Nuclear Magnetic Resonance Study of Configurations and Interionic Separations in $R_4N^+MX_n{}^{3-}$ Ion Pairs

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Abstract: A systematic nmr study was made of line widths and chemical shifts for ion pairs in solution, consisting of tetraethylammonium ions and various complex paramagnetic anions of iron(III) and chromium(III). Anions of identical charge (3−) but of varying size were employed in the study. Solutions in solvent mixtures of D_2O and dimethyl-d_6 sulfoxide were investigated over the temperature range 6-95°. Results of the study indicate that the experimental data are best fit by a model in which there is restricted tumbling of the counterions within the ion pairs. Calculated interionic separations indicate that "contact" ion pairs are formed in dimethyl-d_6 sulfoxide, and "solvent-separated" ion pairs are formed in D_2O. Only minor changes in configuration are observed over the temperature range studied.

Two nmr studies have been reported, the results of which were interpreted assuming the presence of ion pairs in the systems studied. The first study[2] involved the use of various quaternary ammonium ions and hexacyanoferrate(III) ion in aqueous solution. The value of T_{1e}, the electron spin lattice relaxation time, for the paramagnetic hexacyanoferrate(III) ion is relatively short, and chemical shifts due to "pseudocontact" interactions[3] were found to accompany ion-pair formation in these systems. Calculations using the observed "pseudocontact" shifts for the various magnetically equivalent sets of protons in the cations gave some information about the geometry of the ion pairs.

The second study[4] involved the use of quaternary ammonium ions and hexacyanochromate(III) ion in aqueous solution. In this case, the value of T_{1e} for the paramagnetic hexacyanochromate(III) ion is relatively long, and line broadenings, again due to "pseudocontact" interactions,[5] were found to accompany ion-pair formation. Also for these systems, information about the geometry of the ion pairs was obtained from the observed line broadenings for the various magnetically equivalent sets of protons in the cations.

In both systems described above, the interionic separations within the ion pairs were found to be independent of the length of alkyl chain in the cation (R_4N^+). The results were found to be consistent with interionic separations of 8–9 Å for the $R_4N^+Fe(CN)_6{}^{3-}$ ion pairs and 11 Å for the $R_4N^+Cr(CN)_6{}^{3-}$ ion pairs. The relatively large calculated interionic separations and the difference of 2–3 Å between the two very similar systems were surprising, and this prompted additional studies to be made in an attempt to further elucidate the structure of these ion pairs. We presently report nmr studies involving association between tetraethylammonium ions and various complex paramagnetic anions of iron and chromium in the mixed solvent D_2O–dimethyl-d_6 sulfoxide.

Experimental Section

Reagents. The sources for the reagents used are as follows: deuterium oxide (Liquid Carbonic), dimethyl-d_6 sulfoxide (Merck Sharp and Dohme), potassium hexacyanoferrate(III) (Fisher), potassium trisoxalatoferrate(III), potassium trisoxalatochromate(III), and potassium hexafluorochromate(III) (Alfa Inorganics).

The following procedure was used to obtain tetraethylammonium-2-d_3 chloride. Acetic-1-d_3 acid was reduced by the slow addition of the compound to an ether suspension of $LiAlH_4$.[6] Hydrolysis of the intermediate was accomplished through the addition of a stoichiometric amount of water saturated with Na_2SO_4. This yielded an anhydrous ether layer which contained CD_3CH_2OH. The ether was removed and the ethyl-2-d_3 alcohol collected. The alcohol was then treated with P and I_2 to yield ethyl-2-d_3 iodide.[7]

Ethylamine-2-d_3 was obtained through the reduction of CD_3CN with $LiAlH_4$. Hydrolysis of the intermediate was achieved with a solution of NaOH. The amine was released and collected in a cold trap.[8] The synthesis of tetraethylammonium-2-d_3 chloride was accomplished by allowing ethyl-2-d_3 iodide to react with ethylamine-2-d_3 over silver oxide in an aqueous medium at room temperature for 3 to 4 days.

