and changes in the σ and π network could become more competitive. The single point lying drastically off the line is the trifluoromethyl group. CF_3 is well known to behave anomalously, however.[16] Sheppard[16] provided evidence that some electron density is returned to the ring *via* through-space effects to counteract the strong electron-withdrawing power of the group.

In connection with pnigogen–ring interaction it is interesting to compare the chlorine resonances in $(p\text{-}ClC_6H_4)_3As$ to those in $(p\text{-}ClC_6H_4)_3Sb$. It has been shown from ir intensities that, within experimental error, σ_R^0 values for the two groups $(C_6H_5)_2As$ and $(C_6H_5)_2Sb$ are the same.[17] The chlorine resonance frequencies do fall in nearly the same place in both cases indicating that as far as the chlorine atom is concerned, there is little difference between the arsine and stibine. The similarity of the chlorine frequencies in the meta- and para-substituted arsines and stibines suggests that the chlorine atom is not greatly affected by π interactions with the ring. A similar observation was made in extensive studies of substituted chlorobenzenes.[18]

In Tables II and III, the ortho-substituted systems yield higher resonance frequencies than their meta and para counterparts. Tris(p-xylyl)arsine and tris(p-tolyl)arsine have been studied by X-ray crystallography[19] and permit a comparison to be made regarding the effect on molecular geometry of an ortho substituent relative to a para group. The CAsC angle is the same

(16) M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, **88**, 354 (1966); R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *ibid.*, **90**, 1757 (1968); W. A. Sheppard, *ibid.*, **87**, 2410 (1965).

(17) J. M. Angelleli, R. T. C. Brownlee, A. R. Katritzky, R. D. Topsom, and L. M. Yakhontov, *ibid.*, **91**, 4500 (1969).

(18) D. Biedenkapp and A. Weiss, *J. Chem. Phys.*, **49**, 3933 (1968); H. O. Hooper and P. J. Bray, *ibid.*, **33**, 334 (1960).

(19) J. Trotter, *Can. J. Chem.*, **41**, 14 (1963); J. Trotter, *Acta Crystallogr.*, **16**, 1187 (1963).

($102°$) for both, the tip of the rings from a position normal to the C_3 axis ($36, 37°$) is effectively the same, and the AsC bond lengths are quite comparable. ($1.99, 1.96$ Å). The slight increase in the AsC bond lengths of the xylyl compound, if significant, could increase the resonance frequency by decreasing the p_x and p_y orbital populations of arsenic. Through-space effects between the central atom and the ortho group can complicate spectral interpretation, however.

The antimony signals in $(C_6F_5)_3Sb$ are shifted significantly toward higher frequency. The C_6F_5 group has been shown to be a strong π donor of electron density.[20] In $(C_6F_5)_3P$, the ^{19}F nmr spectrum favors $\pi(p\text{-}d)$ ring–phosphorous bonding.[21] $\pi(p\text{-}d)$ bonding may also exist in the stibines but it must be kept in mind that a further important consideration at the antimony atom is the strong σ-withdrawing power of the group. The marked increase in the resonance frequencies is consistent with a decrease in the $p_{x,y}$ orbital population on the antimony atom.

Several substituted triphenylbismuthines have been studied by Petrov, *et al.*[22] The variation in $\nu(^{209}Bi)$ appears not to be governed by any recognizable factors. As pointed out above, the Sternheimer antishielding factor[9] is likely to be an important consideration with the bismuth atom.

(20) M. G. Hogken, R. S. Gay, and W. A. G. Graham, *J. Amer. Chem. Soc.*, **88**, 3457 (1966).

(21) M. Fild, I. Hollenberg and O. Glemser, *Z. Naturforsch. B*, **22**, 253 (1967).

(22) L. N. Petrov, J. A. Kyuntsel, and V. S. Grechiskhin, *Vestn. Leningrad Univ., Fiz. Khim.*, 107 (1969).

