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Electron-Transfer Rate Studies of a Number of Iron(II)–Iron(III) Systems

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The kinetics of isotopic exchange between $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ ions have been extensively studied by quenched-flow[1] and nmr line-broadening methods.[2] The system is a good example of an outer-sphere redox reaction, and it is this type of reaction which is most amenable to theoretical treatment and prediction.[3]

A number of iron(II)– and iron(III)–cyano complexes are known[4,5] in which anions or neutral molecules have replaced cyanide group(s). We have therefore studied the kinetics of reactions of the type

$$Fe(CN)_6^{4-} + Fe(CN)_5NH_3^{2-} \rightleftharpoons Fe(CN)_6^{3-} + Fe(CN)_5NH_3^{3-} \quad (1)$$

by stopped-flow methods and examined the results briefly in terms of the ideas developed by Marcus[6] for the rates of such outer-sphere "cross-reactions."

Experimental Section

Materials. Chemicals used, where possible, were commercial products. A number of complexes were prepared by literature methods and characterized by their spectra. These included (references refer to preparation and spectra) $Na_3Fe(CN)_5NH_3 \cdot 3H_2O$,[7] $Na_2Fe(CN)_5NH_3 \cdot 6H_2O$,[7,8] (reported as a trihydrate when dried over concentrated sulfuric acid[7]), $Na_3Fe(CN)_5H_2O$,[9-11] $Na_2Fe(CN)_5H_2O \cdot H_2O$,[8,9,12] $Na_3Fe(CN)_5P(C_6H_5)_3 \cdot 3H_2O$,[13] $Na_2Fe(CN)_5P(C_6H_5)_3 \cdot 2H_2O$,[13] $K_2Fe(bipy)(CN)_4 \cdot 3H_2O$, and $HFe(bipy)(CN)_4 \cdot 2H_2O$.[14] The ions $Fe(CN)_5N_3^{4-}$ and $Fe(CN)_5CNS^{4-}$[15] were used *in situ*, obtained by mixing solutions of the iron(II) ammine or aquo compound with a large excess (1000-fold) of azide or thiocyanate ion at pH 7–8, in an N_2 atmosphere to avoid aerial oxidation. The preparation of the corresponding iron(III) compounds (without using N_2) required some 2–3 hr for complete conversion.[8]

Kinetic Experiments.—A glass–Lucite stopped-flow apparatus was used. Usually the change of concentration of $Fe(CN)_6^{3-}$ was followed at 420 mμ (ε 1.0 × 10^3) or 303 mμ (ε 1.7 × 10^3) but absorption of $Fe(CN)_5H_2O^{2-}$ at 560 mμ (ε 300), $Fe(CN)_5N_3^{3-}$ at 560 mμ (ε 3.7 × 10^3), and $Fe(CN)_5CNS^{3-}$ at 590 mμ (ε 2.7 × 10^3) was also utilized. The concentration of reactants was determined from the weight of compound and usually checked spectrally. Solutions were used within 15 min of preparation. Most of the work was carried out in the pH 5.5–7.0 region where rates were pH independent, and since any pH changes occurred only slowly and subsequent to the redox process, buffers were found unnecessary. In addition, $Fe(CN)_5NH_3^{2-}$ and $Fe(CN)_5H_2O^{2-}$, for example, were found to interact with buffer constituents such as lutidine and acetate ion. Usually 10^{-4}–10^{-3} *M* reactant concentrations were employed, with sufficient excess of one reagent to ensure both pseudo-first-order kinetics and completion of reaction. This latter occasionally required a high ratio of reactant concentrations. The appropriate kinetic plots were linear over several half-lives. The ionic strength was kept as low as possible to help attain measurable rates with the faster reactions. Errors in k are about ±7%; in ΔH^* errors are ±(1.0–1.5) kcal mol^{-1} and in ΔS^* they are ±(3–5) eu.[16]

Redox Potentials.—These were measured at 25° using Pt and saturated calomel electrodes in conjunction with a Radiometer Type TTTIC titrator. Equimolar concentrations (~10^{-3} *M*) of the pair of the redox couple were used at the ionic strength of the kinetic experiments. In a few cases a full potentiometric titration was used to estimate the redox potential and this value agreed well with the results from the simpler method.

