^{110} - B^{200} - B^{020} + I[B^{111} - B^{201} - B^{021}] + I/2[B^{210} - B^{120} - 3B^{300} - 3B^{030}]$$
(8a)

$$g_1 = I/3[B^{120} - B^{210} + B^{300} - B^{030}]$$
(8b)

or

 $g_0 = g_{02} + Ig_{03}$ (mixed-charged ion) + Ig₀₃ (like-charged ion) (9a)

> $g_1 = Ig_{13}$ (like-charged ion) (9b)

The ion pair term g_{02} is positive only at the lowest concentration (0.5 m), but it becomes negative and decreases steadily with increasing ionic strength. This means that diluting the solution down from 0.5 will promote the formation of like ion pairs $Me_4N^+-Me_4N^+$ consequent to hydrophobic structure making. From 1.0 m up, the formation of mixed ion pairs Me₄N⁺-Na⁺ will be favored over like ion pairs, this tendency increasing as the ionic strength grows. On the other hand, the triplet contributions g_{03} and g_{13} are positive, but starting from 3 m upward the like-charged ion triplet term g_{13} is negligible and we may safely assume that the contribution of mixed-charged ion triplets to the free energy of mixing will be more important than that of triplets formed from three ions of the same charge. In other words a triplet interaction of the form (Me₄N⁺-Br⁻-Na⁺ may be expected. These changes are reflected in the ratio ln $(\gamma_{\rm C}/\gamma_{\rm C}^0)$ in Figure 6 which shows a decrease in the selfsalting-in. The hydrophobic structure making at low concentrations is confirmed by the endothermic heats of mixing found in the same system²⁹ according to Ycung's sign rule,³⁰ which predicts endothermic heats of mixing for ions with the same structure-forming property.

Frank and Evans⁴ proposed that the tetraalkylammonium ions should become hydrophobic structure makers as the size of the alkyl group increases. The evidence is quite strong 5-7,31 in indicating that the tetrapropylammonium ion is a strong hydrophobic structure maker at all concentrations as is the tetramethylammonium ion at low concentration only.^{29,31} However, as the concentration increases, the strong self-interaction of the tetrapropylammonium cation (salting-in) is predominant and masks other effects, while the tetramethylammonium cation behaves as a typical structure breaker, as displayed by the formation of mixed ion pairs. The free energies of mixing¹¹ are small in both cases but the large negative heats of mixing in Pr₄NBr-NaBr indicate that the interactions of the larger tetraalkylammonium ions are predominantly a structural (i.e., entropy) effect, while in the case of the smaller ones the heats of mixing of Me₄NBr with NaBr are endothermic but small so that the structural effect is much less pronounced.

Supplementary Material Available: Tables I, II, V, VI, IX, and X and Figures 5, 6, and 8 (13 pages). Ordering information is available on any current masthead page.

References and Notes

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Nuclear Magnetic Resonance and Infrared Investigation of Adsorbed Pyridine and Thiophene on Molybdena Modified Alumina

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Wide-line NMR measurements have been made that support and extend the ir-based operational distinction between chemisorbed and physically adsorbed species. Physically adsorbed pyridine or thiophene on molybdena-alumina shows liquid-line NMR behavior with considerable and generalized mobility even at low temperatures. These species undergo phase transitions at low temperatures that slow down or eliminate their motions on the surfaces. Chemically adsorbed pyridine is much more rigidly held on the surfaces studied with essentially only a rotation about the C_2 axis of the adsorbed species persisting to very low temperatures. Pretreatment does not affect the behavior of pyridine, but thiophene is physically adsorbed only on H₂ reduced surfaces, and it undergoes a reaction on calcined surfaces. The observed differences in behavior are based on variations exhibited in the line width, line shape, and second moments of the NMR spectra and in the ir spectra of the adsorbed species.

Introduction

The infrared spectra of pyridine adsorbed on aluminas and modified aluminas have been used widely and quite successfully to distinguish Lewis surface acidic sites of various strengths from each other as well as from Bronsted acidic sites.¹⁻⁴ This use of pyridine as an ir probe of surface acidity is possible because of the variations in the spectrum of adsorbed pyridine in the region 1400-1700 cm⁻¹ produced by adsorption to sites of differing types and strengths. Pyridine is adsorbed on a given surface and then subjected to desorption at various temperatures and for various time intervals. The stronger acidic sites retain the bound pyridine (with ir absorptions characteristic of these sites) with increasing temperature and periods of desorption. This operational procedure is also used to distinguish physically from chemically adsorbed pyridine in that the pyridine initially desorbed at temperatures below 150 °C is conventionally defined to be physically adsorbed.¹⁻⁴ Similar successful utilization of NMR techniques has been made to obtain information pertaining to inter- and intramolecular interactions of adsorbed species.⁵

This paper presents NMR and ir data that provide considerable insight both into the differences of physically and chemically adsorbed pyridine and also between adsorption sites of variable strength. The line shapes, line widths, and second moments of the NMR absorptions are utilized here to distinguish physically from chemically adsorbed pyridine. These data tend to validate the ir-based operational assumption with respect to physically and chemically adsorbed pyridine on alumina modified by various transition metals. In addition, these data provide a rather detailed description of the dynamics of the adsorbed species on a molecular level. Finally, information is obtained on the relative strength of the various acid sites through the examination of the spectra of adsorbed thiophene and their contrast to the more strongly adsorbed pyridine on the same modified alumina surfaces.

Experimental Section

The modified aluminas were prepared by standard tech-

niques where MoO_3 was impregnated in the alumina from an aqueous solution of ammonium paramolybdate. The preparations were dried at 100 °C for 2 h, then calcined at 500 °C for 18 h in a current of dry air.

For the ir investigation, samples were ground into 100mg powdered aliquots which were then pressed into 1 in. in diameter wafers at approximately 8000 psi for 1 min. All treatments of the wafers were carried out after the wafer was mounted in a cell, which has been previously described,¹ and attached to a vacuum system in which the ultimate pressure achieved was 10^{-6} Torr.

The wafer was initially evacuated at 500 °C for 16 h. At this point the wafer is considered to be "calcined only". Reduction was accomplished by flowing H_2 at a rate of approximately 20 cc/min for a period of 4 h at 500 °C followed by further evacuation at this temperature for 4 h. Pyridine was added to the wafer surface by exposure to 12 Torr at 150 °C for 1 h, followed by 2-h evacuation at the same temperature. Thiophene was added by exposure to 20 Torr at room temperature for a period of 1 h followed by evacuation, also at room temperature, for 1 min. Other evacuation temperatures and time periods were used and are specified in the text where pertinent.

Infrared spectra were recorded at ambient temperature on a Beckman IR-12 with a special slit width of 4 cm⁻¹. The instrument was continuously purged with dry air.

For NMR investigation, 1 g of sample was contained in a standard solid-sample tube fitted with a side arm, vacuum stopcock, and vacuum joint to permit attachment to the vacuum system. Calcination and reduction conditions were as described above, as was the addition of pyridine and thiophene unless specified differently in the text.

Nuclear magnetic resonance experiments were carried out with a Varian V-4200 wide-line NMR spectrometer. The instrument was equipped with Fieldial for magnetic field scanning and a standard variable temperature probe. The first derivative of the resonance absorption was recorded at 11.09 MHz using 40-Hz audio-modulation of the field with sufficiently low peak-to-peak amplitude to prevent artificial broadening.



Figure 1. Relative intensity of NMR signal due to adsorbed pyridine (A) or thiophene (B) on "calcined-only" (\Box) and reduced (Δ or O) 9% MoO₃/ η -Al₂O₃ as a function of pumping time and temperature. Open symbols are for room temperature evacuations; solid symbols refer to evacuation at 150 °C.

Results and Discussion

A. Ir Results and NMR Line Width Measurements. Pyridine is chemically and physically adsorbed on both η -Al₂O₃ and modified η -Al₂O₃ surfaces. The differentiation between the two types of adsorption is operational in nature. Previous infrared investigations¹ have shown that heating Al₂O₃ with adsorbed pyridine at 150 °C and constant evacuation for 2 h removed the physically adsorbed pyridine, i.e., the species responsible for absorption bands at approximately 1440 and 1600 cm⁻¹.

Figure 1A presents the results for an analogcus experiment utilizing the wide-line NMR signal of pyridine relative to that of dehydrated base alumina. After exposure to pyridine vapor, the modified aluminas were evacuated at room temperature and the spectra recorded at the time intervals shown. After 2 h of room temperature evacuation the samples were heated for 1 h at 150 °C with evacuation. The signal due to the adsorbed pyridine decreased significantly, and in conjunction with the aforementioned infrared spectroscopic results, the residual signal is attributed to chemisorbed pyridine only. The spectra recorded previous to the heat treatment are attributed to both physically and chemically adsorbed pyridine. Figure 1A also shows that H₂ reduction of a 9% Mo/η -Al₂O₃ does not significantly affect the amount of pyridine adsorbed relative to a "calcined-only" sample. There is some initial differ-



Figure 2. Infrared spectra of adsorbed thiophene on 9% MoO₃/ η -Al₂O₃. (A) Sample is "calcined-only". Spectrum A results from 1-min evacuation at room temperature after exposure to thiophene. Spectrum B results from heating the above for 1 h at 150 °C with evacuation. (B) Sample is reduced. Spectrum A results from 1-min evacuation at room temperature after exposure to thiophene. Spectrum B results from 5-min further evacuation at room temperature.

ence in the amount adsorbed, but that difference becomes insignificant after the first few minutes of evacuation. The amount of chemisorbed pyridine does not decrease further even after extensive (4-h) evacuation at 150 °C.

Figure 1B presents the corresponding results for thiophene adsorption on 9% Mo/η -Al₂O₃. The adsorption on the reduced sample is greater than that on the "calcinedonly" sample, with the signal produced from the former of approximately the same magnitude as that produced by adsorbed pyridine.

The infrared spectra of thiophene adsorbed on the modified aluminas, which are presented in Figure 2, show that there is a significant difference between the "reduced" and "calcined-only" samples. Absorption bands occur at 1082, 1252, and 1409 cm⁻¹ on the reduced sample. This spectrum indicates that the thiophene is physically adsorbed because these band maxima are essentially identical with those of liquid thiophene, which occur at 1080, 1250, and 1406 cm⁻¹, and which are assigned to the in-plane deformations.⁶ Also, after approximately 5 min of pumping on the adsorbed thiophene at room temperature, all of the bands with the exception of a weak residual absorption at 1252 cm⁻¹ are removed. The plethora of absorption bands observed for thiophene adsorbed on the "calcined-only" sample indicates that the thiophene has reacted and that the reaction products are adsorbed. Also, these bands were found to remain after heating at 150 °C for 1 h, although the relative intensities were modified. This indicates that the reaction products are chemically adsorbed. The behavior of the above spectra is consistent with the results obtained from the wide-line NMR i.e., the reduced sample contains a significantly greater amount of physically adsorbed thiophene than the "calcined-only" sample.

The wide-line NMR spectra of adsorbed thiophene (Figure 1B) show evidence for some chemically adsorbed thiophene in that there is a residual signal after evacuation at 150 °C for the time interval indicated. The S/N ratio, however, is very low and the amount remaining after each heat treatment is a small fraction of the equilibrium physically absorbed thiophene. It is also of interest to note that the rate of desorption of thiophene from the "calcined-only" sample is considerably greater than from the reduced sample. Essentially, all of the thiophene is removed after about 30 min of pumping. Further information pertaining to the adsorbed thiophene is available from a detailed consideration of the NMR line widths. Thiophene is known to undergo several phase transitions as the temperature is lowered. NMR has been used to detect some of the transitions of thiophene, the NMR absorption line width showing discontinuities at the phase transition temperatures. The experimental second moment of the absorption can be used also for a discussion of such broadenings. Figure 3A presents the variation of the second moment of neat thiophene with decreasing temperature. The solid phase transition occurs at -127 °C, in agreement with previous work.⁷ The variation in the absorption line's second moment for physically adsorbed thiophene on a reduced 9% Mo/η -Al₂O₃ sample is given in Figure 3B. A solid phase transition occurs at -132 °C. The line widths corresponding to the plotted experimental second moments show a closely parallel behavior for the neat and physically adsorbed thiophene. Thus, the behavior of physically adsorbed thiophene is similar to that of the neat liquid when both are solidified at low temperatures. Clearly, the physically adsorbed thiophene remains extremely mobile, showing generalized tumbling and even translational motion at very low temperatures close to the transition temperature. However, even at this transition temperature, there must be some mobility remaining in the adsorbed thiophene for (1) the theoretical moment is 6.8 G,² i.e., considerably greater than the observed value; and (2) as shown by previous work,⁷ there are several phase transitions that neat thiophene undergoes with some mobility remaining down to -160 °C.

The variation of the proton signal line width with decreasing temperature for physically adsorbed thiophene on a reduced 9% M_0/η -Al₂O₃ at two different levels of coverage is given in Figure 4. The differences in coverage were produced by further evacuation at room temperature of the sample initially containing adsorbed thiophene. The sample containing the greater amount of thiophene undergoes a solid phase transition at -127 °C, which is the same temperature as for the pure thiophene. As the amount of physically adsorbed thiophene decreases, the transition temperature shifts to a higher temperature. For the case under consideration, a sample with residual thiophene after 120 °C evacuation at room temperature shows a transition at -110 °C. This indicates that the adsorbed thiophene layers near the surface are under the strong influence of that surface, whereas, the thiophene at the higher coverage behaves more nearly as neat thiophene. It is of further interest to



Figure 3. The experimental second moment of the NMR absorption of neat thiophene (A) and of thiophene adsorbed on reduced 9% MoO₃/ η -Al₂O₃ (B) as a function of temperature.



Figure 4. The line width of physically adsorbed thiophene on reduced $9\% \text{ MoO}_3/\eta$ -Al₂O₃ as a function of temperature. Two different coverages of thiophene are shown: (\Box) represent adsorbed thiophene which has been evacuated at room temperature for 5 min; (O) represents evacuation for 120 min.

note that the line width at a given temperature is greater as the amount of adsorbed thiophene is decreased. This variation of line width as the relative amount of physically adsorbed thiophene is changed can be attributed to the same surface forces responsible for the variation of the transition temperatures with coverage. Similar behavior is observed with both physically adsorbed and chemisorbed pyridine. The line width of pyridine adsorbed on both a reduced and "calcined-only" 9% Mo/ η -Al₂O₃ sample as a function of coverage is given in Figure 5. The line width is seen to be independent of the reducing, or lack of, conditions employed. As observed previously for thiophene, the line width increases as the amount of physically adsorbed pyri-



Figure 5. Line width of NMR adsorption of "physically" (left half of curve, room temperature evacuation) and "chemically" adsorbed pyridine on 9% MoO_3/η -Al₂O₃: (O) represents "calcinec-only" and (Δ) represents reduced modified aluminas.

dine is decreased, reaching a maximum when only chemisorbed pyridine is present on the surface. In fact, there is a tenfold difference in line width between chemisorbed and physically adsorbed pyridine, and this difference could be used as an alternate operational criterion to distinguish chemisorbed from physically adsorbed pyridine.

Another striking difference between chemically and physically adsorbed pyridine is shown in Figure 6. The line width of the chemically and physically adsorbed pyridine has been recorded as a function of temperature, from room temperature to -150 °C. The ir results have been used here for the operational definition of "chemical" and "physical" adsorption. Pyridine that remains on the support after evacuation at room temperature shows a sharp and narrow liquidlike signal that persists in this manner down to about -125 °C. At that temperature, there is a very sharp change taking place with the line width showing a 50-fold increase from about 0.1 to over 5.0 G. On the other hand, the signal due to chemisorbed pyridine, even at room temperature, is a fairly broad one with the ΔH_{pp} being about 3.5 G. The line width for this signal remains unchanged down to about -115 °C at which point there is a transition. The broadening of the chemisorbed species is some 15 °C earlier than the transition of the physically adsorbed one. Also, the broadening is not as great, changing from about 3.5 G to almost 5 G, while for the physically adsorbed, the change is considerably greater. The data below the transition temperature seem to indicate that physically absorbed pyridine broadens to a value some 10% greater than that of chemisorbed pyridine. The difference is probably significant although the spectra at these temperatures are rather poor, especially for the chemisorbed ones with low S/N.

B. Line Shapes and Second Moments of NMR Absorptions. We have examined the line shapes of the resonance absorptions of the various samples with some rather interesting results. The Bloch equations predict Lorentzian line shapes, and this is what is generally observed for liquids.^{8,9} Lorentzian lines are also expected where there exists exchange interaction between like species.

In the absence of exchange broadening, dipolar interactions in randomly distributed solids produce Gaussian NMR absorption lines.⁸ On the other hand, in magnetically dilute systems, dipolar broadening produces Lorentzian lines. Examination of the obtained line shapes further de-



Figure 6. Line width of NMR absorption of chemisorbed (O) and physically adsorbed (\times) pyridine on reduced 9% MoO₃/ η -Al₂O₃ as a function of temperature.

fine the sharp differences that we already noted between chemisorbed and physically adsorbed species.

Figure 7 shows the line shape of physically adsorbed pyridine at various temperatures. Clearly, at high temperatures above the transition point, the observed line is Lorentzian as expected for highly mobile, liquidlike behavior. In the figure this is shown with the \times 's falling exactly on the observed line (-66 and -104 °C spectra) while the Gaussian points (O's) deviate considerably from the observed absorption. The line shape of the signals observed at temperatures below this transition point is pure Gaussian. (Figure 7 also shows the observed signal at -137 °C.) It is interesting that at temperatures immediately before the transition to a broader, solidlike Gaussian signal, the observed signal is actually the superposition of two distinct signals, one extremely narrow and the other much broader. At -118 °C the signal shows large Lorentzian absorption and smaller Gaussian absorption, while closer to the transition (at -128 °C), the relative amounts of the two have been reversed. It is interesting to note that as the transition temperature is approached the line shape begins to deviate from the simple pattern. For example, at -104 °C (Figure 7) the signal is intermediate, i.e., Gaussian toward the center, but in the wings it remains Lorentzian.

For thiophene adsorbed on reduced Mo/Al₂O₃, a similar behavior of the line shape is observed. At temperatures well above the transition point (which occurs at about -130°C), the line shape of the physically adsorbed thiophene is pure Lorentzian; however, at temperatures below the transition, the line shape is Gaussian. The same general pattern is observed with neat thiophene. Its line shape remains essentially Lorentzian down to its transition point, but then below that point the line shape becomes Gaussian. Again the line width of the thiophene above the transition point is liquidlike, but it is broader than the liquid thiophene (0.1 mG vs. 0.1 G).

In sharp contrast to the physically adsorbed pyridine, the line shape of the chemisorbed pyridine is uniformly Gaussian at all temperatures including room temperature and on both sides of the transition point. These various observations are summarized in Table I. No significant difference has been observed in the line shape of pyridine adsorbed on reduced or calcined molybdena-alumina. The results presented here fit a plausible scheme that is deter-



Figure 7. NMR line shapes of physically adsorbed pyridine on reduced 9% MoO₃/ η -Al₂O₃ at various temperatures. The observed line is solid; the X's describe a Lorentzian line shape and the O's a Gaussian curve: (A) -66 °C, Lorentzian line shape; (B) -104 °C, Lorentzian and Gaussian superposition; (C) -137 °C, Gaussian line shape.

TABLE I: NMR Line Shapes Observed for Adsorbed Species on Reduced 9% MoO_3/η -Al₂O₃

Adsorbate	Temp, °C	$\Delta H_{pp}, G$	Line shape ^a	Comments
Thiophene	-6	0.1	L	
1 mophene	-90	0.3	Ĺ	
	-115 to -130			Transition
	-135	3.0	G	
Pyridine	-66	0.1	L	
(physically adsorbed)	-118	0.1	L > G	Two signals
	-128	~ 2	G > L	Two signals
	-130	~3.5	G	Transition
	-137	6	G	
Pyridine	-60	3.2	G	
(chemisorbed)	-115	4.2	G	
	-140	5.0	G	

^a L = Lorentzian; G = Gaussian.

mined by the random distribution of the adsorbed species and of the influence of the system on the mobility of these species.¹⁰ At the higher coverage, where we have more material and less on-the-average influence by the surface for a given species, we should expect a narrow Lorentzian curve. Upon removing the material and thereby increasing onthe-average the influence of the surface, we should expect a somewhat broader (as observed) NMR absorption. The mobility of the species in order to influence the line width of the NMR absorption must be of the order of magnitude of the inverse line width. It could very well be, then, that at the higher coverage the smaller but real influence of the surface causes some slowing down of the species which, when coupled with the random distribution and close proximity of the interacting adsorbed species, gives to the signal some elements of Gaussian behavior. This effect may be enough to give to the physically adsorbed (on the high coverage level at least) some solidlike behavior without greatly affecting the line width. Of course, the line width is not as low as would be expected for a true liquid (ΔH_{pp} at room temperature is a 0.1 mG vs. 0.1 G for the adsorbed species in the case of pyridine). If one restricted further the mobility of the species (e.g., chemisorbed pyridine) then one would expect the signals to become pure Gaussian and to broaden also considerably. As the data presented earlier indicate, this is exactly what is observed both with pyridine (chemisorbed and physically adsorbed) as well as with physically adsorbed thiophene.

Finally we turn briefly our attention to the comparison of calculated and experimental second moments, for they present the possibility of providing some detailed structural and dynamical insight of the behavior of solids and adsorbed species. As shown earlier (Figure 3), there is a close correspondence between the second moment of neat thiophene and adsorbed thiophene over a wide range of temperatures. The theoretical second moment of thiophene is 6.8 G^2 ,⁷ but at no temperature has the observed second moment approached that value at all. The lower observed experimental second moment indicates considerable residual mobility probably of a reorientational nature about the axis perpendicular to the molecular plane.⁷

The situation with pyridine is also instructive. In our experiments, the physically adsorbed pyridine as a function of temperature (Figure 6) corresponds to an initial coverage of 2.2×10^{20} molecules/g of sample (surface area of the catalyst was 200 m²/g). The amount for a monolayer required is 3.9×10^{20} , therefore, in our experiments, less than one monolayer was present. The highest experimental second moment for physically adsorbed pyridine is 6.1 G^2 at the lowest temperature studied, while for the chemisorbed pyridine the corresponding value is 4.2 G^2 . Several observations can then be made with a fairly high degree of confidence using the theoretical and calculated second moment.

The expected *intra* molecular second moment of pyridine is 6.4 G^2 , yet the total observed (6.1 G^2) is less than the intramolecular contribution. Since, (1) upon the onset of rotational motion the intramolecular contribution would be affected first, and (2) the level of coverage is such that we expect some intermolecular contribution for the physically adsorbed pyridine but probably not for the chemisorbed pyridine, then, we must conclude that even below the transition temperature some rotational motion must persist for the physically adsorbed pyridine. The greater second moment of the physically adsorbed relative to that of the chemisorbed pyridine at this low temperature (-130 °C)must be due to intermolecular contributions which are not present in the chemisorbed case because of the lower coverage as well as to possible differences in the intramolecular second moment contribution. The fact that the second moment of the chemisorbed pyridine below the transition has the value of 4.2 G is significant. The intramolecular value of the rigid species (6.4 G^2) is reduced to 4.3 G^2 upon the onset of rotation about the C_2 axis through the nitrogen. Thus, the picture that emerges as far as the pyridine adsorbed on molybdena-alumina at these levels of coverage is the following. The chemisorbed pyridine is attached to the surface sites and it is held quite rigidly with the only apparent motion at a temperature lower than the transition point being a rotation about the C_2 axis. This rotation must have a rate higher than 20 kHz since it does affect the line width of 5 G. At temperatures higher than the transition temperature, there appear(s) additional intramolecular motion(s) since the line width narrows from about 5.0 to 3.5 G and the second moment drops correspondingly from 4.3 to 2.5 G². These additional motions are probably librational in nature, but not generalized tumbling, for the latter would entail a line width and second moment of much lower values as observed with the physically adsorbed species. The generalized motion, including translational motion, is evident for the physically adsorbed pyridine, by the dramatic drop of the line width at its transition point.

These results are in general agreement with certain studies of pyridine on various cation-substituted faujasites reContribution of Charge Transfer Forces to Hydrogen Bonding Systems

ported by Russian workers.¹¹ These workers showed that the width of the NMR lines and their second moments depended on the degree of saturation of the zeolites with pyridine as well as on the nature of the compensating cation of the zeolite.

Conclusions

In conclusion then, the NMR data provided here support the ir based differences between physically and chemically adsorbed species. Pyridine adsorbs both physically and chemically on molybdena modified alumina with the pretreatment of the support not being particularly significant. On the other hand, thiophene adsorbs physically only on the reduced molybdena-alumina while it undergoes reaction on "calcined-only" molybdena-alumina. The physically adsorbed pyridine and thiophene show liquidlike NMR behavior with considerable mobility even at low temperature, but both eventually undergo phase transitions that slow down or eliminate the motion of the adsorbed species. Chemically adsorbed pyridine is much more rigidly held on molybdena-alumina surfaces with apparently only a rotation about the C_2 axis. The NMR data provide alternative definitions to the operational ir definition of chemically and physically adsorbed pyridine by providing some detailed structure and dynamic insight of the adsorbed species.

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Charge Transfer Interaction between Thioacetic Acid or Its Ethyl Ester and Triethylamine

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The interaction between thioacetic acid (TAA) or its ethyl ester (ETA) and triethylamine (TEA) was investigated by means of uv, ir, and NMR measurements in CCl₄, CH₂Cl₂, and ethanol. Two new bands were observed in CH_2Cl_2 and ethanol while only one band was present in CCl_4 for the TAA-TEA system. From the disappearance of the bands characteristic of intermolecular interaction in the case of ETA and TEA and also from the measurements of ir and NMR spectra, the bands due to the interaction of TAA and TEA were attributed to a hydrogen bonding type interaction, which is also supported by the results of absorption spectra for the alkyl thiol-amine system. For the assignment of these bands a semiempirical MO (CNDO-CI) calculation was helpful. The absorption at shorter wavelength in the former, two solvents was assigned to a $\sigma_{S-H-N} \rightarrow \sigma^*_{S-H}$ transition owing to a CT interaction while the absorption at the longer wavelength in the former solvents as well as that in the latter solvent to a $\pi_S \rightarrow \sigma^*_{S-H}$ transition associated with the S-H bond stretched by hydrogen bonding.

There have been a number of studies on the electronic structures of molecular complexes from both theoretical and experimental aspects, since Mulliken proposed the intermolecular charge-transfer (CT) theory.¹ From the point of theoretical interest, molecular orbital (MO) techniques have been applied to various molecular interactions based on Mulliken's theory.² While in experimental fields, spectroscopic investigations have been done on the donor-acceptor interaction by means of several kinds of spectroscopies, uv,³ ir,⁴ NMR,⁵ ESR,⁶ etc. Through these studies,

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the structures and physical properties of CT complexes have been clarified and discussed in some detail.⁷ On the other hand, investigations concerning hydrogen bonding (HB) have been made in connection with various systems of biochemical or theoretical interest.⁸ The contribution of CT forces to HB systems has been discussed and even suggested as one of the significant factors.⁹ However, observations of CT bands in HB systems by spectroscopy in ultraviolet and visible region (uv-vis) have been seldom reported because of much weaker interaction than CT complexes and the absorption of considerably shorter wavelength, usually as in the vacuum ultraviolet region, which is characteristic of these systems. A notable exception is

found in the study of Kubota,¹⁰ where HB type CT complexes between TEA or its N-oxide and several kinds of aromatic hydroxy compounds are investigated, but these HB systems in the case of alkyl compounds as acceptors have not been performed hitherto, so far as we know.

While sulfur compounds have been widely studied in view of several points of chemical interests, of which the contribution of 3d orbital,¹¹ the problem of hypervalency,¹² and the behavior as biochemical model compounds¹³ may be characteristic, many sulfur compounds also behave as the electron donor in the donor-acceptor interaction of chemical and biological systems owing to the lower ionization potential. However, few studies on the donor-acceptor interaction of sulfur compounds as "acceptors" have been done except the works of Miller and others.⁵

In a previous paper,¹⁴ we tried to discuss the difference of the electronic states between thioacetic acid (TAA) and its ethyl ester (ETA). In the present work, an attempt was made to study how TAA and ETA interact with an electron-donating molecule in several kinds of solvents, such as carbon tetrrachloride, methylene chloride, and ethanol, by means of uv-vis spectroscopy. The nature of these interactions was examined also in terms of ir and NMR spectra. Furthermore, MO calculations were performed with the CNDO/2 method in order to make the assignment of CT bands and to obtain the stable configuration of both ground and excited states in these systems, where the configuration interaction (CI) technique was used to describe more correctly the excited states of these systems.