The second salt, tetraethylammonium-1-d_2 chloride, was obtained through the conversion of ethyl-1-d_2 bromide to ethylamine-1-d_2 by treating potassium phthalimide with ethyl-1-d_2 bromide at 200°. The N-ethylphthalimide-1-d_2 was taken up in chloroform, washed with dilute base, taken to dryness, and refluxed for several hours with excess 47% HBr. This solution was then treated with base and heated, and the amine collected in a cold trap immersed in liquid nitrogen.[9]

Solutions 0.05 *M* in tetraethylammonium-1-d_2 chloride and 0.05 *M* in tetraethylammonium-2-d_3 chloride in mixed solvents (D_2O–dimethyl-d_6 sulfoxide) were prepared. The composition of the solvents ranged from pure D_2O to pure dimethyl-d_6 sulfoxide. DDS was added as an internal reference. Successive amounts (generally up to about 0.01 *M*) of salts containing the paramagnetic anions were added directly into nmr tubes containing the solutions, and nmr spectra were recorded. An average of ten spectra was taken for each sample to minimize random error.

Nmr Measurements. The proton magnetic resonance spectra of the solutions were recorded by use of a Perkin-Elmer R-20 nmr spectrometer operating at 60 MHz. The temperature of the sample was varied between 6 and 95°. The deuterium-substituted ammonium salts exhibit essentially broad singlets; only the small couplings with H^2 and N^{14} are present. Chemical shifts relative to the internal reference and line widths were determined from the recorded spectra.

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[1] Presented in part at the Second International Symposium on NMR, São Paulo, July 1968.

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[7] R. Adams, J. Johnson, and C. Wilcox, "Laboratory Experiments in Organic Chemistry," The Macmillan Co., New York, N. Y., p 197.

[8] L. H. Amundsen and L. S. Nelson, *J. Am. Chem. Soc.*, **73**, 242 (1951).

[9] Merck Sharp and Dohme of Canada Ltd., Isotopic Products Department, private communication.

Results and Discussion

The solutions containing tetraethylammonium-1-d_2 chloride and tetraethylammonium-2-d_3 chloride exhibit two closely spaced multiplets (essentially singlets) in the absence of paramagnetic anion. With the addition of paramagnetic anion to the solution, each multiplet becomes the collapsed average of R_4N^+ in the bulk solution and R_4N^+ ion paired with paramagnetic anion. In general, each multiplet is both broadened and shifted due to the dipolar or "pseudocontact" interaction between the protons and unpaired electron(s) in the anion. The chemical shift changes and line broadenings have dependences $\langle(3\cos^2\theta - 1)/r^3\rangle_{\text{av}}$ and $\langle 1/r^6\rangle_{\text{av}}$, respectively,[2,4] where r is the distance between proton and electron(s) and θ is the angle between r and the symmetry axis in the ion pair. Thus the interaction is important to R_4N^+ in ion pairs, but negligible for R_4N^+ in the bulk solution.

The chemical shift for the ith multiplet δ_i is measured relative to the internal reference. That part of the chemical shift which is attributable to the dipolar interaction with the anion is $(\delta_i - \delta_i^0)$, where δ_i^0 is the chemical shift of the multiplet in the absence of paramagnetic anion. For different multiplets, the relative dipolar shifts are given by[2]

$$(\delta_i - \delta_i^0):(\delta_j - \delta_j^0):\cdots = \left\langle\frac{3\cos^2\theta_i - 1}{r_i^3}\right\rangle_{\text{av}}:\left\langle\frac{3\cos^2\theta_j - 1}{r_j^3}\right\rangle_{\text{av}}:\cdots \quad (1)$$

Broadening of any given multiplet is due to broadening of each individual component of that multiplet, and relationships will be developed relating component line width to distance between proton and electron(s). The problem is then one of extracting component line widths from observed multiplet line shapes. This was done by comparing convenient parameters of the observed multiplet with those of multiplets calculated as a function of component line width. The procedure followed was to match observed spectra with calculated spectra which were obtained using an IBM 360 computer. The coupling constants used in the calculated spectra were $J_{\text{HD}} = 1.1$ Hz and $J_{\text{N}\beta} = 2.0$ Hz. In most cases, the lines are so broad that the observed line width differs from the component line width by only a few per cent.

