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Study of Some Cyano–Metal Complexes by Nuclear Magnetic Resonance. I. Chemical Shifts and Line Widths of N^{14} and C^{13} Resonances

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Chemical shifts and line widths of N^{14} n.m.r. in aqueous solutions of various paramagnetic and diamagnetic complex cyanides are reported. The C^{13} resonance was detected in one paramagnetic complex ($K_3Fe(CN)_6$) and in several diamagnetic ones. Temperature and concentration dependence of the resonances for some compounds are also included. The results indicate that in both para- and diamagnetic complexes the line width is determined primarily by the quadrupolar relaxation. Line positions in the diamagnetic complexes do not vary much from complex to complex. In the paramagnetic complexes, on the other hand, considerable shifts have been detected and these are ascribed to the contact term. An exception both with respect to the N^{14} chemical shifts and the line width was found in $K_3Cr(CN)_6$.

Introduction

The nuclear magnetic resonance (n.m.r.) technique has been applied extensively to the study of the structure and dynamic processes of molecules in solution. Most research, however, has been confined to H^1 resonance, which for cyano–metal complexes would yield indirect and limited information on the molecular properties. Thus, for example, the effective magnetic moment for aqueous $K_3Fe(CN)_6$ as calculated from the longitudinal relaxation time, T_1, or the H^1 resonance[2] is only 0.12 B.M. as compared to the value of 2.4 B.M. calculated from the paramagnetic susceptibility. Similar results were obtained for aqueous $K_3Cr(CN)_6$. In the latter complex the electronic spin relaxation time, τ_s, is much longer than in $K_3Fe(CN)_6$. This effect is presumably due to the insensitivity of the environment to the presence of the $Fe(CN)_6^{-3}$ or $Cr(CN)_6^{-3}$ ions which is caused by the chemical inertness of the complexes. Therefore, we have chosen primarily the N^{14} and C^{13} n.m.r. to study the cyano–metal complexes in aqueous solutions.[3a] Proton n.m.r. measurements shall be described in a separate publication.

In this work the measurements of N^{14} and some C^{13} chemical shifts and N^{14} line widths are described. Some of the compounds studied are paramagnetic: $K_3Fe(CN)_6$, $K_3Mn(CN)_6$, $K_4Mn(CN)_6$,[3b] $K_3Cr(CN)_6$; whereas others are diamagnetic: $K_4Fe(CN)_6$, $K_3Co(CN)_6$, $K_2Ni(CN)_4$, $KCu(CN)_2$, $KAg(CN)_2$. The chemical shifts of the N^{14} resonance in the Fe(III), Cr(III), and Mn(III) complexes have previously been reported by Shulman.[4] He found that the N^{14} chemical shift in the Cr complex was significantly smaller than those in the Mn and Fe complexes. Shulman suggested that the shifts in $Mn(CN)_6^{-3}$ and $Fe(CN)_6^{-3}$ are not contact shifts but may be attributed to an anisotropic electronic g tensor which produces a nonvanishing average magnetic field component at the N^{14} nucleus. In this work we assumed that the N^{14} and C^{13} chemical shifts in the paramagnetic complexes would reflect the spin density distribution on the C and N atoms, provided their origin is the contact term. The latter assumption has been verified in the present work for the Fe and Mn complexes. Similar considerations have been used in evaluating the spin densities in various metal–organic complexes.[5] However, the C^{13} resonance could be detected only in $Fe(CN)_6^{-3}$, and thus most conclusions were drawn from the N^{14} shifts only.

The width of the lines, namely $1/T_2$, may be determined by quadrupolar relaxation, and in the case of paramagnetic complexes also by the relaxation of the unpaired electron. If, as turns out to be the case, the first mechanism predominates and assuming $T_1 = T_2$, we may in principle gain information about the quadrupole coupling constants and the correlation times from the measured line widths. The measured positions and widths of the lines shall be described and their significance discussed.

