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Nuclear Magnetic Resonance Study of Ion Association between Quaternary Ammonium Ions and Hexacyanoferrate(III) Ion[1]

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Shifts that occur in the positions of the proton resonance absorption peaks of aqueous quaternary ammonium ions on addition of hexacyanoferrate(III) ion are interpreted as evidence for ion-pair formation. The equilibrium quotient for ion-pair formation in 0.01 to 0.12 M $[(CH_3)_4N]_3Fe(CN)_6$ is 21 M^{-1} at 25°. For other quaternary ammonium salts the values of the quotients are approximately 10 M^{-1} under similar conditions. Evidence is presented that the shifts occur through the "pseudocontact" mechanism. A simple structural model of the ion pairs is proposed and used to explain the observed shifts.

Introduction

Kinetic studies of the isotopic exchange reaction between hexacyanoferrate(II) and -(III) ions in dilute aqueous tetraalkylammonium hydroxide solutions indicated that the reactants may be associated to some extent with the cations.[2] No direct evidence on this point has been reported to our knowledge.

Many polyvalent cations associate with ferricyanide ion in aqueous solution, but of the univalent cations only potassium ion has been reported to associate.[3] The association constant for the K^+–$Fe(CN)_6^{3-}$ ion pair at 25° was estimated to be about 20 from small differences between the conductivities of dilute $K_3Fe(CN)_6$ solutions and the Onsager limiting slope.[4] No evidence has been found for the association of H^+ and $Fe(CN)_6^{3-}$; the association constant is estimated[5] to be <10.

In this paper we present evidence from n.m.r. measurements that ion pairs are formed between quaternary ammonium ions and ferricyanide ion in aqueous solution. The evidence rests on the large shifts that were observed in the positions of proton absorption peaks for the various cations when the paramagnetic ferricyanide ion was added to a solution. Since the shifts are caused by isotropic hyperfine interactions between the unpaired electron and protons,[6] some close association between cation and anion must occur.

While this work was in progress, evidence was presented from n.m.r. measurements for the formation of ion pairs between tetra-*n*-butylammonium ions and several anions in nonaqueous media.[7,8]

Experimental

Reagents.—The following reagents were used without further purification: quaternary ammonium salts (Eastman Organic Chemicals), sodium 3-trimethylsilyl-1-propanesulfonate (Eastman Organic Chemicals), and deuterium oxide (Liquid Carbonic). Potassium ferricyanide (Fisher Scientific) was dried for 1 hr. at 100° before use. Potassium chromicyanide (K and K Laboratories) was recrystallized twice from water and dried for 1 hr. at 100° before use. Tetramethylammonium ferricyanide was prepared by neutralizing tetramethylammonium hydroxide with ferricyanic acid. Tetramethylammonium hydroxide was prepared by treating the bromide with excess silver oxide, filtering, and passing the filtrate through a column of Dowex 1-X4 in the OH^- form. Ferricyanic acid was prepared by passing potassium ferricyanide through a column of Dowex 50W-X4 in the H^+ form; light was carefully excluded.

N.m.r. Measurements.—The n.m.r. spectra of D_2O solutions were determined using a Varian Associates HR spectrometer operating at 56.4 Mc./sec. and equipped with pulsing units to increase base-line stability of paramagnetic solutions. Chemical shifts were measured by the side-band technique. All solutions were 0.04 M in sodium 3-trimethylsilyl-1-propanesulfonate, which was used as an internal standard. One set of solutions also contained tetramethylammonium ferricyanide at concentrations ranging from 0.01 to 0.12 M. Other sets contained 0.04 M quaternary ammonium bromide or hydroxide and 0 to $\sim$1 M potassium ferricyanide or other salts.

Results and Discussion

Plots of the chemical shift δ, relative to the internal reference, of a magnetically equivalent set of protons in quaternary ammonium ion *vs.* concentration of $K_3Fe(CN)_6$ were all found to be curved and to approach zero slope at the higher concentrations of $K_3Fe(CN)_6$ as is illustrated in Figure 1. The shape of the curves suggests ion association, which we assume is limited to formation of ion pairs.

$$R_4N^+ + Fe(CN)_6^{3-} \rightleftharpoons R_4N^+Fe(CN)_6^{3-}$$

The equilibrium quotient K_c for this reaction is given by the equation

$$K_c = \frac{K}{Y} = \frac{[R_4N^+Fe(CN)_6^{3-}]}{[R_4N^+][Fe(CN)_6^{3-}]} \qquad (1)$$

in which K is the equilibrium constant and Y is the appropriate function of molar activity coefficients of the species involved.

