as it relates to the line width of an epr spectrum. The ClO_2 radical is stable and has a suitable line-width variation with the viscosity of the solvent. By making sufficiently dilute solutions and choosing solvents with suitable liquid ranges and viscosities, the effect of spin-rotational interaction could be studied.

The theory developed by Kivelson[5] for spin-rotational interactions in liquids predicts that the line width of the epr spectrum should depend on the temperature and viscosity. The variation of line width as a function of T/η is given by

$$T_2^{-1} = \text{constant}\left(\frac{T}{\eta}\right) \qquad (1)$$

As shown in Figure 4, the line width is a linear function of T/η over a wide temperature and viscosity range. Therefore, in this linear region, ClO_2 appears to follow the spin-rotational interaction theory as given in eq 1. Also, the curves in Figure 4 for the different solvents are superimposed. This shows the line width is primarily a function of the temperature and viscosity of the solvent as predicted by eq 1.

The relationship of line width *vs.* T/η shown in Figure 4 was not linear over the entire range of the experimental data. This curvature, as indicated by the dashed lines, could be due to other line-broadening effects. However, in the line-width regions indicated by dashed lines in Figure 4, the available viscosity data are not accurate enough to test the theory. For the line-width region over which the T/η plot is linear, Figure 4 can be used to estimate the viscosity of the solvent. This is shown by the values in parentheses in Table I.

Atkins, *et al.*,[2] have suggested that there is a different relaxation mechanism for ClO_2 in noninteracting solvents (*e.g.*, CCl_4) than in hydrogen-bonding media (*e.g.*, N_2O, glycerol, H_2SO_4). However, their results could also be explained on the basis of the viscosity of the solvent. In each case in which they indicated that the resolution was increased, there was also an increase in the viscosity. However, from their data it is not possible to make a quantitative comparison with the viscosity of the solvent.

Summary

We have measured the line width of ClO_2 in solvents such as CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, and CF_4 over temperature ranges of 25 to −180°. The isotropic hyperfine splittings due to the Cl^{35} and Cl^{37} isotopes were resolved and found to be 17.0 and 13.7 gauss. The peak height was in the same ratio as their isotopic abundance, and the hyperfine splitting was in almost the same ratio as the isotopic magnetic moment. The measured g value was 2.0103.

The line widths of the individual hyperfine components were found to vary with the solvent and the temperature. The viscosity dependence of the hyperfine line widths agreed with the theory of spin-rotational interaction proposed by Kivelson.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Isotope Exchange in the Iron(II)–Iron(III)–Chloride Ion System in Dimethyl Sulfoxide

BY GORO WADA[1] AND WARREN REYNOLDS

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The isotope exchange reaction between iron(II) and iron(III) in dimethyl sulfoxide (DMSO) is catalyzed by chloride ion. Rate constants for the reaction paths involving $Fe^{2+} + FeCl^{2+}$ and $Fe^{2+} + FeCl_2^+$ are (130 ± 15) M^{-1} sec^{-1} and (1020 ± 150) M^{-1} sec^{-1}, respectively, at 20°. The formation constants β_1 and β_2 for $FeCl^{2+}$ and $FeCl_2^+$ in DMSO are (5.3 ± 0.6) × 10^3 M^{-1} and (5.7 ± 1.2) × 10^5 M^{-2}, respectively. The molar extinction coefficients of Fe^{3+}, $FeCl^{2+}$, and $FeCl^{2+}$ in DMSO at 20° are (840 ± 10), (1180 ± 16), and (2350 ± 130) M^{-1} cm^{-1}, respectively, at 400 mμ.

Despite the fact that net transfer of a hydrogen atom was postulated[2,3] to be a possible mechanism for electron transfer as early as 1952, very few studies on mechanisms of electron-transfer reactions in essentially aprotic or other nonaqueous solvents have been carried out. Maddock[4] reported that electron transfer between iron(II) and iron(III) perchlorates in nitromethane had a half-time of "many days" at room temperature. Sutin[5] found that the rate of the same exchange reaction was about 10^{-8} times

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(1) Goro Wada wishes to gratefully acknowledge leave by Kobe University, Japan.

(2) R. W. Dodson, *J. Phys. Chem.*, **56**, 852 (1952).

(3) R. W. Dodson and N. Davidson, *ibid.*, **56**, 866 (1952).