Experimental

Spectrometer.—All measurements were performed on a Varian DP60 spectrometer equipped with a V4311 4.3-Mc. fixed frequency unit for N^{14} spectra, a V4311 60-Mc. fixed frequency unit for H^1 spectra, and a V4210A variable frequency unit operating at 4.3 or 15 Mc. for N^{14} and C^{13} spectra, respectively. Broad-line technique with a 40 or 20 c.p.s. modulation was used for both N^{14} and C^{13} spectra. To avoid overmodulation, line widths were occasionally measured as a function of the modulation amplitude and the lowest possible amplitude was chosen for routine measurements. The amplitude of the modulation was about 0.3 gauss for lines where the peak to peak separation of the derivative curve was 1.5 gauss. The following procedure was used to measure the modulation amplitude: The H^1 resonance in H_2O is observed on the oscilloscope, and since its line width is less than the modulation amplitude two signals are observed which coalesce into a single peak when the magnetic field is scanned up- or downfield. The separation between the two coalesced peaks is equal to the peak to peak amplitude of modulation. The scanning unit was calibrated by the usual side-band technique. The separation between the two N^{14}

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[2] N. Bloembergen, "Nuclear Magnetic Relaxation" W. A. Benjamin, Inc., New York, N. Y., 1961, p. 97.

[3] (a) For a preliminary report see A. Loewenstein, M. Shporer, and G. Navon, *J. Am. Chem. Soc.*, **85**, 2855 (1963). (b) The authors are indebted to R. G. Shulman for the suggestion to include this compound in the study.

[4] R. G. Shulman, *J. Chem. Phys.*, **29**, 945 (1958).

[5] See, for example, D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).

resonances in a concentrated solution of NH_4NO_3 (5.0 gauss at 4.3 Mc.) was used as a standard.

Samples at room temperature (32°) were contained in 15-mm. o.d. Pyrex tubes. For measurements taken at higher or lower temperatures samples were contained in 8-mm. o.d. Pyrex tubes. These tubes were held in a specially constructed dewar that fitted into the probe of the V4210A radiofrequency unit. Hot or cold air was blown around the sample tube and the temperature was measured by a thermocouple inserted in the solution. The accuracy in the temperature measurements is estimated at $\pm 0.5°$.

The shifts were measured against an external reference in a 5-mm. o.d. tube inserted in the center of the 15-mm. sample tube. A bulk susceptibility correction was not applied since calculation shows it to be negligible.

Materials and Solutions.—The following materials were commercial C.P. reagents: $K_3Mn(CN)_6$ and $K_3Cr(CN)_6$ (A. D. McKay, Inc.), $Na_3Mn(CN)_6$, $K_2Ni(CN)_4$ (City Chemical Corp.), $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, $KAg(CN)_2$ (B.D.H.). Two procedures were used to synthesize $Na_4Mn(CN)_6$: (a) reducing $Na_3Mn(CN)_6$ by sodium dithionite in the presence of excess NaCN, and (b) adding excess NaCN to freshly prepared $MnCO_3$. The acids $H_3Fe(CN)_6$ and $H_4Fe(CN)_6$ were prepared according to the procedure given by Brauer.[6] The alkali and alkaline earth salts of $H_4Fe(CN)_6$ were prepared by adding equivalent amounts of the appropriate base to the acid and evaporating the solution to dryness. The analogous salts of $H_3Fe(CN)_6$ were prepared by precipitating the silver salt, $Ag_3Fe(CN)_6$, and then dissolving it with the corresponding alkali or alkaline earth chloride. The filtrate was evaporated to dryness.

Various complexes were prepared with KCN[7] enriched to 15 atom % with C^{13}. The compound $K_3Fe(C^{13}N)_6$ was prepared using a procedure similar to that given by Thompson[8]; passing Cl_2 gas through $K_4Fe(C^{13}N)_6$ solution. The latter was prepared from equivalent amounts of $FeSO_4$ and $KC^{13}N$. The preparation procedure of $K_2Ni(C^{13}N)_4$ is given in the literature.[9] The compound $Na_3Mn(C^{13}N)_6$ was prepared by adding $KC^{13}N$ to $Na_3Mn(CN)_6$— the ligand exchange is relatively fast for this complex[10]— the mixture was not separated. The compounds $K_3Cr(CN)_6$ and $K_3Cr(C^{13}N)_6$ were prepared by the procedure given in ref. 9 (p. 203) with a slight modification of using $CrCl_3$ instead of $K_2Cr_2O_7$ as starting material. The procedure given in ref. 9 (p. 225) was used to prepare $K_3Co(CN)_6$ and $K_3Co(C^{13}N)_6$.

Solutions of known concentration were usually prepared by weighing the dry material. In some experiments, especially where hygroscopic materials were involved, concentrations were determined by titrating the $Fe(CN)_6^{-3}$ and $Fe(CN)^{-4}$ ions using standard procedures.