Rapid exchange of R_4N^+ ions between the ion-pair sites and the bulk solution will cause the n.m.r. peak of a set of equivalent protons to be a collapsed singlet with a chemical shift δ given by[9]

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[1] This work was supported by the National Science Foundation under grant No. G-24219.

[2] R. J. Campion, Ph.D. Thesis, Washington University, 1963; R. J. Campion, P. King, and A. C. Wahl, Paper 74, Division of Inorganic Chemistry, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.

[3] C. W. Davies, "Ion Association," Butterworth Inc., Washington, D. C., 1962, pp. 169–171.

[4] J. C. James and C. B. Monk, *Trans. Faraday Soc.*, **46**, 1041 (1950).

[5] J. Jordan and G. J. Ewing, *Inorg. Chem.*, **1**, 587 (1962).

[6] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

[7] R. L. Buckson and S. G. Smith, *J. Phys. Chem.*, **68**, 1875 (1964).

[8] G. N. La Mar, *J. Chem. Phys.*, **41**, 2992 (1964).

[9] H. S. Gutowsky and A. Saika, *ibid.*, **21**, 1688 (1953).

$$\delta = \frac{[R_4N^+]}{[R_4N^+]_T}\delta_0 + \frac{[R_4N^+Fe(CN)_6^{3-}]}{[R_4N^+]_T}\delta_p \qquad (2)$$

where δ_0 and δ_p are the chemical shifts of protons in the bulk solution and in the ion pairs, respectively, and $[R_4N^+]_T = [R_4N^+] + [R_4N^+Fe(CN)_6^{3-}]$.

$[(CH_3)_4N]_3Fe(CN)_6$.—The chemical shift for protons in $(CH_3)_4N^+$ was investigated at 25° as a function of $[(CH_3)_4N]_3Fe(CN)_6$ concentration up to ~0.12 *M*, the solubility. The experimentally determined plot of $(\delta - \delta_0)$ *vs.* concentration may be fit by eq. 1 and 2, employing K_c and $(\delta_p - \delta_0)$ as adjustable parameters. The value of K_c may be concentration dependent, and in attempting to fit the experimental data we have considered several forms of the theoretical expression[10] for Y at 25° as a function of ionic strength, μ.

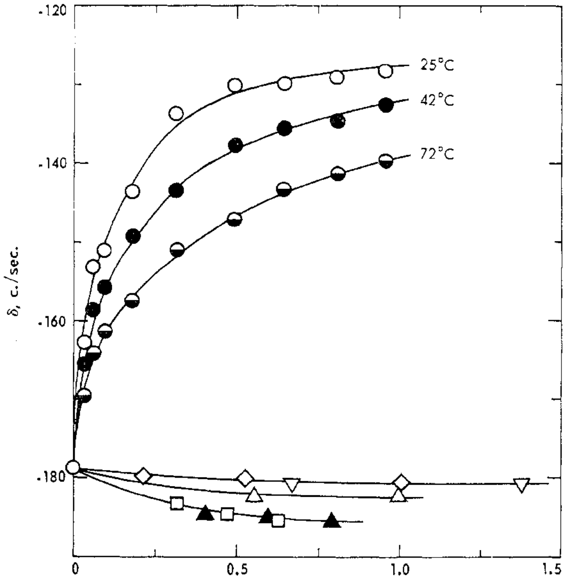

Figure 1.—Proton chemical shift δ, relative to 0.04 *M* sodium 3-trimethylsilyl-1-propanesulfonate, of 0.04 *M* $(CH_3)_4NOD$ as a function of concentration of added electrolyte: ○, ●, ◒, $K_3Fe(CN)_6$; □, $K_4Fe(CN)_6$; ▲, $Na_3Co(CN)_6$; ◇, K_2CrO_4; △, KI; ▽, KCl. Temperature 25°, unless specified otherwise.

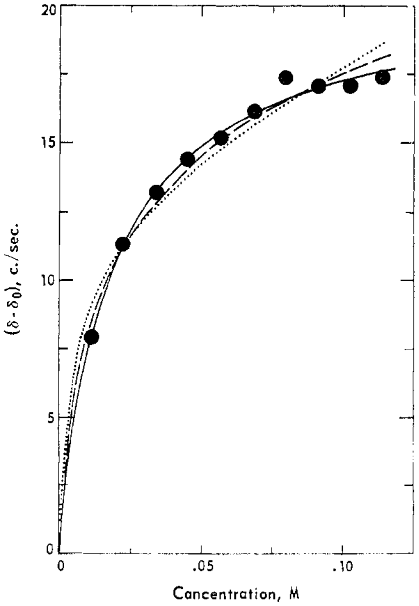

Figure 2.—Chemical shift *vs.* $[(CH_3)_4N]_3Fe(CN)_6$ concentration. δ_0 was determined for $(CH_3)_4NOD$ solutions. Points represent experimental values. Curves are calculated from eq. 1, 2, and 3: ——— for $K_c = 21\ M^{-1}$, $(\delta_p = \delta_0) = 63$ c.p.s., Y constant; — — — for $K = 40$, $(\delta_p - \delta_0) = 85$ c.p.s., $a = 8$ Å., $B = 0$; . . . . . . for $K = 54$, $(\delta_p - \delta_0) = 90$, $a = 1/0.329$, $B = 0.2$.