Results

1. First of all, we carried out measurements of the electronic absorption spectra of TAA and triethylamine (TEA) mixtures in carbon tetrachloride, methylene chloride, and ethanol, varying the concentration of TEA.²² The results obtained are shown in Figures 1-3, which demonstrates that there appeared two kinds of new bands at ca. 335 and 400 nm in methylene chloride and in ethanol, whereas in carbon tetrachloride only one new band at 400 nm was found. Moreover, we can distinctly recognize the increment of these new bands with increasing amount of TEA, reflecting that these bands could be directly correlated to the donor action of TEA. The isosbestic point at 230 nm in the case of ethanol solvent, as is shown in Figure 3, was unconfirmed in other solvents, because of the limit of spectral region due to the absorptions of the solvents themselves. It could be observed by other techniques.

In order to study further these experimental facts, we tried to test the following Benesi-Hildebrand relation,¹⁵ assuming that a 1:1 molecular complex is formed:

$$D + A \stackrel{K}{=} C \tag{1}$$

$$K = C_{\rm C}/C_{\rm D}C_{\rm A} = C_{\rm C}/(C_{\rm D}^0 - C_{\rm C})(C_{\rm A}^0 - C_{\rm C})$$
(2)

where $C_{\rm C}$ is the concentration of the complex (TAA-TEA), $C_{\rm A}^0$ is the original concentration of TAA, and $C_{\rm A}$ is the concentration of noncomplexed TAA; similar designations are applied to TEA (component D). From eq 2

$$1/K = C_{\rm D}{}^{0}C_{\rm A}{}^{0}/C_{\rm C} - C_{\rm D}{}^{0} - C_{\rm A}{}^{0} + C_{\rm C}$$
(3)

The absorbance A is defined as

$$A = \epsilon_{\lambda} dC_{\rm C} \tag{4}$$

where ϵ_{λ} is called the molar extinction coefficient (in units



Figure 1. Uv-vis spectra of the TAA-TEA system in CCl₄ at 15 °C. The concentration of TAA is 7.07×10^{-2} M. The concentrations of TEA are (1) 2.82 $\times 10^{-1}$, (2) 4.25 $\times 10^{-1}$, (3) 5.64 $\times 10^{-1}$, (4) 7.07 $\times 10^{-1}$, and (5) 1.43 M.



Figure 2. Uv-vis spectra of the TAA-TEA system in CH₂Cl₂ at 15 °C. The concentrations of TAA in the region of 335 and 410 nm are 7.07 \times 10⁻³ and 7.07 \times 10⁻² M, respectively. The concentrations of TEA in the region of 335 and 410 nm are 1.43 \times 10⁻¹ \sim 1.43 and 3.57 \times 10⁻² \sim 5.64 \times 10⁻¹ M, respectively.



Figure 3. Uv-vis spectra of the TAA-TEA system in C₂H₅OH at 15 °C. The concentrations of TAA in the region of 250, 335, and 400 nm are 7.07×10^{-5} , 7.07×10^{-3} , and 7.07×10^{-2} M, respectively. The concentrations of TEA in the region of 250, 335, and 400 nm are $7.07 \times 10^{-6} \sim 7.07 \times 10^{-5}$, $7.06 \times 10^{-4} \sim 7.07 \times 10^{-3}$, and $4.95 \times 10^{-2} \sim 7.08 \times 10^{-1}$ M, respectively.

of M^{-1} cm⁻¹) and d is the length in a cell (in cm). Substituting eq 4 into eq 3, one can obtain the following equation:

$$1/K = \epsilon_{\lambda} dC_{\rm C}/A - C_{\rm D}^0 - C_{\rm A}^0 + C_{\rm C}$$
⁽⁵⁾

When $C_D^0 \gg C_A^0 > C_C$, the third and the last terms in eq 5 can be neglected and eq 5 is reduced to



Figure 4. Plots of $C_D^0 C_A^0 / A_C$ vs. $(C_D^0 + C_A^0)$ for the TAA-TEA system in CCI₄ (at 410 nm).



Figure 5. Plots of $C_D{}^0C_A{}^0/A_C$ vs. $(C_D{}^0 + C_A{}^0)$ for the TAA-TEA system in CH₂Cl₂ (O, 335 nm; •, 410 nm). The right coordinate of the vertical axis in this figure corresponds to the absorption band at 335 nm.

$$dC_{\rm A}^{0}/A = 1/(K\epsilon_{\lambda}C_{\rm D}^{0}) + 1/\epsilon_{\lambda}$$
(6)

In the case of $C_D^0 \approx C_A^0 > C_C^0$

$$dC_{\rm D}{}^{0}C_{\rm A}{}^{0}/A = 1/(K\epsilon_{\lambda}) + (C_{\rm D}{}^{0} + C_{\rm A}{}^{0})/\epsilon_{\lambda}$$
(7)

Then, we tried to apply eq 6 and 7 to the above three systems, which results are shown in Figures 4–6. From the straight lines of this figure and the existence of the isosbestic point for the ethanol solvent system, it is permitted to attribute these absorption bands to the 1:1 complex. Values



Figure 6. Plots of $C_D{}^0C_A{}^0/A_C$ vs. ($C_D{}^0 + C_A{}^0$) for the TAA-TEA system in C_2H_5OH (O, 335 nm; \bullet , 400 nm).

of the equilibrium constant K and the molar extinction coefficient ϵ_{λ} obtained from these straight lines are summarized in Table I.

2. Secondly, measurements of uv and visible spectra of ETA-TEA mixtures were carried out in ethanol to decide whether the complex of TAA and TEA is due to the charge transfer from the nitrogen lone pair electron to the σ^* orbital of the S-H bond or to the carbonyl π^* orbital. In the ETA-TEA system, we found neither new absorption bands nor any remarkable change of both position and intensity of the absorption band of ETA itself at 232 nm even with the use of a considerably large amount of TEA. This fact indicates that there appears no formation of molecular complexes between ETA and TEA in ethanol. The difference between TAA and ETA in these phenomena may obviously be attributed to the replacement of hydrogen atom of the S-H group by an alkyl substituent. Hence the two new absorption bands in TAA-TEA mixtures might reasonably be explained in terms of the formation of a HBtype complex.

3. Furthermore, spectral work on the *n*-propanethiol-TEA system was performed to clarify experimentally whether there exists an interaction between the carbonyl group of TAA and TEA or not. The resultant spectra were similar to those of the TAA-TEA system, that is, in CH_2Cl_2 solvent there also appeared two new bands located at somewhat shorter wavelengths, 300 and 340 nm, and in the case of $CHCl_3$ solvent only one new band at 340 nm. The behavior of absorption bands, remarkably depending on the solvent polarity, are also similar to that of the TAA-TEA system. Therefore, it is asserted that two new bands in the case of TAA should not be attributed to the interaction of the carbonyl group of TAA but that of the thiol group with TEA.

4. In order to provide grounds for the above inference, we measured the change of proton chemical shift of the thiol group of TAA by varying the amount of TEA in CCl₄ and CH₂Cl₂. The results obtained are summarized in Table II, from which we can easily recognize that the S-H proton

		Eq 6 (C _D	$^{\circ} >> C_{A}^{\circ} > 0$	$C_{\rm C}$)	Eq 7	Eq 7 ($C_D^{\circ} \approx C_A^{\circ} >> C_C$)		
Solvent		250 nm	335 nm	400 ~ 410 nm	250 nm	335 nm	400 ~ 410 nm	
CCI.	K			4.91			6.53	
•	Ex			4.74			4.98	
CH.CI.	K		52.67	5.14		66.71	7.22	
011,01,	ۓ		105.7	5.33		107.1	5.40	
C,H,OH	ĸ	$39.36 \sim 126.0^{a}$	36.08	8.23	111.7	45.00	10.50 ^b	
	ϵ_{λ}	$6.29 \sim 2.47 \times 10^{4}$	15.13	7.23	2.28×10^4	12.35	23.81	

TABLE I: Equilibrium Constants and Molar Extinction Coefficients of the TAA-TEA System in Three Kinds of Solvents (15 °C)

^a As is seen from Figures 1-3, this was found to be off of the straight line. Such a result may be easily realized from the fact that we could not find the CT band at 250 nm, in the case of excess donor. ^b This result is after 24 h, since the equilibrium constant K in the instant measurement after mixing TAA with TEA was negative $(K = -12.91, \epsilon_{\lambda} 4.23)$ from the straight line using eq 7. This result could be attributed to the interaction of solvent with TAA or TEA.

TABLE II: Proton Chemical Shifts for the CH₃COSH and N(CH₂CH₃)₃ System in CCl₄ and CH₂Cl₂ (in δ Value, ppm)

		C	Cl ₄		CH ₂ Cl ₂			
Mole ratio ^a	CH ₃	SH	-CH ₂ -	-СН,	CH,	SH	-CH ₂ -	-CH ₃
1:0.0	2.33	4.64						
1:0.1	2.30	6.47	3.18	1.26				
1:0.3	2.35	8.57	3.23	1.33				
1:0.5	2.31	9.47	3.18	1.33	2.32	7.50	3.09	1.26
1:0.7	2.30	10.35	3.12	1.27				
1:1.0	2.30	10.77	3.03	1.27	2.32	10.39	3.07	1.25
1:1.2	2.27	10.91	3.10	1.27				
1:2.0	2.27	12.39	2.80	1.14	2.28	10.89	2.80	1.14

^a The concentration of TAA is 4.95×10^{-1} M, and the concentrations of TEA varied from 5.02×10^{-2} to 9.98×10^{-1} M at 20 °C.

signal of TAA largely shifts toward the downfield as increasing concentrations of TEA, i.e., from 4.64 ppm (1:0) to 10.77 ppm (1:1) in δ value in CCl₄ and from 4.64 ppm (1:0) to 10.39 ppm (1:1) in CH₂Cl₂.

In addition, an ir measurement was made with respect to the TAA-TEA system in CCl₄, indicating that the stretching frequency of ν_{S-H} at 2550 cm⁻¹ (m) shifted toward low frequency, 2515 cm⁻¹ (w) and δ_{S-H} at 830 to 810 cm⁻¹ (w), while the shift of $\nu_{C=O}$ at 1690 cm⁻¹ (s) was small compared with that of ν_{S-H} . This result also affords support to the previous conclusion that TAA forms a complex essentially attributable to the formation of a hydrogen bond with TEA.

5. Moreover, thermodynamic data were obtain in regard to the complexation of TAA and TEA in methylene chloride. The values of ΔH and ΔS were estimated by use of the relation, $\ln K = -\Delta H/RT + \Delta S/R$, in which the values of the equilibrium constant K were obtained from eq 7. The values of ΔH and ΔS are given in Figure 7, which are found much larger than usual cases of simple HB formation. These results also favor the CT character of the interaction between TAA and TEA, particularly in polar solvents such as CH₂Cl₂ or ethanol. Values of equilibrium constants and thermodynamic data obtained from similar procedures mentioned above are smaller in the n-propanethiol-TEA system¹⁶ than those in the TAA-TEA system, as is shown in Table III. These results indicate a weaker CT interaction in the former due to the relatively weak ability of n-propanethiol as a proton donor compared to TAA.

Discussion

As mentioned in the previous section, the TAA and TEA system forms a considerably strong HB type CT complex. In order to confirm this conclusion from uv-vis, ir, and NMR studies, we carried out an MO calculation by means



Figure 7. Plots of log K vs. 1/T for the TAA and TEA system in methylene chloride: O, 335 nm; \bullet , 410 nm.

of the CNDO/2 method.²³ We have treated the system composed of TAA and NH₃ in place of the TEA and also the system of CH₃SH and NH₃ for the sake of comparison.²⁴ To begin with, the most stable conformations of these two systems in their ground states were determined, varying the parameters of both r_1 (the distance of S-H) and r_2 (the distance of N-H). Optimized values of r_1 and r_2 as well as the change of the net charge density distributions are shown in Figure 8. The change of S-H bond length and the amount of charge transferred from the nitrogen lone pair to the sulfur atom indicate that the CT interaction of TAA with NH₃ is much stronger than that of CH₃SH and NH₃. This result seems consistent with the experimental facts that CT bands of the TAA-TEA system have larger intensity and are located at longer wavelengths than those of the alkyl thiol and TEA system and that the equilibrium constant K of the former is a factor of $10 \sim 10^2$ larger than that of the latter by uv-vis and NMR studies.¹⁶ This trend may be related to the acid strength; the pK_a value of TAA is 3.33 and that of alkyl thiol is $10 \sim 12$.

In order to understand in more detail the nature of the

TABLE III: Equilibrium Constants, Molar Extinction Coefficients, and Thermodynamic Data for the n-Propanethiol-TEA System in Two Kinds of Solvents (15°C)

Solvent	λ _{max} , nm	<i>K</i> , ^{<i>a</i>} M ⁻¹	$\epsilon_{\lambda}{}^{a}$	<i>−∆H</i> , kcal/mol	$-\Delta S$, eu
CHCI,	339	0.67	1.09		
CH,CI,	300	0.64	6.75	4.18	15.9
	342	1.67	0.95	5.22	16.6

^a These values were obtained from eq 6, since this system was measured by absorption spectra under the condition of an excess of TEA.



Figure 8. Geometry and charge distribution in the systems, CH₃SH + NH₃ and CH₃COSH + NH₃.

ground states as well as the excited states of the TAA-TEA system, we examine the molecular orbitals (MO) of both a few occupied and unoccupied ones in the case of simplified TAA-NH₃ system. In Table IV, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are designated to the asymmetric σ_{S-H-N} orbital due to the HB interaction of the σ_{S-H} orbital with the nitrogen lone pair and the σ^*_{S-H} orbital owing to the destabilization accompanied with a lengthening of the S-H bond, respectively. Other orbitals are also done in a similar manner as is shown in parentheses in Table IV. The change of orbital levels between the TAA monomer and the TAA-NH₃ system is shown in Figure 9, the change of the σ_{S-H} orbital is drastic while that of σ^*_{S-H} is not and no and $\pi_{\rm S}$ orbitals are both elevated by about 2.0 eV through the HB. This result demonstrates that the HB interaction of this system plays an important role in the ground state rather than in the excited state.

Now by using these MO's, we tried to interpret the two bands, 3.02 and 3.70 eV, characteristic to the HB interaction observed in ethanol and methylene chloride and only one absorption band in carbon tetrachloride. The calculated singlet excitation energies and oscillator strengths of both the TAA monomer and the TAA-NH₃ system are shown in Table V, with the results using the CI technique. The characteristics seen from this table are that the σ_{S-H-N} $\rightarrow \sigma^*_{S-H}$ transition shifts toward considerably longer wavelength (ca. 2.6 eV) by the HB interaction and the $\pi_S \rightarrow$ σ^*_{S-H} transition is located at the longest wavelength in the TAA-NH₃ system in place of the $n_0 \rightarrow \pi^*_{C=0}$ one for the TAA monomer. These trends are closely related to the pre-

								Ē	genvector	20							
		C((1)			S(2	(ŏ	3)		H(4)		N(5)		1
Eigenvalues, eV	s	P _x	Py	$\mathbf{P}_{\mathbf{z}}$	s	\mathbf{P}_{x}	Py	Pz	s	P _x	Py	Pz	s	s	Px	٩	P _z
$5.80 (\sigma^*_{C-S})$	0.44	0.09	-0.40	0.0	-0.02	0.09	-0.58	0.0	-0.11	-0.14	-0.06	0.0	-0.04	0.0	0.17		0 15
5.24 $(\pi^*_{C=0})$	0.0	0.0	0.0	-0.71	0.0	0.0	0.0	0.17	0.0	0.0	0.0	0.65	0.0	0.0	0.0		
$3.17 (0^* S-H)$	0.04	0.01	-0.05	0.0	-0.16	-0.47	-0.08	0.0	0.01	-0.03	0.0	0.0	0.74	-0.33	0.19		
-9.97 (0S-H-N)	0.01	0.14	-0.11	0.0	0.03	-0.77	0.11	0.0	0.01	-0.18	0.08	0.0	-0.31	0.22	-0.33	0.0-	0.0
$-10.62 (\pi_{S})$	0.0	0.0	0.0	-0.04	0.0	0.0	0.0	0.94	0.0	0.0	0.0	-0.33	0.0	0.0	0.0	0.0	0.0
-10.88 (n _O)	-0.08	-0.15	0.31	0.0	0.08	-0.26	-0.60	0.0	0.0	0.33	-0.49	0.0	-0.09	-0.07	-0.11	0.0	0.0

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ТА	A monomer	TAA-NH ₃ system (before CI)				TAA-NH ₃ sys	stem (after CI)	TAA- TEA
$\Delta E_{\rm calcd}$	Assgn	ΔE_{calcd}	f	Assgn	ΔE_{calcd}	f	Assgn	$\Delta E_{\rm obsd}$
5.85	$n_0 \rightarrow \pi^* c = 0$	5.41	5.64 × 10 ⁻⁴	$\pi_S \rightarrow \sigma^*_{S-H}$	5.17	5.05 × 10 ⁻⁴	$\pi_S \rightarrow 0^*_{S-H}$	3.02
5.99	$\pi_{S} \rightarrow \sigma^{*}_{S-H}$	6.29	6.60 × 10 ⁻⁶	$n_{O} \rightarrow \pi^{*}C = O$	5.31	5.52 × 10 ⁻⁴	$n_0 \rightarrow \pi^* C = 0$	
7.19	$\pi_S \rightarrow \sigma^*_{C-S}$	7.60	1.38×10^{-1}	$\pi_S \rightarrow \sigma^*_{C-S}$	6.83	1.86 × 10 ⁻³	$\pi_S \rightarrow \sigma^*_{C-S}$	
8.86	$n_0 \rightarrow \sigma^*_{S-H}$	7.71	9.15×10^{-2}	$n_0 \rightarrow \sigma^*_{S-H}$	7.21	8.38 × 10 ⁻¹	$\sigma_{S-H-N} \rightarrow \sigma^*_{S-H}$	3.70
10.03	$n_0 \rightarrow \sigma^*_{C-S}$	7.91	1.08	$\sigma_{S-HN} \rightarrow \sigma^*_{S-H}$	7.32	5.32 × 10⁻⁵	$n_{O} \rightarrow \sigma^{*}_{S-H}$	
10.39	$\pi_S \rightarrow \pi^*_{C=0}$	8.06	1.90×10^{-1}	$\sigma_{S-H-N} \rightarrow \sigma^*_{C-S}$	7.84	9.86 × 10 ⁻⁴	$\sigma_{S-H-N} \rightarrow \sigma^*C-S$	
10.56	$\sigma_{S-H} \rightarrow \sigma^*_{S-H}$	8.56	9.13 × 10 ⁻⁵	$\sigma_{S-H-N} \rightarrow \pi^*C=0$	8.50	1.78×10^{-1}	$\pi_S \rightarrow \pi^* C = 0$	4.96
	5 6	9.81	3.49×10^{-1}	$\pi_s \rightarrow \pi^* c = 0$			5 6 5	

TABLE V: Electronic Transition Energies (ΔE , eV) and Oscillator Strength (f) for the TAA Monomer and TAA–TEA System by Means of the CNDO–CI Method



Figure 9. The molecular orbital levels in the TAA monomer and the TAA-NH_3 system.

vious discussion of orbital levels. Here, we should keep in mind the following fact before assignments for the two bands, that is, the spectra of alkyl thiol-amine system (without carbonyl group) show a similar result with the present TAA-TEA system, although both of the bands are located at somewhat shorter wavelength (3.65 and 4.13 eV). This fact demonstrates that two observed bands of the TAA-TEA system are not due to the existence of the carbonyl group as altered above. Accordingly, we can exclude the possibility of the $n_O \rightarrow \sigma^*_{S-H}$ transition and therefore also the n₀ $\rightarrow \pi^*_{C=0}$ and $\sigma_{S-H-N} \rightarrow \pi^*_{C=0}$ ones. In addition, the fact that the $n_0 \rightarrow \pi^*_{C=0}$ transition shifts toward shorter wavelength by the HB interaction is consistent with the previous conclusion for the TAA anion.¹⁴ Furthermore, the $\pi_{\rm S} \rightarrow \sigma^*_{\rm C-S}$ and $\sigma_{\rm S-H-N} \rightarrow \sigma^*_{\rm C-S}$ transitions are also eliminated because of their very small intensities. From the result after CI treatment as well as these considerations mentioned above, we can reasonably assign these two observed bands, 3.02 and 3.70 eV, to $\pi_{\rm S} \rightarrow \sigma^*_{\rm S-H}$ and $\sigma_{\rm S-H-N} \rightarrow \sigma^*_{\rm S-H}$ transitions, respectively.

Next, we should discuss the only absorption band at 3.02 eV in carbon tetrachloride, where the HB interaction between the σ_{S-H} orbital and the nitrogen lone pair becomes weaker than in the case of a polar solvent such as methylene chloride or ethanol. Accordingly, the σ_{S-H} bond may not be so weakened as in the case of polar solvents and hence the HOMO may become a π_S orbital in place of a σ_{S-H-N} one. Consequently, the band for the $\sigma_{S-H-N} \rightarrow$ σ^*_{S-H} transition shifts toward considerably shorter wavelength, probably with weakened intensity. On the other hand, the absorption band of the $\pi_{S} \rightarrow \sigma^{*}_{S-H}$ transition is not much influenced since the σ^*_{S-H} orbital is almost not changed by this HB interaction. Thus the only band observed in carbon tetrachloride may be also be assigned to the $\pi_S \rightarrow \sigma^*_{S-H}$ transition which increases in intensity as if adding a quantity of TEA.

Finally, we dared to note that the band at 4.96 eV in ethanol is assigned to the $\pi_S \rightarrow \pi^*_{C=0}$ transition owing to the TAA anion. This experimental phenomenon also seems to be in accord with previous discussion.¹⁴

Experimental Section

A. Solvents. Carbon tetrachloride, chloroform, and methylene chloride were commercial grade and were further purified by distillation before use. Ethanol was spectrograde commercial quality and used without further purification.

B. Compounds. Commercial thioacetic acid (TAA), npropanethiol, and triethylamine (TEA) were distilled before spectroscopic measurements. Ethylthioacetate (ETA) was prepared by conventional synthetic methods^{20,21} from ethylmercaptan and acethyl chloride of commercial qualities, and distilled before use. Freshly prepared solutions of TAA and ETA as well as n-propanethiol with TEA in two or three kinds of solvents were always employed avoiding the effect of air oxidation.

C. Measurements. Electronic absorption spectra (uv-vis) were measured by means of a Hitachi recording spectrophotometer (ESP-3T type) with quartz cells (1.0-cm light path). Temperatures of the absorption cells were kept constant during the measurements by using a thermospacer through which water of constant temperature was circulating and the regions of variable temperatures were from 5 to $25 \,^{\circ}$ C. Measurements of ir and NMR spectra were carried out using a Hitachi grating infared spectrometer and a Varian HR-220 spectrometer system, respectively, and the former was at room temperature and the latter at a constant temperature, 20 $^{\circ}$ C. Contribution of Charge Transfer Forces to Hydrogen Bonding Systems

Conclusion

It was shown from experiments and MO calculations that there exists a 1:1 HB type interaction between TAA and TEA which gives, in the uv-vis region, two kinds of absorption bands in polar solvents such as ethanol and CH₂Cl₂, while in CCl₄ being a nonpolar solvent only the one at longer wavelength exists. This fact indicates that the nature of the interaction is very sensitive to solvent polarity, probably due to the stabilization of solvation for solutes, the mixture of TAA and TEA. The above experimental phenomena characteristic to the present systems are also reasonably explained in terms of the degree of the destabilization of the σ_{S-H-N} orbital obtained from MO calculation including the CI treatment in the TAA-NH₃ system. In addition, the trends of calculated transition energies and oscillator strengths are consistent with experimental ones. The values of the equilibrium constants K, which are different (ca. a factor of 10) for these two bands, and the thermodynamic data of ΔH and ΔS are much larger than in the case of so-called simple HB interaction. These results lead to the following conclusion that the TAA-TEA system forms a molecular complex owing to strong hydrogen bonding with considerable charge transfer as to make the quantitative discussions possible by means of electronic absorption spectra.

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Structures of Dimethyl Disulfide and Methyl Ethyl Disulfide, Determined by Gas-Phase Electron Diffraction. A Vibrational Analysis for Mean Square Amplitudes

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Diffraction data were reduced via least-squares fitting of the radial distribution functions and the scattered intensity patterns. The following structural parameters were obtained: for dimethyl disulfide: $r_g(C-S) = 1.816 \pm 0.003$ Å, $r_g(S-S) = 2.029 \pm 0.003$ Å, $r_g(C-H) = 1.105 \pm 0.005$ Å, $\angle SSC = 103.2 \pm 0.2^\circ$, $\angle SCH = 111.3 \pm 0.6^\circ$, and the rotational angle about the S–S bond, $\Phi_3(CS-SC) = 85.3 \pm 3.7^\circ$; for methyl ethyl disulfide: $r_g(C-S) = 1.817 \pm 0.004$ Å, $r_g(S-S) = 2.031 \pm 0.003$ Å, $r_g(C-C) = 1.540 \pm 0.007$ Å, $r_g(C-H) = 1.111 \pm 0.005$ Å, $\angle CCS = 112.4 \pm 1.6^\circ$, $\angle SSC = 103.2 \pm 0.3^\circ$, and $\Phi_3(CS-SC) = 84.4 \pm 6.9^\circ$. The angle parameters are given in terms of the r_α structures and the uncertainties are the estimated standard errors. Normal mode analyses were carried out using Urey-Bradley force fields, with force constants carried over from analogous molecules. These are accurate enough for estimating mean square amplitudes and vibrational corrections of the structural parameters. With respect to rotational isomerism about the CC-SS bond in methyl ethyl disulfide, the present diffraction data, in the absence of additional information, do not lead to a unique conclusion. It is evident that: (i) more than one conformer is present; (ii) the trans isomer comprises a substantial fraction of the total; (iii) the diffraction data can be fitted equally well by a range of compositions, which depend on the assumed relative stabilities of the cis, two gauche, and two skew structures.

Introduction

Considerable attention has been devoted recently to the structures and the conformational preferences of simple alkyl disulfides. These serve as model compounds for probing some of the structural features of protein conformations with respect to the -C-S-S-C- group. At present the minimum energy orientation about the S-S bond in disulfide groups has been well established; the dihedral angle is nearly 90°.1-5 However, the conformational isomers about the C-S bond in -C-C-S-S- groups have not been clearly identified. The Raman spectra of methyl ethyl disulfide (EtS_2Me) in the liquid state⁵ were interpreted as though the gauche isomer (G) were more stable than the trans (T) by 0.9 \pm 0.2 kcal/mol and that only the G form was present in the solid state. (The variety of possible isomers is illustrated in Figure 1.) The G' conformation, which is one of the two nonequivalent gauche forms, was not considered by these authors because the apparent steric interaction of the two CH₃ groups presumably raises its energy. This assumption was also used by Scott and El-Sabban⁶ in their discussion of the infrared spectrum of this molecule. Restudy⁷ of the temperature dependence of the Raman spectra casts serious doubts on the validity of these assumptions. A recent CNDO/2 calculation⁸ of EtS_2Me suggests that the cis $(\Phi_2 = 0 \sim 30^\circ)$ form is the lowest energy conformation rather than gauche ($\Phi_2 = 60^\circ$), and there is a higher minimum in the potential function at the trans ($\Phi_2 = 180^\circ$) position. Since no structure determination of EtS₂Me has been published, Professor H. A. Scheraga proposed that the present study be undertaken to provide information on the geometrical parameters and rotational isomers of this molecule in the gas state. At the same time, the structure of dimethyl disulfide (MeS₂Me) was reinvestigated. In a previous electron diffraction report⁴ the authors ignored shrinkage corrections due to molecular vibrations. In fact, the vibrational corrections proved to be significant based on the present normal mode analysis.