Viscosities were measured with an Ostwald viscosimeter at 32°.

Results and Discussion

The chemicals shifts and line widths of N^{14} resonances and the positions of the detectable C^{13} resonances are given in Table I. The N^{14} resonance positions are close to the position of N^{14} resonance in CH_3CN and almost equal for all diamagnetic complexes. The shifts do not depend on the type of coordination or on the nature of the central metal atom, which indicates that they are predominantly determined by the C≡N bond. The N^{14} line widths do not vary much from one diamagnetic complex to the other; they are, however, much larger than the N^{14} line width in CH_3CN, which is about 0.3 gauss.

TABLE I
POSITIONS AND LINE WIDTHS (IN GAUSS) OF N^{14} AND C^{13} RESONANCES AT 32°

Compound[g]	N^{14} position[a]	Width of N^{14} resonance[b]	C^{13} position[c]
$K_3Mn(CN)_6$	−15.0	2[f]	...[d]
$K_3Fe(CN)_6$	−10.9	1.5–2.0[e]	+50
$Na_4Mn(CN)_6$	−8.7	4[f]	...[d]
$K_3Cr(CN)_6$	−5.4	5[f]	...[d]
$K_4Fe(CN)_6$	−0.7	1.8–2.2[e]	+0.8
$K_3Co(CN)_6$	−0.8	2–3	0[f]
$KCu(CN)_2$	−0.3[f]	2–3	...
$K_2Ni(CN)_4$	−0.3[f]	2[f]	0[f]
$KAg(CN)_2$	−0.3[f]	2[f]	...

[a] Measured relative to N^{14} resonance in CH_3CN. [b] Full width between peaks of derivative curve. [c] Measured relative to C^{13} resonance in C_6H_6. [d] Unsuccessful attempts to detect the C^{13} resonance in C^{13}-enriched samples. [e] Concentration dependence—see Table II. [f] Approximate values. [g] Saturated solutions, except $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$.

On the other hand, both the positions and widths vary from one paramagnetic complex to the other. The shift in $K_3Cr(CN)_6$ is the smallest but still much larger than previously reported by Shulman.[4] The temperature dependence of the N^{14} and C^{13} resonance positions in some paramagnetic complexes is shown in Figure 1. The temperature dependence of the N^{14} resonance in $K_4Mn(CN)_6$ was not measured and in $K_3Cr(CN)_6$ the change in its position is less than 0.5 gauss in the temperature range 25–83°. Analysis of the data shows that for $K_3Fe(CN)_6$ and $K_3Mn(CN)_6$

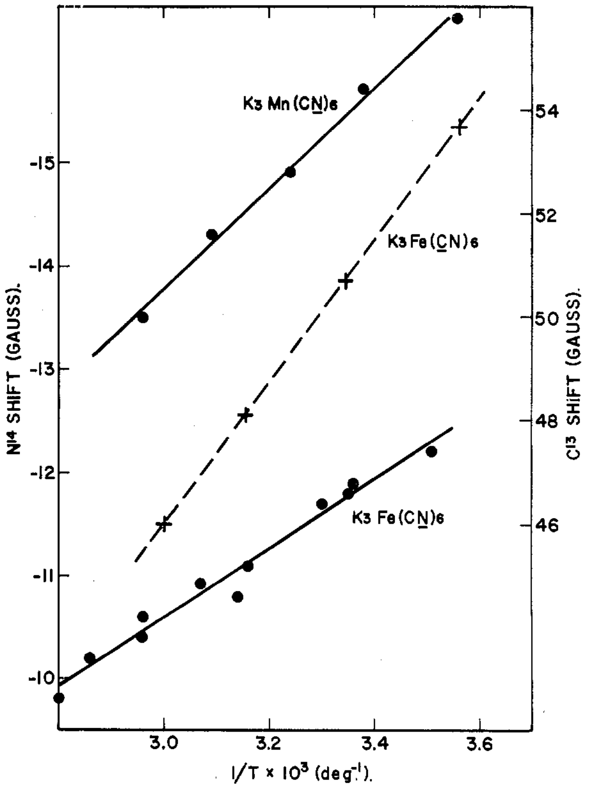

Figure 1.—Temperature dependence of N^{14} resonances (measured relative to CH_3CN) and of C^{13} resonances (measured relative to C_6H_6). N^{14} resonances shift to higher field and C^{13} resonances to lower field with increasing temperature.