The component line width at half-maximum for the ith Lorentzian component $(\Delta\omega_{1/2})_i$ is related to the proton transverse relaxation time for the component T_{2i} by

$$(\Delta\omega_{1/2})_i = \frac{2}{T_{2i}} \quad (2)$$

The component has a small line width in the absence of the dipolar interaction, $2/T_2$, and thus the parameter $(1/T_{2i}) - (1/T_2)$ is that part of the half line width attributable to the dipolar interaction. For different sets of protons, the relative half line broadenings are given by[4]

$$\left(\frac{1}{T_{2i}} - \frac{1}{T_2}\right):\left(\frac{1}{T_{2j}} - \frac{1}{T_2}\right):\cdots = \langle r_i^{-6}\rangle_{\text{av}}:\langle r_j^{-6}\rangle_{\text{av}}:\cdots \quad (3)$$

Table I. Observed and Calculated[a] Chemical Shift and Line-Broadening Ratios for $R_4N^+MX_n^{3-}$ Ion Pairs in D_2O

MX_n^{3-}	Obsd ratio	Calcd ratio	R, Å
CrF_6^{3-}	0.56[b]	0.55[d]	9
$Cr(CN)_6^{3-}$	0.66[c]	0.66[d]	11
$Cr(C_2O_4)_3^{3-}$	0.73[b]	0.73[d]	13
$Fe(CN)_6^{3-}$	0.61[c]	0.65[e]	8–9
$Fe(C_2O_4)_3^{3-}$	0.72[b]	0.73[d]	13

[a] Calculated from previously proposed model (ref 2 and 4). [b] This work. [c] See ref 2 and 4. [d] Calculated from eq 3. [e] Calculated from eq 1.

Equations 1 and 3 relate relative chemical shifts and line broadenings for various multiplets to geometric factors. Table I presents experimental chemical shift and line-broadening ratios for various paramagnetic anions which interact with R_4N^+ in D_2O solution. The ratios are the methylene parameter/methyl parameter. Also presented in Table I are calculated ratios and the integer values of R (the interionic separation) which best fit the observed ratios. The calculation is made by use of eq 1 and 3 and geometric factors from the previously proposed model[2,4] for ion pairs of the type R_4N^+-MX_n^{3-}. The fit of the experimental data can of course be made exact by using noninteger values for R, but the crudeness of the model used makes such a refinement in the calculation unwarranted.

The values of R shown in Table I clearly indicate that the interacting counterions are separated by at least one layer of D_2O molecules. However, the possibility exists that the calculation is sensitive to the model chosen for the ion pair, especially since there is a difference of 2–3 Å in the interionic separations for ion pairs of $Fe(CN)_6^{3-}$ and $Cr(CN)_6^{3-}$, two anions of identical size and charge. To investigate this possibility, a less restrictive model was used in the calculation. Examination of space-filling molecular models suggests use of the model illustrated in Figure 1. The cation is assumed to exist in the configuration used previously,[2,4] *i.e.*, the alkyl groups form intersecting zigzag chains with the N atom in the center. The molecular models indicate that the N–C bonds must assume the tetrahedral configuration or very nearly that to accommodate all four ethyl groups around the central nitrogen. Configurations for the C–C bond other than the staggered one were found to cause little change in the results of the calculation. In any case, the major contribution will come from conformations close to the staggered one because nonbonded interactions are minimized in this rotamer. The position of the anion on the sphere is described by angle ϕ and boundary angle α. The model used for the calculations in Table I is obtained when $\alpha = 0$ and is equivalent to an ion pair in which there is no tumbling of the counterions relative to one another. The value $\alpha = 0$ (the symmetry axis of the cation) was used in previous calculations[2,4] since it gives the position at which the anion is least sterically hindered by the alkyl groups from approaching the positive nitrogen center of the cation. The molecular models indicate that steric hindrance by the alkyl groups increases as α increases but that the immediate region about the symmetry axis offers relatively little steric hindrance. The model will presently be considered in which the

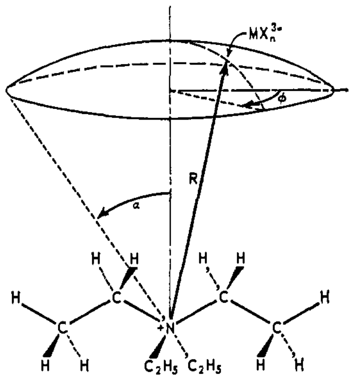

Figure 1. Diagram of model for ion pairs of the type $(C_2H_5)_4N^+$-MX_n^{3-}. MX_n^{3-} occupies any position on the spherical section of radius *R*. The center of the sphere is the N atom in the cation.