Experimental Section

The samples of MeS_2Me and EtS_2Me used in the present study were kindly provided by Dr. Francis Cardinaux of Cornell University. His gas-chromatographic analyses showed that the purity of the former was better than 99.9% and that of the latter was 98.4%, where the major impurity (1.6%) was MeS₂Me. Electron diffraction photographs were taken with the Cornell apparatus,⁹ with the sample reservoirs at room temperature. Patterns were recorded at two nozzle-to-plate distances, 286.57 ± 0.13 mm (HVL) and 128.55 ± 0.14 mm (HVS); the accelerating voltage was about 60 kV (λ 0.04853₉ Å). Photographs of CS₂ (99.97%: Matheson Coleman and Bell) were taken concurrently with those of the samples to provide checks on possible systematic errors. Exposure times were between 10 and 40 s, with a beam current of 0.8 μ A. During the exposure the apparatus pressure was maintained at $1 \sim 3 \times 10^{-6}$ Torr. The optical densities for the three sets of photographs ranged from $0.3 \rightarrow 0.9$ (HVL) and $0.4 \rightarrow 0.9$ (HVS).

The photographic densities were assumed to be directly proportional to the diffraction intensities, and sector corrections were applied. Least-squares analysis of the CS₂ diffraction patterns gave scale correction factors of 0.12% for distances and -4.6% for the mean square amplitudes, obtained by comparing the electron diffraction patterns with values calculated from spectroscopic data.¹⁰ The data reduction procedure followed was that described in previous publications from this laboratory.⁹ The contribution from the 1.6% MeS₂Me impurity to the EtS₂Me photographs was substracted from the intensity function for the



Figure 1. Atom and parameter designations for EtS_2Me . The various conformations are shown projected along the C_5S_8 bond.

latter, even though that contribution was much less than the random noise in the intensity measurements.

Analysis

Choice of Geometric Parameters. Eight parameters were selected to specify the molecular structure of MeS_2Me : three bond distances (C-S, S-S, and C-H), two bond angles (\angle CSS and \angle SCH), and three dihedral angles (Φ _{SS}, Φ _{CS}, and Φ_{CS} '), where Φ_{SS} is the dihedral angle between the two SSC planes, measured from the cis configuration, while Φ_{CS} and Φ_{CS} are the rotational angles of the two methyl groups. When Φ_{CS} (or Φ_{CS}) is set at 0 or $\pm 60^{\circ}$, the model is in the eclipsed or staggered position around the C-S axis, respectively. To fully specify the structure of MeS_2Me , the following addition assumptions had to be made. (a) Each CH_3 group has local $C_{3\nu}$ symmetry with respect to the C-S axis. (b) All C-H bond distances are equal. (c) The skeleton, C-S-S-C, has at least C_2 symmetry. For EtS₂Me additional assumptions were introduced in order to reduce the number of structural parameters which had to be determined. (d) The SCH bond angle was set equal to 111.5°, as in MeS_2Me . (e) The CCH bond angle in the C-CH₃ group was set at 111.5°, equal to that in ethane.¹¹ (f) The HCH bond angle of the CH₂ group was set at 107.8°, equal to the corresponding group in propane.¹² The assumptions concerning the location of the hydrogen atoms did not introduce any serious systematic errors in the sought-for structural information since the contribution of the hydrogenhydrogen pairs to the total scattered intensity is small; indeed, the assumed values were checked by trial-and-error analyses of observed radial distribution curves, and con-

TABLE I: Assumed Force Constants^a

2.20	H(CSS)	0.15
1.70	F(CSS)	0.25
2.37	Y(C-C)	0.15
4.40	$Y(C_m - S)^b$	0.054
4.30	$Y(C_e-S)^b$	0.060
0.44	Y(S-S)	0.147
0.07	$\chi(CH_2)$	0.03
0.186	$\chi(CH_3)$	0.008
0.54	$t(CH_{2}CH_{2})$	0.136
0.15	$g(CH_3CH_2)$	-0.051
0.39	$l(CH_2)$	0.057
0.052		
0.056		
	$\begin{array}{c} 2.20\\ 1.70\\ 2.37\\ 4.40\\ 4.30\\ 0.44\\ 0.07\\ 0.186\\ 0.54\\ 0.15\\ 0.39\\ 0.052\\ 0.056\end{array}$	$\begin{array}{cccc} 2.20 & H(\text{CSS}) \\ 1.70 & F(\text{CSS}) \\ 2.37 & Y(\text{C}-\text{C}) \\ 4.40 & Y(\text{C}_{\text{m}}-\text{S})^b \\ 4.30 & Y(\text{C}_{\text{e}}-\text{S})^b \\ 0.44 & Y(\text{S}-\text{S}) \\ 0.07 & \chi(\text{CH}_2) \\ 0.186 & \chi(\text{CH}_3) \\ 0.54 & t(\text{CH}_3\text{CH}_2) \\ 0.15 & g(\text{CH}_3\text{CH}_2) \\ 0.39 & l(\text{CH}_2) \\ 0.052 \\ 0.056 \end{array}$

^d Modified Urey-Bradley force constants for $S_2(CH_3)_2$ and $S_2(CH_3)(C_2H_5)$. K, H, and F are stretching, angle deformation, and nonbonded interaction force constants (mdyn/Å), respectively. Y is a force constant (mdyn/Å) for torsional oscillation. χ , t, g, and l are constants of internal tension, trans and gauche angle interaction of CH₃-CH₂, and angle interaction of CH₂ (mdyn Å). More detailed definitions are given in ref 12 and 13. ^b The subscript m and e indicate that the atoms belong to the methyl and ethyl groups, respectively.

TABLE II: Mean Square Amplitudes (l_{ij}) and Vibrational Corrections $(\delta_{ij} = r_a - r_{\alpha})$ for S₂(CH₃)₂ at 298 K

Atom pair ^a	l _{ij}	δ _{ij} (× 10⁴ Å)
S-S	486	9
S-C	562	64
$\mathbf{S} \cdot \cdot \cdot \mathbf{C}$	906	2
S: · ·H	1131	262
$(\mathbf{S} \cdot \cdot \cdot \mathbf{H})_{\mathbf{S}}$	2205	36
$(\mathbf{S} \cdot \cdot \mathbf{M})_{\mathrm{L}}^{\mathrm{T}}$	1127	123
C·_··C	1818	-75
C-H	795	532
$(C \cdot \cdot \cdot H)_S$	3036	-138
$(\mathbf{C}\cdot\cdot\cdot\mathbf{H})_{\mathbf{M}}$	2867	-64
$(\mathbf{C}\cdot\cdot\cdot\mathbf{H})_{\mathbf{L}}$	2163	6
H H	1293	805

^a The subscripts S, M, and L refer to the smaller, medium, and longer distance pairs, respectively. The remaining hydrogen-hydrogen pairs are not listed.

firmed with preliminary least-squares analyses of molecular intensities.

On that basis the following ten independent parameters were chosen for EtS₂Me: four bond distances (C-C, C-S, S-S, and C-H), two bond angles (\angle CSS and \angle CCS), and four dihedral angles (Φ_1 , Φ_2 , Φ_3 , and Φ_4 ; see Figure 1). Φ_1 , Φ_4 , and Φ_3 are defined in the same way as are the corresponding angles Φ_{CS} , Φ_{CS}' , and Φ_{SS} for MeS₂Me; Φ_2 is the dihedral angle between the CCS and SSC planes and defines the orientation of the ethyl group around the C-S axis, as illustrated in Figure 1. The name designations for Φ_2 equals 0, 60, -60, 120, -120, and 180° are cis, gauche, gauche', skew, skew', and trans, respectively.

Mean Square Amplitudes of Vibrational Corrections. Normal mode analyses of MeS_2Me and EtS_2Me were carried out using Urey-Bradley force fields¹³ with force constants carried over from analogous molecules: polyethylene disulfide,¹⁴ 1,2-ethanedithiol,¹⁴ n-propyl mercaptan,¹⁴ and 2-thiabutane.¹⁵ These estimated values are compiled in Table I. The present results for the normal vibrations of MeS_2Me and EtS_2Me do not differ significantly from the previous calculations based on the valence force fields used 620

Ator	n pair	Tr	ans	Gau	Gauche		Gauche'		Cis	
i	j	l _{ij}	δ _{ij}	l _{ij}	δ _{ij}	l _{ij}	δ_{ij}	l _{ij}	δ _{ij}	
8	9	486	50	486	30	486	46	486	25	
5	8	558	63	558	50	558	72	558	78	
1	8	1382	84	1382	89	1382	56	1382	47	
5	9	906	48	908	8	908	29	908	14	
1	9	1056	12	2720	-135	2711	-185	2431	-108	
9	11	1115	345	1115	445	1115	445	1115	473	
6	8	1144	246	1114	225	1144	239	1114	312	
2	8	2247	256	2247	291	2247	212	2247	232	
8	11	2204	119	2204	170	2204	115	2204	149	
3	9	2134	82	3851	-150	3949	-237	3876	-206	
2	9	2134	82	3944	-175	3828	-230	3876	-206	
7	9	2182	91	2150	0	1134	157	1752	102	
6	9	2182	91	1136	97	2150	51	1752	102	
4	8	1338	178	1338	178	1338	163	1338	166	
8	13	1127	214	1127	216	1127	177	1127	185	
4	9	1341	67	2688	-17	2672	-47	2681	-27	
1	5	527	398	527	380	527	382	527	376	
1	10	2192	-74	3407	-247	3509	-255	3732	-342	
5	10	1816	5	1817	-10	1817	-60	1817	-39	
1	2	790	539	790	509	790	564	790	540	
2	5	1070	736	1070	719	1070	751	1070	740	
1	6	1088	352	1088	585	1088	617	1088	624	
1	11	3719	-188	3433	-121	4521	-356	4210	-281	
2	10	3720	-133	3757	-150	4368	-227	5414	-679	
3	10	2132	54	5111	-532	5279	-604	4471	-305	
5	11	3034	-51	3034	-20	3034	-72	3034	-35	
1	13	2354	-2	4059	-219	4026	-195	4132	-235	
1	12	3439	-116	4273	-277	4119	-124	4878	-502	
4	10	2631	-46	3630	-182	3993	-248	4108	-285	
5	13	2161	107	2162	81	2162	30	2162	40	
7	10	3000	-78	2856	15	2112	7	2987	-90	
5	12	2865	-7	2866	34	2866	-24	2866	11	
ő	10	2859	76	2167	28	2943	-130	1973	44	

TABLE III: Mean Square Amplitudes (l_{ij}) and Vibrational Corrections $(\delta_{ij} = r_a - r_\alpha)$ for $S_2(CH_1)(C_2H_2)$ (× 10⁻⁴ A)²

^a The hydrogen-hydrogen pairs are not listed.

by Scott and El-Sabban; our calculated frequencies are in good agreement with the observed frequencies cited in their paper.⁶ The assumed force constants are accurate enough for estimating mean square amplitudes (l_{ij}) and vibrational corrections $(\delta_{ij} \equiv r_a - r_a)$ for our electron diffraction analysis. The l_{ij} and δ_{ij} were calculated for all atomic pairs in MeS₂Me and EtS₂Me for 298 K (We estimate that sample cooling due to jet expansion brings the temperature down to 256 K. This has a minimal effect on the l_{ij} 's and δ_{ij} 's, which were calculated via our standard program.); the results are listed in Tables II and III. For EtS₂Me, only the values for C, G, G', and T are given.

It is worth noting that the torsional force constants, Y(S-S) of 0.147 mdyn Å and Y(C-S) of 0.05 mdyn Å for MeS₂Me, correspond to barrier heights of 10.5 and of 1.6 kcal/mol, respectively, when twofolc [S-S] and threefold [C-S] cosine potentials are assumed for the internal rotations. A thermochemical estimate for the former is 9.5 kcal/mol;¹⁶ for the latter a microwave stucy¹⁷ gave 1.6 kcal/mol. Furthermore Tables II and III show that vibrational corrections (δ_{ij}), i.e., shrinkage effects, are not negligible for these molecules because of the presence of low frequency torsional vibration.

Structural Parameters. The experimental radial distributions, f(r), and molecular intensity curves, qM(q), for MeS₂Me and EtS₂Me are plotted in Figures 2 and 3 (dotted) and compared with the corresponding functions calculated for the "best fit" models. From the well resolved f(r) peaks the bonded distances (C-H, C-C, C-S, and S-S) and bond angles (\angle SCH and \angle SSC) were readily obtained, as in-

dicated in Figure 2. Information on rotational isomers about the CC-SS bond in EtS₂Me appears in the 3-5-Å region of the f(r) function, which is derived from the qM(q)function in the corresponding small angle region (<~30 Å⁻¹), as illustrated in Figure 3. This dicotomy is advantageous in that the major structural parameters, i.e., the bonded distances and bond angles, may be derived from the 30-120-Å⁻¹ portion of the scattering pattern without complications due to rotational isomerism. On the other hand, because the contributions from the rotational isomers to the molecular intensity function appear over 10 <q < 30, which is relatively small compared to the total molecular intensity, special care must be taken in the analysis of the data to extract the interesting conformational information. Because of the insensitivity of the diffraction pattern to the orientation of the CH_3 groups in MeS_2Me the structural parameters chosen in the previous section were determined by least-squares fitting of the qM(q) curve with the additional assumptions: the CH₃ groups in MeS₂Me and EtS₂Me were placed in staggered positions (i.e., $\Phi_{CS} = \Phi_{CS}' = 0$, and $\Phi_1 = \Phi_4 = 0$). For EtS₂Me we assumed that the trans ($\Phi_2 = 180^\circ$) fraction was 25% of the total, as estimated from the early spectroscopic measurements.⁵ Indeed, the orientations of the CH₃ groups introduce no significant systematic error in the other parameters; furthermore, their staggered position in MeS₂Me was justified by the "background analysis", used in the following section. In EtS₂Me the only torsional angle parameter that influences the structural parameters is Φ_2 , as anticipated. This feature is analyzed in detail in the following



Figure 2. Radial distribution curves for the two disulfides; experimental values at 0.04-Å intervals are dctted. The computed curve for EtS_2Me is for a mixture of 25% T and 75% G.



Figure 3. The observed (dots) and calculated molecular scattering functions for the two disulfides. The irregular curve marked (A) is the difference between the observed and the calculated function for 25% T and 75% G for EtS₂Me. The curve designated (B) is the calculated difference between the T and G functions, while the corresponding difference curve for the C–G function is designated (C).

section. Thus, in the least-squares analysis the l_{ij} and δ_{ij} values listed in Tables II and III were used and the results are summarized in Table IV. The estimated standard errors are $(\sigma_r^2 + \sigma_s^2)^{1/2}$, where σ_r is the least-squares standard deviation, and σ_s is the estimated experimental error (0.2% of the distances) due to the scale factor. Other systematic errors imposed by constraints introduced in the analysis were found to be insignificant compared with σ_r . The error matrices are listed in Tables V-VIII.

Rotational Isomerism of EtS_2Me . The region of the f(r)

TABLE IV: Structural Parameters Derived by Least-Squares Fitting of $qM(q)_{calcd}$ to $qM(q)_{expt}$

	S ₂ (CH ₃) ₂	$S_2(CH_3)(C_2H_5)$
C-S	1.816 ± 0.003	1.817 ± 0.004
S–S	2.029 ± 0.003	2.031 ± 0.003
C-C		1.540 ± 0.007
C-H	1.105 ± 0.005	1.111 ± 0.005
∠CCS		$112.4 \pm 1.6^{\circ}$
∠SSC	$103.2 \pm 0.2^{\circ}$	$103.2 \pm 0.3^{\circ}$
∠SCH	$111.3 \pm 0.6^{\circ}$	(111.5)
Φ(CS−SC) ^μ	$85.3 \pm 3.7^{\circ}$	$84.4 \pm 6.9^{\circ}$
$\Phi(CC-SS)^b$		66.8 ± 7.6°
k,	1.00 ± 0.01	0.98 ± 0.02
k,	0.97 ± 0.02	0.96 ± 0.03

^a Rotational angle about the S–S bond. ^b Rotational angle (Φ_2) about the CC–SS bond, see Figure 1, on the assumption that the trans $(\Phi_2 = 180^\circ)$ and gauche isomers coexist in the ratio of 25 to 75%, and that the angle Φ_2 of the gauche isomer was determined by the least-squares fitting. Distances, r_g (A); angles, r_α structure; k_1 , k_2 , indices of resolutions (dimensionless); (HVL) and (HVS), respectively.



Figure 4. Portions of the f(r) curves over the region 2.5–5.5 Å, wherein the experimental functions are compared with those calculated for 100% of each of the designated conformers.

curve which is sensitive to the rotational conformations of EtS_2Me is shown in Figure 4, where the derived values (circles) are compared with the theoretical curves for T (100%), G (100%), G' (100%), and C (100%). The vertical bars in the figure indicate the peak positions of the S_{9^-} - C_1 pair for the respective configurations (Figure 1). Please note that the position of the S_{9^-} - C_1 distance is the single important feature which characterizes this rotational conformation; contributions from the other nonbonded pairs, as well as from the C_{1^-} - C_{10} pairs, to the total distribution curve are unfortunately too small. This is an inherent limitation.

TABLE V: Recorded Intensities and Derived Backgrounds for MeS₂Me

q	I(q)	B(q)	q	I(q)	B(q)	q	I(q)	B(q)
	HVL							
11	0.2620	0.2604	37	0.6556	0.6613	80	0.8019	0.7936
12	0.2832	0.2690	38	0.6543	0.6667	81	0.8022	0.7938
13	0.3019	0.2785	39	0.6614	0.6721	82	0.7999	0.7939
14	0.3098	0.2887	40	0.6758	0.6774	83	0.7960	0.7940
15	0.3096	0.2993	41	0.6905	0.6827	84	0.7907	0.7940
16	0.2999	0.3103	42	0.6994	0.6879	85	0.7867	0.7939
17	0.2917	0.3215	43	0.7030	0.6930	86	0.7863	0.7939
18	0.2960	0.3327	44	0.7012	0.6981	87	0.7882	0.7938
19	0.3140	0.3437	45	0.7010	0.7031	88	0.7914	0.7936
20	0.3497	0.3546	46	0.7043	0.7080	89	0.7952	0.7935
21	0.3829	0.3651	47	0.7093	0.7128	90	0.7973	0.7934
22	0.4054	0.3753	48	0.7161	0.7175	91	0.8002	0.7933
23	0.4138	0.3849	49	0.7221	0.7221	92	0.7984	0.7932
24	0.4137	0.3939	50	0.7272	0.7266	93	0.7956	0.7932
25	0.4136	0.4023	51	0.7300	0.7310	94	0.7926	0.7933
$\frac{1}{26}$	0.4143	0.4100	52	0.7342	0.7352	95	0.7900	0.7934
27	0.4166	0.4170	53	0.7386	0.7393	96	0.7885	0.7936
28	0.4158	0.4233	54	0.7418	0.7432	97	0.7887	0.7939
29	0.4139	0.4289	55	0.7443	0.7470	98	0.7923	0.7944
30	0.4149	0.4337	56	0.7469	0.7507	99	0.7963	0.7949
31	0.4221	0.4377	57	0.7504	0.7542	100	0.7980	0.7957
32	0.4363	0.4411	58	0.7574	0.7575	101	0.8009	0.7966
33	0.4499	0.4438	59	0.7657	0.7607	102	0.8027	0.7977
34	0.4578	0.4460	60	0.7728	0.7638	103	0.8006	0.7990
35	0.4587	0.4475	61	0.7765	0.7667	104	0.8015	0.8005
36	0.4535	0.4487	62	0.7763	0.7694	105	0.8009	0.8023
37	0.4455	0.4494	63	0.7732	0.7720	106	0.8005	0.8043
38	0.4417	0.4499	64	0.7679	0.7744	107	0.8039	0.8066
39	0.4437	0.4502	65	0.7678	0.7767	108	0.8084	0.8092
40	0.4513	0.4504	66	0.7700	0.7788	109	0.8120	0.8121
41	0.4570	0.4508	67	0.7757	0.7807	110	0.8173	0.8154
42	0.4596	0.4515	68	0.7830	0.7825	111	0.8208	0.8191
43	0.4589	0.4525	69	0.7883	0.7842	112	0.8246	0.8231
44	0.4548	0.4541	70	0.7922	0.7857	113	0.8291	0.8276
45	0.4542	0.4565	71	0.7936	0.7870	114	0.8332	0.8325
46	0.4562	0.4599	72	0.7935	0.7882	115	0.8367	0.8378
			73	0.7907	0.7893	116	0.8430	0.8437
	HVS	6	74	0.7876	0.7903	117	0.8488	0.8500
32	0.6267	0.6344	75	0.7866	0.7911	118	0.8566	0.8569
33	0.6484	0.6398	76	0.7846	0.7918	119	0.8650	0.8643
34	0.6623	0.6451	77	0.7869	0.7924	120	0.8725	0.8723
35	0.6666	0.6505	78	0.7913	0.7929			
36	0.6624	0.6559	79	0.7967	0.7933			

Hence the electron diffraction data do not provide a basis for discriminating the G from G' form (or S from S'), since, in each of these pairs the same magnitudes appear for the S₉- - C_1 scattering. In Figure 4 G and G' give essentially identical contours.

Despite the above limitation the following conclusions may be deduced from Figure 4. The small peak around 4.4 Å is clearly present in the experimental curve, though the calculate curve in this region is slightly model dependent. Since this peak, which corresponds to the trans S_{9} - - C_1 pair, does not arise in any other conformer, the trans isomer must be present, but clearly at less than 100%. The G and G' isomers (if present at 100%) give reasonably good fits except at the 4.4 Å, indicating a small fraction of T must be included. However, the possibility of obtaining other reasonable fits by inserting various combinations of T + C, T + S (or S'), instead of $\overline{T} + G$ (or G') still must be considered. To obtain further information on this point, the following "background analysis" was undertaken using the small angle region of the intensity curve. This has been successfully applied to the study of rotational isomerism in n-butane,¹⁸ n-propyl chloride,¹⁹ methyl ethyl ketone,²⁰ and ethylenediamine.²¹ In this method one applies a "smoothness" criterion to the background function, $I_{b}(q)$, defined by

$$I_{\rm b}(q) = g(q)I_{\rm T}(q) \left/ \sum_{i} \left[(Z_i - F_i)^2 + S_i \right] [1 + kM_0(q)]$$
(1)

where g(q) is an empirical algebraic function introduced to "level" the observed total intensity, $I_{\rm T}(q)$, and k is a constant, designated as the "index of resolution"; Z_i , f_i , and S_i are the atomic number, elastic, and inelastic scattering factors for atom i. The $I_{\rm b}$ curve thus defined should be free from any oscillations which have a period that corresponds to the nonbonded distances in question, in this case 3–5 Å, when the $qM_0(q)$ is based on a correct model. Several examples of the $I_{\rm b}$ curve are plotted in Figure 5; k was set to unity, and a moderate quadratic function, g(q), was used to level the recorded scattered intensities.

This analysis shows that the I_b curves for the G and G' conformers $[\Phi_2 = 60 \text{ and } -60^\circ]$ have the least fluctuations, if one assumes that a single conformer is present. The previous analysis of the radial distribution curve show that the T form was always present to a moderate extent. The question then remains which mixture should be incorporated with the trans isomer to generate the smoothest I_b curve.

TABLE VI: Intensity (I)	and Background	(B) for EtS, Me
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q	<i>I(q)</i>	B(q)	q	<i>I</i> (<i>q</i>)	B(q)	<i>q</i>	<i>I(q)</i>	B(q)
	HVL							
11	0.3396	0.3521	36	0.5595	0.5586	78	0.6914	0.6927
12	0.3678	0.3662	37	0.5579	0.5638	79	0.6971	0.6931
13	0.3997	0.3812	38	0.5597	0.5690	80	0.7014	0.6934
14	0.4211	0.3968	39	0.5686	0.5742	81	0.7007	0.6937
15	0.4288	0.4128	40	0.5818	0.5794	82	0.6991	0.6938
16	0.4221	0.4291	41	0.5931	0.5845	83	0.6954	0.6939
17	0.4132	0.4455	42	0.6019	0.5896	84	0.6917	0 6940
18	0.4189	0.4617	43	0.6052	0.5946	85	0.6882	0 6940
19	0.4443	0.4777	44	0.6029	0.5995	86	0.6876	0.6940
20	0.4869	0.4932	45	0.6038	0.6044	87	0.6876	0.6939
21	0.5294	0.5082	46	0.6059	0.6092	88	0.6903	0.6938
$22^{$	0.5616	0.5226	47	0.6100	0.6138	89	0.6932	0.6938
23	0.5734	0.5362	48	0.6156	0.6184	90	0.6979	0.6937
24	0.5726	0.5490	49	0.6211	0.6229	91	0.6996	0.6937
25	0.5698	0.5610	- 50	0.6254	0.6273	92	0.6982	0.0337
26	0.5714	0.5720	51	0.6310	0.6315	93	0.6955	0.0530
27	0.5772	0.5820	52	0.6351	0.6356	94	0.6938	0.0337
28	0.5835	0.5911	53	0.6394	0.6396	95	0.0000	0.0538
29	0.5856	0.5991	54	0.6429	0.6435	96	0.6911	0.0535
30	0.5887	0.6062	55	0.6450	0.6472	97	0.6931	0.0542
31	0.5960	0.6123	56	0.6484	0.6508	98	0.6940	0.0940
32	0.6109	0.6176	57	0.6521	0.6542	99	0.0340	0.0900
33	0.6267	0.6219	58	0.6589	0.6575	100	0.0505	0.0936
34	0 6345	0.6255	59	0.6662	0.6607	100	0.0570	0.0904
35	0.6361	0.6284	60	0.6709	0.6637	101	0.7000	0.0973
36	0.6322	0.6307	61	0.6734	0.6665	102	0.7007	0.0984
37	0.6258	0.6326	62	0.6737	0.6692	103	0.7014	0.0997
38	0.6252	0.6341	63	0.6711	0.6717	104	0.7003	0.7012
39	0.6289	0.6353	64	0.6679	0.6741	105	0.7012	0.7030
40	0.6391	0.6366	65	0.6686	0.6763	100	0.7026	0.7050
41	0.6469	0.6380	66	0.6714	0.6784	107	0.7005	0.7073
42	0.6524	0.6398	67	0.6767	0.6804	108	0.7103	0.7099
43	0 6523	0.6421	68	0.6821	0.6821	109	0.7124	0.7128
44	0.6463	0.6452	69	0.6874	0.6838	110	0.7173	0.7160
45	0 6464	0 6492	70	0.6907	0.6853	111	0.7211	0.7196
46	0.6500	0.6546	71	0.6922	0.6866	112	0.7201	0.7236
10	0.0000	0.0010	72	0.6913	0.6879	110	0.7292	0.7280
	HVL		73	0 6897	0.6890	114	0.7327	0.7328
32	0.5319	0.5378	74	0.6877	0.6899	115	0.7307	0.7381
33	0.5443	0 5430	75	0.6859	0.6908	117	0.7420	0.7438
34	0.5551	0.5482	76	0.6856	0.6915	118	0.7400	0.7500
35	0.5592	0.5534	77	0.6885	0.6921	110	0.7000	0.7007
00	0.0002	0.0004		0.0000	0.0321	190	0.7037	0.7040
						140	0.1143	0.7718

TABLE VII: Error Matrix for $S_2(CH_3)_2^a$

	k,	k,	C–S	S–S	C-H	Φ_{SS}	∠SSC	∠ SCH
k,	135	-72	-24	15	4	-61	-16	33
k,		213	31	-22	-6	-27	14	-48
C–S			15	10	4	66	-9	-9
S–S				16	11	90	-7	17
C-H					42	76	8	-38
Φ_{SS}						646	34	72
∠ŠŠC							32	-9
∠SCH								98

 ${}^{a}k_{1}$, k_{2} , dimensionless (× 10⁻⁴); distances, × 10⁻⁴ Å; angles, × 10⁻⁴ radians.

As expected, a mixture of 25% T and 75% G gave an acceptable I_b . Unfortunately this is not a unique combination. Any T-X mixtures where X is an isomer with $\Phi_2 \leq 120^\circ$ led to acceptable I_b curves, when a large amount (50~60%) of the trans fraction was incorporated. An example of a T-C mixture (60-40%) is illustrated in Figure 5. This can be understood by noting that the magnitude and the phase of the I_b fluctuations for the 100% trans I_b curve has a comparable magnitude and is out-of-phase with the cther 100% models, except for those of G and G'. Thus the I_b analysis led to a qualitative conclusion only. Lengthy trial-anderror calculations are needed to determine the limits of error, and quantitatively the ratios of the acceptable mixtures.