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(6) G. Brauer, "Handbuch der Praparativen Anorganischen Chemie," Vol. II, Ferdinand Enke Verlag, Stuttgart, 1960, pp. 1315, 1316.

(7) The authors wish to thank Professor G. Stein of the Hebrew University, Jerusalem, for kindly providing this material.

(8) R. C. Thompson, *J. Am. Chem. Soc.*, **70**, 1045 (1948).

(9) W. C. Fernelius and J. J. Burbager, *Inorg. Syn.*, **2**, 227 (1946).

(10) D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 78.

the temperature dependence of the chemical shift is proportional to the chemical shift at 32°, whereas for $K_3Cr(CN)_6$ this proportionality is not obeyed. These results indicate that in $K_3Fe(CN)_6$ and $K_3Mn(CN)_6$ the shift is mainly due to the unpaired electron (paramagnetic shift) which might not be the case for the Cr(III) complex. Furthermore, comparison of the N^{14} chemical shifts with the effective magnetic moments[11] shows proportionality between these two quantities except for the Cr(III) complex. In Cr(III) complexes there is only one unpaired electron in each t_{2g} d-orbital, whereas in Mn(III), Mn(II), and Fe(III) complexes some of the t_{2g} electrons are paired. The t_{2g} orbitals are of π-symmetry and can interact only with π-orbitals of the ligands.[12] In all the complexes the e_g levels, which are of σ-symmetry, are unoccupied. Assuming that for the contact shift mixing of the t_{2g} levels with the lowest e_g level is needed, we may seek inverse proportionality between the energies of the lowest optical $t_{2g} \rightarrow e_g$ transitions and the N^{14} chemical shifts. The values for these transitions found in the literature are: $Cr(CN)_6^{-3}$ 26,700 cm.$^{-1}$,[13] $Fe(CN)^{-3}$ 18,200 cm.$^{-1}$,[14] and $Mn(CN)_6^{-3}$ 9500 cm.$^{-1}$ (ref. 12, p. 250). Thus, indeed, an inverse proportionality to the chemical shifts *including* the $Cr(CN)_6^{-3}$ is obeyed. No data were available for $Mn(CN)_6^{-4}$ (ref. 12, p. 248). All these arguments point to the conclusion that the major contribution to the chemical shift is due to the contact term but other effects, such as the anisotropic *g* factor suggested by Shulman,[4] should not be excluded. Assuming that in $K_3Fe(CN)_6$ the shifts originate predominantly from the contact term, the ratio spin densities on the C and N nuclei would be *approximately* equal to the ratio of their chemical shifts, namely 5:1 with *opposite* signs.[15a] It is unfortunate that C^{13} resonances could not be detected in other paramagnetic complexes since this could provide us with additional useful information regarding this problem.[15b]

The N^{14} resonance line widths in the paramagnetic complexes also vary, being the largest in $Cr(CN)_6^{-3}$. However, in comparison with the widths in diamagnetic complexes, they are of comparable magnitude. It is thus evident that the line widths are predominantly determined by quadrupolar relaxation and not by the electron spin relaxation. The electon spin relaxation, τ_s, seems to be quite short, as is also evident from the fact that no electron paramagnetic resonance (e.p.r.) signals were observed for most of the complexes in solution.[16] An exception is $Cr(CN)_6^{-3}$—the e.p.r. spectrum of this ion has been observed in aqueous solution[17] indicating a longer life time of the electronic spin which may cause additional broadening of the N^{14} resonances. The same may apply, to a lesser extent, to $K_4Mn(CN)_6$, where e.p.r. lines in the solid are relatively sharp.[18] The effects of complexation with cations, which will be discussed in the following paper, may contribute to the electrical field gradient at the N^{14} nucleus, *i.e.*, to the quadrupolar relaxation and to the line width. However, the complexation constants of K^+ with $Co(CN)_6^{3-}$ (diamagnetic) and $Fe(CN)_6^{3-}$ (paramagnetic) are almost identical,[19] and still their N^{14} line widths are of the same order of magnitude. This supports the assumption that the dominant relaxation term is quadrupolar and that the paramagnetic contribution is relatively unimportant. In other words, the quantity $3/8(1 + \eta^2/3)(e^2qQ/h)^2\tau_q$ is usually larger than $\tau_s A_N{}^2$, where A_N is the hyperfine interaction constant, except for $K_3Cr(CN)_6$ and probably $K_4Mn(CN)_6$, where the two terms might be of the same order of magnitude. The correlation time, τ_q, was measured[20] from the n.m.r. line widths of nuclei with quadrupole moment e^2qQ and asymmetry factor η.

