

Some Observations on Equilibria Involving Monomeric and Dimeric Pentacyanoiron(II) Complexes in Aqueous Solution

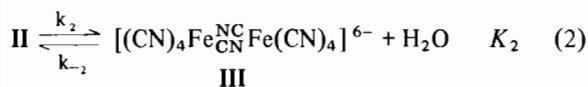
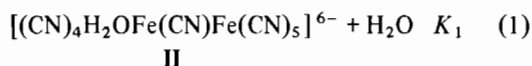
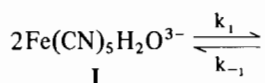
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Although many mononuclear transition metal cyano complexes have been characterized in the solid state and in solution, relatively little is known about the factors leading to the formation and stabilization of cyano-bridged transition metal dimers in solution.¹

Recent work in our laboratory has been aimed at elucidating the properties of the inner-sphere water molecules in the low-spin iron(II) species I and II in aqueous sodium perchlorate.



At $[\text{Fe}^{\text{II}}]_{\text{T}} \leq 5 \times 10^{-5} \text{ M}$ and $\text{pH} \leq 8.0$, the spectral and kinetic properties³ of deoxygenated aqueous solutions⁴ of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ reflect only the presence of I, which has a spectral absorption maximum at 440 nm. However, at $\text{pH} \geq 8.5$, the wavelength of maximum absorbance slowly shifts to the 380–390 nm region and the kinetic properties of the solutions are now consistent with the presence of both monomeric and dimeric pentacyanoiron(II) species.^{6,7}

Addition of a large excess of a complexing ligand X such as isonicotinamide or cyanide to these iron(II) solutions results in the quantitative formation of monomeric $\text{Fe}(\text{CN})_5\text{X}^{n-}$ (ref. 3, 7). However, the rate of reaction of I with X is much faster than are the corresponding reactions with II and III,^{3,7} which allows spectrophotometric determination of the ratio $R = [\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}]/[\text{Fe}^{\text{II}}]_{\text{T}}$ at a given time after dissolution of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ in 1M NaClO_4 . After 15 min standing at 25.0°, R at $[\text{Fe}^{\text{II}}]_{\text{T}} = 2 \times 10^{-4} \text{ M}$ was found⁷ to be 0.38 at pH 10.5, 11.5 and 12.5, while at $[\text{Fe}^{\text{II}}]_{\text{T}} = 2 \times 10^{-5} \text{ M}$ the

corresponding ratios were 0.76, 0.65 and 0.65 at pH 9.5, 12.2 and 12.7, respectively. At fixed $[\text{Fe}^{\text{II}}]_{\text{T}} \leq 10^{-3} \text{ M}$, the total amount of $\text{Fe}(\text{CN})_5\text{X}^{n-}$ formed on addition of a large excess of X decreased as the standing time of the reactant iron(II) solution increased beyond ca. 15 min.

These observations are consistent with the following conclusions.

1) The slow attainment of equilibria (1) and (2) in deoxygenated aqueous solutions of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ is accompanied by decomposition at $[\text{Fe}^{\text{II}}]_{\text{T}} \leq 1 \times 10^{-3} \text{ M}$ and $\text{pH} \geq 8.5$.

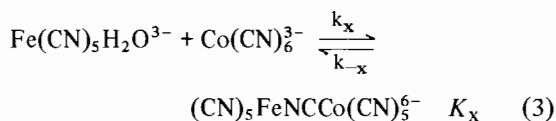
2) The initial rate of conversion of I to II and III increases with increasing $[\text{Fe}^{\text{II}}]_{\text{T}}$ and pH. The effect of acidity in this system may reasonably be attributed to the acid-base properties of II, since I is essentially non-acidic up to pH 12.8.⁷