The following least-squares analyses of the small q region of the qM(q) curve $[q = 11 \rightarrow 40 \text{ Å}^{-1}]$ were then carried out based on the assumptions: (i) the trans conformer is present (possibly 15-85%); (ii) any T-X pair can be accepted to represent the electron diffraction data provided the ratio of the mixture is appropriately chosen. Then the optimum amount of the trans fraction and the index of resolution were determined by a least-squares analysis, for a sequence of Φ_2 values; the remaining structural parameters were fixed at the values listed in Table IV, with the l_{ij} and δ_{ii} given in Tables III. The best combinations are plotted in Figure 6, where the open circles show the converged leastsquares proportions and the bars given the corresponding standard deviations. It appears that each "best fit" was equally acceptable within the estimated errors of the molecular intensity curve. Keeping in mind that for each pair G,G' and S,S' the diffraction patterns are essentially indistinguishable, then on the premise that the mixture at about 250 K (the estimated temperature of the sample²² at the

TABLE VIII: Error Matrix for S₂(CH₃)(C₂H₅)^a

	k.	k,	C-C	C–S	S–S	С-Н	Φ _{CS}	Φςς	∠CCS	∠ SSC
	220	-100	-23	-40	23	42	-132	144	-156	-17
k ₂		252	55	48	-19	-12	177	105	11	-31
C-C C-S			67	21 24	16 14	25 19	134	83	-54 16	-18 -19
S-S					19	22	115	86	-21	-16
С-н Фсs						60	1326	-882	-367	-192
Φ _{SS}								1204	226	120
∠CCS ∠SSC									292	85 58
	• •		0-41 1.4		-4	10-4	4:			

 a_{k_1} and k_2 , dimensionless (× 10⁻⁴); distances, × 10⁻⁴ A; angles, × 10⁻⁴ radians.



Figure 5. The calculated backgrounds (on the basis of eq 1) utilizing the "leveled" intensity shown at the top of the figure, for the several conformers and combinations thereof as designated in the right column.

point of diffraction) consists of trans plus one more type, Figure 6 states the following. (a) The minimum fraction of trans is about 36%. (b) Were the fraction of trans restricted to the range 36-45%, the other conformers must be gauche. Thus, the diffraction data are compatible with the revised Raman spectral analysis⁷ which suggests [G] > [T] > [G'].

TABLE IX: Rotational Constants of S₂(CH₁)₂ in MHz

	MW(obsd) ^a	This study ^b	EDc
A	8163.64	8276 ± 140	8393 ± 57
B	2816.42	2812 ± 50	2815 ± 17
С	2570.37	2517 ± 7	2562 ± 12

^a Rotational constants, A_0 , B_0 , and C_0 for the ground state, ref 16. ^b Calculated from the r_{α} structure of the present ED study. ^c Calculated from the previous ED study (ref 4).



Figure 6. "Best values" for the percent trans present in binary mixtures of T with various conformers, based on the sequence of assumed values for Φ_{SS-CC} , derived from the least-squares fitting of the qM(q) function over the region $q = 0 \rightarrow 40$.

(c) Were more than half of the sample comprised of trans, an undetermined number of combinations could be found to fit the data. Furthermore, in view of the low barrier indicated for rotation about the S_8-C_5 bond,⁷ it is doubtful that diffraction patterns of samples at much lower temperatures would provide a sharper demarkation of compositions.

Discussion and Conclusion

Structural Parameters. The C-S, S-S, and C-H distances, the CSS bond angle and the rotational angle about the S-S bond in EtS₂Me are equal to the corresponding parameters in MeS₂Me within their estimated standard errors; see Table IV. It is interesting to compare the detailed structures of MeS₂Me with the reported rotational constants for this molecule;¹⁷ Table IX. For a rigorous comparison one should use rotational constants based on the r_z structure (microwave) and the r_a^0 structure (electron diffraction), after introducing minor vibrational corrections.²³ The A_{α} , B_{α} , and C_{α} based on the present electron diffraction analysis are consistent with the A_0 , B_0 , and C_0 within their experimental errors, in contrast to the previous electron diffraction results which lead to a considerably larger A than A_0 ; the large uncertainties in A were mainly due to the experimental error in $\Phi(S-S)$.

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Low Frequency Raman Spectra of Dimethyl, Methyl Ethyl, and Diethyl Disulfides, and Rotational Isomerism about Their Carbon–Sulfur Bonds¹

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In conjunction with a gas-phase electron diffraction investigation of the structures of dimethyl and methyl ethyl disulfides (accompanying paper), the Raman spectra of dimethyl, methyl ethyl, and diethyl disulfides have been studied from 80 to 800 cm^{-1} . The variations in the positions and intensities of the fundamentals in the spectra of methyl ethyl and diethyl disulfides as a function of temperature from ~ 77 to 320 K have been found to be consistent with the presence of three rotational isomers differing in their conformations about their C-S bonds. This disagrees with the results of an earlier study of these same molecules which were interpreted in terms of the existence of only two rotamers. Bands due to the high energy rotamer, whose S-S stretching frequency lies at 524 cm⁻¹, nearly disappear when the temperature is reduced to ~ 77 K. However, significant amounts of the other two rotamers, both of which have S-S stretching frequencies of 508 cm⁻¹, persist down to \sim 77 K, indicating that they are of nearly equal energy. The results of the electron diffraction study on methyl ethyl disulfide indicate the existence of a substantial fraction of molecules with a trans conformation about their C-S bonds. In addition, Raman data on dithioglycolic acid, which is known from x-ray studies to have a trans conformation about its C-S bonds, indicate that its S-S stretching frequency is about 508 cm⁻¹. These two results imply that the rotamer responsible for the S-S stretching mode at 524 cm⁻¹ in the alkyl disulfides studied here is not the trans rotamer, as has been assumed by other workers.

I. Introduction

The Raman spectra of several alkyl disulfides have been studied recently, and a correlation between their S-S stretching frequencies, $\nu(S-S)$, and the conformations about their C-S bonds has been proposed.^{3,4} However, the potential function for rotation about the C-S bonds in these molecules is not yet known accurately. As a result, the number and conformations of the rotamers due to internal rotation about the C-S bonds of these disulfides have thus far been assumed.^{3,4} In the accompanying

paper,⁵ Yokozeki and Bauer have carried out a gas-phase electron diffraction study of the structures of dimethyl and methyl ethyl disulfides. In order to interpret the electron diffraction data for methyl ethyl disulfide, which exists as a mixture of at least two conformations, it is necessary to know the number and relative energies of the rotamers present. Hence, in conjunction with the electron diffraction investigation, we have studied the temperature dependence of the low-frequency Raman spectra of methyl ethyl and diethyl disulfides to determine the number and relative

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energies of the rotamers present. Our results differ from those of a similar study reported earlier by other workers.⁴

II. Experimental Section

Materials. Dimethyl and diethyl disulfides were obtained from Eastman Chemical Co. Each was fractionally distilled twice under reduced pressure to remove impurities. Methyl ethyl disulfide was synthesized according to the procedures of Milligan and Swan⁶ from sodium ethyl thiosulfate (Bunte salt) and methyl mercaptan; this synthesis is described in Appendix I (see miniprint material).

Raman Measurements. The Raman spectra were obtained using a SPEX 1401 spectrometer with excitation from the 514.5-nm line of a Coherent Radiation Model 52G-A argon ion laser. A narrow-band interference filter was used to remove plasma lines from the laser. The power at the sample was about 300 mW. The light scattered at 90° to the laser beam was focused through a polarization scrambler onto the entrance slit of the spectrometer. All measurements were made with an instrumental resolution of 1 cm^{-1} , except where stated otherwise. The spectrometer stepping motor and the photon counting system were interfaced to a Model 70 Interdata computer, and data were collected in digital form. The number of photons counted at each setting of the spectrometer was stored in the computer and later transferred to paper tape. The data on these tapes were subsequently transferred to a PDP-9 computer and the spectra plotted on a Houston Instruments Complot plotter. The plotting software contained options for scaling the heights and widths of the spectra as well as for smoothing out statistical fluctuations in the data. The positions of the bands were calibrated with the emission lines of the argon ion laser; for sharp bands, the reported values are accurate to ± 1 cm⁻¹. In a typical run, the spectrometer was stepped in 1 cm⁻¹ increments, and data were collected at each wavelength for between 1 and 5 min. In this manner, exceedingly high-quality spectra with between 10^5 and 10^6 counts per step were obtained. No background fluorescence was encountered. The instrument was occasionally operated in a catting (computerization of average transients) mode and yielded spectra identical with those taken with a single, long-time sweep.

The measurements at liquid nitrogen temperatures were made on unannealed solids sealed in capillary tubes in thermal contact with a copper block (which was maintained at \sim 77 K) in an evacuated cryostat that was kindly made available by Professor D. B. Fitchen. Unfortunately, with the available equipment, the samples could not be annealed to make them crystalline. The temperature variation of a methyl ethyl disulfide sample between about 200 K and room temperature was achieved by blowing cold nitrogen over a sample in a sealed capillary tube. The temperature was determined by a thermocouple which was also sealed into the capillary tube in direct contact with the sample, and was controlled to ±3 K.

III. Results

The Raman spectra of dimethyl, methyl ethyl, and diethyl disulfides at room temperature between 150 and 800 cm^{-1} are shown in Figures 1A and 1B. The 80–150- cm^{-1} region of dimethyl disulfide, in which there is a single broad band at about 116 cm^{-1} , is also shown at the top right of Figure 1A. A similar band, although less well resolved, appears at almost the same frequency in the spectra of methyl ethyl and diethyl disulfides. The 730–800- cm^{-1} regions ٩.



Figure 1. Raman spectra of neat dimethyl, methyl ethyl, and diethyl disulfides at 296 K between 100 and 800 cm⁻¹. The intensity scale between 730 and 800 cm⁻¹ is increased by a factor of 5. The 80–150-cm⁻¹ region in dimethyl disulfide is shown at the top of A as an insert. All spectra are at 1-cm⁻¹ resolution.

of methyl ethyl and diethyl disulfides are shown on an expanded intensity scale $(\times 5)$ in this figure.

The temperature dependence of the low-frequency Raman spectrum of methyl ethyl disulfide between \sim 77 and 320 K is shown in Figure 2. Certain very distinct changes are apparent in these spectra as the temperature is lowered. These changes result from mainly two effects. First, at lower temperatures, all of the bands sharpen up considerably, allowing the resolution of peaks that were superimposed at room temperature. In addition, since it is anticipated that there are bands in these spectra that are attributable to individual rotational isomers, those due to the higher energy rotamers should decrease in intensity as the temperature is lowered while those due to lower energy rotamers should increase in intensity. The solid, whose spectrum was recorded at ~77 K, may consist of a mixture of rotamers, since it was unannealed and noncrystalline.

The broad and fairly intense band between 150 and 220 cm^{-1} in Figure 2 appears to be the superposition of three bands with frequencies of about 179, 197, and 202 cm^{-1} . The band at 197 $\rm cm^{-1}$ decreases in intensity as the temperature is lowered while those at 179 and 202 cm^{-1} do not seem to change very much. The presence of three bands in this region is more evident from spectra in which the polarization of the scattered light was analyzed with a polaroid filter. The band at 197 cm^{-1} is more highly polarized than those at 179 and 202 cm⁻¹ and is, therefore, more pronounced when the analyzer is parallel. The intense band at 241 cm^{-1} changes its shape as the temperature is lowered. It has a shoulder at about 245 cm⁻¹ at 320 K which gradually disappears as the temperature is lowered, indicating the presence of two bands of nearly equal frequencies in this region. The position of this band in spectra taken with an analyzer in the parallel and perpendicular positions moves from 240 to 243 $\rm cm^{-1}$, respectively, indicating that this band is, in fact, due to the near superposition of two bands with somewhat different depolarization ratios and frequencies.

The band in Figure 2 which appears as a shoulder at about 274 cm⁻¹ in the room temperature spectrum is resolved at \sim 77 K. In fact, at this low temperature, this band is sharp enough to allow the detection of a shoulder on it,


Figure 2. Variation of the low frequency Faman spectrum of methyl ethyl disulfide with temperature. All measurements were made at 1-cm⁻¹ resolution.

between 280 and 285 cm⁻¹. Due to the narrowing of the bands at lower temperatures, a weak band at about 310 cm⁻¹ becomes visible. The band at 327 cm⁻¹ decreases in intensity (relative to that at 363 cm⁻¹), but does not change its shape or position with decreasing temperature. The band at 363 cm⁻¹ (at 320 K) increases in intensity and sharpens up as the temperature is lowered. At \sim 77 K, there appears to be a band at 361 cm^{-1} with a shoulder at about 365 cm^{-1} .

The temperature dependence of the 450-700-cm⁻¹ region of methyl ethyl disulfide was also studied, but the spectra are not shown. The bands at 524 and 669 cm^{-1} decrease in size as the temperature is lowered. These two bands, and the one at 327 cm^{-1} , have been attributed⁴ to a high energy rotamer coexisting with a more stable one (which is responsible for the bands at 363, 508, and 642 cm^{-1}). These rotamers reportedly differ with respect to the conformations about their C-S bonds. By using the ratio of the peak intensities of the pairs of bands at 327 and 363, 508 and 524, and 642 and 669 cm^{-1} as equilibrium constants at temperatures between 200 and 320 K, and applying the van't Hoff relation, the enthalpy differences between the rotamers responsible for each pair of bands were calculated to be 780 \pm 200, 300 \pm 100, and 380 \pm 160 cal/ mol, respectively.

The Raman spectra of diethyl disulfide between 150 and 400 cm⁻¹ at room temperature and at \sim 77 K are shown in Figure 3. The room temperature spectrum exhibits an intense band at 178 cm^{-1} with a shoulder at about 200 cm^{-1} ; these two peaks are resolved at \sim 77 K. The 197-cm⁻¹ band of methyl ethyl disulfide is not observed in Figure 3. Also the intense bands at 241 and 274 cm^{-1} in the spectrum of methyl ethyl disulfide are absent in the spectrum of diethyl disulfide. However, weak bands are now visible at about 258 and 280 cm⁻¹. This 280 cm⁻¹ band may be the same as



the one that was responsible for the shoulder on the 274 cm^{-1} band at liquid nitrogen temperature in methyl ethyl disulfide. The 258-cm⁻¹ band might have been present in methyl ethyl disulfide also, but obscured by the intense bands near 241 cm^{-1} .

There are two bands, at 311 and 327 cm^{-1} , in Figure 3 which decrease in intensity at lower temperatures. The 363-cm⁻¹ band, which showed evidence of splitting in methyl ethyl disulfide only at liquid nitrogen temperature, is already split in diethyl disulfide at room temperature and clearly resolved into two bands at 354 and 364 cm⁻¹ at ~77 K. The spectra for the 450-700-cm⁻¹ region were also recorded at low temperatures and show a decrease in the intensities of the 669- and 524-cm⁻¹ bands, as in methyl ethyl disulfide. With the exception of bands at 197, 241, 274, and 693 cm⁻¹, which are missing from the spectrum of diethyl disulfide, the latter shows peaks at the same frequencies as methyl ethyl disulfide. The observed frequencies of all three disulfides studied are summarized in Table I.

IV. Discussion

Band Assignments. The Raman spectrum of dimethyl disulfide has been discussed in detail elsewhere.⁷ In order to help establish group frequencies which will be useful for making band assignments in the low frequency spectra of methyl ethyl and diethyl disulfides, the assignments of the skeletal modes in dimethyl disulfide will be reviewed briefly. This molecule has 24 fundamentals that can be grouped into 16 internal methyl modes, which are observed above 700 cm^{-1} , and 8 skeletal modes (including methyl torsions), which lie below 700 cm⁻¹. The band at about 116 cm⁻¹ is the S-S torsion, τ (S-S). The two methyl torsions, τ (CH₃-S), are too weak to be seen directly, but have been

 $\Delta \nu (cm^{-1})$ Figure 3. Variation of the low frequency Raman spectrum of diethyl disulfide with temperature. All measurements were made at 1-cm

300

200



296°K

400

78

TABLE I: Observed Frequencies and Vibrational Assignments of Dimethyl, Methyl Ethyl, and Diethyl Disulfides⁴

Dimethyl disulfide		Methyl ethyl disulfide		Diethyl disulfide			
Frequency, cm ⁻	Possible ^b assignment(s)	Frequency, cm ⁻¹	Possible ^b assignment(s)	Frequency, cm ⁻¹	Possible ^b assignment(s)		
116	$\tau(S-S)$	~116	$\tau(S-S)$	~116	$\tau(s-s)$		
239	$\gamma(CH,SS)$	179		178			
273	$\gamma(CH, SS)$	197 }	$\gamma(-CH_2SS)$	}	$\gamma(-CH_2SS)$		
508	$\nu(S-S)$	202		202			
693	$\nu(C-S)$	241					
		~245 (sh)	$\gamma(CH_3SS)$	258	$\tau(CH_3-C)$		
		274					
		~280	$\tau(CH_3-C)$ or $\gamma(CCS)$	2 80	$\tau(CH_3-C)$ or $\gamma(CCS)$		
		310	τ (CH ₃ -C), γ (CCS), or (202 + 116)	311	τ (CH ₃ -C), γ (CCS), or (202 + 116)		
		327	$\gamma(CCS)$	327	$\gamma(CCS)$		
		361)	Fermi resonance	354)	Fermi resonance		
		\$	$(2 \times 179) + \gamma(CCS)$	}	$(2 \times 178) + \gamma(CCS)$		
		365 (sh)	or both $\gamma(CCS)$	364	or both $\gamma(CCS)$		
		508	$\nu(S-S)$	508	$\nu(S-S)$		
		5 2 4	v(S-S)	524	$\nu(S-S)$		
		~ 530	$\nu(S-S)$?	~530	$\nu(S-S)$?		
		~618	$\nu(C-S)$?	~ 618	$\nu(C-S)$?		
		642	$\nu(-CH_2S)$	642	$\nu(-CH_2-S)$		
		669	$\nu(-CH_2 - S)$	669	$\nu(-CH_2-S)$		
		693	$\nu(CH_3-S)$				
		759	$\gamma_r(-CH_2-)$	759	$\gamma_{\rm r}(-{\rm CH_2}-)$		
				778	$\gamma_r(-CH_2-)$		

^a sh, shoulder; τ , torsion; ν , stretch; γ , deformation; γ_r , rock. ^b These modes are almost certainly due to coupled motions. The designations given are motions comprising a large percentage of the change in potential energy associated with the vibration in question.

shown,⁷ from their combination bands, to lie at about 134 cm⁻¹. The bands at 239 and 273 cm⁻¹ are the symmetric and antisymmetric CSS deformations, γ (CH₃SS), respectively. The 508-cm⁻¹ band is due to the ν (S-S) mode and the band at 693 cm⁻¹ to both the symmetric and antisymmetric C-S stretching modes, ν (CH₃-S), which are nearly degenerate since they do not interact mechanically.

Methyl ethyl disulfide has 33 fundamentals per rotamer that can be grouped into 16 internal methyl and 6 internal methylene modes, which are observed above 700 cm^{-1} , and 11 skeletal modes, all but one of which (the C-C stretch) should lie below 700 cm⁻¹. The two C-S torsions, τ (-CH₂-S) and τ (CH₃-), and τ (S-S) should lie below 150 cm⁻¹, as in dimethyl disulfide. This leaves seven fundamentals per rotamer that would be expected to lie in the 150-700-cm⁻¹ region. Of these seven, however, the methyl torsion, $\tau(CH_3-C)$, is expected to be weak. Three of the seven fundamentals for methyl ethyl disulfide lie in the 450-700-cm⁻¹ region shown in Figure 1B. These are easily assigned because of their similarity to corresponding modes in the spectrum of dimethyl disulfide. The 508- and 524 cm^{-1} bands are due to ν (S-S) modes, the bands at 642 and 669 cm⁻¹ are due to ν (-CH₂-S) modes (because of the presence of at least two rotamers), and the band at 693 cm^{-1} is due to the $\nu(CH_3-S)$ mode. There are weak bands in the spectra of methyl ethyl and diethyl disulfides (Figure 1B) at about 530 and 618 cm^{-1} . These are in the region of the $\nu(S-S)$ and $\nu(CH_2-S)$ modes, respectively, and may be due to a rotamer present in very small proportions. The possibility that these bands are difference bands between higher frequency modes cannot be ruled out. The band at 759 cm^{-i} is a methylene rocking mode, $\gamma_r(CH_2)$, and is not one of the fundamentals under discussion.

The remaining four fundamentals lie between 150 and 400 cm⁻¹ (see Figure 2), and are harder to identify unambiguously. The γ (CH₃SS) modes for these rotamers would

be expected to lie near the 240–270-cm⁻¹ region, as they do in dimethyl disulfide. The γ (-CH₂SS) modes, then, should lie somewhat lower. For this reason, the three bands at 179, 197, and 202 cm⁻¹ are thought to be due to γ (-CH₂SS) modes and the bands at 241, 245, and 274 cm⁻¹ due to γ (CH₃SS) modes.

It is of interest to consider the possibility that some of these bands in the $\gamma(-CH_2SS)$ and $\gamma(CH_3SS)$ regions might be due to binary combinations (summations or differences) of fundamentals from other regions of the spectrum. It should be pointed out first, however, that these bands are not weak; if they were, they would not be observable, even as shoulders, on these fairly intense deformation modes which involve motions of the highly polarizable sulfur atoms. Since summation bands are weak compared to fundamentals, and difference bands are even weaker,8 it is unlikely that any bands in this region are due to combinations, with the possible exception of those at 197 and 245 cm⁻¹ which do not persist at low temperatures. The possibility that either of these two bands (197 and 245 $\rm cm^{-1}$) are due to summations can be ruled out, however, since only the weak torsional modes, which are barely observable directly, lie at lower frequencies. The possibility that either of these bands are due to differences can be checked easily, since the Raman shift of a difference band must be exactly equal (within experimental error) to the difference of the two fundamental frequencies.⁸ From consideration of all pairs of fundamentals (and requiring at least one in each pair to be fairly intense) from 247 to 3000 cm^{-1} , no bands are found that meet this criterion;⁹ hence, these are not difference bands either.

The remaining bands at ~280, 310, 327, 361, and 365 cm⁻¹ (Figure 2) are still to be accounted for. The γ (CCS) mode would be expected to be near the corresponding bands in ethyl mercaptan¹⁵ and 2-thiabutane,¹⁶ which have been observed at 332 and 352 cm⁻¹, respectively. The 327,

361, and 365 bands are in this region and, hence, may be due to γ (CCS) modes. The splitting of the 361-cm⁻¹ band may be due to Fermi resonance between a γ (CCS) mode and the overtone of the γ (-CH₂SS) mode at 179 cm⁻¹. In diethyl disulfide (Figure 3), this splitting (attributed to Fermi resonance) is even more pronounced, which is consistent with the greatly increased intensity of the 178-cm⁻¹ band for this substance. Furthermore, such an explanation accounts for the disagreement between the enthalpy values calculated by using the pair of bands at 327 and 363 cm⁻¹ and the values calculated from the other pairs of bands, since an involvement in Fermi resonance would cause the intensity of the 363-cm⁻¹ band(s) to vary abnormally.

The band at 311 cm⁻¹ could be a combination band of the $\gamma(-CH_2SS)$ band at 202 cm⁻¹ with the 116-cm⁻¹ band due to the $\tau(S-S)$. Since this band is stronger in diethyl than in methyl ethyl disulfide, in spite of the fact that the 202-cm⁻¹ band is not, this band may actually be a fundamental. If it is a fundamental, it is probably a $\tau(CH_3-C)$ band, which was expected to be weak. Such a mode would be expected to be more intense in diethyl disulfide due to the presence of two $\tau(CH_3-C)$ modes per molecule. The broad band which lies at about 258 cm⁻¹ in diethyl disulfide, and which could also be present, but obscured, in methyl ethyl disulfide; is also probably a $\tau(CH_3-C)$ mode. Finally, the 286-cm⁻¹ band (which is visible in diethyl disulfide, and might be present in methyl ethyl disulfide) could be either a $\gamma(CCS)$ or $\tau(CH_3-C)$ mode.

All of the bands in the Raman spectra of diethyl disulfide shown in Figure 3 have their counterpart in Figure 2, with the possible exception of the band at 258 cm^{-1} . This remarkable similarity in the frequencies of the bands associated with the ethyl halves of the molecules [i.e., all the bands not in either the ν (CH₃-S) or γ (CH₃SS) regions], indicates that vibrational coupling between opposite sides of the molecule in these two compounds is either weak or very similar in both methyl ethyl and diethyl disulfides. The data shown in Figures 1-3 and summarized in Table I suggest that the conformation about the C-S bond on a given side of the molecule determines, in large part, the frequencies of the vibrational modes localized on that side of the molecule. This means that, e.g., a trans conformation about a C-S bond in either methyl ethyl or diethyl disulfide will result in, e.g., γ (-CH₂SS) modes at nearly the

same frequencies. For this reason, the band assignments listed in Table I for diethyl disulfide, which closely parallel those of methyl ethyl disulfide, are not discussed in detail here. The major differences between the spectra of these two molecules, other than the γ (CH₃SS) and ν (CH₃-S) bands, lie in the dissimilar intensities of their bands. This probably reflects both different rotamer populations and the different numbers of these various modes per molecule. The increased intensity of the 178-cm⁻¹ band in diethyl disulfide is of interest. This intense band probably obscures a weak band at 197 cm⁻¹, which is expected, since the other bands at 327, 524, and 669 cm⁻¹, which are also associated with the rotamer responsible for this 197-cm⁻¹ band, are observed.

Rotational Isomerism. Returning now to methyl ethyl disulfide, it is of interest to interpret its vibrational spectrum in terms of the number of rotamers present. Between 150 and 400 cm⁻¹, one should observe, at most, four fundamentals per rotamer. In fact, one observes three γ (-CH₂SS) modes, three γ (CH₃SS) modes, at least two and maybe more γ (CCS) modes, and at least one and maybe more τ (CH₃-C) modes, for a total of at least nine fundamentals. In addition, two ν (S-S) and two ν (-CH₂-S) modes are apparent from the data of Figure 1B. This evidence is consistent with the coexistence of at least three rotational isomers. The rotamer of highest energy has bands at 197, 245, 327, 524, and 669 cm⁻¹ which decrease in intensity quite markedly with decreasing temperature. These bands all have almost disappeared at liquid nitrogen temperature. Even near 77 K, however, sizeable bands remain at 179 and 202 cm⁻¹ in the γ (-CH₂-SS) region and at 241 and 274 cm^{-1} in the τ (CH₃SS) region. This is consistent with the presence of sizeable portions of two rotamers, at 77 K, of nearly equal energy, which have different frequencies for their skeletal deformations, but the same v(S-S) and ν (-CH₂-S) frequencies. Some interesting observed intensity effects are discussed in Appendix II (see miniprint material).

