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Kinetics and Mechanism of the Thiocyanate-Catalyzed Dissociation of $Fe_2(CN)_{10}{}^{6-}(aq)$ in Aqueous Sodium Perchlorate Solution

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The kinetics of the second stage of complexation of aquated $Fe(CN)_5NH_3{}^{3-}(aq)$ species by excess X = isonicotinamide, pyrazine, dimethyl sulfoxide, thiourea, $NO_2{}^-$, $SO_3{}^{2-}$, and SCN^- have been investigated by stopped-flow spectrophotometry under conditions where reactions of monomeric and dimeric iron(II) can be kinetically resolved. The rate-determining step in the second (dimer) reaction with all ligands except SCN^- was found to be acid-independent first-order bond rupture in the dicyano-bridged dimer $Fe_2(CN)_{10}{}^{6-}(aq)$ to give a common monocyano-bridged species which reacts rapidly with 2 mol of X to give 2 mol of mononuclear $Fe^{II}(CN)_5X^{n-}(aq)$ product. The rate constant for this process is $(1.63 \pm 0.01) \times 10^{-2}$ s^{-1} at 25°C, with $\Delta H_1{}^{\ddagger} = 25$ kcal mol^{-1} and $\Delta S_1{}^{\ddagger} = 18$cal deg^{-1} mol^{-1} at 25.0 °C and ionic strength 1.0 M. The first-order rate constant for reaction of $Fe_2(CN)_{10}{}^{6-}(aq)$ with excess SCN^- is given by $k_{obsd} = A[SCN^-]/(B + [SCN^-])$, with $A = 1.27 \pm 0.02$ s^{-1} and $B = (1.53 \pm 0.07) \times 10^{-2}$ M at 25.0 °C. The proposed mechanism for this latter reaction involves rate-determining dissociation of $[(SCN)(CN)_4Fe(CN,NC)Fe(CN)_4]^{7-}(aq)$ to give the monocyano-bridged species $[(SCN)(CN)_4FeCNFe(CN)_5]^{7-}(aq)$, which reacts rapidly with 1 mol of SCN^- to give 2 mol of mononuclear $Fe(CN)_5(SCN)^{4-}(aq)$. The activation parameters for dissociation of the dicyano-bridged intermediate are $\Delta H_3{}^{\ddagger} = 19.8 \pm 0.1$ kcal mol^{-1} and $\Delta S_3{}^{\ddagger} = 8.4 \pm 0.1$ cal deg^{-1} mol^{-1} at 25.0 °C and ionic strength 1.0 M. Although the spectral changes on mixing iron(II) dimer containing solutions with excess HS^- at pH 11 could not be resolved, the time scale for complete reaction suggests that dimer dissociation is also catalyzed by $HS^-(aq)$ and/or $S^{2-}(aq)$.

Introduction

Current interest in the properties of water molecules coordinated to low-spin iron(II) centers has prompted a recent investigation[1] in our laboratory of the kinetics of complexation of $Fe(CN)_5H_2O^{3-}(aq)$ (generated in situ by aquation of $Fe(CN)_5NH_3{}^{3-}(aq)$[2,3]) by a wide range of ligands and of its oxidation by oxygen, hydrogen peroxide, and *tert*-butyl hydroperoxide. Higher analytical iron(II) concentrations than previously employed[2–4] were necessary in the oxidation studies because of the relatively small spectral changes observed in the redox reactions.[1] Deoxygenated sodium perchlorate solutions of aquated $Fe(CN)_5NH_3{}^{3-}(aq)$ containing $[Fe^{II}] = (5–40) \times 10^{-5}$ M did not obey Beer's law and their spectra changed with time in a manner consistent with the slow formation of dimeric $Fe_2(CN)_{10}{}^{6-}(aq)$.[5] The two-component nature of such solutions was reflected by the appearance of two distinct kinetic processes on mixing with a complexing ligand such as isonicotinamide. Kinetic data for the first reaction with a given ligand were in good agreement with those obtained at much lower $[Fe^{II}]$,[1,2–4] indicating that in this case the observed process was complexation of $Fe(CN)_5H_2O^{3-}(aq)$. In this paper we describe our results for the subsequent complexation processes, which are postulated to involve reactions of $Fe_2(CN)_{10}{}^{6-}(aq)$.