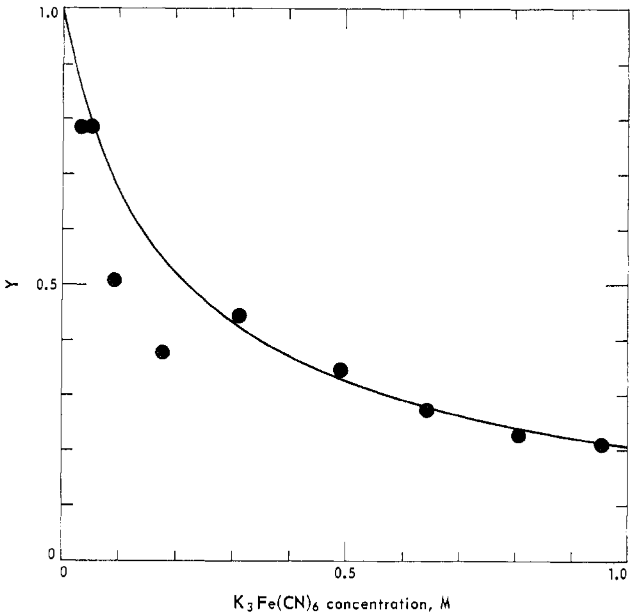

Figure 3.—Variation of Y for $(CH_3)_4NOD$, $K_3Fe(CN)_6$ solution *vs.* $K_3Fe(CN)_6$ concentration at 25°. Points are calculated from measured $(\delta - \delta_0)$ values and eq. 1 and 2 with $(\delta_p - \delta_0) = 63$. Complete dissociation of $K_3Fe(CN)_6$ is assumed. The line represents the expected variation in Y if $K_c' = 1.8\ M^{-1}$ (Y' constant).

$$\log Y = \Delta z^2 \left\{\frac{0.509\sqrt{\mu}}{1 + 0.329a\sqrt{\mu}} - B\mu\right\} \qquad (3)$$

Several curves calculated for $\Delta z^2 = 6$ are shown in Figure 2 with the experimental points. The continuous line was calculated for Y being constant in the concentration range investigated, a situation which is predicted approximately by eq. 3 when $a = 8$ Å. and $B = 0.2$, the calculated values of Y ranging from 2.4 to 3.2. The broken and dotted lines were calculated for other reasonable or frequently assumed values of a and B. The values, given in the figure caption, result in considerable variation of Y with concentration. As can be seen the curves represent the data almost equally well. It is not possible, therefore, to choose between the various expressions for Y or to obtain a unique or "best" value for K. However, for simplicity we have adopted the treatment with Y constant (continuous line in Figure 2) for the $[(CH_3)_4N]_3Fe(CN)_6$ solutions, which will serve as reference for other solutions.

The variation of the methyl proton chemical shift in solutions of $(CH_3)_4NOD$ ranging from 0.02 to 1.0 *M* was found to be less than 1.0 c.p.s. Thus the contribution to $(\delta_p - \delta_0)$ due to variation of the $(CH_3)_4N^+$ concentration is negligible.

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[10] C. B. Monk, "Electrolytic Dissociation," Academic Press, New York, N. Y., 1961, p. 153.

$(CH_3)_4NOD$ and $K_3Fe(CN)_6$.—The chemical shift of $(CH_3)_4N^+$ was also investigated as a function of $K_3Fe(CN)_6$ concentration to 1.0 M, the concentration of $(CH_3)_4NOD$ being constant at 0.04 M. As the concentration of $K_3Fe(CN)_6$ increased the chemical shift increased as shown in Figure 1.

The data may be interpreted by use of eq. 1, 2, and 3 as was done in the previous section if $K_3Fe(CN)_6$ is assumed to be completely dissociated. However, values of K_c and $(\delta_p - \delta_0)$ were obtained that differed from those obtained for $[(CH_3)_4N]_3Fe(CN)_6$ solutions, and, if the value of $(\delta_p - \delta_0)$ determined for the $[(CH_3)_4N]_3Fe(CN)_6$ solutions was adopted, the value of K_c, and therefore Y, varied with $K_3Fe(CN)_6$ concentration. This effect is illustrated in Figure 3, where the values of Y relative to the value in $[(CH_3)_4N]_3Fe(CN)_6$ solutions are plotted. The variation of Y is not surprising since a larger concentration range was investigated than for the $[(CH_3)_4N]_3Fe(CN)_6$ solutions and additional ions, K^+ and OD^-, were present, the former at large concentrations. The effect may be due in part to ion association between K^+ and $Fe(CN)_6{}^{3-}$.