If our main interest were the unambiguous assignments of the remaining bands to individual rotamers, it would have been necessary to anneal the samples. However, since such experiments on annealed samples would provide no further information about our primary objective, viz., the number and the conformations of the rotamers present, no

Appendix I Synthesis of Hethyl Ethyl Disulfide

Sodium ethyl thiosulfate (Bunte salt):16,17 A solution of 19.4 ml of ethyl bromide in 25 ml of absolute ethanol was added slowly, with constant stirring, to 50 gm of Na28203-5H20 (0.2 mole) in 100 ml of degassed water at 35°-40°. Aliquots were titrated with N/100 iodine and starch indicator to assay for S_2O_3 ; after 18 hours, more than 90% of the S_2O_3 had reacted. The reaction mixture was concentrated in vacuo and the syrupy residue evaporated several times with absolute ethanol. The residue was extracted with 70 ml of warm ethanol and the inso' uble MaBr and Ma₂S₂O₃ removed by filtration. Upon cooling the extract in ice. 26.1 g of product was obtained. Recrystallization from 1.65 ? of hot 10% ethanol gave 22.4 g (68% yield) of colorless, odorless plates. The product slowly decomposes up storage at room temperature. mp: sinters above 50°, dec. above 115". A solution acidified with HNO3 gave no precipitate with AgNO3 (absence of bromides). A sample titrated with N/100 indine show ed less then 0.2% thiosulfate. (Bunte salts do not react with iodine at room temperature. 18)

Nethyl ethyl disulfide: Over a period of 30 minutes, 6.1 ml of CH₅SH (0.11 mole, previously dried with GaCl₂ and condensed, b.p. 6.4[°]) were added in small portions to a solution of 21 gm of sodium ethyl thiosulface (0.11 mol) in 200 ml of degassed 0.5 <u>M</u> phosphate buffer (PH 8.3) under nitrogem, and agitated with a vibromizer at 0°. After 20 minutes, the biphasic rea:-

tion mixture was extracted with three 50 ml portions of ether which were then combined and washed with 25 ml water and 25 ml of saturated NaCl solution and dried over CaCl2, all at 0°. The extract was concentrated in vacuo at -10° to a weight of 11 gm. Gas chromatographic (GC) analysis indicated the presence of 5.2 gms of methyl ethyl disulfide (44% yield) plus 0.2 gms of symmetrical disulfides. The concentrate was then fractionally distilled on a 25" teflon spinning band column. Under a reduced pressure of about 90 torr, 7 fractions (0.5-0.6 ml) were collected at a reflux ratio of 1:30. Fractions of equal purity were combined after GC analysis which indicated a purity of greater than 98.4 mole percent. The GC analysis was carried out on a Varian Aerograph 202 with conductivity detection on a 6 foot stainless steel column with 20% SE-30 on Chromosorh P The oven, injector and detector temperatures were 110°, 150° and 150°, respectively, and the He flow rate was 80 ml/min. The elution volumes (corrected for dead volume) were 93, 137 and 238 ml, for dimethyl, methyl ethyl and diethyl disulfides respectively. When the injector temperature was raised to 175" for methyl ethyl disulfide, larger portions of the symmetrical disulfides appeared on the chromatograms, indicating thermallyinduced disproportionation. Analysis Calc. C. 33.29, H. 7.45, S. 59.26. Found: C. 33.24; H. 7.40, S. 59.39. ng²⁰ -1.5140. [Beilstein, Vol. 1, 4th Ed. np = 1.5146. d²⁰ -1.0224, bp = 135*.1

Appendix II Intensity Effects

It is interesting to note that the relative intensities of the pairs of bands at 179 and 202 cm⁻¹ and at 241 and 274 cm⁻¹ for methyl disulfide (Fig. 2) are not

equal. This implies that the band intensities of similar vibrational modes from different rotamers can be quite different This type of intensity effect is also evident in the spectrum of methyl ethyl disulfide at 296°K (Figure 18). The ratios of the integrated peak areas of the bands at 508 and 524 cm⁻¹ and at 642 and 669 cm⁻¹ are 6.2 and 3.2, respectively. If the "intensity per mole" were the same for all rotamers, these values should have been the same. One obvious implication of these observations is that the ratios of the peas areas of v(S-5) modes cannot be relied upon to reflect rotamer populations accurately. Recently, Brunner et al¹⁹ have reported that, upon selective reduction of one of the three disulfide bonds in basic pencreatic trypsin inhibitor, the intensity of the v(S-S) band is reduced by only 15%. This observation supports our conclusion that there are intensity effects in disulfides that complicate the correlation of rotamer populations with integrated band areas

effort was made to obtain spectra of annealed samples. In fact, crystallization of these disulfices might even complicate matters further since Sugeta, Go, and Miyazawa⁴ have found that the annealing of methyl ethyl disulfide resulted in band splittings not present in the spectra of the neat liquid. We have encountered similar splittings in crystals of other disulfides which complicate the interpretation of their solid-state spectra; these splittings disappear on going to the liquid phase.¹²

It is of interest to consider the results of an electron diffraction study⁵ of methyl ethyl disulfide and other Raman¹² and x-ray diffraction¹³ data on related molecules, together with the data contained herein, in order to establish possible conformations for the rotamers responsible for the S-S stretching bands at 508 and 524 cm⁻¹. From the electron diffraction data, it has been concluded that there exists a substantial fraction of molecules with trans conformations about their C-S bonds. The conformations and proportions of other rotational isomers could not be specified uniquely. From work recently completed in this laboratory,¹² designed to correlate the ν (S-S) frequencies of substituted alkyl disulfides with the conformations about their C-S bonds (determined from x-ray diffraction studies), the frequencies of CCSSCC moieties with CS-SC dihedral angles near $\pm 90^{\circ}$ and with SS-CC dihedral angles in the trans and in both nonequivalent gauche regions have been obtained. Especially relevant to the present work is the finding that dithioglycolic acid, (HOOC-CH₂-S)₂, the only disulfide known thus far from x-ray studies¹³ to have trans conformations about its C-S bonds, exhibits its ν (S-S) at 508 cm⁻¹ in the solid state. The spectrum in 1 N HCl shows broad peaks at the same frequencies as in the solid, except that a shoulder appears on the main $\nu(S-S)$ peak near 520 cm⁻¹. Furthermore, from similar data,¹² it seems that the 524-cm⁻¹ band of methyl ethyl disulfide is also not due to rotamers with either of the two nonequivalent gauche conformations about their C-S bonds since compounds with these conformations also have values of ν (S-S) close to 508 cm⁻¹.¹² This evidence strongly suggests that the 524-cm⁻¹ band is not due to either of the trans or nonequivalent gauche conformations considered earlier,⁴ and further supports the contention above that there exist two rotamers with different conformations about their C-S bonds which have the same (or very nearly the same) value of ν (S–S). It is conceivable that the rotamer responsible for the 524-cm⁻¹ band may have a low value of the SS-CC dihedral angle; its existence was indicated in recent CNDO/2 calculations.14,15

Comparison with Previous Work. The results presented here reaffirm the conclusion of Sugeta et al.^{3,4} that rotational isomers about the C-S bonds of methyl ethyl and diethyl disulfides exist. Our data, however, are consistent with the presence of sizeable amounts of three rotamers at room temperature, rather than just the two that had been considered earlier.^{3,4} A major reason for the differences in the conclusions of these two studies lies in the different number of bands reported in the 150-700-cm⁻¹ region of methyl ethyl disulfide. While Sugeta et al.⁴ report only 10, we have evidence for the existence of at least 18. One possible reason for the differences in the frequencies of some of the bands that have been reported at liquid nitrogen temperature is the fact that Sugeta et al.⁴ obtained infrared, rather than Raman data at this temperature. The reported disappearance⁴ of the bands in the annealed samples of methyl ethyl disulfide at 327, 524, and 669 cm⁻¹ is consistent with the decrease in the intensity of these same bands with decreasing temperature found here. However, Sugeta et al.⁴ also reported a band at 248 cm⁻¹ in this molecule that disappeared when this sample was crystallized. We observe a 241-cm⁻¹ band which is very intense and which shows no reduction in intensity as the temperature is lowered. A possible explanation for this apparent discrepancy is that the 241-cm⁻¹ band observed here is not observable in the infrared, and that the 248-cm⁻¹ band that Sugeta et al. reported as vanishing at 77 K is actually the same band that we observe at 245 cm^{-1} and which also vanishes at low temperatures.

The values of the enthalpy differences found here between the rotamers responsible for the pairs of bands at 508 and 524, and 642 and 669 cm^{-1} are not in good agreement with the values reported by Sugeta et al.⁴ Our values obtained from these two pairs of bands average to $340 \pm$ 100 cal/mol, while those of Sugeta et al. (which also include values obtained from the pair of bands at 327 and 363 cm⁻¹) average to 900 \pm 200 cal/mol. Because of the possibility of involvement of the 363-cm⁻¹ band in Fermi resonance, the value of the enthalpy difference calculated from the pair of bands at 327 and 363 cm^{-1} cannot be assumed to be reliable. In any event, the disagreement between our values is larger than can be accounted for by experimental error. It should be pointed out that, since we believe that each of the bands at 508 and 642 cm^{-1} is due to two different rotamers, the calculated enthalpies cannot be considered to represent the energy differences between any two rotamers. Indeed, a multiple equilibrium between the three of them exists.

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Miniprint Material Available: full-size photocopies of Appendices I and II (3 pages). Ordering information is given on any current masthead page.

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The Crystal and Molecular Structure of the "Metallic Reflector" 1,5-Bis(dimethylamino)pentamethinium Perchlorate

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The crystal and molecular structure of the "metallic reflector" 1,5-bis(dimethylamino)pentamethinium perchlorate has been determined. The crystals are monoclinic, space group Cc, with four polymethinium chains and four perchlorate ions per unit cell. Cell dimensions are a = 12.27(3) Å, b = 9.44(2) Å, c = 12.42(3) Å, $\beta = 114.80(1)^\circ$. The structure was determined by Patterson and heavy atom methods, and refined to a residual of 8.5% for reflections with $I > 2\sigma(I)$, although the accuracy of the structure determination is adversely affected by disordering of the perchlorate ions. The long axes of the dye molecules, i.e., the directions of the transition dipoles, are parallel in pairs, but the angle between the respective pairs is only 1.0° so that all dipoles in the crystal are essentially parallel. The long axis of each dye molecule is close to parallel to the (010) crystal face and makes an angle of 34.8° with the c axis, in good agreement with the spectroscopic predictions of Anex and Simpson.

Introduction

Crystals of the polymethine dye 1,5-bis(dimethylamino)pentamethinium perchlorate (subsequently called BDP) are of interest because of their unusual optical properties.^{2,3} For incident linearly polarized light of a frequency near an intense transition of the isolated molecule, the crystals exhibit almost metallic reflection when aligned in certain orientations, while in other orientations the crystals are essentially transparent.

Metallic reflection also occurs from suitable crystal faces of several other organic molecules with π -electron systems, although interest has concentrated on anthracene and the polymethine dyes. Theoretical explanation of the apparent metallic reflection by these molecules is based on a presumed second singlet transition in the case of anthracene and on the first singlet transition for the polymethine dyes.⁴⁻⁶ The structure of anthracene is well known⁷ and we have previously described the structure of the three-carbon dye 1,3-bis(dimethylamino)trimethinium perchlorate (BDTP).⁸ In this report we describe the crystal structure of the five-carbon analogue BDP, which provides the most striking example of metallike reflection described to date.

The structure determination of BDP was intended to provide accurate coordinates for further analysis of the spectral properties of the polymethine dyes. Also there is interest in predicting the molecular orientation from the spectroscopic measurements and knowledge of the crystal structure would permit testing of the different predictive methods.^{2,9}

The schematic formula of BDP and the numbering used in this study are shown in Figure 1.

Experimental Section

Large crystals of BDP were grown by Mr. Chris Babcock by slow evaporation of an ethanol solution. The crystals are transparent, pale-yellow laths, elongated parallel to the ccell edge, with the forms $\{010\}$ and $\{110\}$ most prominent. Preliminary analysis of Weissenberg and precession photographs indicated that the lattice symmetry was monoclinic, and calculations based on the unit cell dimensions and crystal density implied that four dye molecules and four perchlorates were located in each unit cell (Table I).

The systematic absences h + k = 2n + 1 for (hkl) reflections, h odd and l odd for (h0l) reflections, and k odd for (0k0) reflections indicated that the space group could be either Cc or C2/c.

Three-dimensional data were collected with a card controlled Enraf-Nonius three circle diffractometer, using a crystal cut to the dimensions $0.4 \times 0.5 \times 0.4$ mm. The longest dimension was aligned parallel to the ϕ axis. The calculated absorption coefficient was relatively small (Table I), and no correction was made for absorption.

Filtered Mo K α radiation (λ 0.7107 Å) was used, data being collected to sin $\theta/\lambda = 0.66$ Å⁻¹, i.e., equivalent to the observable limit for Cu K α radiation. Total counting time per reflection was about 50 s. A θ -2 θ scan mode was utilized to measure 1497 reflections of which 923 had intensity $I > 2\sigma(I)$.

Structure Determination

The molecular symmetry permitted either space group Cc or C2/c, and knowledge of the probable molecular orientation as determined optically² did not provide sufficient information to allow a conclusive choice between the two alternatives. In attempting to resolve the space group ambiguity it was decided to use the Patterson function, rather than statistical methods which might be biased by the highly symmetrical nature of the molecule itself. The identification of the chlorine-chlorine vectors alone would not resolve the space group ambiguity since in space group C2/c the perchlorate ions would have to lie on special positions, but the identification of the chlorine-light atom vectors would, at least in theory, allow differentiation between C2/c and Cc. This subsequently proved to be the case; inspection of the Patterson function suggested that the space group was in fact Cc and provided starting coordinates for four atoms, including chlorine.

A Fourier synthesis, phased on these atoms in the usual way, revealed the remainder of the dye molecule and four



Figure 1. Schematic formula and atomic numbering for BDP.

TABLE I: Crystallographic Data

	This work ^a	Ref 13
Unit cell dimensions	a = 12.27(3) Å	12.15 Å
	$b = 9.44(2) \lambda$	9.43 A
	c = 12.42(3) A	12.55 Å
	$\beta = 114.80(1)$ A	115.50°
	$V_c = 1306 \text{ A}^3$	1298 A ³
Space group	Cc	Cc
Four molecules per unit cell		
Density (calcd)	1.284 g cm^{-3}	1.292 g cm^{-3}
Density (obsd)	$1.297(5) \text{ g cm}^{-3}$	1.30 g cm^{-3}
cient (Mo K_{α})	3 .0 cm ⁻¹	

^a The lattice constants were determined by centering 25 reflections and were refined by least-squares methods. The standard deviation of the last place of each value is given in parentheses, as will be done throughout this communication.

perchlorate oxygens. After block diagonal least-squares refinement with isotropic temperature factors converged near a residual of 24%, a difference Fourier synthesis indicated four additional peaks near the chlorine atom which were assumed to correspond to alternate positions for the oxygen atoms. This apparent disorder of the perchlorate ions was incorporated into the model structure by including eight oxygen atoms with fractional occupancy. Further isotropic refinement proceeded to R = 17% and introduction of anisotropic thermal parameters further reduced Rto 9%. Using the low-angle data (sin $\theta/\lambda = 0.32 \text{ Å}^{-1}$), a difference Fourier map revealed peaks near all the anticipated hydrogen positions. The hydrogen atoms were positioned at stereochemically reasonable locations and included in several cycles of refinement with isotropic thermal factors. At convergence, the final R value for the reflections with I> $2\sigma(I)$ was 8.4%. The final parameters are given in Tables II and III, and the observed and calculated structure factors are listed in Table IV.¹⁰ Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.11

Discussion

A primary motivation for this structure determination arose from a desire to correlate the molecular orientation with the optical properties of the crystal. The direction of the dipole transition moment of the dye is parallel to the line between the nitrogen atoms N(1) and N(2) in the polymethinium chain. Spectroscopic analysis² suggests that the transition moments of all the molecules in the crystal are parallel to the *ac* face and inclined to the elongation axis (i.e., *c*) by approximately 33°. The x-ray results show that the long axes of the four molecules in the unit cell, defined as the respective lines joining N(1) and N(2), are parallel in pairs, but that the angle between pairs of lines is only 1.0°. The mean angle between the long axes of the molecules and the *c* axis is 34.8° (Figure 2). Furthermore,



Figure 2. Schematic comparison of alignment of the chromophores as determined spectroscopically and from the structure determination. The figure also shows the morphology of a typical crystal with the Miller indices of the most common faces indicated.

the transition dipoles are perpendicular within experimental error to the *b* axis, i.e., parallel to the predominant crystal face, in good agreement with the spectroscopic predictions. In addition, the x-ray study shows that the plane of the polymethinium chain is tilted so that its normal makes an angle with the *b* axis of 89.3°. If an orthogonal system of axes is defined with axes parallel to a^* , *b*, and c, then the direction cosines of the "average dipole", relative to these axes, are (0.5707, 0, 0.8211).

The nonhydrogen bond lengths and angles are listed in Table V with the standard deviations taken from the final refinement but multiplied by a factor of 2 to allow for underestimation. The hydrogen to nonhydrogen distances range from 0.8 to 1.2 Å and have an average value of 0.99 Å.

The nonhydrogen bond lengths and angles for the BDP molecule are illustrated in Figure 3. The bond lengths of the chemically equivalent segments of the molecule are subject to rather large variations which are attributed in part to the disorder of the perchlorate ion. Oxygen atoms 1, 3, 5, and 6 correspond approximately to one orientation of a tetrahedral perchlorate ion, and oxygens 2, 4, 7, and 8 to an alternative orientation. This is clearly not an adequate model, as indicated by the variation in the chlorine-oxygen bond lengths and angles (Table V), and the inequality of the occupancies of the oxygen atoms (Table II). A number of alternative models for the perchlorate ion were tested but were found to be even less satisfactory. The crystallographic analysis is complicated by the fact that the chlorine is at a pseudocenter of symmetry and a number of the presumed oxygen sites are approximately related by a pseudomirror plane normal to b. Presumably the perchlorate ions assume a number of different orientations throughout the crystal, and cannot be adequately represented by a two-state model. Since the principal motivation for the structure determination was to determine the orientations of the chromophores, and this had been achieved, we did not attempt to define the nature of the disorder of the perchlorate ions more precisely. As a consequence of the disorder, the geometry of the perchlorate ion cannot be determined with precision. The chlorine-oxygen bond lengths and angles quoted in Table V clearly have larger errors than suggested by the quoted standard deviations, which were obtained from the least-squares refinement. These bond lengths and angles are included in order to show the relation between the oxygen sites, and should not be taken as a valid statement of the perchlorate geometry.

In order to improve the accuracy of the bond lengths within the chromophore, similar bonds were averaged. These bond lengths are comparable with the values found in 1,3-bis(dimethylamino)trimethinium perchlorate, BDTP,⁸ (Table VI) and it is interesting to note that in both cases the average bond length between the internal carbon

TABLE II: Nonhydrogen Fractional Coordinates × 10^{4a}

	x	у	z	<i>B</i> ₁₁	B22	B , ,	B ₂₃	B ₁₃	B ₁₂	N
$\overline{C(1)}$	2587(22)	8745(24)	-1544(20)	154(22)	165(28)	114(18)	-035(36)	106(32)	-006(40)	1.0
C(2)	2813(24)	11087(24)	-1013(26)	153(24)	127(22)	164(26)	060(42)	110(40)	-003(40)	1.0
$\tilde{C}(3)$	3769(16)	9206(22)	0520(14)	106(14)	169(24)	088(14)	064(30)	091(24)	022(30)	1.0
C(4)	4334(18)	9959(20)	1508(16)	112(16)	126(20)	100(16)	-029(26)	093(24)	-057(28)	1.0
C(5)	4974(26)	9376(16)	2532(26)	093(10)	138(16)	088(10)	003(44)	068(16)	009(46)	1.0
C(6)	5595(14)	10015(18)	3653(18)	094(12)	141(20)	072(10)	-045(26)	089(17)	-081(26)	1.0
C(7)	6152(12)	9210(14)	4691(12)	084(10)	097(14)	074(11)	-002(20)	093(16)	-002(20)	1.0
C(8)	7323(21)	8555(23)	6732(18)	139(20)	154(24)	091(14)	051(30)	060(25)	094(35)	1.0
C(9)	7035(21)	11143(25)	5990(20)	149(21)	181(27)	116(18)	-023(35)	122(31)	068(42)	1.0
C1	0(0)	10027(10)	0(0)	097(20)	191(7)	137(5)	-078(8)	065(6)	-012(7)	1.0
$\tilde{N}(1)$	3076(15)	9612(19)	-0654(15)	123(16)	185(23)	106(15)	012(30)	111(25)	-005(31)	1.0
N(2)	6799(12)	9682(15)	5698(11)	084(10)	126(15)	066(9)	-007(18)	043(14)	-005(21)	1.0
O(1)	11277(40)	10122(51)	10639(35)	188(50)	396(101)	188(50)	023(89) -	-022(71)	-156(85)	0.77(13)
0(2)	8795(34)	10253(55)	9669(59)	124(39)	412(115)	371(98)	253(140)	244(94)	138(85)	0.67(14)
O(3)	9500(45)	8904(49)	9417(50)	180(63)	132(58)	205(70)	-158(54)	208(104)	-093(92)	0.32(6)
O(4)	10658(72)	11215(65)	10141(59)	209(55)	132(90)	135(75)	-058(115)	135(34)	-258(160)	0.26(7)
0(5)	9805(42)	11270(38)	9069(32)	263(62)	163(53)	126(38)	101(63)	049(69)	132(84)	0.62(8)
O(6)	9865(50)	10924(52)	10964(52)	285(83)	232(76)	277(85)	-208(118)	269(140)	076(106)	0.57(11)
O(7)	10154(48)	9111(64)	9163(58)	209(68)	295(108)	277 (92)	127(144)	047(114)	047(114)	0.50(11)
Ō(8)	9978(71)	8997(74)	10815(80)	501(154)	543(164)	742(416)	179(278)	548(268)	231(221)	0.99(24)

^a The thermal parameters, $B_{ij} \times 10^4$ (Å²), are the coefficients in the expression exp $[-B_{ij}h_ih_j]$, N is the fractional occupancy.

В

4.8(66)

5.0(50)

5.6(70)

7.3(76)

5.8(74)

2.0(52)

3.3(22)

15.0(130)

3.0(36) 1.5(30)

2.1(22)

12.8(112)

9.3(74)

5.1(90)

12.2(114) 11.1(110)

7.8(104)

TABLE III: Fractional	Hydrogen	Coordinates (>	< 10³)	and
Thermal Parameters (A	²)			

У

859(32)

765(26)

895(34)

1144(32)

1153(32)

1165(24)

822(22)

1078(52)

1102(18)

832(16)

822(14)

847(44)

893(36)

766(34)

1114(38)

1198(42)

1132(42)

z

-177(26)

-134(22)

-226(26)

-167(28)

-166(28)

-061(20)

069(18)

153(38)

240(26)

370(16)

467(12)

721(40)

685(38)

628(30)

621(32)

513(40)

668(36)

TABLE	VI:	Comparison of	Averaged	Equivalent	Bond
Lengths				-	

	BDP	BDTP ^a
Nitrogen-methyl carbon	1.44(10) Å	1.450(5) A
Conjugated nitrogen-carbon	1.33(8)	1.308(6)
Carbon-carbon	1.36(4)	1.381(14)
Chlorine—oxygen	1.4 3 (8)	1.429(32)

^a Reference 8.

TABLE	VII:	Deviations	from	the	Best-Fit	Plane
-------	------	------------	------	-----	----------	-------

C(1) 0.04(3) Å H(3)	0.1(2) A
C(2) -0.08(3) H(4)	-0.1(2)
N(1) 0.00(2) H(5)	0.0(4)
C(3) = 0.02(2) = H(6)	0.0(3)
C(4) = -0.02(2) H(7)	0.1(2)
C(5) 0.06(3)	
C(6) -0.00(2)	
C(7) 0.01(2)	
C(8) = -0.08(3)	
C(9) 0.10(3)	

ΤA	۱BL	E	V	:	Bond	Lengths	s and	Ang	les
----	-----	---	---	---	------	---------	-------	-----	-----

x

168(26)

284(22)

272(26)

204(26)

302(28)

346(22)

392(18)

420(40)

485(30)

564(16)

626(12)

688(42)

825(38)

713(30)

780(32)

661(40)

664(36)

H(11)

H(12)

H(13)

H(21)

H(22)

H(23)

H(3)

H(4)

H(5)

H(6)

H(7)

H(81)

H(82)

H(83)

H(91)

H(92)

H(93)

C(1) - N(1)	1.30(3) Å	C(1) - N(1) - C(2)	$113(2)^{\circ}$
C(2) - N(1)	1.45(3)	C(1) - N(1) - C(3)	125(2)
N(1) - C(3)	1.41(3)	C(2) - N(1) - C(3)	123(2)
C(3) - C(4)	1.33(3)	N(1) - C(3) - C(4)	132(2)
C(4) - C(5)	1.30(3)	C(3) - C(4) - C(5)	123(2)
C(5) - C(6)	1.41(3)	C(4) - C(5) - C(6)	130(2)
C(6) - C(7)	1.40(2)	C(5) - C(6) - C(7)	122(2)
C(7) - N(2)	1.25(2)	C(6) - C(7) - N(2)	126(2)
N(2) - C(8)	1.58(2)	C(7) - N(2) - C(8)	116(2)
N(2) - C(9)	1.43(3)	C(7) - N(2) - C(9)	125(2)
		C(8) - N(2) - C(9)	119(2)
Cl-O(1)	1.43(5)		
Cl-O(2)	1.37(5)	O(1) - Cl - O(3)	123(3)
Cl-O(3)	1.29(5)	O(1) - Cl - O(5)	98(3)
Cl-O(4)	1.35(7)	O(1) - Cl - O(6)	89(3)
Cl - O(5)	1.59(4)	O(3) - Cl - O(5)	108(3)
Cl-O(6)	1.53(6)	O(3)-Cl-O(6)	134(3)
Cl-O(7)	1.44(6)	O(5) - Cl - O(6)	98(3)
Cl = O(8)	1.45(8)	O(2)- Cl - $O(4)$	117(4)
		O(2) - Cl - O(7)	109(4)
		O(2)- Cl - $O(8)$	89(4)
		O(4) - Cl - O(7)	109(4)
		O(4)-Cl-O(8)	130(5)
		O(7) - Cl - O(8)	100(4)

a These atoms were not included in the determination of the best plane.



Figure 3. Bond lengths and angles for BDP.

atoms is shorter than the value expected¹² for aromatic compounds (1.395 Å).

The equation of the best-fit least-squares plane through the polymethinium chain is

$$0.9853X + 0.0119Y - 0.1710Z = 4.1885$$
 Å

as determined by using the eleven nonhydrogen atoms in the chain. The equation of this plane is given for coordinates measured in angströms relative to an orthogonal coordinate system with the X axis parallel to a and the Zaxis parallel to c*. The perpendicular distances from the least-squares plane to the eleven atoms in the chain, and to the relevant hydrogen atoms, is given in Table VII. The crystal packing is illustrated in Figure 4. Orientation of the adjacent dye molecules is such that there are numerous mutual intermolecular approaches ranging upward from a minimum value of 3.50 Å for C(2)-C(8). Interaction of the perchlorates with the polymethinium chains is expected to be of ionic character and the closest approaches of this kind occur between O(4) and C(9) (2.95 Å) and O(2) and N(2) (3.20 Å). O(4) has the lowest occupancy of the perchlorate oxygens (Table II).

After the structure determination of BDP had been completed we learned that Neely and Anex had independently carried out an x-ray analysis of crystals of the same compound. The results obtained by Neely and Anex13 are to some extent similar to those reported here, but there is one striking difference which is described below.

The cell dimensions reported by Neely and Anex (Table I) are very close to those obtained by us, although the monoclinic angle differs by 0.7° which is almost certainly significant. In the crystal structure as determined by Neely and Anex¹² the location of the polymethinium chains and the perchlorate groups are similar to those found by us, but the two structures differ significantly in that Neely and Anex found both the perchlorate ions and the polymethinium chains to be disordered, whereas we observed disorder in the perchlorates but not in the chromophores. The distinction between the two structures can perhaps best be visualized in Figure 4b. In the crystals studied by us, the molecules which superimpose in Figure 4b are related by a glide operation parallel to c. As one proceeds through the crystal in this direction, alternate chromophores alternate between the conformations indicated by the open and closed circles. In contrast, in the structure described by Neely and Anex, the polymethine chains are randomly distributed between the open circle and closed circle conformations. The x-ray reflections which are most sensitive to the two alternative modes of crystal packing are those with l odd, since in the structure described by Neely and Anex the average electron density corresponding to the polymethinium chains repeats at c/2. In addition the chlorine ions repeat at the same spacing, although the perchlorate oxygens need not do so. Therefore most of the electron density repeats at spacings of half the c cell edge, so that all reflections with l odd have a small calculated structure amplitude. In contrast, for the crystal packing determined by us, the polymethinium chains do not superimpose exactly when translated by c/2, so that some reflections with l odd will be expected to have moderate intensity, as is observed (Table IV).