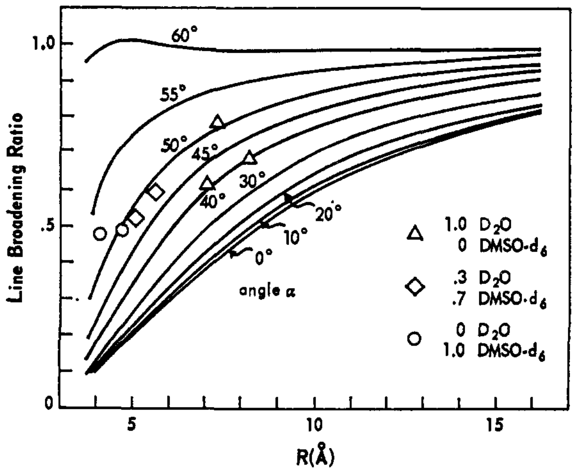

Figure 2. Calculated line-broadening ratios (methyl:methylene) for $(C_2H_5)_4N^+$ protons *vs.* interionic separation (N to M distance) in the ion pair as a function of angle α.

anion is free to occupy any position in the region characterized by radius *R* and boundary angle α. This is equivalent to an ion-pair model in which there is restricted tumbling of the counterions relative to one another.

The line broadening and chemical shift ratios calculated by using this model are shown in Figures 2 and 3, respectively. It can be seen in Figures 2 and 3 that the calculation is extremely model sensitive. For example, the observed line-broadening ratio for $Cr(CN)_6^{3-}$ at 34° is consistent with $R = 4$ Å for $\alpha = 55°$ and with $R = 11$ Å for $\alpha = 0°$.

One feature of the calculation which is of interest is that for all reasonable values of *R*, the calculated line broadening and shift ratios are greater than unity for $\alpha = 90°$. The model with $\alpha = 90°$ is of course equivalent to ion pairs in which there is completely unrestricted tumbling of the counterions relative to one another. Since the observed ratios are in all cases less than unity, this tends to indicate that the tumbling of the counterions is restricted and that the anion prefers to be in the region around the cation in which steric hindrance is small.

In order to determine the value of *R* for a given system, the value of α must be known. It can be seen that if both chemical-shift measurements and line-broadening measurements can be made on the same ion pairs or on different ion pairs with identical geometry, both *R* and α can be determined independently. Also, a check on the calculation can be made by using a solvent of lower dielectric constant and larger in size than water. This should produce associated species in which the counterions are in contact, and the calculated value of *R* should be just slightly larger than the sum of the ionic radii.

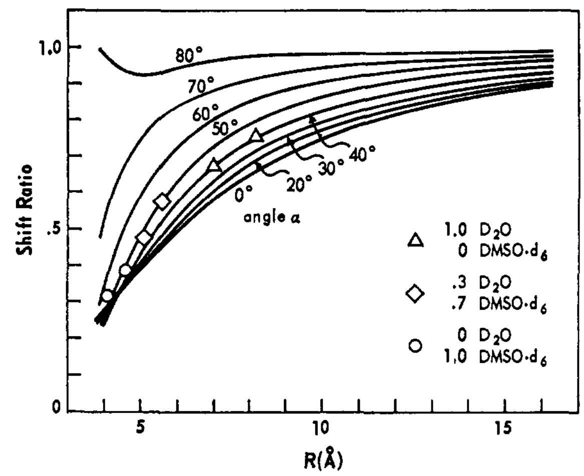

Figure 3. Calculated chemical shift ratios (methyl:methylene) for $(C_2H_5)_4N^+$ protons *vs.* interionic separation (N to M distance) in the ion pair as a function of angle α.