If the effect is attributed entirely to ion-pair formation

$$K^+ + Fe(CN)_6{}^{3-} \rightleftarrows K^+Fe(CN)_6{}^{3-}$$

$$K_c' = K'/Y' = \frac{[K^+Fe(CN)_6{}^{3-}]}{[K^+][Fe(CN)_6{}^{3-}]} \qquad (4)$$

the magnitude of this association can be estimated. The line in Figure 3 represents the variation in Y that would result if $K_c' = 1.8$ (Y' constant). The large deviation of two points from the curve could result from errors of 3 to 5 c.p.s. in the measurements; these errors are larger than our estimated experimental uncertainties of $\backsim$1 c.p.s., so the deviations indicate that the treatment is an oversimplified one.

Use of eq. 3 for estimation of Y and Y' does not improve the fit, but it does increase the complexity of the calculation. (A value of $K' \approx 4$ was obtained when the parameters associated with the broken line in Figure 2 were used.) Therefore, for interpretation of the remaining data we assume that Y is given by the line in Figure 3. Although this line was derived from consideration of a particular way in which the activity of $Fe(CN)_6{}^{3-}$ could be changed, the line by representing the empirical data reasonably well may be considered an empirical correction of the activity coefficient expression to the conditions of the 0.01 to 0.12 M $[(CH_3)_4N]_3Fe(CN)_6$ solutions. The representation of the line by eq. 1, 2, and 4 is of course a convenience.

Figure 1 illustrates the variation of chemical shift with $K_3Fe(CN)_6$ concentration as a function of temperature. We have interpreted the data assuming Y and Y' constant and $(\delta_p - \delta_0)$ proportional to $1/T$. That a $1/T$ proportionality is to be expected will be shown later in the article. Equations 1, 2, and 4 were used to fit the data employing K_c and K_c' as adjustable parameters. It was possible to determine unique values of K_c and K_c' which give the best agreement between the equations and the data. These values are presented in Table I. From plots of log K *vs.* $1/T$, we estimate ΔH values of -6 and -8 kcal./mole for the formation of $(CH_3)_4N^+Fe(CN)_6{}^{3-}$ and $K^+Fe(CN)_6{}^{3-}$, respectively.

TABLE I

EQUILIBRIUM QUOTIENTS FOR FORMATION OF $(CH_3)_4N^+Fe(CN)_6{}^{3-}$ AND $K^+Fe(CN)_6{}^{3-}$

	25°	42°	72°
$(\delta_p - \delta_0)$, c.p.s.	63	60	54
K_c, M^{-1}	21	8	5
K_c', M^{-1}	1.8	0.5	0.3

R_4NBr and $K_3Fe(CN)_6$.—The chemical shifts for a number of quaternary ammonium ions were investigated as a function of $K_3Fe(CN)_6$ concentration. For interpretation of the data eq. 5 was derived[11-14] from eq. 1 and 2. The equation is applicable when ion

$$\frac{[Fe(CN)_6{}^{3-}]}{\delta - \delta_0} = \frac{[Fe(CN)_6{}^{3-}]}{\delta_p - \delta_0} + \frac{1}{K_c(\delta - \delta_0)} \qquad (5)$$

association is limited to ion pairs, when $[R_4N^+Fe(CN)_6{}^{3-}] \ll [Fe(CN)_6{}^{3-}]$, and when Y and K_c are constant. Under these conditions a plot of $[Fe(CN)_6{}^{3-}]/(\delta - \delta_0)$ *vs.* $[Fe(CN)_6{}^{3-}]$ should yield a straight line.

The straightness of the line seems not to be very sensitive to conditions. We obtained straight lines using formal $K_3Fe(CN)_6$ concentrations for $[Fe(CN)_6{}^{3-}]$, although as shown in the previous section both this equality and the constancy of K_c and Y do not hold.