A detailed comparison of the structure factors measured by Neely and Anex with the diffraction data obtained in this study (Table IV) indicates that for reflections with leven, the two data sets are roughly equivalent, but that for

TABLE VIII: Selected Structure Factors for Two Crystal Forms of BDP

-1	Re	f 13	This work		
hkl	Fo	F _c	Fo	F _c	
131	5.3	6.9	39.7	42.6	
ī 5 1	6.7	* 7.8	34.1	30.7	
$\bar{2} 2 1$	7.4	3.8	60.4	59.6	
$\bar{2}$ 4 1	5.5	6.5	25.4	29.7	
331	5.3	4.5	29.8	25.4	
223	26.4	15.5	43.6	40.3	
513	4.7	6.1	27.8	30.8	
533	6.1	6.9	30.7	34.5	
025	7.2	10.9	31.5	30.6	
115	7.9	7.9	37.7	35.9	



Figure 4. The structure of BDP projected down the three cell edges, illustrating the molecular packing. The four perchlorate oxygens shown are O(1), O(3), O(5), and O(6).

reflections with l odd the Neely-Anex data are systematically weaker, resulting, in some instances, in large differences, as indicated in Table VIII. There are two possible explanations for the discrepancy. Either the crystals used by Neely and Anex and those used by us represent two distinct crystal forms of the same compound, or the crystals are the same and the reflections with l odd were incorrectly measured by Neely and Anex. Since both crystals were grown by similar techniques from the same solvent, the former explanation would be surprising, although it is not difficult to visualize (e.g., see Figure 4b) how molecules throughout the crystal could be rotated by 180° about their

Formation of S20⁻ on Magnesium Oxide

long axes with little if any effect on the crystal stabilization energy.

Since the direction of the transition dipoles is not influenced by the order-disorder phenomenon, the crystal structure determined by Neely and Anex would be expected, at least to a first approximation, to have similar optical properties to the crystal structure described here. Nevertheless it should be noted in future that two crystal forms of BDP may be possible, and that it may be important to distinguish between them in order to understand in detail the optical properties of these crystals.

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Supplementary Material Available: Table IV contains structure factor tables (10 pages). Ordering information is given on any current masthead page.

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Electron Paramagnetic Resonance Evidence for the Formation of S₂O⁻ on Magnesium Oxide

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A paramagnetic ion attributed to S_2O^- was formed when H_2S and SO_2 were allowed to react on MgO at 25 °C. The EPR spectrum of S₂O⁻ is characterized by two sets of ³³S hyperfine lines with $a_{xx}(1) = 48.6$ G and $a_{xx}(2) = 32.6$ G. The other principal values of the hyperfine tensor were less than 1 G. No hyperfine structure was detected when ¹⁷O was introduced via SO₂. The principal g values are $g_{xx} = 2.001$, $g_{yy} = 2.030$, and $g_{zz} = 2.010$. The concentration of the surface species was enhanced by irradiation at 254 or 366 nm. The S_2O^- ion was also formed by irradiation of adsorbed COS or CS_2 . A proposed mechanism for the formation of S_2O^- involves the reaction of elemental sulfur as S_2 with oxide ions of the MgO surface.

Introduction

The formation of S_2O^- was first postulated by Morton,¹ who had previously observed the electron paramagnetic resonance (EPR) spectrum of the ion in irradiated thiosulfate single crystals.² The S₂O⁻ ion was identified by comparing the principal g values with the isoelectronic $SO_2^$ and S_3^- ions; however, no hyperfine data were available for a more definitive assignment.

More recently in an EPR study of sulfur-doped synthetic photochromic sodalites, Hodgson et al.³ observed two sulfur-containing radicals. They attributed one spectrum with g = 2.032, 2.012, and 2.002 to an unspecified sulfur-containing species, and another spectrum with g = 2.006 to a defect on oxygen. The unspecified sulfur-containing species was later identified by McLaughlan and Marshall⁴ as S_2O^- by its EPR spectrum, yet again no hyperfine structure was observed.

Evidence is given in this paper for the formation of $S_{2}O^{-}$ by allowing H_2S and SO_2 to react on a clean MgO surface. The surface concentration of the ion is greatly enhanced by irradiation at 254 or 366 nm. The sulfur-33 hyperfine lines have been used to identify the molecule and to establish its electronic structure. In addition to yielding S_2O^- the reaction between H₂S and SO₂ forming elemental sulfur and H₂O (the Claus reaction) is of interest as a practical means of removing either H₂S or SO₂ from effluent streams.⁵ This study provides additional information on the mechanism of the Claus reaction over basic oxide catalysts.

Experimental Section

The method for the preparation of the magnesium oxide samples used in these experiments has been described elsewhere.⁶ In a typical experiment, about 0.01 g of the MgO pellets was placed in an EPR tube of 20 ml volume and was degassed at 300 °C for 2 h and at 500 °C for 1 h under vacuum. The final pressure in the vacuum system was below 1.0×10^{-4} Torr. The pretreated MgO sample was exposed to 3 Torr of H₂S for 10 min, and 3 Torr of SO₂ was subsequently introduced. The sample wes then irradiated with 254- or 366-nm ultraviolet light for periods up to 48 h. Experiments were also carried out by irradiating MgO in 20 Torr of COS or 6 Torr of CS₂.

The EPR spectra of the resulting paramagnetic species were recorded at room temperature or at -196 °C using both Varian E-6S X-band and Varian V-4502 Q-band spectrometers. The g values in the X-band spectra were determined relative to the Cr³⁺ impurity line which has g =1.9797, whereas DPPH which has g = 2.0036 was used as the standard in the Q-band spectrum. The error in estimating the g values is believed to be ±0.001.

The H₂S, anhydrous SO₂, COS, and CS₂ were obtained from commercial sources. They were purified by the freezepump technique prior to adsorption. Isotopically enriched sulfur was purchased from Oak Ridge National Laboratory and the enriched ¹⁷O₂ was obtained from YEDA R&D Co. Ltd. Sulfur-33 enriched SO₂ was prepared by allowing 3 mg of sulfur containing 25.5 or 59.2% ³³S to react with an excess of pure oxygen at 450 °C for 2 h. Oxygen-17 labeled SO₂ was prepared in a similar manner by using 41.7% enriched ¹⁷O₂. Sulfur-33 enriched H₂S was prepared by allowing 5 mg of sulfur containing 25.5% ³³S to react with an excess of pure hydrogen at 300 °C for 10 h. The unreacted gases were removed by the freeze-pump technique prior to adsorption.

In the infrared experiments a self-supported MgO wafer was placed in a fused quartz holder in an ir cell. About 40 mg of the pretreated powder was pressed into a wafer in a steel die at a pressure of 15 tons/in.² The average "thickness" of the wafer was 4 mg/cm². The sample in the ir cell was degassed under the conditions previously stated. The spectra were recorded using a Beckman IR-9 spectrophotometer which was operated in the transmittance mode.

Results

No paramagnetic species were detected after the adsorption of 3 Torr of H_2S on MgO; however, the color of the sample changed immediately from white to yellow after the introduction of 3 Torr of SO₂. An EPR spectrum was observed at 25 °C for a radical which is characterized by three principal g values of $g_{xx} = 2.001$, $g_{yy} = 2.030$, and $g_{zz} = 2.010$ (Figure 1a). The radical in the Q-band spectrum is characterized by $g_{xx} = 2.002$, $g_{yy} = 2.032$, and $g_{zz} = 2.011$ (Figure 1b). For reasons which will be subsequently discussed this radical is identified as S_2O^- .

Upon irradiation with a 254-nm uv lamp for 24 h, the intensity of the spectrum increased by a factor of 3, but no further increase in intensity was observed with longer irradiation times. The maximum spin concentration of this radical is 1.2×10^{17} spins/g. A weak peak at g = 2.049 was frequently detected. The S₂O⁻ spectrum was not affected by pumping off the gaseous H₂S and SO₂ or by reversing the adsorption sequence of H₂S and SO₂. The reaction of H₂S with a small excess (~5 Torr) of SO₂ on the surface of MgO also resulted in the formation of SO₂⁻ ions. A large



Figure 1. EPR spectrum of S_2O^- formed by allowing H₂S and SO₂ to react on magnesium oxide at room temperature, followed by irradiation at 254 nm: (a) X-band, (b) Q-band.

excess (≥ 10 Torr) of either H₂S or SO₂ decreased the concentration of the S₂O⁻ radical upon irradiation.

Four hyperfine lines with a splitting of 47.6 G, centered on g_{xx} , were observed when SO₂ enriched to 25.5% ³³S was used (Figure 2a). When H₂S enriched to 25.5% ³³S was employed, another set of four hyperfine lines with a splitting of 32.6 G, also centered on g_{xx} , was detected as shown in Figure 2b. Both sets of hyperfine lines of approximately equal intensity were observed as the result of the reaction of H₂S with enriched SO₂ which contained 59.2% ³³S (Figure 3a). The hyperfine structure resulting from the adsorption of SO₂ enriched to 41.7% in ¹⁷O was not observed. No change in the EPR spectrum was detected when D₂S was used instead of H₂S.

The spectrum of S_2O^- was also observed, though less intense, following the irradiation of MgO in the presence of COS or CS₂. A smaller concentration of the ion was formed from H₂S and SO₂ on samples of MgO which were activated at 300 °C, but it was not detected on MgO-Mg(OH)₂ which was degassed at 25 °C.

The S₂O⁻ radical was stable at room temperature under vacuum for weeks and was stable in the ambient atmosphere and in pure oxygen for days. In an atmosphere of oxygen gas the sample showed a broader EPR spectrum which indicates that the radical was indeed on or near the surface. Upon pumping off the oxygen gas the spectrum underwent a slight modification which is attributed to the formation of SO₂⁻ ions.⁷ Irradiation of a sample at 366 nm in an ambient atmosphere also produced S₂O⁻ ions on the surface. Heating the adsorbed S₂O⁻ radical in the presence of oxygen at 400 °C yielded SO₂⁻ ions.

The reaction of H₂S and SO₂ on magnesium oxide also resulted in the formation of S₃⁻. The spectrum of this species at -196 °C is characterized by $g_{\perp} = 2.043$ and $g_{\parallel} =$ 2.004 with $a_{\parallel}(1) = 20.7$ G and $a_{\parallel}(2) = 39.0$ G.⁸ The concentration of S₃⁻ grew with increasing time of irradiation and with heating at 100 °C. After heating the sample to 100 °C in vacuo it was greenish and the EPR spectrum showed the formation of yet another radical with $g_1 = 2.049$, $g_2 =$ 2.026, and $g_3 = 2.001$ (Figure 4a). Occasionally this radical was also present following the reaction at 25 °C. Upon heating to 200-300 °C *in vacuo* the sample was yellowish green, and the EPR spectrum was similar to that observed





Figure 2. EPR spectrum of S_2O^- formed by allowing (a) H_2S to react with 25.5% ³³S-enriched SO₂, (b) 25.5% ³³S-enriched H₂S to react with SO₂ on MgO.



Figure 3. (a) EPR spectrum of S_2O^- formed by allowing H₂S to react with 59.2% ³³S-enriched SO₂ on MgO, (b) simulated X-band spectrum for 50% ³³S enrichment, assuming complete isotopic mixing.

by allowing elemental sulfur to react with a partially hydrated magnesium oxide surface at 375 °C.⁸ The intensity of this spectrum decreased upon heating to 350-400 °C, and the color of the sample changed to light blue. Irradiation of the sample at this point produced SO_3^- which is



Figure 4. EPR spectrum of sulfur radicals formed on MgO at (a) 100 °C, (b) 500 °C.

characterized by a symmetric line with $g = 2.0034.^9$ Upon heating the sample to 500 °C the color became white and a radical with $g_1 = 2.052$, $g_2 = 2.033$, and $g_3 = 2.002$ was observed as depicted in the spectrum of Figure 4b. This spectrum has been attributed to $S_n^{-.10,11}$ Heating at 500-800 °C reduced the intensity of the S_n^{-} ions, and no paramagnetic species were observed upon heating over 800 °C.

In the infrared experiments no bands due to adsorbed H_2S were observed following the addition of 3 Terr of H_2S ; however, a broad weak OH stretching band formed near 3600 cm⁻¹. The addition of 3 Torr of D_2S resulted in the observation of an O-D stretching band at 2600 cm⁻¹. After the introduction of 3 Torr of SO₂ a strong band at 1650 cm⁻¹ which is attributed to the H-OH bending mode of molecular water was observed. A broad band from 930 to 1020 cm⁻¹ was also detected. Irradiation at 254 nm did not alter the band intensities or band positions. Reversing the adsorption sequence of H_2S and SO₂ did not affect the results. The broad band from 930 to 1020 cm⁻¹ remained at the same intensity before and after the MgO was allowed to react with H_2S .

Discussion

From the ³³S (I = 3/2) hyperfine splitting observed in Figure 3 it is evident that two sets of four lines result from two nonequivalent ³³S atoms. Although some isotope mixing occurred during the formation of the paramagnetic ion, the results suggest that the hyperfine splitting of 48.6 G was mainly due to the ³³S which originated from SO₂; whereas, the splitting of 32.6 G was mainly due to the ³³S which originated from H₂S. The mixing was more apparent in the spectrum of the more highly enriched (59.2% ³³S) SO₂.

In view of the fact that two sulfur atoms are present in the paramagnetic ion and $g_{yy} > g_e$ with $g_{xx} \simeq g_{zz} \simeq g_e$, it is tempting to assign the spectrum to the S_2^- ion. The spectrum of the S_2^- ion on MgO has not previously been reported; however, Vannotti and Morton¹² have reported its spectrum in alkali halide crystals, and a number of groups have investigated the isoelectronic O2⁻ ion in various crystals and on surfaces.¹³ It is evident from these studies that for a similar crystal field gradient at the ior the greater spin-orbit coupling of sulfur relative to oxygen results in much larger g tensor anisotropy for O_2^- relative to S_2^- . The O_2^- ion on MgO is characterized by $g_{yy} = 2.078$, $g_{zz} =$ 2.009, and $g_{xx} = 2.002$;¹⁴ hence, one would expect the maximum g value of S_2^- on this surface to be considerably greater than g = 2.030. Furthermore, essentially the same spectrum has been observed for sulfur radicals in sodium thiosulfate crystals, sodalites, and now on the surface of MgO, yet the g tensor for S_2^- is very dependent upon the local environment.

Morton originally based the assignment of the S_2O^- ion on a comparison of trends in principal g values for the ions SO_2^- , S_2O^- , and S_3^- where the effect of the larger spinorbit coupling becomes increasingly greater with more sulfur atoms in the molecule. Since the orbitals available for mixing with the ground state are rather far removed in energy, the effect of the local environment is small, and the spectra are reasonably independent of the particular matrix or surface. This is evident, for example, when one compares the spectra of SO_2^- or S_3^- on surfaces and in irradiated crystals, as shown in Table I.

Using a theoretical value of 970 G^{17} for the isotropic interaction in a pure 3s orbital and 59 G for $2\beta^{18}$ in a pure 3p orbital $(2\beta = 4/5\gamma_e\gamma_s/r_{3p}^3)$, one may calculate that the total spin density on the two sulfur atoms is about 93%; 54% in the 3p orbital of one sulfur and 37% in the 3p orbital of the other. By difference the spin density on the oxygen is estimated to be about 7%, although the absence of any oxygen-17 hyperfing structure suggests that the spin density may be considerably smaller than this.

The spin densities of S_2O^- and the isoelectronic $SO_2^$ and S_3^- ions are compared in Table II. The variations in spin density for SO_2^- , S_2O^- , and S_3^- are in agreement with a simple argument based upon electron repulsion. The unpaired electron which occupies a highly antibonding $2b_1''$ orbital is repelled to the less electronegative sulfur atom by the concentration of electron charge in bonding orbitals near the more electronegative oxygen atom. It is expected, therefore, that the central sulfur atom would increase in spin density as one moves up the series from SO_2^- to S_3^- . By a similar argument one would predict that the replacement of an oxygen atom by sulfur in SO₂⁻ would result in a greater charge density but a smaller spin de sity on the remaining oxygen atom.

The absence of any oxygen hyperfine splitting, however, is somewhat difficult to understand since ¹⁷O has a rather large nuclear magnetic moment and even a spin density of 0.05 would result in a separation of approximately 25 G between terminal hyperfine lines. It seems more reasonable that the oxygen in S_2O^- is derived from the oxide ions of the lattice, rather than from the SO_2 . Further justification for this model comes from the observation that S_2O^- could be formed from CS_2 . We suggest that sulfur molecules (S_2 , S_3, \ldots, S_n) are deposited on the surface of MgO by the reaction of H₂S with SO₂ and by irradiation of adsorbed COS or CS_2 . The subsequent reactions

 $S_2 + O^{2-}(MgO) \longrightarrow S_2O^- + e^-$

and

$$S_3 + e^- \longrightarrow S_3^-$$
 (2)

yield the observed paramagnetic ions. It is likely that S_2^- is also formed, but the EPR spectrum is not observed at -196°C because of a short spin relaxation time. The partial pressures of H₂S and SO₂ over the MgO may affect the distribution of molecular weights of the sulfur species, and thereby alter the concentration of S_2O^- . The role of oxide ions is further substantiated by the absence of S_2O^- on $MgO-Mg(OH)_2$, where the surface is covered with hydroxide ions.

The infrared results of Low and Lee,¹⁹ and Deane et al.²⁰

TABLE I: g Values of the Isoelectronic SO₂⁻, S₂O⁻, and S₃⁻

	g 1	g ₂	g 3	Ref
SO_2^-/MgO (A)	2.0097	2.0052	2.0028	7
(B	2.0078	2.0033	2.0014	7
SO_2^- /zeolites	2.009	2.002	2.002	15
SO ₂ -/KCl	2.0100	-2.0071	2.0025	16
S_2O^-/MgO	2.030	2.010	2.001	This
				work
S ₂ O ⁻ /sodalite	2.029	2.011	2.001	4
S ₂ O [−] /Na ₂ S ₂ O ₃ · 5H ₂ O	2.0287	2.0106	2.0035	2
S_3^-/MgO	2.043	2.043	2.004	8
S_3^- /sodalite	2.046	2.036	2.005	4
S ₃ ⁻ /KCl	2.0499	2.0319	2.0026	16

TABLE II: Spin Density of the Isoelectronic SO₂⁻, S₂O⁻, and S₃⁻ on MgO

	$SO_2^-(A)$	$SO_2^-(B)$	S_2O^-	S_3^-
S _{3p} (total)	0.75	0.71	0.91	1.08
S_{3p} (sulfur 1)	0.75	0.71	0.54	0.53
S_{3p} (sulfur 2)			0.37	0.27
S _{3p} (sulfur 3)				0.27
O_{2p} (oxygen 1)	0.14	0.12	0.07	
O _{2p} (oxygen 2)	0.14	0.12		
Ref	7	7	This work	8

show that on magnesium oxide H₂S dissociates upon adsorption, forming surface hydroxide ions and sulfide ions. A band at 2580 $\rm cm^{-1}$ due to the S-H stretching mode was observed only at higher coverages of H2S. This band was not observed in our experiments at the lower pressure of H_2S . The appearance of a band at 1650 cm⁻¹ after the addition of 3 Torr of SO2 indicates that water and presumably elemental sulfur are formed on the surface. Part of the SO_2 also reacts to form sulfite ions, as indicated by the bands at 930 to 1020 cm⁻¹, which have been previously studied on similar samples. It appears that H₂S does not react directly with the sulfite ions since adsorption of SO_2 first, followed by the addition of H_2S , did not alter the band intensities of the bands from 930 to 1020 cm^{-1} .

Conclusions

(1)

The reaction of H_2S and SO_2 on the surface of MgO produces water, elemental sulfur, and a small amount of a radical described as S_2O^- . Upon irradiation at room temperature the elemental sulfur, probably in the form of S_2 , reacts with lattice oxide ions of MgO forming a greater concentration of S_2O^- .

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Phosphorus-31 Spin–Lattice Relaxation of Esters of Orthophosphoric Acid

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Spin-lattice relaxation times are reported for the ³¹P nuclei in various mono-, di-, and triesters of orthophosphoric acid in 0.1 M solutions. The effects of changing cations, the pH, and the solvent are presented and discussed.

With the present widespread use of Fourier-transform (FT) technology in obtaining nuclear magnetic resonance (NMR) spectra, the capability for measuring nuclear relaxation times has become available to many chemical laboratories. Furthermore, one or two orders of magnitude of greater dilution are now open to NMR investigation by use of the FT technique. As a result, biochemists are beginning to employ ³¹P spin-lattice relaxation times (T_1 values) to probe into the chemical structure of living systems.^{1,2} In order that such investigations be firmly based, it is necessary first to establish the relaxation behavior of the simple chemical structures which are analogues of the naturally occurring biochemicals.

In the phosphate family of compounds, the ³¹P spin-lattice relaxation of inorganic orthophosphoric acid has been reported.³ The work presented herein deals with the spinlattice relaxation of its various esters in dilute solution. In an earlier study⁴ confined to several neat triesters, it was shown that in the neighborhood of room temperature the predominant relaxation mechanism for the ³¹P nucleus is spin rotation for (CH₃O)₂PO, with about equal contributions from this and dipole-dipole interactions for $(C_2H_5O)_3PO$. For $(n-C_4H_9O)_3PO$, the dipole-dipole contribution was shown to become the dominant relaxation mechanism in this temperature range.

Experimental Section

NMR Measurements. A Varian XL-100-15 multinuclear spectrometer was employed with an external heteronuclear lock on ²H. The system includes a TT-100 Fourier-transform unit from Nicolet Technology Corp., Inc., using a data system having 20K of 20-bit word storage. The sample temperature in the probe was maintained at 31 \pm 0.5 °C and measurements of the ³¹P spin-lattice relaxation times were

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accomplished by the inversion-recovery method^{5,6} under conditions where a 90% pulse for the ³¹P nuclei was provided in 63 μ s. The value of τ in the 180°- τ -90° sequences was chosen to bracket the inversion point at which $T_1 = \tau/\ln 2$. The reported T_1 values were all finally computed by hand from a plot of ln $(I_{\infty} - I_{\tau})$ vs. τ , where I is the intensity for the peak. In a previous study,³ we found that the standard error in the measurements carried out by this procedure was in the range of 5-8% of the T_1 value for the range of concentrations and relaxation times reported here.

³¹P chemical shifts are reported relative to the usual⁷ standard⁸ of 85% orthophosphoric acid, with positive chemical shifts being associated with increasing field strengths as is customary. The spectrometer frequency for ³¹P was 40.5 MHz (¹H, 100.0 MHz).

Samples Studied. Adenosine 5'-monophosphoric acid and sodium adenosine cyclic 3'-5'-monophosphate (PL Laboratories) and ribose 5-phosphate (Calbiochem) were found to be chromatographically⁹ and spectroscopically¹⁰ pure and were used without further treatment as were the phosphate triesters. The remaining ionic phosphates were prepared from an equilibrated syrupy mixture of orthophosphoric acid with the desired alcohol at a mole ratio of 1:2 by diluting it 10-fold with water, heating on a steam cone for 20 min, then cooling and titrating to pH 6.0 with BaOH. After centrifugation to remove prccipitated inorganic barium orthophosphate, an equivolume of ethanol was added to precipitate the phosphate monoester, and this material was collected by centrifugation. The supernatant solution was treated with additional ethanol until the ³¹P spectrum showed that all of the residual monoester had precipitated. After collecting the monoesters, the alcohol concentration was then increased to 80%, and the precipitated diester salt collected. By further titration of the supernatant solution with absolute ethanol, the symmetrical diester of pyrophosphate was prepared. Each of the salts were then dried at 24 °C in vacuo. All of these barium ester salts were recrystallized from aqueous ethanol to effect final purification.

The various salts used in the NMR study were prepared from the above barium salts or from commercial esters by previously described⁹ ion-exchange procedures employing Dowex 50 hydrogen-exchange resin. Note that all of the ionic phosphate preparations must first be passed through Dowex 50 to purge them of traces of contaminating metal ions.¹⁰ Without such treatment, the ³¹P spin-lattice relaxation times are not reproduceable on replicate preparations and an electron spin resonance (ESR) signal was noted in some of the frozen NMR samples exhibiting shortened ³¹P NMR relaxation times before the cation-exchange treatment. A related problem has also been found with aged so-lutions of tetramethylammonium hydroxide which may also exhibit an ESR signal that is found to be associated with an abnormally short ³¹P spin-lattice relaxation time of a tetramethylammonium phosphate made from it. Great care was taken in this work to employ tetramethylammonium hydroxide that had been freshly prepared by ion exchange from a recrystallized sample of the chloride.

The deuterated preparations were made from the corresponding aqueous samples by successive vacuum evaporations at 24 °C from very high-quality D_2O (selected vials of Mallinckrodt 99.8% deuterium oxide). To obtain reproduceable T_1 values the HDO content of the samples must be reduced below the 0.5% level; and this can be achieved with the phosphates of this study if reasonable care is exercised in the preparation of the samples and the D_2O used meets the stated specifications.

Samples were purged of dissolved oxygen by bubbling nitrogen through them for 5 min while they were in the NMR tubes. This procedure was found³ to be quite satisfactory, and removal of oxygen by the use of several freeze-pumpthaw cycles did not change the values of the measured relaxation times.

Results

Spin-lattice relaxation times of the ³¹P nucleus are reported in Table I for 0.1 M solutions of the symmetrical esters of orthophosphoric acid. In carbon disulfide, the value of T_1 is seen to increase regularly with molecular weight for the three aliphatic esters; and, even with the inclusion of triphenyl phosphate, the value of T_1 varies roughly in proportion to the molecular weight of the ester molecule. This is very different from the neat-liquid results reported by Dale and Hobbs,⁴ whose data correspond at 31 °C to a T_1 of 13.8 s for the trimethyl ester, 20.8 s for the triethyl ester, and 11.3 s for the tri-*n*-butyl ester. Since the spin-rotation mechanism ought to dominate⁴ for a dilute solution in carbon disulfide, our observed consistent increase in T_1 with increasing molecular weight is not surprising.

By changing the solvent from carbon disulfide to deuterium oxide, the observed spin-lattice relaxation time is seen practically to dcuble. Moreover, the value of T_1 for trimethyl orthophosphate is about equal within the experimental error to that of the triethyl ester. Again, one would expect from the studies by Dale and Hobbs⁴ and from the absence of protons in the solvent that the predominate relaxation mechanism would still be spin-rotation. Thus, it seems that the increase in T_1 when going from carbon disulfide to deuterium oxide solution is attributable to the insertion of the esters into the network structure of the water by hydrogen bonding (i.e., ²H bonds). As shown in Table I, the dipole-dipole relaxation by the protons of reg-

ΤА	BLE I:	³¹ P Spin-	-Lattice F	elaxation	Times at 31	°C of
0.1	M Solu	tions of	Triesters o	of Orthop	hosphoric A	cid

Phosphate	Solvent	<i>T</i> ₁ , s
Trimethyl	CS,	11.2
Triethyl	CS,	18.6
Tri-n-butyl	CS.	24.0
Triphenyl	CS.	25.0
Trimethyl	D.Õ	32.0
Triethyl	DÓ	32.8
Trimethyl	НĴО	21.3
Triethyl	H ₂ O	22.1

ular water causes the value of T_1 of the phosphate ester in H_2O to drop to ca. 21 s as compared to 32 s in D_2O . The similar relaxation times of the trimethyl and the triethyl phosphates, when either in D_2O or H_2O , may be attributable to nearly the same aqueous solvation of these two triester molecules.

In Table II, ³¹P spin-lattice relaxation times are reported for 0.1 M aqueous solutions of the diesters of orthophosphoric acid at a sufficiently high alkalinity (pH 11) so that these compounds are fully dissociated, with the phosphorus essentially all present in (RO)₂PO₂⁻ anions. Since it is not uncommon in the chemistry of phosphate anions for the NMR parameters to vary appreciably upon switching from one cation to another similar one,¹² values are presented in Tables II-IV for H₂O solutions made up with several different singly charged cations. Note that the chemical shift of adenosine cyclic 3',5'-monophosphate is seen to vary appreciably in Table II when going from the tetramethylammonium to either the sodium or potassium ion. Likewise in this table, there is a considerable difference in chemical shift between the potassium salt and the sodium and tetramethylammonium salts of the dimethyl orthophosphate anion. However, the value of T_1 as measured for diethyl orthophosphate in H₂O solution does not change significantly when the relatively noncomplexing tetramethylammonium ion is substituted by either sodium or potassium. Also there is not much change in T_1 when going from the dimethyl through the diethyl to the di-n-butyl orthophosphate, while it should be noted that the adenosine cyclic 3',5'-monophosphate exhibits a much shorter relaxation time.