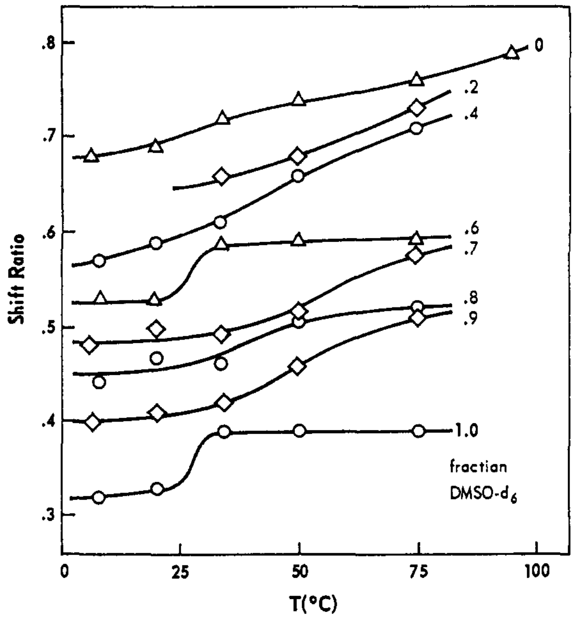

Figure 4. Experimental chemical shift ratios (methyl:methylene) for $(C_2H_5)_4N^+$ *vs.* *T* for $(C_2H_5)_4N^+Fe(CN)_6^{3-}$ ion pairs, as a function of mole fraction DMSO-d_6 in the D_2O-DMSO-d_6 solvent mixture.

The experimental chemical shift ratios for the $R_4N^+Fe(CN)_6^{3-}$ system in solvent mixtures of D_2O and dimethyl-d_6 sulfoxide are shown in Figure 4, and the experimental line-broadening ratios for the $R_4N^+Cr(CN)_6^{3-}$ system also in solvent mixtures of D_2O and dimethyl-d_6 sulfoxide are shown in Figure 5. Measurements were made over the temperature range in which the system remains liquid. Since $Fe(CN)_6^{3-}$ and $Cr(CN)_6^{3-}$ are the same size and have the same charge, their configurations in ion pairs should be very similar,

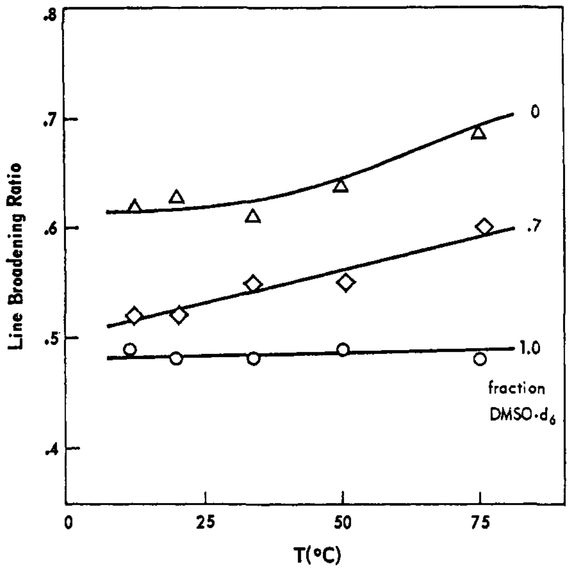

Figure 5. Experimental line-broadening ratio (methyl:methylene) for $(C_2H_5)_4N^+$ *vs.* *T* for $(C_2H_5)_4N^+Cr(CN)_6^{3-}$ ion pairs, as a function of mole fraction DMSO-d_6 in the D_2O–DMSO-d_6 solvent mixture.

and thus their chemical shift ratios and line-broadening ratios should be identical to a first approximation. The chemical shifts are difficult to determine accurately for the $R_4N^+Cr(CN)_6^{3-}$ system since the lines are very broad; however, by using the deuterated compounds which give essentially singlets and by making repeated measurements, Figure 4 was reproduced also for the $R_4N^+Cr(CN)_6^{3-}$ system within experimental error (about ±5%). There is no observable line broadening in the $R_4N^+Fe(CN)_6^{3-}$ system except with dimethyl-d_6 sulfoxide solvent. In this case, the broadening is fairly small, but the broadening ratio agrees within experimental error (again about ±5%) with that shown in Figure 5 for dimethyl-d_6 sulfoxide.

