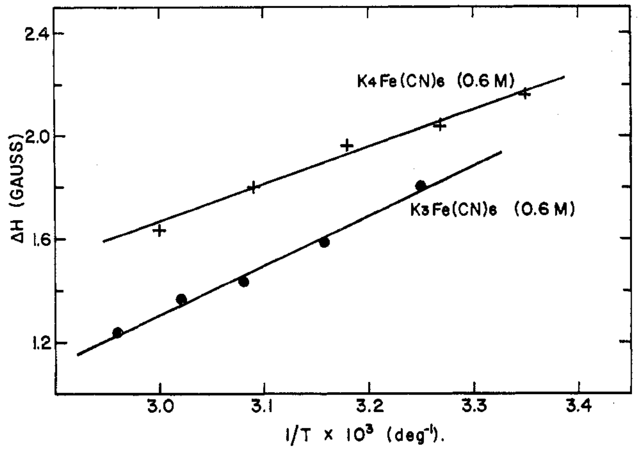

Figure 2.—Temperature dependence of N^{14} line widths in 0.6 *M* solutions of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. The line width is the separation between peaks of the derivative curve.

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).

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(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.

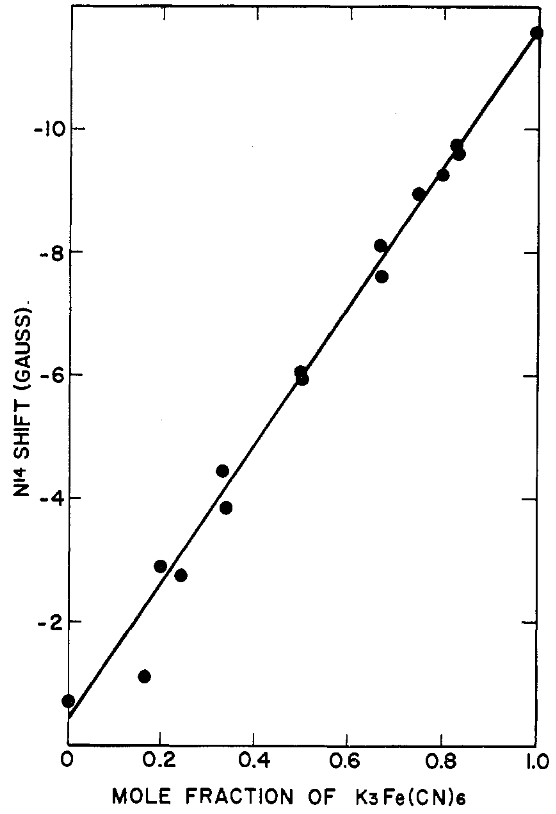

Figure 1.—N^{14} resonance position in mixtures of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ as a function of the "mole fraction" of $K_3Fe(CN)_6$ at 32°. The "mole fraction" is defined as the ratio of the $K_3Fe(CN)_6$ concentration to the sum of the $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ concentrations in the solution.

ity of the N^{14} resonances—about 10^{-3} as compared to H^1 taken as unity—is a severe limiting factor in n.m.r. studies of N^{14}. Furthermore, the sensitivity is usually even lower since N^{14} resonances are commonly much broader than H^1 resonances.

Experimental

The instrument, materials, and measuring procedure were described in paper I.[2]

Results and Discussion

Potassium Ferri- and Ferrocyanide.—Aqueous solutions of mixtures of $K_4Fe(CN)_4$ and $K_3Fe(CN)_4$ show one N^{14} resonance for all practical concentrations. Evidently, two lines would be observed for small concentrations of the two components if the sensitivity of the n.m.r. instrument were increased. The position of the common line is a linear function of the ratio of ferricyanide concentration to the total ferri- plus ferrocyanide concentration in the solution; this is shown in Figure 1. The width of the common line depends on the ratio of $Fe(CN)_6^{-3}$ to $Fe(CN)_6^{-4}$ in the solution and on the temperature. We thus deduce that the rate of electron exchange is fast compared to the reciprocal chemical shift and that in evaluating the rate constants we are justified in using the approximate formula for fast exchange[5]