Experimental Section

Reagents. The preparation and standardization of deoxygenated aqueous solutions of $NaClO_4$, NaOH, $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$, $NaNO_2$, NaCN, pyrazine (pz), isonicotinamide (IN), and thiourea (tu) and the use of certified buffers to calibrate the pH meter were as previously described.[1] Reagent grade NaSCN was recrystallized from water and dried in a vacuum oven overnight at 105 °C. Dimethyl sulfoxide (DMSO), Na_2S, and Na_2SO_3 were reagent grade and were used as supplied.

Apparatus. The stopped-flow apparatus was operated as before.[1] Spectra were recorded on a thermostated Beckman DK spectrophotometer at room temperature and 25.0 °C.

Kinetic Measurements. The kinetics of complexation of aquated $Fe(CN)_5NH_3{}^{3-}$ species in the presence of a large excess of ligand were monitored spectrophotometrically in the stopped-flow apparatus[1] and kinetic traces were analyzed by a combination of analog[6] and on-line[7] computer methods.

A typical total reaction time for all ligands except thiocyanate was 2.5 min, which falls awkwardly between the time scales in conventional and stopped-flow spectrophotometry. The PDP-11A computer was interfaced[7] to record spectral changes for times up to 10 min. Spectral interference due to diffusion[8] in the observation cell of the stopped-flow apparatus was not observed within this period. Iron(II) concentrations were in the range $(1–20) \times 10^{-5}$ M except in the thiocyanate reactions, where $[Fe^{II}] = (2.5–124) \times 10^{-5}$ M. Ligand concentrations varied in the range $(2–200) \times 10^{-3}$ M and the experimental pH range was 8.6–12.5 at 25.0 °C for all ligands except thiocyanate (see below). The ionic strength in all experiments was adjusted to 1.0 M by addition of sodium perchlorate. Reactions with IN and SCN^- were also investigated at 15–35 and 5–25 °C, respectively.

The kinetics of complexation with X = IN, pz, $NO_2{}^-$, and DMSO as ligands were determined by monitoring $Fe^{II}(CN)_5X^{n-}(aq)$ product formation at 400–525 nm, while the kinetic data for X = CN^-, tu, and $SO_3{}^{2-}$ were obtained from the rate of absorbance decrease at 390–430 nm. Complexation with X = SCN^- was monitored both by $Fe(CN)_5(SCN)^{4-}(aq)$ product formation at 390 nm and by iron(II) reactant disappearance at 420 and 455 nm. Experiments with X = HS^- ($pK_a = 12$) at pH 11 gave irreproducible spectral changes which could not be resolved at 375–460 nm.

The relative magnitudes of the two spectral changes observed in the reaction with a ligand such as SCN^- or IN can be used to determine the relative proportions of monomeric and dimeric iron(II) species.[1,5] When reagent solutions were prepared by dissolving $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ in aqueous sodium perchlorate solution at 5.0 or 15.0 °C, the spectral changes due to dimer dissociation to give $Fe(CN)_5(SCN)^{4-}(aq)$ or $Fe(CN)_5IN^{3-}(aq)$ were too small to give kinetic data of acceptable precision. However, when iron(II) solutions at 25.0 °C were cooled to 5.0 °C, enough dimer was initially present to allow a study of its reaction with thiocyanate. This latter method of solution preparation still gave unsatisfactory results in isonicotinamide experiments at 15.0 °C: first-order plots were linear only to 1 half-life. No experiments were attempted above 35 °C since Malin[2] has suggested an upper limit of about 30 °C for experiments with pentacyanoiron(II) species.