The assumption that there are identical shift ratios and identical line-broadening ratios for the $R_4N^+Cr(CN)_6^{3-}$ and $R_4N^+Fe(CN)_6^{3-}$ systems enables both *R* and α to be determined independently; *i.e.*, one assumes identical *R* and identical α values for both ion pairs under the same given conditions. There will then be only one set of *R* and α values which reproduce observed shift and line-broadening ratios for both systems for any given temperature and solvent. These values were determined from Figures 2 and 3, and the points corresponding to explicit values of *R* and α for three solvents are shown in Figures 2 and 3. The results are summarized in Table II. Also shown in Table II are the same results when ϕ (see Figure 1) is restricted to 90 and 270°. The restriction of ϕ to 90 and 270° corresponds to ion pairs in which the motion of the anion is restricted to an arc around the cation. This highly restricted model is not considered to be realistic but was investigated to determine the extent to which relative motion of the counterions must be present to give satisfactory agreement with the experimental data. It was found that this model fits the data as well as the model in which ϕ is unrestricted, giving nearly identical values of *R* and α. The symmetry of the cation is such that variation of ϕ has a much smaller effect on the results of the calculation than does variation of α. This is unfortunate since a complete picture of the ion pairs necessarily involves a knowledge of ϕ values. However, while no information was obtained about ϕ values, the result that α is appreciably different from zero is definitely indicated by the calculation. The more reasonable model in which ϕ is unrestricted will arbitrarily be used for further discussion.

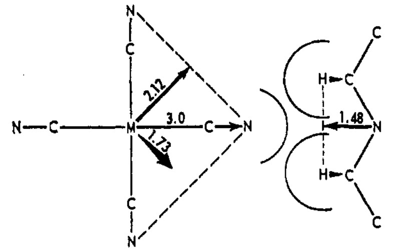

Figure 6. A possible configuration and pertinent distances for $R_4N^+M(CN)_6^{3-}$ ion pairs.

Table II. Calculated[a] Values of *R* and α for $(C_2H_5)_4N^+Fe(CN)_6^{3-}$ and $(C_2H_5)_4N^+Cr(CN)_6^{3-}$ Ion Pairs

Solvent	*T*, °C	*R*, Å	α, deg	
DMSO-d_6	10	4.1	52	ϕ unrestricted
	75	4.7	49	
70% DMSO-d_6 30% D_2O	10	5.1	48	
	75	5.6	48	
D_2O	10	7.0	41	
	75	8.2	40	
DMSO-d_6	10	4.1	45	ϕ = 90°
	75	4.5	45	
70% DMSO-d_6 30% D_2O	10	4.9	45	
	75	5.5	47	
D_2O	10	6.8	44	
	75	8.2	42	

[a] Calculated using the model in Figure 1.

The values of α shown in Table II range from 40 to 52° with an average value about 45°. If α is arbitrarily assumed to be 45° for all ions, values of *R* can be determined for all ions. These values are shown in Table III. Certain features of the data in Table III are of interest. First, the *R* values are much smaller than those in Table I. Second, the differences in the values of *R* at 34° for Cr or Fe complexes approximate the differences in sizes of the anions.

Table III. Calculated Values of Interionic Separations for $R_4N^+MX_n^{3-}$ Ion Pairs in D_2O Assuming ϕ Unrestricted and α = 45°

MX_n^{3-}	*R* (10°), Å	*R* (34°), Å	*R* (75°), Å
CrF_6^{3-}	. . .	6.0	. . .
$Cr(CN)_6^{3-}$	6.5	6.8	7.3
$Cr(C_2O_4)_3$	. . .	7.9	. . .
$Fe(CN)_6^{3-}$	6.8	7.2	7.8
$Fe(C_2O_4)_3$	. . .	7.8	. . .

To further elucidate the structure of the ion pairs, some consideration of the sizes of the ions must be made. Figure 6 illustrates a possible configuration for the ion pairs of $M(CN)_6^{3-}$, along with pertinent interionic distances. The cation may approach a corner, an edge, or a face of the anion octahedron. The value of R for dimethyl sulfoxide is slightly larger than 4 Å. This indicates that in this solvent the cation approaches the face, since other configurations do not allow enough space for the electron clouds. The value of R for D_2O is 7–8 Å. This clearly suggests that regardless of configuration, there is at least one layer of water molecules between the counterions in the ion pair; *i.e.*, the cation lies outside the second coordination sphere of the anion. In 30% D_2O–70% dimethyl sulfoxide, the distance is intermediate, and this suggests an equilibrium between "contact" and "solvent-separated" ion pairs.

The values of R for the other anions in Table III differ by about 1 Å from $M(CN)_6{}^{3-}$. This is consistent with their difference of 1 Å in radius from $M(CN)_6{}^{3-}$, which suggests similar configurations for these anions.