(4) A. G. Maddock, *Trans. Faraday Soc.*, **55**, 1268 (1959).

(5) N. Sutin, *J. Phys. Chem.*, **64**, 1766 (1960).

slower in 2-propanol than in water. In mixtures of acetone, methanol, ethanol, or 1-propanol with water, Horne[6] found that the rate of this exchange decreased with decreasing water concentration, but the water concentration was not reduced to less than a mole fraction of approximately 0.4 to 0.6 for acetone, methanol, and 1-propanol. In ethanol the rate decreased slowly until the water concentration was reduced to approximately 0.143 M and then more rapidly as the water concentration was reduced below this value. Presumably the rate of exchange would have continued to decrease as the water concentration decreased and the exchange would have been extremely slow in the dry, nonaqueous solvent as found by Sutin[5] for 2-propanol. The results obtained in these three studies, although there are several alternative explanations,[5] were not inconsistent with a net hydrogen atom transfer mechanism for the iron(II)–iron(III) electron-transfer process. However, in dimethyl sulfoxide (DMSO) Menashi, Reynolds, and Van Auken[7] found that the rate of the iron(II)–iron(III) exchange in perchlorate media decreased as the nonaqueous solvent was added, passed through a broad minimum between 0.8 to 0.6 mole fraction water, and then increased as the water content was further decreased. In the absence of added water the rate constant was independent of acid concentration over a large range and in the presence of 0.05 mole fraction, or greater, of water the apparent second-order rate constant increased with decreasing acid concentration. The results were interpreted to mean that, in the absence of added water, exchange occurred between iron(II) and iron(III) species containing only DMSO molecules in their coordination shells and that net transfer of a hydrogen atom, involving hydrogen atoms of the methyl groups, could be discounted as an electron-transfer mechanism. The most probable mechanisms for electron transfer are the outer-sphere mechanism between $\mathrm{Fe(DMSO)_6{}^{2+}}$ and $\mathrm{Fe(DMSO)_6{}^{3+}}$ or an inner-sphere mechanism involving an O–S bridge between the two iron ions. Quite surprisingly, the free energy, enthalpy, and entropy of activation in DMSO were approximately equal to those for the uncatalyzed exchange in water, the free energies of activation differing by less than 1 kcal/mole at 20°.

In the present work the catalytic effect of chloride ion on the isotope exchange rate in DMSO was studied. In order to obtain the rate constants for the individual electron-transfer processes it was necessary to determine formation constants for $\mathrm{FeCl^{2+}}$, $\mathrm{FeCl_2{}^+}$, and $\mathrm{FeCl^+}$.

Experimental Section

Chemicals.—Baker's Analyzed Reagent grade DMSO was distilled under reduced pressure; the middle portion was collected and shaken with activated alumina overnight and then redistilled under reduced pressure. Approximately two-thirds of the distillate was retained for experimental purposes.

Anhydrous sodium perchlorate, hexakis(dimethyl sulfoxide)-iron(III) perchlorate, and perchloric acid solutions in DMSO were prepared as described earlier.[7] Sodium chloride was twice recrystallized from water and dried. Hexaaquoiron(II) perchlorate was used for the experiments concerning possible $\mathrm{FeCl^+}$ formation; the small amount of water thus introduced did not exceed that which was present as an impurity in the solvent. This perchlorate was prepared by dissolving reagent grade iron powder in perchloric acid, filtering quickly before all the iron powder had reacted, evaporating at slightly above room temperature under a constant flow of oxygen-free nitrogen until a few crystals began to form, cooling, filtering quickly, washing with a little water, and drying in a vacuum desiccator. The product contained no detectable quantity of iron(III) when analyzed spectrophotometrically using 2,2′-bipyridine in the presence and absence of hydroxylamine which would have reduced any iron(III) present.

Apparatus and Procedure.—The apparatus and procedure for the exchange rate measurements have been fully described elsewhere.[7] One modification of the procedure was necessary to prevent the appearance of a turbidity when total iron concentration was determined in the reaction mixture: 5 ml of reaction mixture was added to a solution containing 1 ml of 0.9 M $\mathrm{HClO_4}$, 1 ml of 0.125 M 2,2′-bipyridine in a 50% ethanol–water mixture, 1 ml of 2% $\mathrm{NH_2OH \cdot HCl}$, and 10 ml of ethanol. After reduction of iron(III) to iron(II) the solution was diluted to 25.00 ml with ethanol and the optical density determined.