Results and Discussion

All of the iron(III) complexes and $Fe(CN)_6^{4-}$ gave a neutral solution[17] and were stable during the course of the kinetic experiments. Upon long standing some showed color and pH changes. All reactions were shown to be second order except those which were too rapid for meaningful concentration variations to be made. All rate constants (Table I) were determined at an ionic strength of 0.05 *M* (largely KNO_3). In this way it was hoped that differences in the relative reactivity of free and associated $Fe(CN)_6^{4-}$ ions[1] would not be an overriding consideration for the survey purposes of this work.[18] The activation parameters were measured at ionic strengths governed by the necessary experimental conditions. They were found not to vary significantly at different ionic strengths. For five reactions involving 2− with 3−, 2− with 4−, and 3− with 4− charged species the enthalpies and entropies of activation fall in the range 1.8–4.0 kcal

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[1] R. J. Campion, C. F. Deck, P. King, Jr., and A. C. Wahl, *Inorg. Chem.*, **6**, 672 (1967).

[2] M. Shporer, G. Ron, A. Loewenstein, and G. Navon, *ibid.*, **4**, 361 (1965); A. Loewenstein and G. Ron, *ibid.*, **6**, 1604 (1967).

[3] For recent accounts and literature see: W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press Co., New York, N. Y., 1966; F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

[4] H. E. Williams, "Cyanogen Compounds," Edward Arnold, London, 1948, gives a thorough account of the earlier literature.

[5] B. M. Chadwick and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8**, 83 (1966), give a comprehensive survey of the transition metal cyanides and their complexes.

[6] R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 1155 (1964).

[7] G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry, Vol. 2, Academic Press, New York, N. Y., 1963, p 1399.

[8] B. Jaselskis, *J. Am. Chem. Soc.*, **83**, 1082 (1961).

[9] K. A. Hofmann, *Ann. Chem.*, **312**, 1 (1900).

[10] S. Ašperger, I. Murati, and D. Pavlović, *J. Chem. Soc.*, 730 (1960).

[11] G. Emschwiller, "Proceedings of Seventh International Conference on Coordination Chemistry," Stockholm, 1962, p 244.

[12] E. F. G. Herington and W. Kynaston, *J. Chem. Soc.*, 3555 (1955).

[13] R. Nast and K. W. Kreiger, *Z. Anorg. Allgem. Chem.*, **341**, 189 (1965).

[14] A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

[15] This formulation is used since the mode of linkage of thiocyanate (through S– or N–) is unknown with these compounds.

[16] A table of detailed data has been deposited as Document No. NAPS-00125 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York, N. Y., 10001. A copy may be secured by citing the document number and by remitting $3.00 for photoprints, or $1.00 for microfiche. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

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

[18] Association of K^+ (and Na^+) ions with $Fe(CN)_6^{4-}$ must occur at our ionic strengths of 0.05 *M* because the thermodynamic association constant of $KFe(CN)_6^{3-}$ is 60 at 25° and I = 0.03 *M*: W. A. Eaton, P. George, and G. I. H. Hanania, *J. Phys. Chem.*, **71**, 2016 (1967).