In the final analysis of the data, the $[Fe(CN)_6{}^{3-}]$ values required for the plot were obtained by solving eq. 1 and 4 by successive approximations. A family of curves, giving $[Fe(CN)_6{}^{3-}]$ as a function of formal $K_3Fe(CN)_6$ concentration, was drawn with K_c as a variable parameter and $K_c' = 1.8$. Values of $[Fe(CN)_6{}^{3-}]$ were taken from this plot for an assumed value of K_c, a plot of $[Fe(CN)_6{}^{3-}]/(\delta - \delta_0)$ *vs.* $[Fe(CN)_6{}^{3-}]$ was made, and the values of $(\delta_p - \delta_0)$ and K_c were obtained from the slope and the intercept of the plot. Then, the whole process was repeated for another assumed K_c value close to the previously calculated K_c value. It was found that the calculated K_c values were quite dependent upon the value of K_c assumed but that the calculated $(\delta_p - \delta_0)$ values were not. In general, calculations were made for assumed K_c values of 6, 10, and 18. The final values of K_c and $(\delta_p - \delta_0)$, presented in Table II, are either values for which the assumed and calculated values of K_c were almost equal, or else are average values obtained from the two calculations giving the best agreement between assumed and calculated values.

Values of $(\delta_p - \delta_0) = 1/\text{slope}$ are considerably more accurate than values of $K_c = \text{slope}/\text{intercept}$. We

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[11] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

[12] S. R. Cohen and R. A. Plane, *J. Phys. Chem.*, **61**, 1096 (1957).

[13] M. Alei, *Inorg. Chem.*, **3**, 44 (1964).

[14] M. W. Hanna and A. L. Ashbough, *J. Phys. Chem.*, **68**, 811 (1964).

TABLE II
INTERACTION BETWEEN QUATERNARY AMMONIUM IONS AND FERRICYANIDE ION AT 25°

Ion	Proton	δ_0, c.p.s.	$(\delta_p - \delta_0)$, c.p.s.	K_c, M^{-1}
$(CH_3)_4N^+$	α^a	−179.0	63	21
$(C_2H_5)_4N^+$	α^a	−183.4	106	8
	β^b	−68.6	64	9
$(C_3H_7)_4N^+$	α	−174.3	104	6
	β	−95.4	88	7
	γ	−52.2	56	6
$(C_4H_9)_4N^+$	α	−179.7	99	6
	δ	−53.1	31	8
$(C_2H_5)_3NCH_3^+$	α	−186.4	111	7
	β	−74.6	59	14
	α'^c	−164.7	85	11
$C_2H_5N(CH_3)_3^+$	β	−72.5	80	4
	α'	−174.8	103	6
$C_6H_5N(CH_3)_3^+$	α'	−209.5	69	10
	ϕ^d	−437.7	55	8

[a] Spin–spin coupling constant between nitrogen and proton, $J_{N\alpha} = 2.0$ c.p.s. [b] $J_{N\alpha} = 0$; $J_{N\beta} = 2.0$ c.p.s.; $J_{\alpha\beta} = 7.4$ c.p.s. [see J. M. Anderson, J. D. Baldeschwieler, D. C. Dittmer, and W. D. Phillips, *J. Chem. Phys.*, **38**, 1260 (1963)]. [c] α' refers to methyl group attached to the nitrogen; α and β refer to other groups. [d] Shifts for all phenyl protons are the same within ~6 c.p.s.

estimate that the uncertainties in the values of $(\delta_p - \delta_0)$ are ~10% and those in the values of K_c are ~50%. For a given cation, values of K_c derived from the shifts for different protons generally agree within this uncertainty. The largest discrepancy is for $(C_2H_5)_3NCH_3^+$; examination of the data shows that an error of 1 c.p.s. in several of the measurements could change the K_c values by about 20% and $(\delta_p - \delta_0)$ values by about 6%.

It should be noted that the use of $K_c' = 1.8$ in the calculation makes activity coefficient corrections relative to the 0.01 to 0.12 M $[(CH_3)_4N]_3Fe(CN)_6$ solutions. Therefore, the K_c values in Table II apply to solutions of such concentrations and not to the more concentrated solutions of $K_3Fe(CN)_6$ used in the measurements.

The value of the association constant K at 25° calculated from Bjerrum's theory of ion association[15] is 18 if the distance of closest approach of the +1 and −3 ions is 8 Å. Although this value cannot be compared directly with the experimental K_c values because of a lack of knowledge of activity coefficients, it is of the correct magnitude. However, the Bjerrum theory predicts an increase in K with temperature, whereas a decrease in K_c is observed (Table I). Also our model for the ion pairs, which is discussed later in the article, describes a discrete entity, not a mixture of all pairs separated by distances less than that for a probability minimum.

$(CH_3)_4$NOD and $K_3Cr(CN)_6$.—The $(CH_3)_4N^+$ proton n.m.r. peaks are very broad in the presence of $Cr(CN)_6^{3-}$, and chemical shifts could not be measured at $Cr(CN)_6^{3-}$ concentrations greater than 0.04 M. In solutions, each 0.0422 M $(CH_3)_4NOD$, 0.04 M in sodium 3-trimethylsilyl-1-propanesulfonate, and (a) 0.013 M, (b) 0.026 M, and (c) 0.039 M in $K_3Cr(CN)_6$, the shifts $(\delta - \delta_0)$ were 4, 11, and 17 c.p.s., respectively, at 25°. These values are the same, within the experimental uncertainty, as those estimated by interpolation in Figure 1 for $K_3Fe(CN)_6$ solutions of corresponding concentrations.