A detailed study of line widths was carried out for the system $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. The concentration and viscosity dependence of the widths are given in Table II and their temperature dependence in Figure 2. Table II shows that the line widths of diamagnetic $K_4Fe(CN)_6$ are definitely bigger than those of paramagnetic $K_3Fe(CN)_6$. The widths are concentration dependent, which could be attributed in part to changes in the viscosity and in part to variations in the complexation constants. The ratio of width to viscosity for $K_4Fe(CN)_6$ *decreases* with increasing concentration, indicating that the ratio[20] τ_c/τ_q is concentration dependent.[21] τ_c is the correlation time computed from the viscosity. In $K_3Fe(CN)_6$ the ratio of width to viscosity seems to remain constant, which means that the increase in τ_c with concentration is accom-

TABLE II

CONCENTRATION AND VISCOSITY DEPENDENCE OF $K_3Fe(CN)_6$ AND $K_4Fe(CN)_6$ LINE WIDTHS AT 32°

$K_3Fe(CN)_6$, *M*	η, cp.	Width, gauss	Width/η	$K_4Fe(CN)_6$, *M*	η, cp.	Width, gauss	Width/η
0.2	0.819	1.54	1.88	0.2	0.856	1.85	2.16
0.5	0.891	1.69	1.90	0.4	0.937	1.94	2.07
1.0	1.086	1.96	1.81	0.6	1.050	2.04	1.94
				0.8	1.203	2.13	1.77

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[11] The values of μ_{eff} are (in B.M.) $K_3Fe(CN)_6$, 2.4; $K_3Mn(CN)_6$, 3.18; $Na_4Mn(CN)_6$, 1.8; $K_3Cr(CN)_6$, 3.72; ref. 10, p. 407.

[12] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 158.

[13] R. Krishnamurthy and W. B. Schaap, *Inorg. Chem.*, **2**, 604 (1963).

[14] C. S. Naiman, *J. Chem. Phys.*, **35**, 323 (1961).

[15] (a) In ref. 3a the C^{13} and N^{14} hyperfine coupling constants were calculated from the chemical shifts and their ratio assumed to be equal to the ratio of the spin densities. This is incorrect. The hyperfine coupling constants are proportional to the spin densities but the proportionality constant contains the gyromagnetic constants. Thus for unlike nuclei the ratio of the chemical shifts is proportional to the spin densities. (b) H. A. Kuska and M. T. Rogers (private communication) report $A_{C^{13}} = -9.8$ gauss for $K_3Cr(CN)_6$ from e.s.r. measurements. The calculated ratio of spin densities on the C and N nuclei in $K_3Cr(CN)_6$ would thus approximately equal 9:1; with opposite signs.

[16] An attempt to observe an e.p.r. signal in $K_3Fe(CN)_6$ solutions at room temperature failed.

[17] R. G. Hayes, Thesis, University of California, 1961.

[18] J. M. Baker, B. Bleaney, and K. D. Bowers, *Proc. Phys. Soc.* (London), **B69**, 1205 (1956).

[19] "Stability Constants," Special Publication No. 7, The Chemical Society, London, pp. 32, 33.

[20] (a) W. B. Montiz and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 1155 (1963); (b) D. E. Reilly and G. E. Schacher, *ibid.*, **39**, 1768 (1963).

[21] A similar effect was found for CH_3CN solutions: A. Loewenstein, unpublished results. For the solvent dependence of this ratio see: D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **7**, 515 (1964).

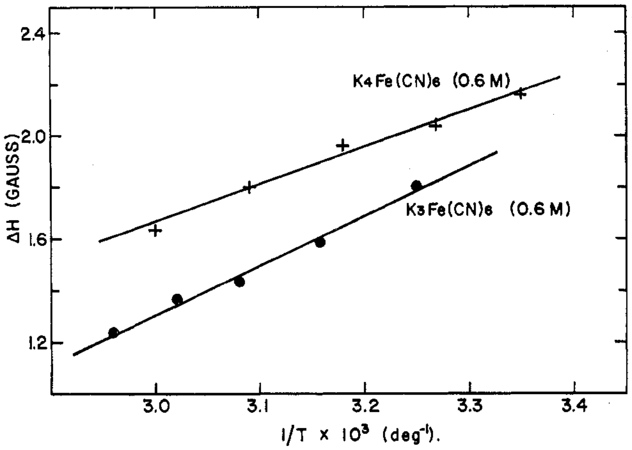

Figure 2.—Temperature dependence of N^{14} line widths in 0.6 *M* solutions of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. The line width is the separation between peaks of the derivative curve.

panied by an increase in τ_q. The latter result may be attributed to increased ionic complexation. In the absence of a detailed calculation of field gradients a more complete analysis is difficult. The effect of other cations, besides potassium, on the line widths will be described in the following paper.