TABLE I

KINETIC AND POTENTIAL DATA FOR Fe(II)–Fe(III) REDOX REACTIONS AT 25° ($I = 0.05\ M$)

Reductant	Oxidant	E_0,[a] V	k, M^{-1} sec^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, eu
$Fe(CN)_6^{4-}$	$Fe(bipy)_3^{3+}$	~1.0	$\geqslant 10^8$ [b]		
	$Fe(bipy)(CN)_4^-$	0.55[c]	8×10^6 [d]		
	$Fe(CN)_5P(C_6H_5)_3^{2-}$	0.54	8×10^4	3.3	−25
	$Fe(CN)_5NH_3^{2-}$	0.33[e]	7×10^3	3.3	−32
	$Fe(CN)_5H_2O^{2-}$	0.54[f]	1×10^3 [g]	3.2	−33
	$Fe(CN)_6^{3-}$	0.40[h]	5×10^3 [i]	4.0	−32
			10^3 [j]	3.6	−24
$Fe(CN)_5N_3^{4-}$	$Fe(CN)_6^{3-}$	0.24	8×10^4	1.8	−30
$Fe(bipy)(CN)_4^{2-}$	$Fe(CN)_6^{3-}$	0.55	2×10^4 [d]		

[a] Potential of substituted complex as oxidant (*i.e.*, all positive values). [b] From the cross reaction $Fe(phen)_3^{3+} + Fe(4,4'\text{-dimethylbipy})_3^{2+}$: B. M. Gordon, L. L. Williams, and N. Sutin, *J. Am. Chem. Soc.*, **83,** 2061 (1961). See also D. W. Larsen and A. C. Wahl, *J. Chem. Phys.*, **43,** 3765 (1965). [c] P. George, G. I. H. Hanania, and D. H. Irvine, *J. Chem. Soc.*, 2548 (1959), report 0.56 V. [d] These values lead to $K_{equil} = 400$; from redox potentials, $K_{equil} = 300$. [e] D. Davidson, *J. Am. Chem. Soc.*, **50,** 2622 (1928), reports 0.37 V. [f] L. Michaelis and C. V. Smythe, *J. Biol. Chem.*, **94,** 329 (1931), report 0.42 V. [g] $I = 0.02\ M$. [h] P. A. Rock, *J. Phys. Chem.*, **70,** 576 (1966), reports 0.37 V. [i] Estimated from ref 1. [j] M. Shporer, G. Ron, A. Loewenstein, and G. Navon, *Inorg. Chem.*, **4,** 361 (1965), report value at $I \simeq 8\ M$.

mol^{-1} and −23 to −33 eu. These values include that for the parent system $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$. The large negative entropies of activation are expected for reactions in which the reactants have high positive charge products.[3]

Isotopic-Exchange Rate Constants.—The different free energies for each reaction had to be allowed for in assessing the influences of substitution on the ease of electron transfer. An effective way of accomplishing this is to use Marcus' relation derived for outer-sphere redox reactions[6]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2)$$

Here k_{11} and k_{22} are the appropriate isotopic-exchange rate constants; *e.g.*, $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ and $Fe(CN)_5NH_3^{3-}$–$Fe(CN)_5NH_3^{2-}$ in reaction 1 are the systems for which k_{12} and K_{12} are the rate and equilibrium constants. Z is the frequency factor, $\sim 10^{11}$. Since we know k_{12}, k_{11}, and K_{12}, we can estimate k_{22} for each complex studied. The isotopic-exchange rate constants thus computed increase in the order $Fe(CN)_5N_3^{4-,3-}$ (3×10^3) < $Fe(CN)_6^{4-,3-}$ (5×10^3) < $Fe(CN)_5NH_3^{3-,2-}$ (10^5) ~ $Fe(CN)_5P(C_6H_5)_3^{3-,2-}$ (10^5) < $Fe(bipy)(CN)_4^{2-,1-}$ (4×10^7) < $Fe(bipy)_3^{2+,3+}$ ($>10^8$); the rate constants (M^{-1} sec^{-1}) at 25° are given in the parentheses. The large effect produced on substitution of only one bipyridyl molecule may be largely as a result of reduced electrostatic repulsions, judging from the results with the ammine and phosphine complexes.