We have previously noted[1] that the reactions of monomeric and dimeric iron(II) species with various ligands can be resolved at pH $\gtrsim$9.5. Nonexponential dimer reaction traces were obtained at pH 7–11 with thiocyanate as the complexing ligand. However, exponential traces were obtained at 390 nm when the pH was maintained at 4.5 or 12.5. Nonexponential traces at pH 9 and at 420 or 455 nm were resolved from the slopes of the two components of a plot of log ($A_\infty - A_t$) vs. time, where A_∞ and A_t are the absorbances at "infinite" time and time *t*, respectively.

It should be noted that the experiments at pH 4.5 do not reflect the amount of dimer present at equilibrium at this pH, because experiments were conducted by mixing iron(II) solutions at pH ~9.5 with thiocyanate solutions whose acidities were adjusted such that mixing would give the desired pH of 4.5.

The complex spectral behavior at pH 9 was shown not to arise from the presence of $NH_3/NH_4{}^+$ produced by aquation of $Fe(CN)_5NH_3{}^{3-}(aq)$ as follows. A solution containing $[Fe^{II}] = 4 \times 10^{-4}$ M at ionic strength 1 M was divided into two equal portions. The

Table I. Kinetic Data for the Reaction of $Fe_2(CN)_{10}^{6-}$ with Complexing Ligands at 25 °C

Ligand, X	pH	$10^2[X]^a$	$10^4 k_{obsd}{}^b$
IN	12.3	1.00[c]	162 (3)
		1.00[d]	160 (4)
		5.00[d]	160 (4)
	11	1.00	161 (3)
		0.20	160 (1)
	12.3	5.00[e]	640 (10)
pz		1.28	163 (1)
	11.5	2.18[f]	166 (3)
DMSO	12.3	5.0	164 (5)
CN^-	12.5	1.00	165 (6)
		4.99	161 (4)
NO_2^-	12.3	1.07	163 (4)
		2.94	170 (6)
		Av	163 ± 1
tu	12.3	5.0	121 (8)
SO_3^{2-}	12.3	14.0[f]	109 (2)

[a] All concentrations are M; $[Fe^{II}] = 10^{-4}$ M at 25.0 °C unless noted otherwise. [b] Units are s^{-1}; errors quoted are one standard deviation. [c] $[Fe^{II}] = 1.0 \times 10^{-5}$ M. [d] $[Fe^{II}] = 5 \times 10^{-5}$ M. [e] Measured at 35.0 °C; data not included in average. [f] $[Fe^{II}] = 2.0 \times 10^{-4}$ M.

pH of the first portion was adjusted to pH 8.6 and the solution was then flushed with deoxygenated N_2 for 10 min. The pH of the second portion was adjusted to 11 by addition of NaOH and it was then flushed with N_2 for 10 min to remove NH_3. Readjustment of the pH of this latter solution to the same pH as the first portion gave two iron(II) solutions which exhibited closely similar spectral changes on mixing with pz in the stopped-flow apparatus.

The first-order rate constants, k_{obsd}, for the reactions with SCN^- are the average of the results of three to ten kinetic runs under fixed concentration conditions. Experiments in other systems usually consisted of three to five runs. All first-order rate constants are reported to ±1 standard deviation. Nonlinear least-squares routines and the procedures used for the determination of activation parameters in the SCN^- system were as previously described.[1]

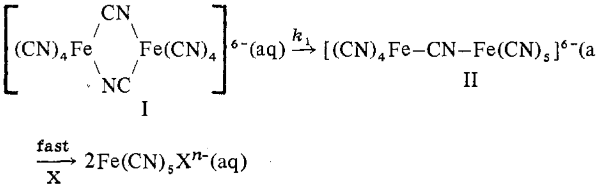
Results and Treatment of Data

Product Spectra. The products of reaction, $Fe(CN)_5X^{n-}(aq)$, from complexation reactions with excess X = IN, pz, NO_2^-, CN^-, and tu were established by comparison of spectra with literature data.[1,9-11] The product with excess SCN^- exhibited an absorption maximum at 383 nm (ϵ 434 M^{-1} cm^{-1}, pH 4.9) or 385 nm (ϵ 542 M^{-1} cm^{-1}, pH 12.1).[12] Formation of $Fe(CN)_5X^{n-}$ was quantitative under all experimental conditions.