$$\Delta\frac{1}{T} \equiv \frac{1}{T_2} - \frac{P_A}{T_{2A}} - \frac{P_B}{T_{2B}} = P_A^2 P_B^2 \Delta\omega^2(\tau_A + \tau_B) \qquad (1)$$

where T_{2A} and T_{2B} are the N^{14} transverse relaxation times in the absence of chemical exchange, P_A and P_B are the N^{14} mole fractions in A and B, $\Delta\omega$ is the chemical shift between A and B, and τ_A and τ_B are the mean lifetimes of species A and B between exchanges. The subscripts A and B refer to the ferri- and ferrocyanide ions.

The values of $(P_A/T_{2A} + P_B/T_{2B})$ were taken as the weighted averages of $Fe(CN)_6^{-3}$ and $Fe(CN)_6^{-4}$ line widths in solutions each of which was equal in concentration to the *sum* of the concentrations of the components in the mixture. For example, for mixtures where the *total* concentration was 0.6 *M*, the quantity $(P_A/T_{2A} + P_B/T_{2B})$ at different temperatures was taken by interpolation from Figure 2 of paper I.[2]

Assuming the reaction to be described by

$$\text{rate} = k[Fe(CN)_6^{-3}][Fe(CN)_6^{-4}] \qquad (2)$$

we obtained the results given[6] in Table I. The average value is $9.2 \pm 1.3 \times 10^4$ sec.$^{-1}$ M^{-1} and the error given is the calculated mean standard deviation. The rate is constant over a 4- to 5-fold change in the concentration of each of the species, which justifies the use of eq. 2. The low solubility of the compounds limits the upper range of concentrations, whereas the lower limit is determined by the sensitivity of the instrument.

The variation of the rate constant with the temperature for solutions containing 0.3 *M* each of $Fe(CN)_6^{-3}$ and $Fe(CN)_6^{-4}$ is given in Figure 2. Since 8-mm. o.d. tubes were used for these measurements the accuracy is low, especially at higher temperatures where the line widths approach the natural line widths. At temperatures lower than 25°, lines were too broad to be measured accurately. The points above 40° were included in Figure 2 (dashed line) in order to demonstrate a trend indicating that *E might* increase with the temperature. It is, however, difficult to ascertain this conclusion because the sharp change in the curvature of the line in Figure 2 may be due to experimental inaccuracy. Further experiments are being planned to check on this point. Between 25 and 40° a good Arrhenius plot was obtained with E = 4.2 kcal./mole and a pre-exponential factor, k_0, equal to 8.5×10^7 sec.$^{-1}$ M^{-1}.

Wahl and co-workers[3] worked at much lower concentrations and obtained a rate equation which is complex and depends on the first and second powers of the potassium ion concentration. Our work was carried out where the K^+ concentration by far exceeded the free ferri- and ferrocyanide concentrations and their catalytic effect on the reaction reached its maximum value. This has also been proved by observing no change in the line width when a mixture containing 0.3 *M* each of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ was saturated with KCl. Nevertheless, when the rate is calculated, using the constants and E given by Wahl and the conditions of this work ($K^+ \simeq 1.75$ *M*), the result is 3.9×10^5 sec.$^{-1}$ M^{-1} at 32°, which is in fair agreement with

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[6] A slightly different result is given by A. Loewenstein, M. Shporer, and G. Navon, *J. Am. Chem. Soc.*, **85**, 2855 (1963), because an erroneous correction of the "natural line width" was applied.