For the determination of formation constants a Beckman Model DU spectrophotometer with a thermostated cell compartment and 1-cm silica cells with ground glass stoppers was used for all optical density measurements.

Results and Discussion

Molar Extinction Coefficients of $\mathrm{Fe(DMSO)_6{}^{3+}}$.—The values of the molar extinction coefficient, ϵ_0, of the solvated iron(III) ion at various wavelengths are: (450, 50), (440, 91), (430, 171), (420, 309), (410, 534), (400, 840), (390, 1340), (380, 1890), (370, 2530), (360, 3150), (350, 3660), (340, 4060), (330, 4230), (320, 4170), (310, 4230), (300, 4550), (290, 5490), (280, 7290), and (270, 9600) in which the wavelength in mμ is given first and the molar extinction coefficient in l. mole^{-1} cm.$^{-1}$ is given last. The solutions obeyed Beer's law up to at least 1.00 mM iron(III). The extinction coefficients were independent of perchloric acid concentration down to 0.02 M acid, the lowest concentration studied.

At low chloride ion concentrations and constant iron(III) concentrations an isosbestic point was observed at 280 mμ indicating the probable formation of one iron(III)–chloride complex from the solvated iron(III) ion. This observation is in agreement with the conclusion of Drago, Hart, and Carlson[8] that only $\mathrm{FeCl^{2+}}$ was being formed in DMSO solutions containing 0.15 mM iron(III) and 0.15 to 0.30 mM chloride ion.

Determination of Formation Constants of $\mathrm{FeCl^{2+}}$ and $\mathrm{FeCl_2{}^+}$ in DMSO.—The analytical concentrations of iron(III) and sodium chloride used and the corresponding absorptivities measured at 400 mμ are given in Table I. A high-speed digital computation method[9] was used to calculate β_1 and β_2, the over-all

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[6] R. A. Horne, Ph.D. Thesis, Columbia University, New York, N. Y., 1955.

[7] J. Menashi, W. L. Reynolds, and G. Van Auken, *Inorg. Chem.*, **4**, 299 (1965).

[8] R. S. Drago, D. M. Hart, and R. L. Carlson, *J. Am. Chem. Soc.*, **87**, 1900 (1965).

[9] Z Z. Hugus, "Advances in the Chemistry of the Coordination Compounds," The Macmillan Company, New York, N. Y., 1961.

TABLE I

AVERAGE MOLAR EXTINCTION COEFFICIENTS OF IRON(III) IN $NaCl-HClO_4-NaClO_4$-DMSO MEDIA

0.02 M $HClO_4$, μ = 0.100, 25°, 400 mμ

[NaCl] $\times 10^4 M$	[Cl^-] $\times 10^4 M$[c]	$\bar{\epsilon}$,[d] M^{-1} cm^{-1}	[NaCl] $\times 10^4 M$	[Cl^-] $\times 10^4 M$	$\bar{\epsilon}$, M^{-1} cm^{-1}
0.80[a]	0.34	893	12.0	9.22	1210
1.60	0.74	940	13.0	10.16	1230
2.00	0.96	960	14.0	11.10	1250
2.50	1.26	990	15.0	12.04	1260
3.00	1.79	1030	16.0	12.99	1280
3.00	1.58	1010	17.0	13.95	1290
4.00	2.28	1050	18.0	14.90	1300
5.00	3.04	1080	30.0[b]	28.24	1440
6.00	3.86	1100	35.0	33.18	1480
7.00	4.74	1120	40.0	38.12	1510
8.00	5.58	1140	45.0	43.08	1540
9.00	6.47	1160	50.0	48.04	1560
10.0	7.38	1170	55.0	53.00	1590
11.0	8.30	1200	60.0	57.96	1610
			65.0	62.93	1630

[a] From 0.80 × 10^{-4} to 18.0 × 10^{-4} M NaCl inclusive the analytical iron(III) concentration was 3.00 × 10^{-4} M, except for the fifth experiment, where it was 2.40 × 10^{-4} M. [b] From 30.0 × 10^{-4} to 65.0 × 10^{-4} M NaCl inclusive the analytical iron(III) concentration was 1.50 × 10^{-4} M. [c] Free chloride ion concentration calculated using the values reported for β_1 and β_2. [d] $\bar{\epsilon} = A/[Fe(III)]$.