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Solvation Numbers of Group III and Group V Representative Halides in Acetonitrile by Proton Magnetic Resonance

By I. Y. AHMED* AND C. D. SCHMULBACH

Proton magnetic resonance spectra of solutions of some group III and group V representative halides in acetonitrile at low temperatures are reported. Under these conditions, separate pmr signals of bulk acetonitrile and acetonitrile molecules in the first coordination sphere of the metal halide solute species can be distinguished. From the relative intensities of these signals the solvation numbers of the metal halides were determined. Variation in the solvation numbers among halides of the same group were observed and are discussed with reference to infrared and conductance measurements previously reported. An apparent solvation number of 1 was observed for boron and gallium trihalides indicating the presence of four-coordinate species, mainly $MX_2(CH_3CN)_2^+$ and MX_4^-. The solvation number of 1.5 observed for $AlCl_3$ indicates the presence of six-coordinate $Al(CH_3CN)_6^{3+}$ and four-coordinate $AlCl_4^+$ ions. Among group V metal halides, the pmr data clearly show that PCl_5 is not solvated to any extent while $SbCl_5$ has a solvation number close to 1 indicating the presence of six-coordinate species $SbCl_4(CH_3CN)_2^+$ and $SbCl_6^-$. The reduction in the solvation numbers of $GaCl_3$ (0.57) and $SbCl_5$ (0.82) from the expected value of 1 is explained on the basis of contact ion pairing which produces nonsolvated four- or six-coordinate dimeric species of the forms Ga_2Cl_6 and Sb_2Cl_{10}, respectively.

Introduction

The results of infrared and conductance measurements of solutions of aluminum trichloride[1] and

boron[2,3] and gallium trihalides[4] in acetonitrile indicated that the halides interact strongly with ace-

(1) C. D. Schmulbach and I. Y. Ahmed, *J. Chem. Soc. A*, 3008 (1968).

(2) I. Y. Ahmed and C. D. Schmulbach, *Inorg. Chem.*, **8**, 1411 (1969).

(3) C. D. Schmulbach and I. Y. Ahmed, *ibid.*, **8**, 1414 (1969).

(4) C. D. Schmulbach and I. Y. Ahmed, *ibid.*, **10**, 1902 (1971).

tonitrile to form adducts which dissociate to a greater or lesser extent to give MX_4^- anions and cations with unspecified numbers of solvent molecules in the first coordination sphere. The possibility that gallium and aluminum cations may possess four- or six-coordination or that chemical equilibrium exists between four- and six-coordinate cationic species prompted the investigation of solvation numbers. The value of nuclear magnetic resonance spectroscopy in determining the solvation numbers, structure, and lability of kinetically distinguishable solute species in nonaqueous solvents is firmly established.[5-10] The principles, limitations, and usefulness of this technique in studying the structure and kinetics of solvated cations have been thoroughly reviewed.[11-13]

Experimental Section

Reagents.—Fisher reagent grade acetonitrile was purified by the method described previously.[1] Gallium(III) chloride and bromide (Alfa), aluminum(III) chloride (Baker), and phosphorus(V) chloride (Baker) were sublimed under vacuum prior to use. Boron(III) chloride (Matheson) and antimony(V) chloride (Baker) were purified by fractional distillation under vacuum in the manner described previously.[1] All solutions were prepared by weight and transferred in a glove bag under an anhydrous nitrogen atmosphere to nmr tubes, which had been baked at 120°. Because of the exothermic reaction, acetonitrile was added to the metal halide samples cooled in liquid nitrogen.

Measurements.—Proton nmr spectra were obtained at 60 Mc with a Varian A-60 spectrometer equipped with a variable-temperature probe (V-6031) and a variable-temperature control unit (V-6040). The temperature was monitored by measuring the peak separation of methanol. The areas under the peaks were obtained by integration of the signals with the electronic integrator.

Results

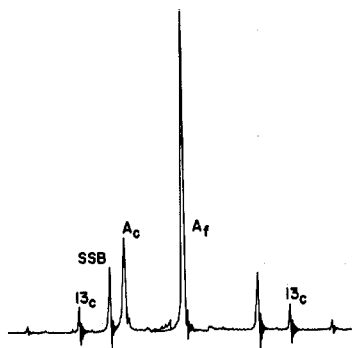Figure 1 shows a representative spectrum of gallium-

Figure 1.—The ^1H nmr spectrum of gallium(III) bromide solution in acetonitrile at −36°. A_f, A_o, SSB, and ^{13}C are designations for free acetonitrile, coordinated acetonitrile, spinning side band, and the free solvent band resulting from ^{13}C splitting, respectively.