Two reactions which we studied are not included in the series above because of their complexity. Oxidation of $Fe(CN)_5CNS^{4-}$ by an excess of $Fe(CN)_6^{3-}$ rapidly produced a transient purple species (with an absorption peak at 550–560 mμ) which changed (*via* an isosbestic point at 575 mμ) to the blue color (absorption peak at 590 mμ) characteristic of the species obtained directly from $Fe(CN)_5NH_3^{2-}$ and SCN^- ions.[3] One possible explanation for these observations is that the iron(II)–thiocyanate complex is N bonded and that rapid and complete oxidation gives an unstable, purple, N bonded $Fe(CN)_5NCS^{3-}$ ion which slowly rearranges to a blue linkage isomer $Fe(CN)_5SCN^{3-}$. This rearrangement is speeded up if $Fe(CN)_5H_2O^{3-}$ is added to the solution possibly through the catalytic process depicted in[19]

$$Fe(CN)_5NCS^{3-} + Fe(CN)_5H_2O^{3-} \longrightarrow Fe(CN)_5NCSFe(CN)_5^{6-} \longrightarrow Fe(CN)_5H_2O^{3-} + Fe(CN)_5SCN^{3-} \quad (2)$$

Thus in the slow oxidation of $Fe(CN)_5NCS^{4-}$ by H_2O_2 or when there is a deficiency of $Fe(CN)_6^{3-}$, enough $Fe(CN)_5H_2O^{3-}$ ions are present to prevent the purple species from being seen. Significantly $Fe(CN)_5N_3^{4-}$ gave *only* a purple species on oxidation, also with a maximum at 560 mμ.

Reaction 3 also behaves in an unexpected manner. Although it is recognized that pentacyanoaquoferrate(III) may be polymeric in solution,[20] its reduction by

$$Fe(CN)_6^{4-} + Fe(CN)_5H_2O^{2-} \rightleftharpoons Fe(CN)_6^{3-} + Fe(CN)_5H_2O^{3-} \quad (3)$$

$Fe(CN)_6^{4-}$ is second order and proceeds easily to completion. In apparent contradiction to this pentacyanoaquoferrate(II) reacts with $Fe(CN)_6^{3-}$, as shown by absorption changes at 420 mμ (*e.g.*, with 3×10^{-4} M $Fe(CN)_6^{3-}$, 3×10^{-3} M $Fe(CN)_6^{3-}$, and $t_{1/2}$ = 70 msec at 25°) but a redox process is not involved, however, since the product of a characteristic absorption at 560 mμ is absent. Such "interactions" have been observed previously[4] and presumably involve the formation of cyanide-bridged dimers or polymers believed present in solutions of pentacyanoaquoferrate(II) itself.[20] The nonsubstituted $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ ions have been shown not to interact.[21] Absorption changes were also observed when a solution of pentacyanoaquoferrate(II) was allowed to react with pentacyanoaquoferrate(III) or even $Fe(CN)_6^{4-}$ ions. These slow reactions did not interfere with observation of the rapid redox reactions.

Thus it is not possible to assign equilibrium constants from redox potential for the reactions involving the aquo- and thiocyanate-substituted iron complexes, and the appropriate substitution in the Marcus equation cannot, therefore, be made.

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(19) We are grateful to Dr. D. H. Huchital for this suggestion. Lability of the coordinated water is shown by a rapid reaction of $Fe(CN)_5H_2O^{3-}$ with N_3^- ion (second-order rate constant estimated as $>10^4\ M^{-1}$ sec^{-1}).

(20) G. Emschwiller, *Compt. Rend.*, **238**, 341 (1954); **260**, 4333 (1965); G. Emschwiller and C. Friedrich, "Proceedings of the 9th International Conference on Coordination Chemistry," St. Moritz-Bad, Switzerland, Sept 1966, p 244.

(21) J. A. Ibers and N. Davidson, *J. Am. Chem. Soc.*, **73**, 476 (1951).