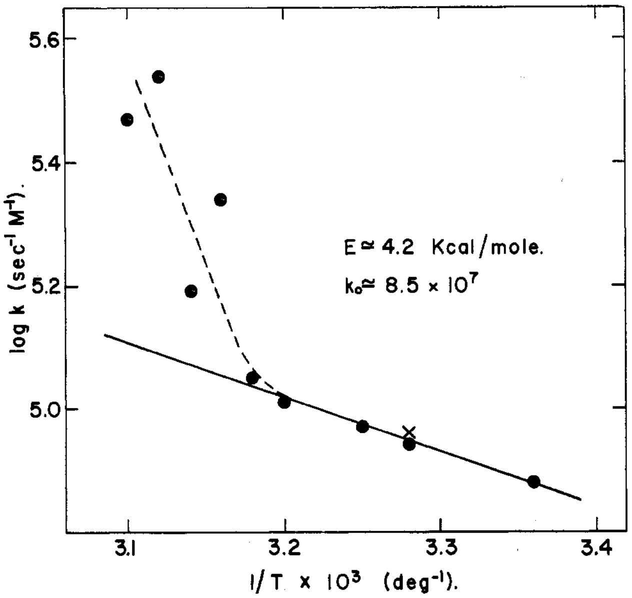

Figure 2.—An Arrhenius plot of the rate of electron transfer between $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. The point marked × is the mean value of log *k* taken from Table I.

TABLE I

KINETIC RESULTS FOR $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ MIXTURES IN AQUEOUS SOLUTION AT 32°

K_3Fe-$(CN)_6$, *M*	K_4Fe-$(CN)_6$, *M*	Width of common line, gauss	$\Delta(1/T)$, gauss	*k*, sec.$^{-1}$ M^{-1}	No. of expts.[b]
0.25	0.25	3.54	1.69	8.3×10^4	4
0.17	0.33	3.06	1.16	10.8×10^4	3
0.40	0.10	2.70	0.94	9.4×10^4	1
0.10	0.40	3.09	1.14	7.8×10^4	1
0.13	0.37	3.09	1.16	9.0×10^4	1
0.33	0.17	3.01	1.31	9.3×10^4	2
0.37	0.13	3.01	1.23	8.4×10^4	1
0.30	0.30	3.16	1.18	9.8×10^4	2
0.12	0.30	3.45	1.56	8.6×10^4	1
0.32	0.32	3.17	1.24	8.9×10^4	1
0.24	0.24	3.66	1.86	7.9×10^4	1
0.15	0.45	2.88	0.68	12.8×10^4	1
0.20	0.20	4.22	2.42	7.2×10^4	1
0.40	0.40	2.55	0.55	15.8×10^4[a]	1
			Av.	$9.2 \pm 1.3 \times 10^4$	

[a] Not taken in the average because of uncertainty in complete solubility. [b] For each experiment four to six spectra were measured.

our result. Furthermore, the activation energy measured by us is close to that quoted by Wahl (4.7 kcal./mole). It is rather surprising that this electron-transfer reaction should obey the same rate equation with the same *E* over such a large concentration range. Cation complexation constants which are included in Wahl's rate equation are expected to change with the concentration unless an activity correction is applied.

The values of ΔS^* and ΔF^* were calculated from *k* and *E* and the results are: $\Delta S^* = -24.3$ e.u. and $\Delta F^* = 10.9$ kcal./mole at 300°K. The value of ΔF^* for this reaction calculated by Marcus[4a] is 10.1 kcal./mole.

Effect of the Other Cations.—It is known that substituting the potassium by other cations affects the rate of the $Fe(CN)_6^{-3}$–$Fe(CN)_6^{-4}$ exchange reaction[3] and other electron-transfer reactions such as the manganate–permanganate exchange.[7] In order to further check this we synthesized the various ferri- and ferrocyanides of the alkali and alkaline earth cations which are soluble in water. Cs^+ was an exception since we were unsuccessful in preparing stable solutions of $Cs_3Fe(CN)_6$. The substitution of potassium by other cations had no measurable effect on the line positions.