(III) bromide solution in acetonitrile at −36°. The spectra of $AlCl_3$, $GaCl_3$, BCl_3, and $SbCl_5$ are similar in appearance to this spectrum. The intensity of the

(5) S. Nakamura and S. Meiboom, *J. Amer. Chem. Soc.*, **89**, 1765 (1967).

(6) J. F. Hon, *Mol. Phys.*, **15**, 57 (1968).

(7) S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, **44**, 3148 (1966); **46**, 4164 (1967).

(8) J. F. O'Brien and M. Alei, *J. Phys. Chem.*, **74**, 743 (1970).

(9) H. Haraguchi and S. Fujiwara, *ibid.*, **73**, 3467 (1969).

(10) W. E. Movius and N. A. Matwiyoff, *Inorg. Chem.*, **8**, 925 (1969), and references therein.

(11) K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, **13**, 107 (1970).

(12) J. Burgess and M. C. R. Symons, *Quart. Rev., Chem. Soc.*, **22**, 276 (1968).

(13) J. F. Hinton and E. S. Amis, *Chem. Rev.*, **67**, 367 (1967).

peak attributed to coordinated acetonitrile is directly proportional to the concentration of the halide. At −40°, the position of this peak in the spectra of the various systems investigated is around 40 ± 5 Hz downfield from the bulk acetonitrile peak. The bands resulting from ^{13}C splitting of free acetonitrile are also readily discerned. No coordinated solvent peak is observed in the spectra of PCl_5 solutions over a wide range of concentrations and temperatures. The separate acetonitrile peaks in solutions of aluminum and gallium halides are distinguishable even at room temperature although the coordinated solvent peak is quite broad due to solvent exchange. In boron(III) chloride and antimony(V) chloride solutions, the coordinated solvent peaks are broad at low temperatures and completely disappear when the temperature is raised to around 0 and −20°, respectively. The results of kinetic studies of solvent exchange in these solutions will be reported in a separate publication.

The solvation number was determined from the molar ratio of the metal halide and acetonitrile in solution and the ratio of the areas under the signals of coordinated and bulk acetonitrile in the spectra. Because the amplitude of the signals differ appreciably for some solutions, it was not always possible to record both signals at the same recorder input level and obtain an accurate area for both. Instead, the area of one of the peaks resulting from ^{13}C splitting, measured at the same signal amplitude as that of coordinated acetonitrile, was used to calculate the relative area of bulk acetonitrile. The results from the ^{13}C splitting peak agreed well with those obtained from bulk acetonitrile peak and thus provided a check on the accuracy of the results. The calculated solvation numbers at the respective temperature and solute concentration are summarized in Table I. An attempt to measure the solvation number of BI_3, which is expected to show a solvation number of 2, was not successful due to its limited solubility in acetonitrile.

Discussion

An experimental solvation number of 1 for boron(III) chloride is consistent with both a molecular structure $CH_3CN \cdot BCl_3$ and an ionic structure $(CH_3CN)_2$-BCl_2^+,BCl_4^-. Since solutions of boron(III) chloride in acetonitrile have been shown[1] to contain appreciable concentrations of BCl_4^-, as revealed by infrared measurements, but exhibit low conductance, the ions must be present predominantly as ion pairs. There is not direct evidence for the existence of the molecular adduct in solution such as the appearance of two bands for coordinated acetonitrile in the spectra due to $CH_3CN \cdot BCl_3$ and $(CH_3CN)_2BCl_2^+$. However, the presence of two solvated boron species in solution would produce a single resonance band if either the actual chemical shifts of the two species are experimentally indistinguishable or rapid solvent and/or chloride exchange between the species produced an average chemical shift. In view of the similar chemical shifts of coordinated acetonitrile observed in the spectra of various halide solutions, it is conceivable that the two solvated boron species would have very close, if not identical, chemical shifts. The broadening and disappearance of the coordinated acetonitrile signal in BCl_3 solutions at temperatures well below those ob-