The ³¹P spin-lattice relaxation times of 0.1 M aqueous solutions of the monoesters of orthophosphoric acid, also at pH 11 where the phosphate anion should be essentially fully dissociated, are reported in Table III. The findings presented in this table roughly parallel those reported for the diesters in Table II. However, the difference in spinlattice relaxation time upon going from tetramethylammonium to either sodium or potassium as the counterion is more pronounced, as might be expected for a doubly charged anion, (RO)PO3²⁻, as compared to a singly charged anion, (RO)₂PO₂⁻. The last two items in Table II represent the symmetrically substituted dialkyl pyrophosphate anions, $(RO)(O_2^-)P-O-P(O_2^-)(OR)$, which are related to the dialkyl orthophosphates in that each PO₄ group bears a single charge and which are also the anhydrides of the monoalkyl orthophosphoric acids. Interestingly, the spin-lattice times for these structures turns out to be very close to the values obtained for the same alkyl groups in the monoesters and diesters of orthophosphoric acid.

In order to complete the comparison of the effect of counterions on these partially esterified orthophosphoric acid molecules, data are presented in Table IV for the spin³¹P Spin–Lattice Relaxation of Esters of Orthophosphoric Acid

TABLE II: ³¹ P Spin-Lattice Relaxation Times and
Chemical Shifts at 31 °C of 0.1 M Aqueous Solutions of
Diesters of Ortho- and Pyrophosphoric Acids at pH 11

Phosphate	Cation	Solvent	T ₁ , s	δ, ^a ppm
Dimethyl	(CH,),N+	H,O	19.4	-1.83
	(CH ₃) ₄ N ⁺	D,0	29 .0	
	K+	H,O	22.7	-1.87
	Na ⁺	H ₂ O	20.0	-1.85
Diethyl	$(CH_3)_4N^+$	H,O	19.7	-0.82
-	(CH ₃) ₄ N ⁺	D_2O	29.3	
	K+	H,O	19.2	0.83
	Na ⁺	H,O	20.0	0.80
Di-n-butyl	(CH ₃) ₄ N ⁺	H,O	17.4	-1.00
-	(CH ₃) ₄ N ⁺	$D_{2}O$	26.5	
	K+	H,O	17.7	-1.05
	Na ⁺	H,O	18.0	-1.03
Adenosine cyclic	(CH ₃) ₄ N ⁺	H,O	7.97	1.39
3',5'-monophosphat	e (CH ₃)₄N ⁺	D,O	12.1	
	K+	H,O	9.93	-0.94
	Na ⁺	H,O	10.14	-1.00
P,P'-dimethyl	(CH ₃)₄N ⁺	H,O	19.9	10.89
pyrophosphate ^b	K+	Н,O	21.1	10.77
	Na ⁺	H,O	19 .8	10.79
P.P'-diethyl	$(CH_1)_{A}N^+$	Н,O	20.3	12.73
pyrophosphate ^b	K ⁺	Н,O	21.1	12.77
	Na ⁺	H ₂ O	19.8	12.70

^a Chemical shift referenced to 85% H₃PO₄. ^b Compounds of the formula: $(RO)(O_2^{-})POP(O_2^{-})(OR)$.

TABLE III: ³¹P Spin–Lattice Relaxation Times and Chemical Shifts at 31 °C of 0.1 M Aqueous Solutions of Monoesters of Orthophosphoric Acid at pH 11

Phosphate	Cation	Solvent	<i>T</i> , s	δ, ppm
Methyl	(CH ₃) ₄ N ⁺	H,O	19.4	-4.75
	$(CH_3)_A N^+$	D,O	29.3	
	K+	н,о	20.5	-3.66
	Na+	н,о	20.2	-3.67
Ethyl	$(CH_1)_A N^+$	н,о	21.7	-3.70
2	$(CH_{3})_{A}N^{+}$	D,O	32.9	
	Ň K+	H,O	20.4	-3.80
	Na ⁺	H,O	20.2	-3.83
n-Butyl	$(CH_3)_A N^+$	н,о	14.0	-3.59
5	$(CH_3)_A N^+$	D,O	20.7	
	K ⁺	н,́О	16.1	-3.85
	Na+	н,о	20.0	-3.86
Ribose 5-phosphate	(CH ₃)₄N ⁺	Н,́О	14.1	-3.83
• •	(CH ₁) ₄ N ⁺	D,O	21.2	
	K ⁺	H,O	13.3	-3.93
	Na ⁺	н,о	13.1	-3.72
Adenosine	$(CH_3)_A N^+$	Н,́О	7.44	-3.82
5'-monophosphate	$(CH_3)_A N^+$	D,O	10.8	
• •	`Ќ́+́	H,O	7.91	-3.88
	Na ⁺	H ₂ O	7.37	-3.88

lattice relaxation times measured for 0.1 M orthophosphoric acid in 2.5 M aqueous solutions of tetramethylammonium, potassium, and sodium hydroxides. At these concentrations even the third very weakly acidic hydrogen of orthophosphoric acid should be essentially fully dissociated. The percentage change in T_1 due to the counterion effect in H₂O solution is particularly pronounced for the inorganic orthophosphate anion as compared to its simple alkyl esters. Furthermore, the measured relaxation times in H₂O solution are considerably smaller than those observed for any of the esters.

In our previous study³ of the spin-lattice relaxation of orthophosphoric acid, the spin-lattice relaxation time was found to vary in an oscillatory manner when the acid was titrated with a strong base or an acid stronger than itself,

TABLE IV: ³¹P Spin-Lattice Relaxation Times and Chemical Shifts at 31 °C of 0.1 M Inorganic Orthophosphoric Acid in 2.5 M Aqueous Base Solutions

Cation	Solvent	T_1 , sec	δ , ppm
(CH ₁), N ⁺	H,O	10.5	-4.19
	D,0	15.5	-4.50
К+	H,O	1 2 .5	-5.34
	D,0	30.0	-5.38
Na ⁺	н,О	8.18	-5.77
	D,O	23.2	-5.73

with the higher T_1 values corresponding to the equivalence points in the titration curve and the minima to the pKvalues. In other words, the presence of equal amounts of the two different ions at a pK value offers an additional pathway for relaxation. A similar study has been carried out for several monoesters of orthophosphoric acid and two diesters of pyrophosphoric acid, with the results being reported in Table V. Of these dibasic esters, only the monoesters of orthophosphoric acid exhibits a weakly dissociable hydrogen. In Table V, spin-lattice relaxation data are reported for the equivalence points on either side of the pK value for this weak hydrogen, along with the relaxation time corresponding to the pK value. In all cases, the spinlattice relaxation time corresponding to the pK value was considerably shorter than those corresponding to the equivalence points. For the pH values corresponding to pK_2 and pK_3 of orthophosphoric acid, we previously found that the spin-lattice relaxation time was related³ to those at the neighboring equivalence points by the following empirical equation:

$$(1/T_1)_{pK} = (1/T_1)_{equiv A} + (1/T_2)_{equiv B}$$
(1)

Equation 1 has been applied to the data of Table IV and the results are reported in the last column of this table, from which it can be seen that this equation very adequately predicts the experimental findings. Indeed, the somewhat poor agreement in the case of the ethyl orthophosphate is almost certainly due to the difficulty of adjusting the pH to exactly the proper values. Using the pH values associated with the pK_2 of pyrophosphoric acid and its neighboring equivalence points, no diminution in T_1 is observed for the symmetrical dialkyl pyrophosphoric acid, since the weakly acidic hydrogens corresponding to pK_3 and pK_4 of inorganic pyrophosphoric acid have been abolished from the molecule by the esterification.

Discussion

It is possible to estimate the percentage of the observed spin-lattice relaxation attributable to dipole-dipole interaction of the ³¹P nucleus with the hydrogen atoms of the solvent water. From the standard equation for dipole-dipole interaction and the fact that the observed $(1/T_1)$ is composed of the sum of the various $(1/T_1)$ contributions, we can set up the following equation:³

$$\frac{(1/T_1)_{\rm H} - (1/T_1)_{\rm x}}{(1/T_1)_{\rm D} - (1/T_1)_{\rm x}} = \frac{3\gamma_{\rm H}^2}{4(2\gamma_{\rm D}^2)} = 15.91$$
(2)

where $(1/T_1)_H$ and $(1/T_1)_D$ refer to the observed ³¹P relaxation in the H₂O solution and in the D₂O solution, respectively, and $(T_1)_x$ represents the spin-lattice self-relaxation time in a hypothetical aqueous solvent which contributes no dipole-dipole relaxation to the phosphorus nucleus. This equation has been applied (see Table VI) to those compounds for which appropriate data are reported in the

Phosphate monoester	рН	$\frac{\mathbf{Exptl}}{T_1, \mathbf{s}}$	$\begin{array}{c} \text{Calcd}^{a} \\ \text{p}K_{a} \ T_{1} \end{array}$
Methyl	11.19	19.42	
-	6.81	8.89	8.73
	4.26	15.87	
Ethyl	10.90	21.74	
2	6.87	11.43	9.51
	4.13	16.90	
n-Butyl	11.08	14.00	
2	6.81	6.04	6.04
	4.30	10.62	
Ribose 5-phosphate	11.00	14.14	
	6.93	6.01	5.83
	3.96	9.92	
Adenosine	11.16	7.44	
5'-monophosphate	6.84	1.60	1.63
0	4.00	2.09	
P.P'-dimethyl	11.21	19.9	
pyrophosphate	6.89	20.7	
FJF	4.07	19.8	
P P'-diethyl	11.16	20.3	
pyrophosphate	6.83	19.8	
FJF -F	4.16	20.1	

TABLE V: pH Variations of the T_1 Values of 0.1 M Aqueous Solutions at 31 $^\circ\mathrm{C}$

^a Calculated from the experimental T_1 values determined at the equivalence points of the mono- and dianionic phosphate species according to the equation: $(1/T_1)_{dianion} + (1/T_1)_{monoanion} = (1/T_1)_{pK_a}$.

TABLE VI: Values of $(T_1)_x$ and the Solvent Dipole–Dipole Relaxation of the Phosphates in 0.1 M Aqueous Solutions at 31 °C

Phosphate	Cation	$(T_1)_{\mathbf{X}}$	% dd re- laxation
$\overline{\mathrm{PO}_{4}^{2^{-}}}$	(CH ₃) ₄ N ⁺	16.0	34
	K+	36.5	66
	Na ⁺	26.4	69
CH ₃ OPO ₃ ²⁻	(CH ₃) ₄ N ⁺	30.3	36
$C_1 H_5 OPO_3^{2-}$	$(CH_3)_4 N^+$	34.1	36
C ₄ H ₆ OPO ₃ ²⁻	$(CH_{3})_{4}N^{+}$	21.4	35
Ribose 5'-OPO ₃ ²⁻	$(CH_{3})_{4}N^{+}$	21.9	36
Adenosine 5'-OPO,2-	$(CH_3)_4N^+$	11.1	33
(assoc)			
(CH ₃ O) ₂ PO ₂ ⁻	(CH₃)₄N+	30.0	35
$(C_2H_5O)_2PO_2^{-1}$	(CH₃)₄N+	30.3	35
$(C_4H_9O)_2PO_2^-$	(CH ₃)₄N+	27.5	37
Adenosine PO_2 (assoc)	$(CH_3)_4N^+$	12.5	36
(CH ₁ O) ₁ PO	None	33.1	64
$(C_2H_5O)_3PO$	None	33.9	65

preceding tables. In H₂O solution, the percentage of the total ³¹P spin relaxation contributed by the dipole-dipole interaction between the hydrogen atoms of the water and the respective phosphorus atoms equals $100[1 - (T_1)_{\rm H}/(T_1)_{\rm x}]$. These values are presented in the last column of Table VI which shows that for all of the tetramethylammonium salts, regardless of the degree of esterification or the choice of esterifying group, about 35% of the observed spin-lattice relaxation in 0.1 M aqueous solution at 31 °C is due to the relaxing effect of the hydrogen atoms of the water. However, this value is practically doubled (to ca. 65% by replacing the tetramethylammonium by sodium or potassium ions in the case of the completely unesterified orthophos-

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phate ion, and this also applies to the un-ionized trialkyl phosphates for which there are of course no counterions.

In view of the fact that the dipcle-dipole relaxation mechanism exhibits an r^{-6} dependence (where r is the distance between the interacting spin-active nuclei), we interpret these findings to mean that the orthophosphate PO₄ group in the presence of sodium and pctassium counterions is associated with closely lying water molecules in about the same way as is the PO₄ group of the neutral orthophosphate triesters; but the tetramethylammonium salts of the orthophosphate ion and its various mono- and diesters are less closely solvated. In other words, the tetramethylammonium cation seems to "protect" its phosphate counterion from the relaxing influence of the protons of the water.

The values of $(T_1)_x$ in Table VI show that the self-relaxation process for the monoesters is about the same as that for the equivalent di- and triesters. Although most of the esters exhibit about the same value of $(T_1)_x$, it is found that the adenosine derivatives show an unusually short self-relaxation time and that the self-relaxation time of the simple orthophosphate ion is also quite short when in the presence of the tetramethylammonium counterion.

Even where the spin-lattice relaxation time at the pKvalues is considerably smaller than that observed at the neighboring equivalence points, it is found that the difference between the effect of one ester group and another ester group is relatively independent of the solution pH. This means that the change, ΔT_1 , upon replacing one ester group with another is quite constant with pH. In the case of both the mono- and diesters, the spin-lattice relaxation times are found not to change much from one ester to another, except when an adenosyl group is substituted for another group. Both cyclic and the linear adenosine monophosphates exhibit unusually short relaxation times, whereas ribose 5-phosphate exhibits a relaxation time close to that of monobutyl phosphate, which has about the same molecular weight. We believe that the anomalous behavior of the adenosyl derivatives may be related to the interaction¹³ of the phosphate moiety with the nucleotide aromatic ring or to the fact that these molecules are extensively associated¹⁴ ("stacked") in aqueous solution. In the case of the polyphosphoryl chlorides,¹⁵ we found that the ³¹P atoms of the higher-molecular weight species exhibited relatively short relaxation times and, by analogy, suggest that the stacking of the adenosyl derivatives may lead to the short T_1 .

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Stereodynamics of Acyclic Alcohols, Ethers, and *N*,*N*-Dimethylurethanes. Potential Barriers to Rotation about Carbon–Carbon and Carbon–Nitrogen Bonds

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Examination of the ¹H DNMR spectra of a series of acyclic alcohols and methyl ethers showed changes consistent with slowing rotation about carbon-carbon single bonds and allowed an assessment of the relative hindering potential to *tert*-butyl rotation of hydroxyl, methoxyl, and various alkyl groups. Both hindered *tert*-butyl and N,N-dimethyl rotation were observed in an acyclic N,N-dimethylurethane and N,N-dimethylthiourethane.

Although the potential barrier to threefold rotation in ethane (2.9 kcal/mol) is well established experimentally,³ a quantitative theoretical assessment of various energy components contributing to the barrier is elusive.⁴ It is apparent that van der Waals repulsions can account for only a fraction of the barrier height in ethane and an orbital-control mechanism has been proposed to account for the hindering potential.⁵ In more complicated systems,⁶ van der Waals repulsions become more important and in many instances, the barriers to rotation about carbon-carbon single bonds are large enough to be accessible to measurement by the dynamic nuclear magnetic resonance (DNMR)⁷ technique.

Although a large number of polyhalogenated ethanes and butanes have been examined by the DNMR method,⁶ there has been little effort to assess the effect of hydroxyl or alkoxyl on the barrier to carbon-carbon single bond rotation.⁸ This report concerns the DNMR measurement of the rate of *tert*-butyl rotation in a series of selectively deuterated acyclic alcohols, methyl ethers, and urethanes. The *tert*-butyl rotor was selected in order to provide a symmetrical threefold potential surface for rotation and eliminate the need to determine more than one potential barrier for a given compound. The *tert*-butyl group has also been useful in establishing stereodynamical trends in trialkylamines,⁹ trialkylphosphines,¹⁰ and trialkylphosphine complexes.^{11,12}

Results

For the purpose of DNMR spectral simplification, a number of specifically deuteriated alcohols (1-5) and

methyl ethers (6-9) were prepared by standard methods (see Experimental Section).

$$\begin{array}{c} CH_{3} R \\ | & | \\ H_{3}C - C - C - C - OR'' \\ | & | \\ CH_{3} R' \\ CD_{3} R' = CD_{2}CD_{3} R'' = D \\ \mathbf{2}, R = CD_{3}; R' = CD_{2}CD_{3}; R'' = D \\ \mathbf{3}, R = R' = CH_{2}CD_{3}; R'' = D \\ \mathbf{4}, R = CD_{3}; R' = CH_{2}C_{0}H_{5}; R'' = D \\ \mathbf{5}, R = CD_{3}; R' = CH_{2}C_{0}H_{5}; R'' = D \\ \mathbf{6}, R = R' = CD_{3}; R' = CH_{3} \\ \mathbf{7}, R = CD_{3}; R' = CD_{2}CD_{3}; R'' = CH_{3} \\ \mathbf{7}, R = CD_{3}; R' = CH_{2}CD_{3}; R'' = CH_{3} \\ \mathbf{8}, R = R' = CH_{2}CD_{3}; R'' = CH_{3} \\ \mathbf{9}, R = CD_{3}; R' = t \cdot C_{4}H_{9}; R'' = CH_{3} \\ \mathbf{10}, R = R' = CH_{3}; R'' = C(O)N(CH_{3})_{2} \\ \mathbf{11}, R = R' = CH_{3}; R'' = C(S)N(CH_{3})_{2} \end{array}$$

Examination of the ¹H DNMR spectrum of 5 (4% v/v in CH₂CHCl) at -37.0 °C (Figure 1) revealed a singlet resonance for the *tert*-butyl protons (δ 1.045) consistent with rapid *tert*-butyl rotation on the DNMR time scale. At temperatures below -37.0 °C, the *tert*-butyl resonance broadens and is separated at -111.9 °C (Figure 1) into three singlet resonances at δ 0.980 (3 H), 1.046 (3 H), and 1.129 (3 H) consistent with slow *tert*-butyl rotation on the DNMR time scale and the symmetry experienced by a static *tert*-butyl (eq 1). Total DNMR line shape analyses at various



Figure 1. Experimental ¹H DNMR spectra (60 MHz) of the tert-butyl group of 5 (4% v/v in CH2CHCI) and theoretical spectra calculated as a function of the rate of tert-butyl rotation (k = first-order rate constant for conversion of one tert-butyl rotamer to one other rotamer).



temperatures (Figure 1) using a substantially modified local version of computer program DNMR313 gave the rate of tert-butyl rotation at various temperatures. The activation parameters derived from a weighted least-squares fit of an Eyring plot and slow exchange tert-butyl chemical shifts are compiled in Table I.

Changes in the ¹H DNMR spectrum of 1 were observed at slightly lower temperatures than for 5 with the slow exchange spectrum of 1 at -124 °C (Figure 2) consistent with the symmetry of 1 and slow tert-butyl rotation. Analogous changes in the ¹H DNMR spectra were observed for 2 and 4. Alcohol 3 did not show a separation of the ¹H tert-butyl resonance in both CH_2CHCl or $CBrF_3$ to about -150 °C due most likely to a small or zero chemical shift difference between the stereochemically nonequivalent methyls of the tert-butyl group. Pertinent data are compiled in Table I. Also compiled in Table I are activation parameters for tertbutyl rotation in 5 in a variety of solvent systems.

Examination of the ¹H DNMR spectra of the methyl ethers 7 (Figure 3; 5% v/v in CH₂CHCl) and 9 (Figure 4; 5%

	∆G‡, kcal/mol (−100 °C)	2.7 8.73 ± 0.10 3.4 8.91 ± 0.10	2.6 8.93 ± 0.10	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.10 9.99 ± 0.10	1.9 9.95 ± 0.10	2.3 9.57 ± 0.10	9.34 ± 0.40	2.8 8.49 ± 0.10	$1.4 9.43 \pm 0.10$	0.0 9.38 ± 0.10
OR"	ΔS‡, gibbs	-1.4 ± 2	0.8 ± 2	1.5 ± 4 -1.3 + 1	-0.6 ± 2	0.6 ± 3	-0.1 ± 2		0.0 ± 2	0.8 ± 3	-0.8 ± 2
t-C4H,(R)(R')C(ΔH ‡, kcal/mol	8.5 ± 0.4 8.7 ± 0.6	9.1 ± 0.4	9.8 ± 0.8 9.6 + 0.2	9.9 ± 0.4	10.1 ± 0.7	9.6 ± 0.4		8.5 ± 0.4	9.6 ± 0.6	9.2 ± 0.4
ters for tert-Butyl Rotation in	'H chemical shifts, ppm from TMS	0.873 (3 H); 0.969 (6 H) 0.843 (3 H); 0.940 (3 H); 0.867 (3 H);	0.961 (6 H); 1.045 (3 H)	0.980 (3 H); 1.046 (3 H); 1.129 (3 H) 0.955 (3 H): 1.043 (3 H):	1.120 (3 H) 0.946 (3 H); 1.036 (3 H);	1.109 (3 H) 0.968 (3 H); 1.054 (3 H);	1.120 (3 H) 0.946 (3 H); 1.021 (3 H);	1.112 (3 H) 0.859 (3 H); 0.889 (6 H)	0.821 (3 H); 0.922 (6 H)	0.913 (3 H); 0.983 (3 H);	1.089 (3 H) 0.863 (3 H); 0.992 (6 H)
nange and Activation Parame	Solvent (v/v% of alcohol or derivative)	CH ₂ CHCl (4%) CH ₂ CHCl (4%)	CH, CHCI (4%) CH, CHCI (4%)	CH ₂ CHCI (4%) 90:10 CH_CHCI-	CH, OH (4%) 75:25 CH, CHCI-	CH ₃ OH (4%) 45:55 CH ₂ CHOI–	$CH_{3}OH (4\%)$ 60:40 $(CH_{3})_{2}O-$	(CH ₃), NCHO (4%) CH, CHCI (5%)	CH, CHCI (5%)	CH ₂ CHCI (5%)	CH, CHCI (5%)
Shifts at Slow Exch	R."	QQ	000	n				CH,	CH,	CH3	C(O)N(CH ₃) ₂
VMR Chemical	R	CD, CD,CD,	CH, CD, CH, C, H,	r-C4H,				cD,	CD,CD,	<i>t</i> -C ₄ H	CH,
ert-Butyl 'H P	R	CD,	CH,CD, CD,	۲D ،				CD,	CD, CH, CH	CD, CD,	CH ₃
TABLE I: t	Compd	2	ω 4 r	ß				9	r- 0	6	10



Figure 2. Experimental ¹H DNMR spectra (60 MHz) of the *tert*-butyl group of 1 (4% v/v in CH₂CHCi) and theoretical spectra calculated as a function of the rate of *tert*-butyl rotation (k = first-order rate constant for conversion of *one tert*-butyl rotamer to *one* other rotamer).

v/v in CH₂CHCl) also revealed changes at low temperature consistent with slowing *tert*-butyl rotation on the DNMR time scale. While it might be reasonable to expect three *tert*-butyl methyl resonances with slow *tert*-butyl rotation in 7, only two peaks are resolved (Figure 3). It is apparent that the effective diamagnetic anisotropies of CD₃ and CD₂CD₃ toward *tert*-butyl are the same in 7. A comparison of Figures 1 and 2 with Figures 3 and 4 also shows generally longer T_2 values (sharper lines) for the ethers as compared to the alcohols. In the case of 6, the small chemical shift difference between the different *tert*-butyl methyl resonances precluded extraction of accurate ΔH^{\ddagger} and ΔS^{\ddagger} values from a complete line shape analysis and only a ΔG^{\ddagger}

The ¹H DNMR spectra of urethane 10 (Figure 5; 5.5 wt % in CH_2Cl_2 above -20 °C and 5 wt % in CH_2CHCl below -20 °C) showed changes consistent with slowing rotation about the carbonyl carbon-nitrogen bond and with slowing tert-butyl rotation. The activation parameters for $N(CH_3)_2$ rotation in 10 ($\Delta H^{\pm} = 15.4 \pm 1.4 \text{ kcal/mol}; \Delta S^{\pm} = 0.3 \pm 5$ gibbs; $\Delta G^{\pm} = 15.3 \pm 0.1$ kcal/mol at 6.3 °C) were determined from a complete ¹H DNMR line shape analysis. NMR and activation parameters for *tert*-butyl rotation in 10 are compiled in Table I. Similar changes in the ¹H DNMR spectra of thiourethane 11 were also observed (Figure 6; 5.5 wt % in CCl₂CCl₂ above 25 °C and 5 wt % in CH₂CHCl below -20 °C). Complete DNMR line shape analyses yielded the activation parameters for N(CH₃)₂ rotation ($\Delta H^{\pm} = 19.6 \pm 0.8 \text{ kcal/mol}; \Delta S^{\pm} = 8 \pm 2 \text{ gibbs};$ $\Delta G^{\pm} = 17.0 \pm 0.1$ kcal/mol at 53.0 °C) and tert-butyl rotation (Table I). The barriers to $N(CH_3)_2$ rotation in 10 and



Figure 3. Experimental ¹H DNMR spectra (60 MHz) of the *tert*-butyl group of 7 (5% v/v in CH₂CHCI) and theoretical spectra calculated as a function of the rate of *tert*-butyl rotation (k = first-order rate constant for conversion of *one tert*-butyl rotamer to *one* other rotamer).

11 seem typical¹⁴ and are higher than those for tert-butyl rotation.

It should also be noted that for those compounds in Table I which show changes in the *tert*-butyl ¹H DNMR spectra at low temperatures, the slow exchange spectrum consists of two or three *singlets*. This is of course consistent with rapid rotation on the DNMR time scale of the *individual* methyls of each *tert*-butyl group.¹⁵

Discussion

A perusal of Table I reveals *some* trends which can be correlated with conformational parameters from other systems. For example, the conformational requirements of various alkyl groups as measured by preference for the equatorial conformer in the monosubstituted cyclohexane $(-\Delta G^{\circ} \text{ or } "A \text{ value"})^{16}$ reveals methyl (A = 1.7 kcal/mol)to be slightly smaller than ethyl $(A = 1.8 \text{ kcal/mol})^{16}$ which is in turn comparable in size to benzyl $(A = 1.8 \text{ kcal/mol})^{17}$ The sequence of barriers to *tert*-butyl rotation in proceeding from compound 1 to 2 to 4 parallels reasonably well the corresponding A values for methyl, ethyl, and benzyl.

However, the A value of tert-butyl (~5 kcal/mol) is very large compared to methyl or ethyl and the relatively small increase in the barrier to tert-butyl rotation in 5 as compared to 1, 2, or 4 (Table I) reveals the potential inadequacy of employing A values to predict quantitative trends in potential barriers to rotation. Unexpectedly low barriers to tert-butyl rotation have also been observed in 2,2,3,4,4pentamethyl-3-chloropentane^{6d} which is an analogue of 5. Two approaches may be taken to rationalize the small barrier increase in 5, one involving ground state geometry and 646



Figure 4. Experimental ¹H DNMR spectra (60 MHz) of the *tert*-butyl group of **9** (5% v/v in CH₂CHCl) and theoretical spectra calculated as a function of the rate of *tert*-butyl rotation (k = first-order rate constant for conversion of *one tert*-butyl rotamer to *one* other rotamer).



Figure 5. ¹H DNMR spectra (60 MHz) of 10 (5.5 wt % in CH_2CI_2 from 23.8 to -17.7 °C and 5 wt % in CH_2CHCI from -85.9 to -116.1 °C).



Figure 6. Experimental ¹H DNMR spectra (60 MHz) of the N(CH₃)₂ group of **11** (5.5 wt % in CCl₂CCl₂) and the *tert*-butyl group (5 wt % in CH₂CHCl) with theoretical spectra calculated as a function of the respective rates of rotation.

the other transition state geometry. Examination of a model of 5 keeping all bond angles at 109.5° and all vicinal substituents perfectly staggered (12; projection down



C-CD₃ bond) shows severe 1,3-dimethyl repulsions analogous to the 1,3-dimethyl repulsions (~4 kcal/mol) in the diaxial chair conformation of cis-1,3-dimethylcyclohexane. In light of recent electron diffraction and molecular mechanics studies of tri-tert-butylmethane¹⁸ and di-tertbutylmethane,¹⁹ it is highly probable that the geometry of minimum potential energy for 5 is not 12 and that significant deviations from perfect staggering, from local T_d symmetry at each carbon, and normal carbon-carbon bond lengths (1.53 Å) occur. In tri-tert-butylmethane,¹⁸ the central carbon-carbon bond length is stretched to 1.611 Å, the central $(t-C_4H_9)C(t-C_4H_9)$ bond angle opens up to 116.2°, and each tert-butyl group is rotated about 10° away from perfect staggering. All of these adjustments in molecular geometry as compared with less hindered systems are consistent with relief of nonbonded repulsions involving the large tert-butyl groups and are analogous to trends observed in hindered N-tert-butyl-N,N-dialkylamines.9 In di-tert-butylmethane,19 the central carbon-carbon bond length is nearly normal at 1.545 Å while the central (t- C_4H_9)C(t-C_4H_9) bond angle opens up to 128°!