formation constants of $FeCl^{2+}$ and $FeCl_2^+$, respectively, and ϵ_1 and ϵ_2, the molar extinction coefficients of these two species, respectively, in DMSO. The value of ϵ_0, the molar extinction coefficient of Fe^{3+} in DMSO, was taken to be 840 M^{-1} cm^{-1} at 400 mμ and 25°. The values of β_1 and β_2 obtained were (5.3 ± 0.6) × 10^3 M^{-1} and (5.7 ± 1.2) × 10^5 M^{-2}, respectively, at 25°; the values of ϵ_1 and ϵ_2 were 1180 ± 16 and 2350 ± 130 M^{-1} cm^{-1}, respectively.

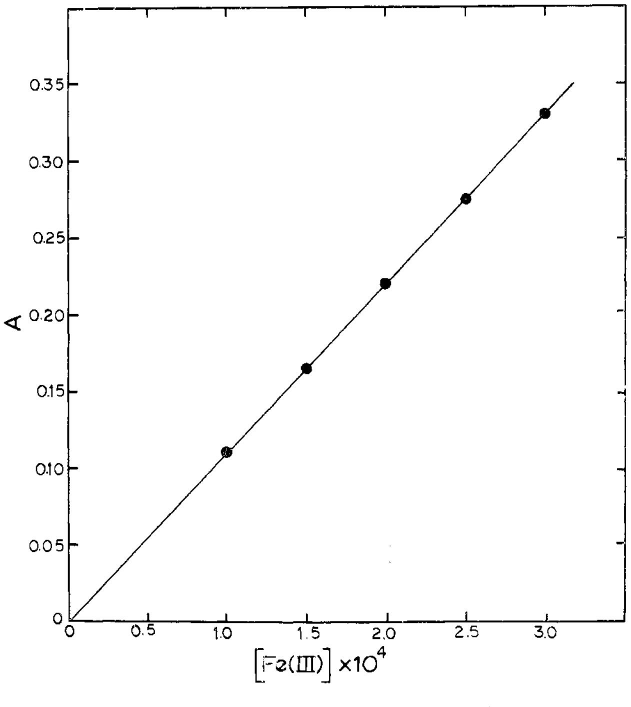

Figure 1.—Absorbance *vs.* iron(III) concentration at constant free chloride ion concentration but variable total chloride concentration: $HClO_4-NaClO_4$ media in DMSO; μ = 0.10 M.

Using these values of β_1 and β_2 the quantities of NaCl necessary to give a free chloride ion concentration of 3.00 × 10^{-4} M at various iron(III) concentrations were calculated. The measured optical densities and analytical iron(III) concentrations (mM) were (0.112, 0.100), (0.166, 0.150), (0.233, 0.200), (0.276, 0.250), and (0.330, 0.300) and are plotted in Figure 1. It is seen that optical density is strictly proportional to the analytical iron(III) concentration over the range studied and that the line passes through the origin. It was concluded that the calculated values of β_1 and β_2 predicted the free chloride ion concentration with satisfactory accuracy and that negligible quantities of polynuclear iron(III) species were being formed.

The measured optical densities were not dependent on perchloric acid concentration over the range 0.020 to 0.070 M. It was assumed that the equilibrium constants were independent of acid concentration over this range. The ionic strength of the solutions was kept at 0.10 with anhydrous sodium perchlorate.

No evidence for formation of $FeCl^+$ was obtained spectrophotometrically at 330 and 350 mμ using Job's method and the sum of the iron(II) and chloride ion concentrations equal to 2.00 mM.[10]

Dependence of Reaction Rate on Concentrations.—If it is assumed that in the anhydrous NaCl-DMSO solutions isotope exchange occurs by the mechanism

$$Fe(DMSO)_6^{2+} + {}^*Fe(DMSO)_6^{3+} \rightleftharpoons Fe(DMSO)_6^{3+} + {}^*Fe(DMSO)_6^{2+} \quad (1)$$

$$Fe(DMSO)_6^{2+} + {}^*Fe(DMSO)_5Cl^{2+} \rightleftharpoons Fe(DMSO)_5Cl^{2+} + {}^*Fe(DMSO)_6^{2+} \quad (2)$$