TABLE I
SOLVATION NUMBERS OF METAL HALIDES IN ACETONITRILE

Molality, m	Temp, °C	Solvation no., n	Av n
		AlCl₃	
0.6343	−40	1.40	1.50 ± 0.03
	−17	1.50	
0.8464	−50	1.60	
	−40	1.64	
	−25	1.49	
0.9562	−40	1.45	
	−26	1.43	
		BCl₃	
0.6115	−40	0.96	1.04 ± 0.02
1.029	−40	1.00	
1.064	−40	1.08	
1.288	−40	1.11	
1.843	−40	1.07	
		GaCl₃	
0.5335	−40	0.61	0.57 ± 0.01
0.6022	−40	0.55	
	−27	0.61	
0.6770	−42	0.51	
	−35	0.51	
	−28	0.54	
0.7130	−40	0.51	
1.072	−44	0.58	
	−40	0.65	
1.079	−25	0.59	
		GaBr₃	
0.2521	−40	0.94	1.02 ± 0.01
0.2802	−40	1.00	
0.3184	−31	1.04	
0.3295	−40	1.06	
0.4220	−46	0.96	
0.5438	−34	1.04	
0.8665	−40	1.02	
0.9847	−40	1.03	
	−17	1.10	
		SbCl₅	
0.3342	−40	0.79	0.82 ± 0.01
1.062	−40	0.82	
1.163	−40	0.86	
1.438	−40	0.79	
1.772	−40	0.83	

served in the spectra of gallium and aluminum halide solutions indicate rapid ligand exchange. While the solvation number gives no information as to the relative amounts of molecular species and ion pairs, it clearly indicates that ion pairs of the type $(CH_3CN)_2BCl_2^+,Cl^-$ cannot be present in any significant amount since it would increase the solvation number well above 1.

Raman spectral measurements of concentrated solutions of aluminum(III) chloride in acetonitrile[14] showed that the tetrachloroaluminate ion is present in high concentrations. The apparent solvation number of 1.5 can be explained on the basis of the equation $4AlCl_3 + 6CH_3CN \rightarrow Al(CH_3CN)_6^{3+} + 3AlCl_4^-$, where ion aggregates (*e.g.*, $(CH_3CN)_6Al(AlCl_4)_2^+$, etc.) exist in solution. The low conductance and irregular Λ *vs.* $C^{1/2}$ plots[1] of aluminum(III) chloride solutions in acetonitrile, which show a decrease of molar conductance with increasing concentrations through a minimum and then an increase to a flat maximum at high concentrations, require that a variety of ion aggregates be present in equilibrium. Our results are in excellent agreement with recent proton and aluminum-27 nmr studies of aluminum(III) chloride in acetonitrile.[6,8,9] They are in disagreement with the conclusion reached from con-

ductance measurement results by Libus[15] in which the ionization $2AlCl_3 + 4CH_3CN \rightarrow AlCl_2(CH_3CN)_4^+ + AlCl_4^-$ was proposed. A solvation number of 2 is required in this case. Aluminum(III) chloride is unique among the group III elements studied in that no halide ion is associated with the cation and a coordination number of 6 is thermodynamically preferred.

The question of whether gallium(III) halides in acetonitrile assume ionic configurations like those in the solid state can now be answered. In the solid state the complexes are formulated as $[(CH_3CN)_2GaX_2^+,GaX_4^-]$ with the gallium in both the cation and anion being four-coordinate.[4] The solvation number of 1 for the strongly conducting acetonitrile solutions of gallium(III) bromide over wide concentration and temperature ranges can be accounted for only if the species present are $(CH_3CN)_2GaBr_2^+$ and $GaBr_4^-$ and their ion pairs. Infrared studies established the existence of $GaBr_4^-$ in solution and conductance measurements indicated slight ion association.[4] The presence of measurable amounts of six-coordinate species (such as $(CH_3CN)_4GaBr_2^+$, $(CH_3CN)_6Ga^{3+}$, or $(CH_3CN)_5GaBr^{2+})$ or five-coordinate species (*e.g.*, $(CH_3CN)_3GaBr_2^+$, $(CH_3CN)_4GaBr^+$, or $(CH_3CN)_5Ga^{3+})$ or any solvated four-coordinate species of the type $(CH_3CN)_2GaBr_2^+,Br^-$ that would increase the solvation number above 1 is eliminated. The possibility that the solution contains a mixture of these species along with unsolvated Ga_2Br_6 or $Ga_2Br_6 \cdot CH_3CN$ to give apparent solvation number of 1 is unlikely in view of the invariance of the solvation number with concentration and the behavior of gallium(III) bromide as a slightly associated 1:1 electrolyte of the type GaX_2^+,GaX_4^-. The existence of molecular species of the type $CH_3CN \cdot GaBr_3$ in small concentrations cannot be excluded. The preference of gallium, in acetonitrile solutions of gallium(III) bromide, for four-coordination is firmly established.