Kinetics. Uncatalyzed Dimer Dissociation. The rate law for the second, slower reaction of excess IN, pz, NO_2^-, CN^-, tu, DMSO, and SO_3^{2-} with aquated $Fe(CN)_5NH_3^{3-}$ solutions at pH ≥11 was found to be

$$\frac{-\mathrm{d}\ln[\text{dimer}]}{\mathrm{d}t} = \frac{\mathrm{d}\ln[Fe^{II}(CN)_5X^{n-}]}{\mathrm{d}t} = k_{obsd} \tag{1}$$

for at least 90% reaction in all cases. The experimental data collected in Table I indicate that, except with X = tu or SO_3^{2-}, k_{obsd} is independent of the identity and concentration of the complexing ligand as well as of the presence of NH_3/NH_4^+, pH, and analytical [iron(II)]. The mean value of k_{obsd} for all X except tu and SO_3^{2-} at 25.0 °C is $(1.63 \pm 0.01) \times 10^{-2}$ s^{-1}, where the error quoted is the standard deviation of the mean.[13] A mechanism consistent with these findings is



I

II

(2)

Here, the rate-determining step is postulated to be first-order bridge rupture of the dicyano-bridged dimer $Fe_2(CN)_{10}^{6-}(aq)$[5e,14] to give a monocyano-bridged dimer[15] which is rapidly "scavenged" by X to give mononuclear $Fe(CN)_5X^{n-}(aq)$ products, with $k_{obsd} = k_1$. The data at 25.0 and 35.0 °C for reaction with IN (see Experimental Section) gave $\Delta H_1^\ddagger = 25$ kcal mol^{-1} and $\Delta S_1^\ddagger = 18$ cal deg^{-1} mol^{-1} at 25.0 °C and ionic strength 1 M. No estimate of errors was made because acceptable data were obtained at only two temperatures.

When conditions outside those in Table I were employed, the observed spectral changes were more complicated. When [IN] = 0.1 M at pH >11, the rate constant for reaction of the dimer appeared to be slightly greater than those in Table I ($k \approx 0.02$ s^{-1}), but the traces had poor infinite absorbances. An accurate estimate of the rate constant could not be obtained at $[OH^-] = 0.3$ M. The first-order rate constant continually decreased with time, probably indicating ligand decomposition.

At pH ~11, with $[X] \leq 2.0 \times 10^{-3}$ M, the initial portions of first-order plots were slightly curved, indicating incomplete resolution of the two reactions. Below pH 11, even with the highest ligand concentrations employed, the spectral changes were complex and evidence was found for a third reaction. At the iron(II) concentrations typically used in this study, significant amounts of dimer were usually not present except at pH ≳8.5. Between pH 8.5 and 9.5, reaction traces were always nonexponential and reactions of both the monomer and dimer appeared rapid and inseparable. Above pH 9.5, the monomer reaction could be studied without dimer complications if ligand concentrations were sufficiently high,[1] but the dimer reaction, when monitored in the pH 9.5–11 region, gave nonlinear first-order plots. Considering the time scale employed, the monomer reaction should have been complete and the spectral changes should only reflect dimer behavior. Since rate constants for the monomer reaction in this pH region with several ligands agree with those obtained at lower and higher pH,[1] the curved plots cannot be directly attributed to monomer reaction interference.

In the reaction with HS^-, the experimental pH was chosen to avoid the predominance of S^{2-} ligand species while keeping pH ≳10.5 (see above). Despite this precaution, the spectra of the products were unstable and no monitoring wavelength could be found where less than two closely coupled processes were apparent. Although no useful kinetic data could be obtained from this system, the time scale of the spectral changes was similar to that for SCN^- reactions, suggesting the occurrence of similar kinetic phenomena.