TABLE II

EFFECT OF CATIONS ON THE ELECTRON-TRANSFER REACTION AT 32°

	Width, gauss				
Cation	Fe-$(CN)_6^{-3}$[a]	Fe-$(CN)_6^{-4}$[a]	Width in mixture,[b] gauss	$\Delta(1/T)$, gauss	Rate constant, sec.$^{-1}$ $M^{-1} \times 10^{-4}$
H^+	2.1	2.2	2 unbroadened lines	...	<0.4[c]
Li^+	2.6	2.9	2 overlapping lines	...	<3[c]
Na^+	2.0	2.3	4.4	2.25	5.8
K^+	1.7	2.0	3.5	1.65	7.9
Rb^+	1.7	2.2	2.9	0.95	13.1
NH_4^+	1.7	2.1[d]	3.3	1.40	8.4
Mg^{+2}	3.4	7.2	Very broad (10–12)	...	...
Ca^{+2}	3.8	7.0	Very broad (7–9)	...	...
Sr^{+2}	3.0	4.1	5.5	2.05	6.7

[a] Concentration 0.5 *M*. [b] Concentration 0.25 *M* of each. [c] Estimated from formula for slow exchange approximation. [d] Average value between K^+ and Rb^+ since N^{14} resonances of NH_4^+ and $Fe(CN)_6^{-4}$ overlap.

The measured widths and the calculated rate constants are given in Table II. Columns 2 and 3 of Table II show the following facts related to the line widths: (a) The widths of the N resonances in the diamagnetic ferrocyanides are invariably larger than the corresponding values in the paramagnetic ferricyanides. (b) The lines become narrower from Li^+ to Rb^+ and from Mg^{+2} to Sr^{+2} with H^+ being an exception. (c) Line widths in the case of alkaline earth ferri- and ferrocyanides are much greater than for the alkali ferri- and ferrocyanides. The explanation of the changes in line widths must be given in terms of their effect on the electrical field gradient, *q*, at the N^{14} nucleus. Divalent positive ions would increase *q* more than monovalent ions and thus reduce T_1 and T_2, which implies an increase in the line width. On the other hand, changes of the line width due to cations carrying the same charge may be related to their effective distance from the N^{14} nucleus. This distance is determined by their size, hydration, and tendency to complex with the anion. Assuming that the complexation constants are of the same order of magnitude[8] (except for H^+), it seems that the effective distance between the center of the cation and the N nucleus increases from Li^+ to Rb^+ and from Mg^{+2} to Sr^{2+}. This can be taken as evidence that the increase in ionic

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(7) O. L. Myers and J. C. Sheppard, *J. Am. Chem. Soc.*, **83**, 4739 (1961).

(8) "Stability Constants," Special Publication No. 7, The Chemical Society, London, 1958 pp. 32, 33.

radii more than compensates for the decrease of hydration, or that the complexes form ion pairs with no water molecules between cation and anion.[9] The position of NH_4^+ is close to that of K^+ both with respect to width and catalytic effect. The proton is strongly bonded to the $Fe(CN)_6^{-4}$, whereas no evidence for complex formation in $H_3Fe(CN)_6$ is known.[8] A simple explanation for the widths in this case cannot be given.

The second part of Table II shows the effect of the cations on the rate. The transition from two separate resonances observed in mixtures of $H_3Fe(CN)_6$ and $H_4Fe(CN)_6$ to a single, rather sharp, line in mixtures of $Rb_3Fe(CN)_6$ and $Rb_4Fe(CN)_6$ is striking. Although rates are accurate only within ±15%, there is a definite 30–40-fold increase in rate comparing H^+ to Rb^+. The rates for Mg^{+2} and Ca^{+2} were not evaluated since the lines were too broad to be measured accurately. These rates are, however, smaller than in Sr^{+2} and obey the expected order $Ca^{+2} > Mg^{+2}$.

A separate experiment to check the effect of Cs^+ was performed. CsCl was added to a mixture of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. The results are given in Table III and indicate that the catalytic effect of Cs^+ exceeds that of Rb^+. A direct comparison is not permissible, because the conditions differ.

TABLE III

CATALYTIC EFFECT OF CsCl ON THE ELECTRON TRANSFER[a]

CsCl, M	$\Delta(1/T)$, gauss	Rate constant, sec.$^{-1}$, M^{-1}
None	1.7	8.2×10^4
2.9×10^{-2}	1.3	10.5×10^4
8.8×10^{-2}	1.2	11.3×10^4
16.6×10^{-2}	1.0	13.7×10^4

[a] 0.25 M $K_3Fe(CN)_6$; 0.25 M $K_4Fe(CN)_6$; 32°.