$$Fe(DMSO)_6^{2+} + {}^*Fe(DMSO)_4Cl_2^{+} \rightleftharpoons Fe(DMSO)_4Cl_2^{+} + {}^*Fe(DMSO)_6^{2+} \quad (3)$$

that the formation and dissociation of the chloride complexes is rapid compared to the rate of isotope exchange, and that no other complexes are formed to an appreciable extent, the apparent second-order rate constant will be given by

$$k_{app} = \frac{k_0 + k_1\beta_1[Cl^-] + k_2\beta_2[Cl^-]^2}{1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2} \quad (4)$$

in which k_0, k_1, and k_2 are the second-order rate constants for reactions with zero, one, and two chloride ions in the activated complex and [Cl^-] is the concentration of free chloride ion. The analytical concentrations of iron(II), iron(III), and sodium chloride used and the values of k_{app} are listed in Table II. The listed values of k_{app} were calculated from

$$k_{app} = -2.303S/[Fe] \quad (5)$$

in which [Fe] is the sum of the iron(II) and iron(III) concentrations, S is the slope of the linear plot of log

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(10) The preliminary results reported for the formation constants of $FeCl^+$ and $FeCl_2^+$ are in error (G. Wada and W. L. Reynolds, paper presented at the I.A.E.A. Symposium, Brookhaven National Laboratories, Upton, N. Y., May 31–June 4, 1965). A possible explanation of the incorrect results is that polynuclear iron(III) species were formed at the high (0.01 M) concentrations employed which gave a reproducible but misleading maximum at a 2:1 ratio for Cl^- to iron(III) when Job's method was used. The conclusion that $FeCl^{2+}$ formation was negligible was incorrect and the maximum at a 1:1 ratio for Cl^- to iron(II), when Job's method was applied to the latter system, was due to traces of iron(III) inpurity in the iron(II) salt.

TABLE II

DEPENDENCE OF k_{app} ON CHLORIDE ION CONCENTRATION

0.02 M $HClO_4$, μ = 0.10 at 20°

[NaCl] $\times 10^4 M$	[Cl^-] $\times 10^4 M$	[Fe(II)] $\times 10^5 M$	[Fe(III)] $\times 10^5 M$	k_{app}, M^{-1} sec^{-1}
0.50	0.46	6.20	1.85	50.8
1.00	0.93	5.21	2.12	61.3
1.50	1.43	4.78	1.66	71.5
2.00	1.93	5.00	1.41	72.0
2.00	1.97	2.99	0.69	87.2
2.50	2.44	2.93	1.09	82.9
3.00	2.91	0.88	1.35	104
3.00	2.93	5.16	1.06	106
3.00	2.97	1.41	0.46	104
3.00	2.99	2.42	0.19	123
3.50	3.46	0.68	0.56	125
3.50	3.43	2.47	1.03	117
4.00	3.93	3.14	0.92	103
4.00	3.97	2.77	0.52	139
4.00	3.94	4.18	0.87	116
4.00	3.94	2.39	0.84	136
4.00	3.95	1.76	0.68	133
4.00	3.97	1.83	0.44	128
4.50	4.45	3.37	0.79	122
5.00	4.99	1.25	0.19	113
5.00	4.95	4.78	0.65	119
5.00	4.92	1.90	1.01	132
5.45	5.35	4.29	1.25	122
5.45	5.37	1.63	0.98	125
5.50	5.47	1.79	0.38	127
5.50	5.46	2.33	0.49	126
6.00	5.98	0.81	0.21	135
6.00	5.97	2.26	0.35	145
6.00	5.95	2.82	0.71	171
6.00	5.96	2.22	0.60	154
6.00	6.00	6.17	0.05	138
6.00	5.97	3.86	0.43	160
6.00	5.95	1.41	0.63	169
6.00	5.93	4.24	0.87	159
6.50	6.42	2.99	0.95	172
6.50	6.43	2.55	0.82	163
7.00	6.93	2.01	0.76	162
7.00	6.93	1.85	0.77	165
7.50	7.45	1.79	0.60	145
7.50	7.42	2.06	0.87	170
8.00	7.92	1.60	0.87	176
8.00	7.92	1.69	0.89	159
10.0	9.90	3.49	1.10	200
15.0	14.9	1.95	0.85	215
20.0	19.9	1.73	1.03	273
20.0	19.9	1.69	1.00	257
20.0	19.9	0.82	0.84	278
20.0	19.9	0.95	1.33	285
20.0	19.9	1.78	0.56	277
20.0	20.0	1.56	0.36	267
20.0	19.9	2.92	0.76	273
20.0	20.0	0.41	0.31	270

$(1 - F)$ *vs.* time,[11] and F is the fraction of exchange at time t.