Thiocyanate-Catalyzed Dimer Dissociation. The reaction of $Fe_2(CN)_{10}^{6-}(aq)$ with SCN^- was much faster than that observed with all the other complexing ligands of this study. The kinetic data are collected in Table II. Figure 1 shows a plot of the pseudo-first-order rate constant k_{obsd} vs. $[SCN^-]$ at pH 4.4 and 12.5. These data are consistent with the acid-independent empirical rate law

$$k_{obsd} = \frac{A[SCN^-]}{[SCN^-] + B} \tag{3}$$

where A and B are empirical parameters. A nonlinear least-squares fit of the data to eq 3 gave $A = 1.27 \pm 0.02$ s^{-1} and $B = (1.55 \pm 0.07) \times 10^{-2}$ M at 25.0 °C.

The following mechanisms are consistent with empirical rate law (3).

Mechanism A is as follows

$$\mathrm{I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{II} \xrightarrow[SCN^-]{k_2} [(SCN)(CN)_4Fe\text{–}CN\text{–}Fe(CN)_5]^{7-}(aq)$$

$$\xrightarrow[\text{fast}]{SCN^-} 2Fe(CN)_5(SCN)^{4-}(aq) \tag{4}$$

In this mechanism, assumption of a steady state in [II] leads

Table II. Kinetic Data for the Reaction of $Fe_2(CN)_{10}^{6-}$ with Thiocyanate

Temp, °C	pH	$10^3[SCN^-]^a$	$10^2k_{obsd}{}^b$
5.0	12.3	150^c	10.8 (0.1)
15.0		100^d	39.1 (1.8)
		150^d	39.4 (0.4)
		200^d	39.3 (0.8)
25.0	4.4	2.58	16.0 (0.4)
	4.1	5.00	28.1 (0.6)
	12.5		33.2 (0.1)
		10.0^e	43.2 (0.4)
		10.0^c	43.2 (0.3)
	4.5	15.0^e	61.0 (0.9)
	12.5	15.0^f	64.1 (1.0)
	4.3	25.0	87.5 (1.6)
	12.5	25.0^f	82.4 (0.3)
	9.1	$50.0^{f,g}$	112 (3)
		$50.0^{f,h}$	122 (2)
	12.5	50.0^f	108 (2)
	6.5	100	115 (1)
	12.5	100^f	110 (2)
	4.4	150	105 (2)
	12.5	150^i	113 (3)

[a] All concentrations are M; $[Fe^{II}] = 5.0 \times 10^{-5}$ M unless noted otherwise. [b] Units are s^{-1}; errors quoted are one standard deviation. [c] $[Fe^{II}] = 6.2 \times 10^{-4}$ M. [d] $[Fe^{II}] = 5.0 \times 10^{-4}$ M. [e] $[Fe^{II}] = 2.5 \times 10^{-5}$ M. [f] $[Fe^{II}] = 10^{-4}$ M. [g] Measurements at 420 nm. [h] Measurements at 455 nm. [i] $[Fe^{II}] = 2.0 \times 10^{-4}$ M.

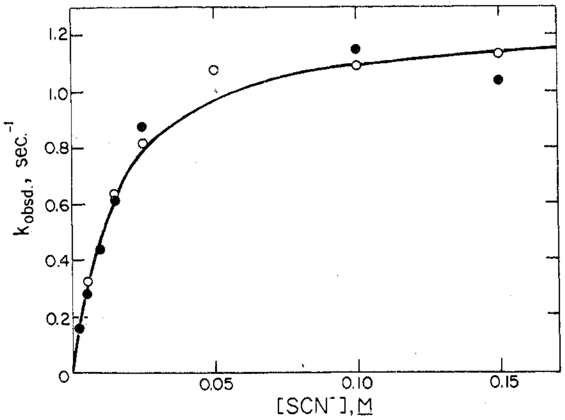


Figure 1. Plot of k_{obsd} vs. $[SCN^-]$ for thiocyanate-catalyzed dimer dissociation at $[Fe^{II}] = (2.5\text{–}20) \times 10^{-5}$ M, 25.0 °C, and ionic strength 1.0 M. Open and filled circles refer to data at pH 12.5 and 4.4, respectively.