One additional point deserves comment. All line widths given in Table I are one order of magnitude larger than that of N^{14} in CH_3CN (approximately 0.3 gauss). The reason for this seems to lie in the differences in molecular radii, *a*, which appears in the equation for τ_c as a^3. Thus if the diameter of CH_3CN is 2.27 Å. and that of $Fe(CN)_6^{-3}$ 4.5 Å.,[22] the ratio of a^3 would be about 8, which explains the enormous difference in widths.

Attempts to observe the C^{13} resonance in paramagnetic complexes other than $K_3Fe(CN)_6$ failed (Table I). This might be due to the excessive width of the C^{13} resonance in these complexes or to improper experimental conditions (sweep rate, modulation amplitude, radiofrequency intensity). It would be desirable to repeat these experiments with samples more enriched in C^{13} and with a proper radiofrequency unit. The width of C^{13} resonances could not be determined accurately enough with our equipment, and thus no information is derived from this quantity in the present work.

[22] R. A. Marcus, *J. Chem. Phys.*, **26**, 867 (1957).

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Study of Some Cyano–Metal Complexes by Nuclear Magnetic Resonance. II. Kinetics of Electron Transfer between Ferri- and Ferrocyanide Ions

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The kinetics of the electron-transfer reaction between $Fe(CN)_6^{-3}$ and $Fe(CN)_6^{-4}$ ions in aqueous solutions was studied by measuring the N^{14} n.m.r. line width. The reaction obeys a rate equation: rate = $k[Fe(CN)_6^{-3}][Fe(CN)_6^{-4}]$ with $k = 9.2 \pm 1.3 \times 10^4$ sec.$^{-1}$ M^{-1} at 32° and an Arrhenius activation energy of 4.2 kcal./mole in the temperature range 25–40°. The effect of replacing the potassium by other alkali and alkaline earth cations is reported. The rate increases from H^+ to Cs^+ and from Mg^{+2} to Sr^{+2}. Possible mechanisms, in view of the catalytic effect of the cations, are discussed. The effect of the presence of various cations on the N^{14} line width is reported and discussed.

Introduction

The general features of N^{14} n.m.r. spectra of iron hexacyanide ions have been described previously.[2] The present communication reports the study of the kinetics of the electron exchange between the ferri- and ferrocyanide ions by means of the N^{14} n.m.r. spectra. The temperature dependence of this reaction and the effect of various cations on this reaction rate are also described. This electron-transfer reaction has been studied previously both experimentally,[3] by isotope labeling, and theoretically.[4] Their data shall be discussed later with reference to the results obtained in this work. It should be noted that the ferri–ferrocyanide system is rather unique in the sense of the application of n.m.r. to the study of rate processes. The reasons are that both dia- and paramagnetic lines can be observed and are of comparable widths, and the changes in their line shapes are identical with those of a simple collapsing doublet.[5] This situation is strikingly different from most n.m.r. electron-exchange studies where the concentration of one species, usually the diamagnetic, predominates in the equilibrium mixture. The kinetic analysis was made difficult by the high concentrations that had to be used. The low sensitiv-

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[2] M. Shporer, G. Ron, A. Loewenstein, and G. Navon, *Inorg. Chem.*, **4**, 358 (1965) [paper I].

[3] (a) A. C. Wahl, *Z. Elektrochem.*, **64**, 90 (1960); (b) P. King, C. F. Deck, and A. C. Wahl, Abstracts, 139th National Meeting of the American Chemical Society, 1961, p. 30R; (c) A. C. Wahl, R. J. Campion, and P. King, Abstracts, 142nd National Meeting of the American Chemical Society, 1962, p. 32N; (d) for a recent review on electron-exchange reactions, see N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 299 (1962).

[4] (a) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); **26**, 867 (1957); (b) W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

[5] (a) A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Physik. Chem.*, **67**, 280 (1963); (b) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, Chapter 10.