The variation in R over the temperature range 10–75° is quite small (about 1 Å maximum) and suggests that the ion pair undergoes only minor configuration changes in this temperature range.

The previous studies[2,4] involved use of tetraalkylammonium ions with chain lengths up to *n*-butyl. As the chain length increases and as concentration increases, the greater will be the probability of micelle formation.[10] In the present study, both the length of the alkyl chain (ethyl) and the concentration of the cation (0.05 M) are such that it is unlikely that micelles are present.[10] It was also observed that when the concentration of the cation is increased fivefold, the observed interaction parameter ratios are unchanged within experimental error, indicating that micelles are also not present in this system even at the higher concentrations.

The Solomon relaxation model[5] is not strictly speaking applicable to the present case. In these systems with strongly anisotropic g factors, T_2 will have an angular dependence. This dependence could be taken into account by using the Solomon treatment if g-factor components in solution were known. Unfortunately, neither the components themselves nor the extent to which ion pairing influences the components is known, so the effect cannot be explicitly accounted for in our calculations. However, examination of the Solomon equations indicates that inclusion of g-factor anisotropy would result in an expression which would be the sum of a large number of terms, each containing the geometric factor r^{-6}. If the expression excluding the geometric factor has the same or approximately the same numerical value for both methyl and methylene protons (when averaged over all configurations), then eq 3 will be at least approximately correct. Since the ion-pair model involves many configurations and since the cation itself is highly symmetric, the approximation is probably justified. Certainly the reasonable results of the calculations support the approximation.

Acknowledgments. We thank Mr. Raymond F. Novak for synthesizing some of the compounds used in this study. Support of the Office of Water Resources Research through Grants A-012-MO and A-022-MO is gratefully acknowledged.

[10] C. W. Davies, "Ion Association," Butterworth Inc., Washington, D. C., 1962, pp 117–127.

Hydrolysis and Nucleophilic Substitution of the Hexachloroantimonate(V) Ion in the pH Range 2–12

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Abstract: The hydrolysis reaction of $SbCl_6{}^-$ has been investigated in the pH range 2–12. The final product of the reaction is the $Sb(OH)_6{}^-$ ion. The rate of the reaction has been measured by use of a spectrophotometric method in acetate, phosphate, borate, ammonia, and carbonate buffers. In the acid region the rate is independent of pH. In the basic region the reaction is catalyzed by OH^- and by the basic component of the buffer. In ammonia buffers at ionic strength = 0.10, the pseudo-first-order rate constant is given by $k = k_0 + k_{OH^-}[OH^-] + k_{NH_3}[NH_3]$, where $k_0 = 2.74 \times 10^{-5}$ sec^{-1}, $k_{OH^-} = 1.56$ sec^{-1} M^{-1}, and $k_{NH_3} = 8 \times 10^{-5}$ sec^{-1} M^{-1}. Intermediates of measurable lifetime are formed with the buffer bases. The behavior in basic solution provides a good example of an SN2 mechanism in the substitution reactions of an octahedral complex.

In hydrochloric acid solution the hexachloroantimonate(V) ion, $SbCl_6{}^-$, undergoes hydrolysis at a measurable rate.[2] The observations are consistent with the interpretation that the hydrolysis occurs stepwise, with only the rate of the first step being measurable.

$$SbCl_6{}^- \xrightarrow{k} Sb(OH)Cl_5{}^- \xrightarrow{\text{fast}} Sb(OH)_2Cl_4{}^-, \text{ etc.}$$

The final product of the hydrolysis depends on the H^+ and Cl^- concentrations, but in any case is an equilibrium mixture of complexes of type $Sb(OH)_xCl_{6-x}{}^-$.

Quantitative measurements of the rate were made by Neumann and Ramette.[3] Using a spectrophotometric method they determined rates under conditions where the reaction was pseudo first order; *i.e.*, rate = $k_h \cdot [SbCl_6{}^-]$. The reaction was accelerated by hydrogen ions. At a total chloride concentration of 6 M, the

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[1] Taken in part from a thesis submitted by S. B. Willis in partial fulfillment of the requirements for the M.S. degree, June 1966.

[2] H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 2611 (1954).

[3] H. M. Neumann and R. W. Ramette, *ibid.*, **78**, 1848 (1956).