Libby[4b] and Marcus[4a] developed the theory for "outer-sphere" electron-transfer reactions which refers to the case discussed here. Calculations in this model are based on the assumption that the transition of the electron from $Fe(CN)_6^{-4}$ to $Fe(CN)_6^{-3}$ is direct and obeys the Franck–Condon principle. Marcus[4a] assumes that both anions are of similar size and thus the rate-determining step is the reorientation of the water molecules in the hydration sphere. In the concentrated solutions described in this work the predominant species presumably[8] are $KFe(CN)_6^{-2}$ and $K_2Fe(CN)_6^{-2}$, and thus the calculations of Marcus[4a] are not applicable directly. The result that in dilute solutions the rate constant is about five orders of magnitude smaller than in the concentrated solutions described here suggests that the cations play an important role in the reaction mechanism. The catalytic action of the cations may be described qualitatively by two mechanisms.[10]

(a) The only role of the cations in the reaction is to facilitate the approach of two anions in the solution while the electron is transferred *directly* from one anion to the other obeying the Franck–Condon principle. Since the effective distance between cation and the N nucleus increases from H^+ to Cs^+ it might be expected that the rate should *decrease* in the same sequence. The experimental results are contrary to this expectation. The same argument might be applied to the divalent cations. Another possibility is that the cations differ in their ability to create the conditions required for a Franck–Condon transition between the reactants (similarity of states). From electrostatic considerations we may assume that the small cations (such as Li^+) are more firmly attached to the anions and thus are less effective in bringing the reacting species to a similar state as compared to bigger cations, such as Cs^+. A similar argument has been applied[4] to explain the result that electron-transfer rates usually increase with increasing size of the reactants. It is not evident, however, that the cations act merely as inert agents in the transfer but may have a more involved function.

(b) The second proposed mechanism suggests that the electron is actually transferred *by the cation* which serves as a bridge between the two anions. In the limiting case of this mechanism the reaction might be described by two steps: (1) $A^{-4} + M^+ \rightleftarrows A^{-3} + M$; (2) $M + A^{-3} \rightleftarrows M^+ + A^{-4}$, where A represents the anion and M the cation. However the mechanism is more likely to be of a *simultaneous one-step* form. Admittedly this is a rather vague description of the mechanism. The activated complex would accordingly be described by the structure

$$(KFe(CN)_6)^{-2} \cdots\cdot K^+ \cdots\cdot (Fe(CN)_6K)^{-3}$$

with an analogous structure for other cations replacing the potassium. In this model the polarizability and the slight difference in complexation constants should play a dominant role in catalyzing the reaction. The greater polarizability of the large cations[11] is in accord with their increased catalytic activity and supports this model. A similar effect of ligand polarizability was considered in describing electron transfer between metal ions bridged by organic ligands.[12] The relatively high value of negative ΔS^* also seems to be in favor of the suggested type of activated complex.

The oxidation–reduction potentials represent the over-all tendency of the system to donate and accept electrons and are expected to be related to the electron-transfer rate. Oxidation–reduction potentials for the $Fe(CN)_6^{-3}$–$Fe(CN)_6^{-4}$ system in the presence of various cations were measured by Kolthoff and Tomsicek,[13] who found that they increase from Li^+ to Cs^+ in the same order as do the rates.

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

[10] A discussion of the role of cations in electron-transfer reactions is given by H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

[11] J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., Amsterdam, 1958, p. 91.

[12] J. Halpern and L. E. Orgel, *Discussions Faraday Soc.*, **29**, 32 (1960); R. T. M. Fraser, *J. Am. Chem. Soc.*, **83**, 4920 (1961); P. V. Manning, R. C. Jarnagin, and M. Silver, *J. Phys. Chem.*, **68**, 265 (1964).

[13] I. M. Kolthoff and W. J. Tomsicek, *ibid.*, **39**, 945 (1935).