At $\text{pH} > 11$, reaction of aqueous solutions of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ with excess X in a stopped-flow spectrophotometer gives rise to kinetic traces with two easily resolvable first-order components. The first reaction with fixed [X] has kinetic parameters which closely agree with data obtained from experiments at low $[\text{Fe}^{\text{II}}]_{\text{T}}$ and pH 7, where only I is present.^{3,7} However, the rate of the second, slower reaction is independent⁷ of the identity and concentration of X, and can thus be assigned to the slow, spontaneous conversion of III to II in eq 2 followed by rapid reaction of II (in its equilibrium form at $\text{pH} > 11$) with excess X to give 2 mol of $\text{Fe}(\text{CN})_5\text{X}^{n-}$ (ref. 8). Studies with a range of widely different ligands give $k_{-2} = (1.63 \pm 0.01) \times 10^{-2} \text{ sec}^{-1}$ with $\Delta H_{-2}^\ddagger = 25 \text{ kcal mol}^{-1}$ and $\Delta S_{-2}^\ddagger = 18 \text{ cal deg}^{-1} \text{ mol}^{-1}$ at 25.0 °C^{7,9} and ionic strength 1.0 M.

Emschwiller¹⁰ (working with pentacyanoiron(II) species prepared by Hofmann's method¹¹) obtained a value of $K_1K_2 = 1700 \text{ M}^{-1}$ at 10 °C, pH 10 (borate-buffered 1.0 M aqueous NaClO_4) by quantitating $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}]$, as described above, with excess X = nitrosobenzene. Emschwiller¹⁰ employed $[\text{Fe}^{\text{II}}]_{\text{T}} = (0.1-1.0) \times 10^{-1} \text{ M}$ with the result that equilibrium is rapidly attained in this system in the absence of significant cyanide loss from the iron(II) centers (see above). He also estimated $k_{-2} = 3 \times 10^{-3} \text{ sec}^{-1}$ at 10 °C, which is in fairly good agreement with our extrapolated estimate^{7,9} of $1.6 \times 10^{-3} \text{ sec}^{-1}$ at this temperature. However, estimates of the other rate constants in eqs 1 and 2 cannot be obtained directly from Emschwiller's studies and we are therefore encouraged to attempt an indirect, kinetic assignment of this system at pH 10 and 10 °C.

Higginson's¹² direct measurement of the rate constant for reaction of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ with the iso-

electronic species $\text{Co}(\text{CN})_6^{3-}$ at 9.4°C (eq 3)



can be used to approximate $k_x = k_1 = 3.5 \text{ M}^{-1} \text{ sec}^{-1}$ in eq 1, and the stability constant¹² $K_x = (2 \pm 1.5) \times 10^3 \text{ M}^{-1}$ is a reasonable approximation for K_1 in eq 1 at 10°C . When the error in $K_x = K_1$ is accounted for, these assumptions lead to $k_{-1} = (1-7) \times 10^{-3} \text{ sec}^{-1}$ at 10°C in eq 1. Since $K_1K_2 = k_1k_2/k_{-1}k_{-2} = 1700 \text{ M}^{-1}$ (see above), it follows that $k_2 = (0.8-5.6) \times 10^{-3} \text{ sec}^{-1}$ at 10°C and pH 10.

Emschwiler's¹⁰ calculated value of the apparent rate constant for dimer formation, $k_f = 5.1 \text{ M}^{-1} \text{ sec}^{-1}$ at 10°C and pH 10, is now seen to be consistent with the assignment $k_f = K_1k_2$ in eqs 1 and 2. If K_1 is taken to be $2 \times 10^3 \text{ M}^{-1}$ (see above), then k_2 would be $2.5 \times 10^{-3} \text{ sec}^{-1}$, which is in the range derived above and serves as an independent check of the model we are proposing for this system.¹³