$(CH_3N)_4$OD and Diamagnetic Salts.—The chemical shift for $(CH_3)_4N^+$ protons was investigated for 0.04 M $(CH_3)_4NOD$ solutions as a function of salt concentration to 1.0 M. The salts were KCl, KI, $Na_3Co(CN)_6$, and $K_4Fe(CN)_6$. As shown in Figure 1, the chemical shifts observed were small $(\delta - \delta_0 < 6$ c.p.s.) and negative (downfield) as contrasted to the large positive shifts caused by paramagnetic salts.

The large positive shifts observed with $K_3Fe(CN)_6$ and $K_3Cr(CN)_6$ may then be the sum of two shifts, one the large upfield shift due to the paramagnetic anions and the other the smaller downfield shift due to the intrinsic diamagnetism of the anions. This view is supported by our observation that 0 to 1 M solutions of K_2CrO_4, which has a small temperature-independent paramagnetism,[16] cause a chemical shift of the $(CH_3)_4N^+$ protons of less than 2 c.p.s. (see Figure 1). Apparently the paramagnetic and diamagnetic contributions cancel one another.

An attempt was made to investigate association between $(CH_3)_4N^+$ and $Fe(CN)_6^{4-}$ by changing the $K_4Fe(CN)_6$ concentration in solutions of constant $(CH_3)_4NBr$ and $K_3Fe(CN)_6$ concentrations. It was anticipated that increasing the concentration of $K_4Fe(CN)_6$ would, through association of $Fe(CN)_6^{4-}$ with $(CH_3)_4N^+$, decrease the chemical shift caused by association of $(CH_3)_4N^+$ and $Fe(CN)_6^{3-}$. Some decrease was observed, but it was small, so association between $(CH_3)_4N^+$ and $Fe(CN)_6^{4-}$ must have been small in the solutions investigated. This could be due either to a small association constant, about one-half that for $(CH_3)_4N^+$ and $Fe(CN)_6^{3-}$, which would be surprising in view of the ionic charges, or to extensive association between K^+ and $Fe(CN)_6^{4-}$, so that little free $Fe(CN)_6^{4-}$ was present in the solutions.

Mechanisms of Interaction.—The small shift caused by diamagnetic anions can be explained in terms of small changes of the electric field at a proton arising from other parts of the molecule or from neighboring molecules.[17,18] Such field changes generally cause changes in chemical shifts of the order of 0.1 p.p.m., which is the magnitude of the changes shown in Figure 1 for the diamagnetic anions.

Two types of interactions between unpaired electrons in a paramagnetic anion and a proton may be con-

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(15) N. Bjerrum, *Kgl. Danske Videnskab. Selskab*, **7**, No. 9 (1926); H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, p. 70.

(16) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 205.

(17) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(18) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

sidered[19,20] as giving rise to the observed shifts. The interactions have been designated the "contact" and "pseudo-contact" contributions to the isotropic hyperfine interaction. The contact interaction may be considered to arise from σ-overlap of the Fe(III) t_{2g} orbital which contains the magnetic electron with a proton in the ion pair.[13] The contact shift is related to the hyperfine coupling constant, a_i, by the equation[21]

$$\left(\frac{\Delta f}{f}\right)_i = a_i \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{3kT} \qquad (6)$$

where Δf_i is the shift in the resonance frequency, f_i, upon formation of an ion pair, γ_e and γ_H are the gyromagnetic ratios of the electron and the proton, respectively, g and S are the spectroscopic splitting factor and the spin, respectively, of the unpaired electron(s) in the paramagnetic anion, and β is the Bohr magneton.

The pseudo-contact interaction arises from the dipole field of the net induced paramagnetic moment which is seen by the proton and is dependent upon g factor anisotropy. The pseudo-contact shift is given by the relationship[20]

$$\left(\frac{\Delta f}{f}\right)_i = -\frac{\beta^2 S(S+1)(3\cos^2\chi_i - 1)}{27 r_i^3 kT}(g_\parallel + 2g_\perp)(g_\parallel - g_\perp) \qquad (7)$$

where r_i is the distance between the paramagnetic anion and the proton i and χ_i is the angle between the radius vector $\vec{r}_i$ and the crystal-field axis z of the paramagnetic anion (see Figure 4). Equation 7 applies when $T_{1e} >> \tau$, where T_{1e} is the spin-lattice relaxation time of the electron and τ is the characteristic correlation time of the tumbling motion. If T_{1e} for the metal complex is very short, the condition may not hold. For the case $T_{1e} << \tau$, the pseudo-contact shift will be given by[20]

$$\left(\frac{\Delta f}{f}\right)_i = -\frac{\beta^2 S(S+1)(3\cos^2\chi_i - 1)}{45 r_i^3 kT}(3g_\parallel^2 - g_\parallel g_\perp + 4g_\perp^2) \qquad (7a)$$