to eq 5, which is of the same form as eq 3 with $A = k_1$ and

$$k_{obsd} = \frac{k_1[SCN^-]}{k_{-1}/k_2 + [SCN^-]} \tag{5}$$

$B = k_{-1}/k_2$. This mechanism can be discarded because A from eq 3 is not identical with k_1 for the uncatalyzed dissociation reaction (see eq 2), as would be the case if this mechanism were valid.

Mechanism B is given by

$$\begin{aligned} &SCN^- + I \overset{\text{fast}}{\rightleftharpoons} \underset{\text{III}}{[(SCN)Fe_2(CN)_{10}]^{7-}(aq)} \quad K \\ &\xrightarrow{k_3} [(SCN)(CN)_4FeCNFe(CN)_5]^{7-}(aq) \\ &\xrightarrow[SCN^-]{\text{fast}} 2Fe(CN)_5(SCN)^{4-}(aq) \end{aligned} \tag{6}$$

Here, III is postulated to be a di-μ-cyano-bridged dimer with seven- and six-coordinated iron(II) atoms. This mechanism predicts that k_{obsd} will be given by eq 7. Comparison of eq

$$k_{obsd} = \frac{k_3[SCN^-]}{1/K + [SCN^-]} \tag{7}$$

7 with eq 3 gives $A = k_3$ and $B = 1/K$. Thus, $k_3 = 1.27 \pm 0.02$ s^{-1} and $K = 65 \pm 3$ M^{-1} at 25.0 °C. Data at 5.0 and 15.0 °C obtained at high $[SCN^-]$, where the first term in the denominator of eq 7 can be neglected, were used in a nonlinear least-squares fit of the data to calculate $\Delta H_3^{\ddagger} = 19.8 \pm 0.1$ kcal mol^{-1} and $\Delta S_3^{\ddagger} = 8.4 \pm 0.1$ cal deg^{-1} mol^{-1} at 25.0 °C and ionic strength 1.0 M.

The initial absorbance, A_0, at fixed wavelength and [iron(II)] on the time scale of the dimer dissociation studies is determined by the equilibrium constant K_X for equilibrium 8, together with the molar absorptivities of $Fe(CN)_5H_2O^{3-}$,

$$Fe(CN)_5H_2O^{3-} + X \rightleftharpoons Fe(CN)_5X + H_2O \quad K_X \tag{8}$$

$Fe_2(CN)_{10}^{6-}$, and $Fe(CN)_5X$ and the fraction of [iron(II)] in the dimeric form at the time at which a kinetic run is performed (the spectra of pentacyanoiron(II) solutions are time dependent in the absence of X except at low [iron(II)] and pH 6.5–9[1]). At a fixed time after preparation of a given iron(II) reagent solution, the initial absorbance for a kinetic run on the time scale appropriate for observation of dimer dissociation behavior in the presence of excess X was independent of [X] except when X = SCN^-.

This observation indicates that the only monomeric iron(II) species present at $t = 0$ for dimer dissociation is $Fe(CN)_5X$ except when X = SCN^- and is consistent with $K_{SCN} = 90 \pm 30$ M^{-1} in eq 8,[17] which is the smallest value of K_X for the ligands of this study. Thus, A_0 will vary since the ratio $[Fe(CN)_5SCN^{4-}]/[Fe(CN)_5H_2O]$ is a function of $[SCN^-]$. This dependence of A_0 (for dimer dissociation) on $[SCN^-]$ even at $[SCN^-] = 1.5 \times 10^{-1}$ M and the time-dependent nature of iron(II) reactant solutions precluded an accurate spectrophotometric determination of K in eq 6.