The properties of aqueous solutions of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ at $9 \leq \text{pH} \leq 11$ are consistent with the presence of at least *three* species (including I) under such conditions,⁷ as suggested by the magnitudes of K_1 and K_2 from our indirect analysis, which predicts the presence of comparable proportions of II and III at 10°C . This situation is reflected by the phenomena observed on mixing $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$ solutions with a large excess of X, when at least two kinetic events take place with very similar rate constants on the time scale for dissociation of III at $\text{pH} \geq 11$.⁷ These events are presumably connected with dissociation and conversion to $\text{Fe}(\text{CN})_5\text{X}^{n-}$ of both II and III, the former process involving displacement of H_2O in II. The increased importance of II at $\text{pH} \leq 11$ may reasonably be attributed to a change from coordinated OH^- to H_2O with decreasing pH. The latter form of the inner-sphere aquo-ligand would appear to stabilize II relative to III. The fact that only one dimer dissociation step III \rightarrow I is observed at $\text{pH} > 11$ indicates⁸ that an OH^- ligand in II is more rapidly displaced by X than is H_2O , and would also be consistent with an increase in k_2 with increasing pH, since in this case it is a potential bridging cyanide which is the substituting ligand. This tentative explanation of the apparent stabilization of II at pH 9-11 also suggests that inner-sphere H_2O in II is considerably less labile to substitution than is the aquo ligand in monomeric $\text{Fe}(\text{CN})_5\text{H}_2\text{O}_{\text{aq}}^{3-}$ (ref. 3, 7).

References

- 1 Previous studies have been made of equilibria involving pentacyanoiron(III) species in solution.² Dimeric pentacyanoiron(III) complexes are considerably less thermodynamically stable in alkaline solution than are their iron(II) analogs.
- 2 J. H. Espenson and S. Wolenuk, *Inorg. Chem.*, **11**, 1034 (1972) and references therein.
- 3 J. M. Malin and H. E. Toma, *Inorg. Chem.*, **12**, 2080 (1973); H. E. Toma, *Inorg. Chim. Acta*, **15**, 205 (1975).
- 4 Malin and Toma⁵ have shown that dissolution of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ in deoxygenated aqueous sodium perchlorate results in rapid hydrolysis to produce aquopentacyanoiron(II) species.
- 5 J. M. Malin and H. E. Toma, *Inorg. Chem.*, **13**, 1772 (1974).
- 6 G. Emschwiler, *Compt. Rend.*, **265**, 281 (1967) and references therein.
- 7 G. Davies and A. R. Garafalo, *Inorg. Chem.*, in the press, and references therein.
- 8 The rate-determining process at $\text{pH} > 11$ must be III \rightarrow II, since (i) II offers a co-ordination site (a replaceable aquo ligand) and (ii) the rate of dissociation of the $(\text{CN})_4\text{XFe}(\text{CN})\text{Fe}(\text{CN})_5^{n-}$ dimer formed would be expected to vary with the nature of X, which is not a rate-determining factor at $\text{pH} > 11$.
- 9 No estimate of errors was made since only the data at 25.0 and 35.0°C were used for the calculation of activation parameters. Data at lower temperatures indicate interference from another rate-determining step (see text) and higher temperatures are unsuitable for kinetic studies because of the thermal instability of pentacyanoiron(II) species.³
- 10 G. Emschwiler, *Compt. Rend.*, **238**, 341 (1954).
- 11 K. A. Hofmann, *Annalen*, **312**, 1 (1900); S. Ašperger, I. Murati and D. Pavlovic, *J. Chem. Soc. A*, 2044 (1969).
- 12 A. James, R. Murray and W. Higginson, *J. Chem. Soc. Dalton*, 1273 (1974).
- 13 The relaxation time observed on diluting aqueous solutions of pentacyanoiron(II) species with aqueous sodium perchlorate at fixed pH and ionic strength could, in principle, provide a means of determining the rate constants of eqs. 1 and 2. However, a knowledge of the equilibrium constants K_1 and K_2 , together with the concentrations of the various iron(II) species present at the instant of mixing, would be required (the system is never at equilibrium at $[\text{Fe}^{II}]_T \leq 10^{-3} \text{ M}$ and $\text{pH} \geq 9$). In addition, our analysis shows that k_{-1} , k_2 and k_{-2} are of similar magnitude at pH 10 and 10°C which would make analysis of the relaxation data unusually difficult.¹⁴
- 14 G. Czerlinski, "Chemical Relaxation", Dekker, New York, N.Y., 1966, Chapter 3.