The low solvation number of 0.57 for gallium(III) chloride can occur only if significant concentrations of four-coordinate, chlorine-bridged gallium species are present. The unsolvated dimeric gallium(III) chloride or $(CH_3CN)Cl_2Ga-ClGaCl_3$ are examples of such species. These species are produced if contact ion pairing occurs whereby acetonitrile molecules in the first coordination sphere of the cation are completely or partially replaced by the anion. Similar results were obtained for $GaCl_3$ solutions in aqueous acetone mixtures.[16] The solvation number decreased from 6 in pure aqueous solution to 2.6 in an aqueous solution mixture with a dielectric constant (ϵ 36) similar to that of acetonitrile. Reduction in the solvation number of other ions in acetonitrile solutions had been reported.[17] The greater strength of the GaCl bond in the dimeric gallium halides[18-20] must be responsible for this variation in solvation numbers of the two halides.

The absence of a resonance signal for coordinated acetonitrile in the spectrum of phosphorus(V) chloride solution over a wide temperature and concentration range indicates that the solute species are not solvated

(14) C. D. Schmulbach, *J. Inorg. Nucl. Chem.*, **26**, 745 (1964).

(15) W. Libus and D. Puchalska, *J. Phys. Chem.*, **71**, 3549 (1967).
(16) A. Fratiello, R. E. Lee, and R. E. Schuster, *Chem. Commun.*, 37 (1969).
(17) L. D. Supran and N. Sheppard, *ibid.*, 832 (1967).
(18) S. C. Wallwork and I. J. Worall, *J. Chem. Soc.*, 1816 (1965).
(19) H. Brode, *Ann. Phys. (Leipzig)*, **5**, 344 (1940).
(20) P. A. Akishin, V. A. Naunov, and V. M. Tatowski, *Kristallografiya*, **4**, 194 (1959).

to any extent in acetonitrile. The possibility that this might be due to limited solubility is rejected since two resonance signals, assigned to PCl_4^+ and PCl_6^- ions, were observed in the ^{31}P nmr spectrum of phosphorus-(V) chloride in acetonitrile under the same conditions.[1] The absence of a coordinated acetonitrile signal confirms our previous conclusion based upon infrared data[1] that acetonitrile is not entering into the first coordination sphere of the PCl_4^+ ion to alter its tetrahedral symmetry.

Although infrared spectral measurements[1,21] showed the presence of $SbCl_6^-$ ion in solutions of antimony(V)

(21) I. R. Beattie and M. Webster, *J. Chem. Soc.*, 38 (1963).

chloride in acetonitrile, no evidence could be found in the spectrum for tetrahedral $SbCl_4^+$ ion. The apparent solvation number of 0.82 indicates that two acetonitrile molecules are present in the first coordination sphere of the cation and supports the suggestion[1,21] that the cation is present as *trans*-$(CH_3CN)_2SbCl_4^+$. The possibility that $SbCl_5 \cdot CH_3CN$ is also present cannot be entirely excluded since it too has a solvation number of 1. However, in view of the high conductance of the solution[1] it cannot be present in any significant amounts. The slight reduction in the solvation number from the expected value of 1 indicates the presence of species of decreased solvation number such as Sb_2Cl_{10} or $(CH_3CN)Cl_4Sb^+, SbCl_6^-$.
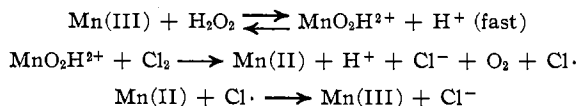

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Catalysis of the Chlorine–Hydrogen Peroxide Reaction by the Manganese(III)–Manganese(II) Ion Pair