La Mar[8] proposed that the pseudo-contact mechanism was responsible for the shifts that he observed for protons in tetra-*n*-butylammonium ion associated with the paramagnetic anions $[(C_6H_5)_3P]CoI_3^-$ and $[(C_6H_5)_3P]NiI_3^-$ in deuteriochloroform solution. He explained the different direction of the shifts caused by the two anions by assuming different signs of the $(g_\parallel - g_\perp)$ factors in eq. 7.

We also propose that the pseudo-contact mechanism is responsible for the shifts that we observed for the protons in a quaternary ammonium ion associated with $Fe(CN)_6^{3-}$. Assumption of this mechanism allows a reasonable explanation for the approximately equal shifts caused by $Fe(CN)_6^{3-}$ and $Cr(CN)_6^{3-}$ and, with a simple model for the ion pairs, calculation of the relative shifts for different sets of equivalent protons in various quaternary ammonium ions.

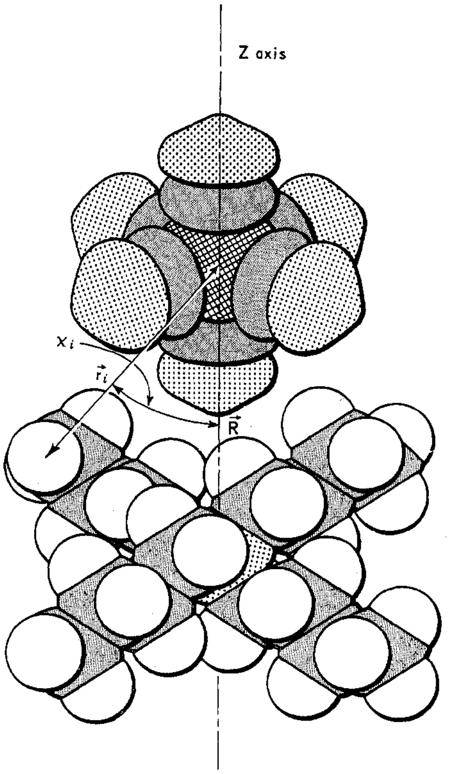

Figure 4.—A model of the ion pair between tetra-*n*-butylammonium and ferricyanide ions. The C atoms are darkly shaded, the N atoms are lightly shaded, the Fe atom is cross hatched, and H atoms are unshaded. The nitrogen atom in $(C_4H_9)_4N^+$ is only partly visible; R is the distance from its center to the center of the iron atom.

The $Fe(CN)_6^{3-}$ and $Cr(CN)_6^{3-}$ ions have spins of $^1/_2$ and $^3/_2$, respectively, so the ratio of the $S(S+1)$ factors is 5 for either the contact or pseudo-contact interaction. To account for the approximately equal $(CH_3)_4N^+$ proton shifts caused by the two anions the ratio of the other factors must be $\sim ^1/_5$. The two anions have the same charge and are nearly the same size so the association constants and geometries of the two ion pairs should be essentially the same. The $(g_\parallel - g_\perp)$ factor for $Fe(CN)_6^{3-}$ in solid $K_3Fe(CN)_6$ is about 1.4,[22] and a value of about 1.0 for an aqueous ion pair can account for shifts if the model described in the next section is assumed. For free $Cr(CN)_6^{3-}$ the $(g_\parallel - g_\perp)$ factor should be zero, and in an ion pair it should be small, a value of 0.2 to 0.3, as required for the explanation, being reasonable. Of course, for the contact mechanism to apply the product $a_i g$ from eq. 6 could be a factor of about five greater for $(CH_3)_4N^+Fe(CN)_6^{3-}$ than for $(CH_3)_4N^+Cr(CN)_6^{3-}$, although we know of no reason for assuming so.