The determination of the order of the reaction with respect to iron(II) and iron(III) concentrations was difficult because predetermined values of these concentrations were not obtained in the solutions. Fresh solutions of iron(II) were always prepared for each rate experiment by dissolving a small amount of iron(II) perchlorate. The concentration of iron(II) was always determined spectrophotometrically as the 2,2′-bipyridine complex on duplicate samples at the end of the experiment. Since the iron(II) perchlorate invariably contained some iron(III) impurity it was necessary to determine the iron(III) concentration in each experiment also. This was done by determining the total iron concentration[12] in duplicate samples at the end of an experiment and subtracting the iron(II) concentration. Examination of the results obtained at 6.0 × 10^{-4} and 20.0 × 10^{-4} M Cl^- does not reveal any marked dependence of k_{app} on either iron(II) or iron(III) concentrations. Although the product [Fe(II)][Fe(III)] varied as much as 20-fold, k_{app} was independent of this product within the sizable experimental error resulting from approximately 20% zero-time exchange.

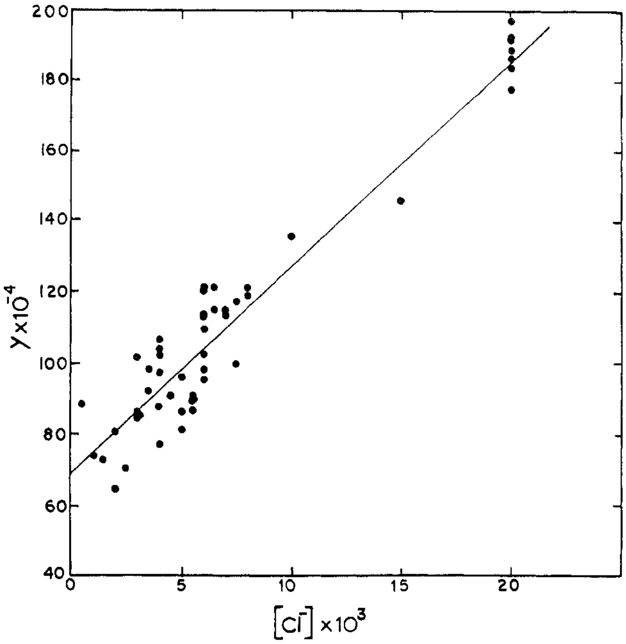

Figure 2.—Y *vs.* total chloride concentration: 0.020 M $HClO_4$, 0.080 M $NaClO_4$, 20°, μ = 0.10 M.

Equation 4 may be rearranged to give

$$Y = \frac{Dk_{app} - k_0}{[Cl^-]} = k_1\beta_1 + k_2\beta_2[Cl^-] \qquad (6)$$

in which D is the denominator in eq. 4. All quantities on the left-hand side were known; hence the left-hand side was plotted *vs.* [Cl^-] in Figure 2. The slope and intercept were calculated by the method of least squares. From the intercept and the known β_1 value k_1 was calculated to be (130 ± 15) M^{-1} sec^{-1}; from the slope and the known β_2 value k_2 was calculated to be (1020 ± 150) M^{-1} sec^{-1}. (Although the formation constants were determined at 25° they may be used here without appreciable error since the temperature coefficient for the formation constants apparently did not exceed approximately 6 kcal mole^{-1}.)

These results do not permit one to distinguish between inner-sphere and outer-sphere activated complex mechanisms. However, it is interesting to note that the ratio k_1/k_0 in DMSO is approximately equal to 6

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[11] R. J. Prestwood and A. C. Wahl, *J. Am. Chem. Soc.*, **71**, 3137 (1949).