BY JACK I. MORROW* AND LAWRENCE SILVER

The Mn(III)–Mn(II) ion pair catalyzes the Cl_2–H_2O_2 reaction by initiating a free-radical mechanism. In the saturation region ($[Mn(II)] \geq 0.01\ M$) the reaction is first order with respect to both Cl_2 and H_2O_2. A mechanism consistent with the data is
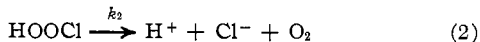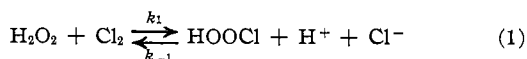
$$Mn(III) + H_2O_2 \rightleftharpoons MnO_2H^{2+} + H^+ \text{ (fast)}$$

$$MnO_2H^{2+} + Cl_2 \longrightarrow Mn(II) + H^+ + Cl^- + O_2 + Cl\cdot$$

$$Mn(II) + Cl\cdot \longrightarrow Mn(III) + Cl^-$$

Introduction

The oxidation of hydrogen peroxide by chlorine in acid media

$$H_2O_2 + Cl_2 \longrightarrow 2H^+ + 2Cl^- + O_2$$
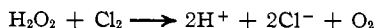
has been the subject of a number of investigations.[1-3] A mechanism for this reaction was suggested by Connick[3]

$$H_2O_2 + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOOCl + H^+ + Cl^- \qquad (1)$$

$$HOOCl \overset{k_2}{\longrightarrow} H^+ + Cl^- + O_2 \qquad (2)$$

This leads to the rate expression

$$-\frac{d[Cl_2]}{dt} = \frac{k_1 k_2 [H_2O_2][Cl_2]}{k_{-1}[H^+][Cl^-] + k_2} \qquad (I)$$

When the [HCl] is large and constant, this reduces to

$$-\frac{d[Cl_2]}{dt} = k_0 [H_2O_2][Cl_2] \qquad (II)$$

where $k_0 = k_1 k_2 / k_{-1}[H^+][Cl^-]$ and is the pseudo-second-order rate constant.
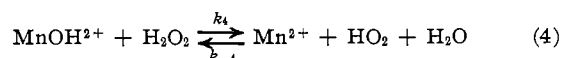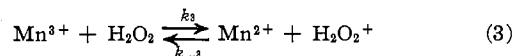
The present study was undertaken to determine the catalytic effect of the Mn(III)–Mn(II) pair on the Cl_2–H_2O_2 reaction. This pair has previously been used to

(1) B. Makower and W. C. Bray, *J. Amer. Chem. Soc.*, **55**, 4765 (1933).
(2) B. Makower, *ibid.*, **56**, 1315 (1934).
(3) R. E. Connick, *ibid.*, **69**, 1509 (1947).

catalyze a number of other redox reactions[4,5] causing them to occur through a free-radical mechanism. Davies, Kirschenbaum, and Kusten[6] did a kinetic study of the reaction between Mn(III) and H_2O_2 in perchloric acid solutions and proposed the rate-determining steps

$$Mn^{3+} + H_2O_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Mn^{2+} + H_2O_2^+ \qquad (3)$$

$$MnOH^{2+} + H_2O_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Mn^{2+} + HO_2 + H_2O \qquad (4)$$

where at 25.0° $k_3 = 7.3 \times 10^4\ M^{-1}\ sec^{-1}$ and $k_4 = 3.2 \times 10^4\ M^{-1}\ sec^{-1}$. Other metal ions causing the rapid formation of the $HO_2\cdot$ free radical include Ce(IV)[7] and Co(III).[8]

As in these other studies the presence of the Mn(III)–Mn(II) pair causes the Cl_2–H_2O_2 reaction to proceed *via* a free-radical mechanism.

Experimental Section

Reagents.—Triply distilled water was used in the preparation of all solutions.

(4) H. Taube, *ibid.*, **69**, 1418 (1947).
(5) H. Taube, *ibid.*, **70**, 3928 (1948).
(6) G. Davies, L. J. Kirschenbaum, and K. Kusten, *Inorg. Chem.*, **7**, 146 (1968).
(7) G. Czapski, B. H. J. Bielski, and N. Sutin, *J. Phys. Chem.*, **67**, 201 (1963).
(8) J. H. Baxendale and C. F. Wells, *Trans. Faraday Soc.*, **53**, 800 (1957).