Model for Ion Pairs.—For a system containing more than one set of equivalent protons and having the

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dominant contribution to the isotropic shift from the pseudo-contact interaction mechanism, it has been observed,[23] and is indicated by eq. 7 or 7a, that the relative shifts can be described solely in terms of molecular geometry, *i.e.*

$$\left(\frac{\Delta f}{f}\right)_i : \left(\frac{\Delta f}{f}\right)_j : \ldots = \left(\frac{3\cos^2\chi_i - 1}{r_i^3}\right) : \left(\frac{3\cos^2\chi_j - 1}{r_j^3}\right) : \ldots \quad (8)$$

La Mar[8] suggested a model for the ion pairs between $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ and $[(\text{C}_6\text{H}_5)_3\text{P}]\text{CoI}_3^-$ or $[(\text{C}_6\text{H}_5)_3\text{P}]\text{NiI}_3^-$ in which the cation tumbles rapidly with this center at an approximately fixed distance from a metal atom along the C_3 axis opposite the triphenylphosphine ligand. La Mar invoked tumbling to explain the observations that there were single resonance absorption lines for equivalent sets of protons in the cation and that shifts caused by ion-pair formation decreased for protons in the order α, β, γ, δ protons. However, tumbling is not necessary to explain the single lines since the rapid exchange at a frequency of $>10^3$ sec.$^{-1}$ between free cations and those in ion pairs is sufficient. Also, although La Mar's arguments based on tumbling explain qualitatively the relative shifts, the shifts may also be explained by a model of an ion pair with fixed geometry.

The model we propose for the ion pairs between tetraalkylammonium ions and ferricyanide ion is illustrated in Figure 4. Values of r_i and χ_i were calculated using this model and assuming a constant value of R = 8 Å. for all the tetraalkylammonium ions. Bond lengths of 1.47, 1.54, and 1.10 Å. were assumed for the C–N, C–C, and C–H bonds, respectively.[24] Bond angles were assumed to be the tetrahedral angle.

The calculated factors $(3\cos^2\chi_i - 1)/r_i^3$, calculated shifts, and observed shifts for the symmetrical tetraalkylammonium ions (normalized to methylene protons of tetraethylammonium ion using eq. 8) are presented in Table III. The normalization corresponds to the use of eq. 7 with $g_\parallel = 2.8$ and $g_\perp = 1.6$ or eq. 7a with $g_\parallel = 1.8$ and $g_\perp = 1.0$.

It is seen that calculations based on the simple model account satisfactorily for the observed shifts. Precise agreement is not expected since some factors of possible importance were not included in the model. These include shielding of protons from the paramagnetic dipole by solvent molecules and by carbon atoms between the proton and the iron atoms, variation of the distance R for different ion pairs, and deviation of some carbon chains from the zigzag structure.

TABLE III

CALCULATED SHIFTS[a] FOR PROTONS IN TETRAALKYLAMMONIUM–FERRICYNAMIDE ION PAIRS

(R = 8 Å.)

Carbon proton is attached to	$\frac{3\cos^2\chi_i - 1}{r_i^3} \times 10^{-22}$		$(\delta_p - \delta_0)_{\text{calcd}}$		$(\delta_p - \delta_0)_{\text{obsd}}$	
	CH$_2$	CH$_3$	CH$_2$	CH$_3$	CH$_2$	CH$_3$
1	0.418	0.386	(103)[b]	95	106[d] 104[e] 99[f]	63[c]
2	0.287	0.271	71	67	88[e]	64[d]
3	...	0.197	...	49	..	56[e]
4	...	0.122	...	30	..	31[f]

[a] C.p.s. [b] Reference. [c] Tetramethylammonium ion. [d] Tetraethylammonium ion. [e] Tetra-*n*-propylammonium ion. [f] Tetra-*n*-butylammonium ion.

The greatest difference between observed and calculated shifts is for $(\text{CH}_3)_4\text{N}^+\text{Fe(CN)}_6^{3-}$, for which the formation constant also differs from those for the other ion pairs; and, therefore, the structure or distance R of the ion pair may differ somewhat from the others.

The model is supported to some extent by other measurements. Raman[25] and X-ray[26] measurements show that the zigzag configuration of carbon chains is the most stable one and indicate that the most stable form of tetraalkylammonium ions may be one having two intersecting planar zigzag chains of atoms with bond angles very close to the tetrahedral angle, as is illustrated in Figure 4. Also, dipole-moment[27] measurements on alkyl halides indicate that polarity is not effectively transmitted along the chain, so it is reasonable to consider the positive charge of the tetraalkylammonium ion to be largely localized at the nitrogen atom. Thus, a negative cyanide ligand would be attracted to that point as proposed in the model.

The gradual decrease in $(\delta_p - \delta_0)$ values in going from α to δ protons is additional evidence for the "pseudocontact" mechanism. Assuming that ion-pair formation occurs only near the nitrogen atom in R_4N^+, the contact mechanism could cause the gradual decrease in $(\delta_p - \delta_0)$ values only if spin density were effectively transmitted down the alkyl chain, and e.s.r. studies indicate that this does not occur.[28]

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