[12] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, D. Van Nostrand Co., New York, N. Y., 1949, p 316.

as it is for aqueous systems at 25° where it is known[13] that electron transfer between Fe^{2+}(aq) and $FeCl^{2+}$(aq) occurs by both mechanisms although the bridged, inner-sphere mechanism predominates; the effect of introducing a Cl^- ion (probably in place of a solvent molecule) into the activated complex has very much the same effect when the rest of the ligands are DMSO molecules as when they are water molecules. This suggests, but does not prove, that the role of Cl^- in reaction 2 is the same as it is in the aqueous system. Thus, not only are the free energy, enthalpy, and entropy of activation of reaction 1 approximately equal to those for the corresponding reaction between hexaaquo iron ions,[7] but the effect on the free energy of activation in both solvents is essentially the same when Cl^- is added to the activated complex. Some difference for the two solvents is indicated by the fact that k_2/k_1 is approximately 7 in DMSO but 2 in water and that at Cl^- concentrations above 2.00×10^{-3} M the value of k_{app} begins to increase rapidly indicating a third chloride-catalyzed path. Since no indication of a third chloride species was found spectrophotometrically at similar chloride concentrations no formation constant for this species had been determined and the kinetic studies at the higher Cl^- concentrations were discontinued.

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(13) R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 4591 (1964).

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Nuclear Magnetic Resonance Studies on Exchange Reactions of Trimethylantimony Dihalides

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Proton magnetic resonance spectra for the four trimethylantimony dihalides, $(CH_3)_3SbF_2$, $(CH_3)_3SbCl_2$, $(CH_3)_3SbBr_2$, and $(CH_3)_3SbI_2$, show methyl proton signals of considerably different chemical shifts. The spectrum at −32° of a chloroform solution containing any pair of the previously mentioned compounds shows three methyl proton signals, two of which are characteristic of the two parent dihalides, $(CH_3)_3SbX_2$ and $(CH_3)_3SbY_2$, and a third signal which has been identified as the mixed halide, $(CH_3)_3SbXY$. All six of the solutions made by pairwise combinations of the dihalides show a similar temperature dependence. The initial result of increasing the temperature above −32° is the broadening of the three methyl signals. At higher temperatures the signal of the heavier dihalide (X_2) and the mixed halide (XY) coalesce to a broad intermediate signal which is closer to that of the mixed halide. At still higher temperatures the lighter dihalide (Y_2) signal begins to merge with this intermediate signal. Finally, a single, somewhat broadened signal with a chemical shift corresponding to that of the mixed halide is attained for the dibromide–diiodide solution at 70°, dichloride–dibromide at 80°, and difluoride–dichloride at 150°. These results are explained on the basis of a series of exchange equilibria. In addition, ^{19}F chemical shifts are reported for the fluorine-containing species.

For some time we have been interested in trigonal bipyrimidal molecules that have several dissimilar groups attached to the central atom, *e.g.*, MA_3BC and MA_2B_2C. A problem encountered in the study of these compounds is the fact that elemental analysis cannot distinguish between a pure compound and certain mixtures. Thus, materials which have an elemental analysis corresponding to MA_3BC may be either the pure compound or a series of mixtures each containing equimolar quantities of MA_3B_2 and MA_3C_2.

In a preliminary experiment we noted that the pmr chemical shifts of the trimethylantimony dihalides, $(CH_3)_3SbF_2$, $(CH_3)_3SbCl_2$, $(CH_3)_3SbBr_2$, and $(CH_3)_3SbI_2$, differ considerably. This suggested that the presence of a mixed halide, $(CH_3)_3SbXY$, could be detected by observation of the methyl proton chemical shift. The synthesis of the pure mixed halide probably would be difficult.[1] However, if disproportionation between two dihalides, $(CH_3)_3SbX_2$ and $(CH_3)_3SbY_2$, occurs readily, the presence of the mixed halide, $(CH_3)_3SbXY$, could be detected by the observation of a pmr signal that does not correspond to that of either of the two starting materials. Also, if one of the dihalides is $(CH_3)_3SbF_2$, we should be able to confirm the disproportionation by observation of different ^{19}F nmr signals for the difluoride and for the mixed derivative. Reported in this paper are the pmr chemical shifts for the trimethylantimony dihalides, the results of experiments to prepare and detect the mixed halides, and some of the interesting equilibria observed in solutions of these compounds.

Experimental Section

The ^1H and ^{19}F nmr studies were carried out using a Varian HA-100 high-resolution spectrometer equipped with a variable-

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[1] G. O. Doak and G. G. Long, *Trans. N. Y. Acad. Sci.*, **28**, 402 (1966).