In light of these observations, it is virtually certain that the central carbon atom in the most stable geometry of 5 does not possess local T_d symmetry and that the central $(t-C_4H_9)C(t-C_4H_9)$ bond angle will be greater than 109.5° and the *tert*-butyl group will rotate away from perfect staggering, i.e., rotate toward the transition state geometry for *tert*-butyl rotation. Any deviation from T_d symmetry at the central carbon of 5 also precludes achieving any geometry via tert-butyl rotation in which all three methyl groups of tert-butyl are perfectly eclipsed with the three other vicinal atoms on the central carbon of 5 bonded to hydroxyl. Thus, partial rotation of *tert*-butyl in the ground state and less-than-perfect eclipsing in the transition state for tertbutyl rotation would tend presumably to compress the energy difference between ground and transition states and lower the barrier. In addition to these effects of geometry on the barrier to tert-butyl rotation, it is very likely that the potential energy increase associated with one tert-butyl group in 5 rotating against the other may be optimized (i.e., minimized) via a concomitant rotation of both tert-butyl moieties. Other workers^{6d} have suggested such a cog-wheel mechanism in analogues of 5. All of these effects would tend to lower the barrier to tert-butyl rotation below what one would predict by analogy with the A value of tertbutyl.

It is noteworthy that the barrier to *tert*-butyl rotation in 5 in a variety of solvent systems (Table I) having different polarities and capacities to hydrogen bond varies to only a small degree indicating an almost negligible contribution of hydrogen bonding to restricting *tert*-butyl rotation in these relatively hindered systems.

In considering the methyl ethers (6-9; Table I) of interest in this study, a comparison of alcohols 1-5 with ethers 6-9 reveals hydroxyl to be roughly comparable to methoxyl in hindering tert-butyl rotation. However, in proceeding from ether 6 to 7 to 8, there is a clearly defined decrease in the barrier to tert-butyl rotation as steric bulk around the central carbon increases. In ether 9, the barrier then increases reflecting the presence of a much larger tert-butyl group. This inverse dependence of the barrier to tert-butyl rotation in ethers 6-8 on steric bulk is analogous to a similar but more pronounced dependence of the barrier to inversion-rotation about nitrogen in a series of N-tert-butyl-N,N-dialkylamines.⁹ For the ethers 6-8, such a trend is very likely due to yet-to-be-determined adjustments in ground state geometry resulting from the crowding of several bulky groups around the central atom. An important point to be made is that no simple approach can be taken to predict barrier trends in these encumbered systems without knowledge of the intimate details of ground state geometry. It is quite possible that methoxyl exerts a more pronounced buttressing effect than hydroxyl leading to more internal crowding in the ethers than in the alcohols and differences in preferred ground state geometry.

A number of studies have now appeared in which the DNMR method was used to measure the rate of rotation about carbon-carbon single bonds.⁶ In addition, the rate of rotation about the carbonyl carbon-nitrogen bond of several urethanes has been measured using the same technique.¹⁴ In light of these data and the barriers compiled in Table I, it was then possible to predict qualitatively the temperature dependence of the ¹H DNMR spectra of urethanes 10 and 11 (Table I; Figures 5 and 6). Separation of the N(CH₃)₂ resonance of 10 or 11 into two singlets of equal intensity at low temperatures is consistent with slowing the N(CH₃)₂ rotation (eq 2) and a significant degree of π bond-



TABLE II: Free Energies of Activation ($\Delta G \ddagger$) for *tert*-Butyl Rotation in *t*-C₄H₉C(CH₃)₂X

x	ΔG^{\pm} , kcal/mol	Ref
Н	6.9	6e,f
F	8.0	20
Cl	10.4	6d,e
Br	10.7	6d,e
I	11.1	20
OH	8.7	This work
OCH ₃	9.3	This work

ing across the carbon-nitrogen bond.¹⁴ The barriers to $N(CH_3)_2$ rotation in 10 ($\Delta H^{\pm} = 15.4 \pm 1.3 \text{ kcal/mol}; \Delta S^{\pm} = 0.3 \pm 5 \text{ gibbs}; \Delta G^{\pm} = 15.3 \pm 0.1 \text{ kcal/mol}$ at 6.3 °C) and 11 ($\Delta H^{\pm} = 19.6 \pm 0.8 \text{ kcal/mol}; \Delta S^{\pm} = 8 \pm 2 \text{ gibbs}; \Delta G^{\pm} = 17.0 \pm 0.1 \text{ kcal/mol}$ at 53 °C) are typical of such ure-thanes.¹⁴ The barriers to *tert*-butyl rotation in 10 and 11 (Table I) reveal the carbamate moiety to be very similar to methoxyl and hydroxyl in its ability to restrict *tert*-butyl rotation.

Finally, it is interesting to compare the abilities of various functionalities incorporated into the same basic carbon skeleton to hinder tert-butyl rotation (Table II). It is not surprising to note that hydrogen is the least effective substituent in restricting rotation. The ability of halogens to hinder tert-butyl rotation (Table II) seems to be more a function of van der Waals radius and does not parallel A value trends.¹⁶ Indeed the A values of methoxyl (0.55 kcal/ mol)¹⁶ and non-hydrogen-bonded hydroxyl (~0.6 kcal/ mol)¹⁶ are almost identical with chlorine $(0.53 \text{ kcal/mol})^{16}$ and yet hydroxyl and methoxyl are significantly less hindering to tert-butyl rotation than chlorine. These comparisons point up the possible pitfalls of using conformational parameters from cyclic compounds to predict trends in both conformational preferences and barriers to rotation in acyclic systems.

Experimental Section

The 60-MHz ¹H DNMR spectra were obtained using a Varian HR-60A spectrometer equipped with a custombuilt variable temperature probe.²¹ The 100-MHz ¹H DNMR spectra were obtained using a Varian HA-100-15 spectrometer equipped with a Varian variable temperature probe and temperature controller.

The theoretical ¹H DNMR spectra¹³ were calculated using DEC PDP-10 and RCA Spectra 70/46 computers and plotted using a Calcomp plotter.

3,3-Dimethyl-2-butanone-1,1,1-d₃ (13) was prepared by repeated exchanges with refluxing deuterium oxide and a trace of sodium carbonate. Alcohols 1, 2, 4, and 5 were prepared by reaction of CD_3MgI , CD_3CD_2MgI , $C_6H_5CH_2MgBr$, and t- C_4H_9MgBr respectively with 13 and worked up in deuterium oxide. Alcohol 3 was prepared by reaction of 2 M equivalents of CD_3CH_2MgI with the ethyl ester of pivalic acid followed by work-up in deuterium oxide.

Methyl ethers 6-9 were prepared from the corresponding alcohols above by initial conversion to the potassium alkoxide using the potassium hydride procedure of $Brown^{22}$ followed by treatment with methyl iodide.

Urethanes 10 and 11 were prepared by treating potassium alkoxide²² of 1 ($R = R' = CH_3$) with N,N-dimethylcarbamoyl chloride and N,N-dimethylthiocarbamoyl chloride, respectively.

Communications to the Editor

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COMMUNICATIONS TO THE EDITOR

Molecular Covolumes of Sphere and Ellipsoid of Revolution Combinations

Sir: In the analysis of equilibrium sedimentation, light scattering, or osmotic pressure results on polydisperse or interacting macromolecular systems it is required to express nonideality effects in terms of activity coefficients that are functions of solution composition. This implies that even for relatively simple interacting systems several self- and cross-term second virial coefficients must either be evaluated from the experimental results or assigned numerical values on the basis of molecular covolume and charge considerations. The former endeavor is formidable and has not been achieved without simplifying assumptions,^{1,2} whereas the latter requires expressions for covolumes. Of particular interest in the protein field are covolume expressions for interactions between various combinations of spheres and ellipsoids of revolution (prolate or oblate). Recently, Ogston and Winzor³ formulated expressions for sphere and prolate ellipsoid combinations, but left unanswered two basic questions. The first pertains to the corresponding expressions for oblate ellipsoids and the second to the correlation of their formulation with the Isihara⁴ treatment of self-covolumes of ellipsoids of either type.

The basic set of equations considered by Ogston and Winzor³ in relation to their Figure 1 was $\left| \frac{x^2}{a^2} + \frac{y^2}{b^2} \right|$ = 1, $X = x + r \sin \theta$, $Y = y + r \cos \theta$, $dy/dx = \tan \theta$ where a and b refer to the semimajor and semiminor axes, respectively, of the ellipse, which is tangential at the point (x,y)to a circle of radius r and center (X, Y). This same set of equations applies to the sphere-oblate ellipsoid problem, the difference being that in this instance rotation of the ellipse is considered about the y axis. Formulation of the covolume expressions requires consideration of the volume enclosed by the locus of the point (X, Y) which may be formulated in terms of circular transverse sections. In these terms the molecular covolume U is given by

$$U = 2 \int_{x=0}^{x=a} \pi Y^2 \,\mathrm{d}X \qquad \text{(prolate)} \tag{1a}$$

$$U = 2 \int_{y=0}^{y=b} \pi X^2 \,\mathrm{d}Y \qquad \text{(oblate)} \tag{1b}$$

The indicated integrations may be performed directly once the quantities $Y^2 dX$ and $X^2 dY$ are written (with the use of the basic set of equations) as functions of the respective single variables x and y. Indeed, the required integrals (12 in each case) are in standard form when the substitutions are made that $\epsilon^2 = 1 - (b^2/a^2)$ for the prolate case and $(a^2/b^2) - 1 = \epsilon^2/(1 - \epsilon^2)$ for the oblate case, where ϵ is the eccentricity. With collection of terms the results are:

$$U = \frac{4\pi r^3}{3} \div \frac{4\pi a b^2}{3} + 2\pi a b r \left| (1 - \epsilon^2)^{1/2} + \frac{\sin^{-1} \epsilon}{\epsilon} \right| + 2\pi a r^2 \left| 1 + \frac{(1 - \epsilon^2)}{2\epsilon} \ln \frac{(1 + \epsilon)}{(1 - \epsilon)} \right| \qquad \text{(prolate)} \quad (2a)$$

$$U = \frac{4\pi r^3}{3} + \frac{4\pi a^2 b}{3} + \frac{2\pi a b r}{(1-\epsilon^2)^{1/2}} \left| 1 + \frac{(1-\epsilon^2)}{2\epsilon} \ln \frac{(1+\epsilon)}{(1-\epsilon)} \right| + \frac{2\pi b r^2}{(1-\epsilon^2)^{1/2}} \left| (1-\epsilon^2)^{1/2} + \frac{\sin^{-1}\epsilon}{\epsilon} \right| \quad \text{(oblate)} \quad \text{(2b)}$$

At first sight eq 2a appears to differ from the corresponding solution given by Ogston and Winzor³ in their eq 17, where the substitution $\sin \alpha = b/a$ was employed. However, on noting the identities that $\sin^2 \alpha = 1 - \epsilon^2$, $\cos \alpha =$ $\sin \{(\pi/2) - \alpha\} = \epsilon$, and $\{(\pi/2) - \alpha\} = \sin^{-1} \epsilon$, the solutions prove to be identical. It is also noted that when a = b = r'(sphere-sphere covolume), $\epsilon = 0$ and both eq 2a and 2b become $U = 4\pi (r + r')^3/3$ (as required), since power series expansions show that $\sin^{-1} \epsilon/\epsilon = 1$ and $(\frac{1}{2}\epsilon) \ln \left[(1+\epsilon)/(1-\epsilon) \right]$ ϵ)] = 1 when ϵ is zero. In an experimental context eq 2a and 2b may themselves be directly relevant to the calculation of the covolumes of a globular (spherical) protein and an asymmetric macromolecule; but they also form the basis for formulating expressions for other covolumes pertinent to such a system.

Ogston and Winzor³ made this extension by using a symmetry argument in relation to their analog of eq 2a to write an expression for the covolume of two different prolate ellipsoids of revolution (embodied in their eq 18). A similar treatment applied to eq 2b for two different oblate ellipsoids with axial ratios a_1/b_1 and a_2/b_2 gives

$$U_{1,2} = \frac{4\pi a_1^{2} b_1}{3} + \frac{4\pi a_2^{2} b_2}{3} + \frac{\pi C_1 D_2}{4} + \frac{\pi C_2 D_1}{4}$$
(3a)

$$C_{1} = \frac{2a_{1}b_{1}}{(1-\epsilon_{1}^{2})^{1/2}} \left| 1 + \frac{(1-\epsilon_{1}^{2})}{2\epsilon_{1}} \ln \frac{(1+\epsilon_{1})}{(1-\epsilon_{1})} \right|$$
(3b)

$$D_1 = \frac{2b_1}{(1 - \epsilon_1^2)^{1/2}} \left| (1 - \epsilon_1^2)^{1/2} + \frac{\sin^{-1} \epsilon_1}{\epsilon_1} \right|$$
(3c)

with similar expressions in a_2 , b_2 , and ϵ_2 for C_2 and D_2 . The difficulty arises that there is no a priori justification for use of a symmetry argument. However, justification is provided by two observations. First, when $a_2 = b_2 = r$ eq 3 becomes eq 2b, as required. Secondly, the formulations embodied in the present eq 3 and the previous eq 18 may be shown by the following means to be entirely consistent with that given by Isihara.⁴ Combination of eq 2, 22, and 28 of Isihara,⁴ which refer to the self-covolume of either prolate or oblate ellipsoids of revolution, gives, in present terminology

$$U_{1,1} = v \left| 2 + \frac{3}{2} \left[1 + \frac{\sin^{-1} \epsilon}{\epsilon (1 - \epsilon^2)^{1/2}} \right] \times \left[1 + \frac{(1 - \epsilon^2)}{2\epsilon} \ln \frac{(1 + \epsilon)}{(1 - \epsilon)} \right] \right\}$$
(4)

where $v = 4\pi ab^2/3$ (prolate) or $v = 4\pi a^2 b/3$ (oblate). Equation 4 is also obtained by placing $a_1 = a_2$, $b_1 = b_2$, $(C_1D_2 =$ C_2D_1) in eq 3 and by placing $a_1 = a_2$, $b_1 = b_2$, $(A_1B_2 = a_1)$ A_2B_1) in eq 18 of Ogston and Winzor.³ In other words the basic conclusion drawn by Isihara⁴ that the same expression may be used to calculate the self-covolumes of either prolate or oblate ellipsoids of revolution is also reached by (5a)

employing a symmetry argument to rigorously defined expressions for sphere-ellipsoid covolumes.

It is now seen that the two questions posed in the introductory paragraph have been answered. In the first place the basic approaches used by Isihara⁴ and by Ogston and Winzor³ have been correlated. Secondly, expressions are now available for the calculation of covolumes involving spheres and oblate ellipsoids (eq 2b), and two oblate ellipsoids of dissimilar axial ratio (eq 3), which extend the selfcovolume treatment of Isihara⁴ (eq 4). Finally, by again resorting to symmetry arguments it is possible to postulate the covolume of a prolate ellipsoid with axial ratio a_1/b_1 and an oblate ellipsoid with axial ratio a_2/b_2 as

 $U_{1,2} = \frac{4\pi a_1 b_1^2}{3} + \frac{4\pi a_2^2 b_2}{3} + \frac{\pi A_1 D_2}{4} + \frac{\pi C_2 B_1}{4}$

where

$$A_{1} = 2a_{1}b_{1}\left|(1-\epsilon_{1}^{2})^{1/2} + \frac{\sin^{-1}\epsilon_{1}}{\epsilon_{1}}\right|$$
(5b)

$$B_1 = 2a_1 \left| 1 + \frac{(1 - \epsilon_1^2)}{2\epsilon_1} \ln \frac{(1 + \epsilon_1)}{(1 - \epsilon_1)} \right|$$
(5c)

$$C_2 = \frac{2a_2b_2}{(1-\epsilon_2^2)^{1/2}} \left| 1 + \frac{(1-\epsilon_2^2)}{2\epsilon_2} \ln \frac{(1+\epsilon_2)}{(1-\epsilon_2)} \right|$$
(5d)

$$D_2 = \frac{2b_2}{(1 - \epsilon_2^2)^{1/2}} \left| (1 - \epsilon_2^2)^{1/2} + \frac{\sin^{-1} \epsilon_2}{\epsilon_2} \right|$$
(5e)

Equation 5 meets the requirement that it should simplify to eq 2a or 2b when the appropriate ellipsoid is replaced by a sphere.

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The Pfeiffer Effect in Heavy Water. **Evidence for Hydrophobic Bonding**

Sir: The Pfeiffer effect refers to an anomalous change in optical rotation observed when a racemic mixture of a certain complex is added to a solution containing a stable chiral compound called an environment compound. Several possible mechanisms for the Pfeiffer effect have been proposed, viz., configurational activity, differential association, equilibrium shift, hydrogen bonding, hydrophobic bonding, etc. Among them, the concept of configurational activity proposed first by Dwyer et al.¹ has been recently examined by Craig et al.^{2,3} using quantum electrodynamics, and hydrophobic bonding proposed by Brasted and his coworkers⁴ is one of the most important concepts in the field of colloid chemistry as well as biochemistry.⁵

It seems somewhat strange, however, that the Pfeiffer effect is well observed in systems of the same charge, e.g., the $[Zn(phen)_3]^{2+}-l$ -stryH⁺ and -d-cinchoH⁺ systems in water, despite the electrostatic repulsion between the complex cation and the cationic environment compounds (phen = o-phenanthroline, l-stryH⁺ = l-strychninium cation, and d-cinchoH⁺ = d-cinchoninium cation). In fact, the Pfeiffer effect of the above systems was found to be greatly enhanced by the addition of inorganic anions.⁶ This has been interpreted in terms of reduced electrostatic repulsion by added anions and of the resulting increase in the number of the complexes interacting with the chiral environment compound.⁷ It follows that these systems bear a close resemblance⁸ to aqueous cationic surfactant solutions, wherein cationic surfactants attract each other against their mutual repulsion to form micelles by hydrophobic bonding⁹ and their critical micelle concentration (cmc) is greatly influenced (lowered) by added anions.¹⁰ Thus, hydrophobic bonding is probably an important mechanism in Pfeiffer systems composed of hydrophobic solutes such as tris-phen complexes and l-stryH⁺, d-cinchoH⁺, or d-BCS⁻, as was suggested first by Brasted et al.^{1b} (d-BCS⁻ = $d \cdot \alpha$ bromocamphor- π -sulfonate anion).

Recently the cmc of some ionic surfactants has been measured in D₂O by several workers^{11,12} and found to be a little lower than in H₂O. They attributed the increased micelle stability in D₂O to the enhanced hydrophobic bonding arising from the higher "structuredness" of D₂O.¹³ That is, when a hydrophobic solute is dissolved, the entropy loss in D_2O is greater than in H_2O (i.e., hydrophobic solvation is more extensive in D₂O). Thus, the hydrophobic bond formation is more favored in D_2O , since it is accompanied by an entropy gain.⁵ In this respect, it seems of great value to compare the magnitude of the Pfeiffer effect in D₂O with that in H_2O . A number of experimental results¹²⁻¹⁴ such as conductance, enthalpy and entropy of solution, heat capacity, molar volume, etc. support the view that hydrophobic interaction including hydrophobic solvation and bonding is, slightly but definitely, stronger in D₂O. Thus, an enhanced Pfeiffer effect is expected in D₂O irrespective of the charge type of the Pfeiffer systems.

Sample solutions containing $[Zn(phen)_3]SO_4$ were prepared by dissolving zinc sulfate and o-phenanthroline in a mole ratio of 1:3 in H₂O and D₂O. To these solutions was added the chiral environment compound *l*-stryH-0.5SO₄ or *d*-BCSNH₄.¹⁵ The purity of these compounds was checked by both elemental analysis and optical rotation measurements. The D₂O used had an isotope composition of 99.8% of D₂O. Optical rotations were measured at 405 nm in a 5-cm cell at 25 ± 0.1 °C with a Union-Giken PM-71 polarimeter.

Table I lists independently observed rotations in H_2O and D_2O of the two chiral environment compounds used. From the table, it is seen that their optical rotations are not subject to the so-called solvent isotope effect within experimental error and that the effect of the difference in refractive index of H_2O and D_2O is negligible.¹⁶

Figures 1 and 2 show the plots of observed optical rotations at 405 nm of the $[Zn(phen)_3]^{2+}-l$ -stryH⁺ and

TABLE I: Comparison of Observed Optical Rotations at 405 nm in H_2O and D_2O at 25 °C in a 5-cm Cell

	d-BCSNH₄ ^a	l-stryH•0.5SO₄ ^b
H_2O	+0.952°	-0.159°
	+0.950°	-0.158°
D_2O	+0.948°	-0.158°
-	+0.946°	-0.157°

^a In 0.02 M. ^b In 0.01 M.



Figure 1. Plots of observed optical rotations (in degrees) at 405 nm in a 5-cm cell vs. the concentration of $[Zn(phen)_3]SO_4$ for the $[Zn(phen)_3]^{2+}$ -*k*-stryH⁺ system in H₂O and D₂O.



Figure 2. Plots of observed optical rotations (in degrees) at 405 nm in a 5-cm cell vs. the concentration of $[Zn(phen)_3]SO_4$ for the $[Zn(phen)_3]^{2+}$ -*d*-BCS⁻ system in H₂O and D₂O.

 $[Zn(phen)_3]^{2+}-d$ -BCS⁻ systems, respectively in H₂O and D₂O vs. molar concentration of $[Zn(phen)_3]SO_4$, where the concentration of *l*-stryH·0.5SO₄ and *d*-BCSNH₄ is kept constant (0.01 and 0.02 M, respectively) and individual circles correspond to completely independent observations. It is clearly seen in these figures that an approximately liner relationship¹ is observed between the observed rotation and the concentration of the complex both in H₂O and

 D_2O_1 , and that the magnitude of the Pfeiffer rotation¹ is slightly but definitely greater in D₂O than in H₂O (by 8% on an average), as is expected. Therefore, our experimental results reported here, we believe, provide additional evidence suggesting that hydrophobic bonding is an important mechanism for the Pfeiffer effect examined here.

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Crystal Structure and Melting Behavior of *m*-Nitrophenol

Sir: In the course of studies on the melting of disubstituted benzenes Tewari¹ and others noted that there was considerable premelting in the case of m-nitrophenol (MNP) and the liquid can be supercooled to ~ 30 °C below the melting point. A literature²⁻⁴ search indicated that the melting point of MNP has been quoted variedly as 95, 96, or 97 °C. The exact crystal structure of MNP has not been reported so far. Thus it was of interest to take a closer look at the structure and melting behavior of this compound.

MNP (BDH laboratory reagent) was recrystallized several times from ethyl alcohol and purified by zone melting. Using a microscope and a hot stage the melting point was found to be 96.8-97 °C. Dilatometry was undertaken to determine the melting point more accurately and measure the volume change on melting.⁵ A known weight of MNP was sealed in a bulb to which a precision bore capillary was attached vertically. The tube was evacuated and the solid mass devoid of air bubbles was covered under vacuum with an indicator liquid (purified Hg or silicon oil). The dilatometer was kept in an oil bath regulated to ± 0.1 °C. Volume changes were measured over 80-110 °C by noting the level of the indicator liquid with a cathetometer reading to 0.001 mm. Plots of volume changes vs. temperature indicated premelting from 95 °C onward with a sharp increase in volume at 96.9-97 °C, corresponding to the melting point. The volume increase over 95-96.9 °C is $\sim 10\%$ of the change at the melting point. The total volume change over the range 95-97 °C was 9.5 \pm 0.3 cm³/mol. The premelting effects could be due to presence of more than one form of MNP. For example, in the case of 2,3- and 2,6-dimethylnaphthalenes Al Mahdi and Ubbelohde⁶ reported nonreproducibility of molar volumes near the melting point and attributed this to the possible existence of polymorphism.

The melting of the compound was observed under a microscope in polarized light. Two morphologically distinct forms, needles and prismatic platelets, could be discerned. Some amount of the compound was found to sublime a few degrees below the melting point. Once melted, the compound cools to \sim 35-40 °C below the melting point before freezing. The matrix thus obtained is a mixture of small birefringent crystallites brilliantly colored under polarized light and globules of what is probably glass.

The melting was also studied by a differential scanning calorimeter (DSC 1, Perkin-Elmer) using an In standard calibration. About 4 mg of MNP was weighed and sealed in the sample cell and the melting and freezing runs were observed at various rates of heating/cooling (16-4 °C/min). A typical trace of differential temperature vs. sample temperature is shown in Figure 1 (cf. Table I). For all heating rates the peak near the melting point is broad extending from 90 to 98 °C. The freezing point is sharper (within a 2 °C range) but occurs in the region 55-60 °C, i.e., 40 °C below the melting point. At higher cooling rates there is a distinct auxiliary maximum, extending to within 10% of the total area covered by the peak at the freezing point. This auxiliary maximum was repeatedly observed at 6-8 °C below the freezing point.

Attempts were made to grow single crystals of the two morphologically different forms and determine their structure by x-ray crystallography. It was not possible to grow and isolate sufficiently large prismatic crystals on a plate. However, since conditions of zone melting are conducive to single crystal formation attempts were made to isolate such crystals from the zone-melted matrix. Irregular blocks, slightly cloudy but displaying clean faces and edges, could be separated. A piece of one of these blocks was cleaved off and mounted on a goniometer head for precession photography. A prominent row of reflections was aligned with the spindle using setting strips and zero layer film taken at spindle setting of 191.7°: $\mu = 26^{\circ}$, R = 20 mm, S = 41.5mm, T = 16 h. The pattern showed mm symmetry with a twofold absence perpendicular to the spindle. A second

TABLE I: Peaks on DSC 1 Plots for MNP



Figure 1.

film was taken 90° away at a spindle setting of 100.7°. The pattern was oblique, suggesting a monoclinic system. A first layer was taken at this position which showed one axis to be halved indicating a glide absence. It was now possible to assign the space group P21/C to the specimen and measurement of the lattice parameters gave a cell of (7.35 × 6.86 × 12.88) Å, $\beta = 108.59^{\circ}$, cell volume = 615 Å³. If there are four molecules in the unit cell then $\rho_{expt} = 1.50 \text{ g cm}^{-1}$ and the mean electron density = 0.47 electrons/Å³. The solid density quoted in the literature⁴ at 20 °C = 1.485 g cm⁻³.

Needle-shaped single crystals were grown by sublimation at 95 °C. Whiskers grew on the original sample itself and were detached and mounted in succession to find a crystal of acceptable quality for Weissenberg photography.⁷ The needle axis was set by eye to align with the spindle and oscillation photographs were taken for each. These matched and the spacing corresponded to a repeat distance of 8.16 Å, but there were slight differences in intensity above and below the zero line indicative of a close approximation to

mirror symmetry perpendicular to the needle. A zero-level Weissenberg photograph was taken and exhibited mm symmetry and twofold absences on both axial zones. The first-layer photographs showed slight curvature of axial rows confirming that the needle axis was not a unique direction. In addition, one axis was seen to contain the double spots of the zero layer which again suggested the monoclinic space group P21/C. Measurement of the zero layer photograph gave a monoclinic cell of dimensions (6.95 \times 22.3 \times 8.16) Å, β near 90°, cell volume = 1265 Å³. If there are eight molecules in the unit cell then $\rho_{expt} = 1.46 \text{ g cm}^{-1}$ and the mean electron density = 0.46 electrons/Å³. The implication of Z = 8 is that there are two differently disposed molecules in the cell of the needles, which is double the cell-volume of the prisms. Although there is approximate agreement between the lengths of the b axis of prisms and the *a* axis of needles, it is not possible to simply relate the orientations or reduce one cell mathematically to half the other.

The results taken together indicate the existence of at least two different forms of MNP: prismatic crystals of cell volume = 615 Å³ with four molecules in the unit cell and needle-shaped crystals of cell volume 1265 Å³, with eight molecules in the unit cell. The ordinary chilled sample may in addition have a glass component. The peculiar feature noted around and at the melting point may be the result of various factors such as the melting of the glass, existence of polymorphism, vaporization below the melting point, etc. Preliminary NMR investigations indicate that molecular motion of a rotational character sets in at 89–90 °C.

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