Discussion

Emschwiller[5e] has isolated $Pb_3[Fe_2(CN)_{10}]$ from concentrated pentacyanoaquoiron(II) solutions prepared by the method of Hofmann.[18] However, other workers[2] have noted difficulties in working with such preparations, and, like them, we have chosen the alternative route to monomeric and dimeric cyanoiron(II) species via aquation of $Fe(CN)_5NH_3^{3-}(aq)$. The isolation of the above lead salt does not necessarily prove that the complex $Fe_2(CN)_{10}^{6-}(aq)$ is the only dimeric iron(II) species in solution, but Emschwiller's observations[5] and those reported here do suggest, at least at pH >11, that there are only two major cyanoiron(II) components, a monomer and a dimer, in such solutions. Emschwiller noted two reactions on addition of the complexing ligand nitrosobenzene, PhNO. The first, which may be readily attributed to complexation of $Fe(CN)_5H_2O_{aq}{}^{3-}$, was too fast to be followed by conventional means, but the second, slower reaction to form $Fe(CN)_5PhNO_{aq}{}^{3-}$ proceeded with an activation energy of 28–29 kcal mol^{-1}, which is similar to that of the present study with IN, where the observed reaction is that of spontaneous dissociation of $Fe_2(CN)_{10}^{6-}(aq)$ (Table I). By taking advantage of the difference in rates of reaction of $Fe(CN)_5H_2O^{3-}(aq)$ and $Fe_2(CN)_{10}^{6-}(aq)$ with PhNO, Emschwiller determined the equilibrium constant $K_D \approx 1700$ M^{-1} at 10 °C and pH 10 in borate-buffered 1 M sodium perchlorate solution[5d] for the reaction

$$2Fe(CN)_5H_2O^{3-} \rightleftharpoons Fe_2(CN)_{10}^{6-}(aq) + 2H_2O \quad K_D \tag{9}$$

The enthalpy and entropy changes for reaction 9 were estimated to be –(10–15) kcal mol^{-1} and –35 cal deg^{-1} mol^{-1}, respectively.[5d]

Monomer–dimer equilibration in this system is significantly slower under our conditions (ref 1 and this work) than was the case in Emschwiller's studies[5d] at much higher $[Fe^{II}]$; although experimental data are lacking in the latter report,[5d] an essential conclusion was that equilibrium 9 shifted to the left with increasing temperature. Our observations suggest that equilibrium 9 shifts to the left with *decreasing* temperature[19] (see also Experimental Section).

Although we have been unable to resolve the complicated spectral behavior observed on mixing aquated $Fe(CN)_5NH_3^{3-}(aq)$ with HS^-, we suspect that this ligand, like SCN^-, catalyzes the dissociation of $Fe_2(CN)_{10}^{6-}(aq)$. It is notable that the "soft" ligand CN^- is not able to act as an efficient catalyst for this process, which is also the case in CN^- substitution at $Fe(CN)_5X^{n-}$ ($X = SO_3^{2-}$,[10] py,[17] or nitrosobenzene[20]), where the rate-determining process is spontaneous Fe–X bond breaking.

Except for SCN^-, the kinetic data for other sulfur-containing ligands of this study indicate that these species do not catalyze $Fe_2(CN)_{10}^{6-}(aq)$ dissociation, despite the fact that the $Fe(CN)_5X^{n-}(aq)$ products (particularly with X = DMSO[21]) are all very thermodynamically stable.[17] This result indicates that catalysis by SCN^- arises from accessibility of the sulfur atom in this ligand.

We suggest that the product of reaction with $X = SCN^-$ is $(CN)_5FeSCN^{4-}(aq)$ based on the following arguments. Gray[22] has shown that the iron(III) analogue is $(CN)_5FeNCS^{3-}(aq)$ (λ_{max} 590 nm). Oxidation[23] of $Fe(CN)_5(SCN)^{4-}(aq)$ by $Fe(CN)_6^{3-}$ produces a transient purple intermediate (λ_{max} 550–560 nm) which converts via an isosbestic reaction at 575 nm to $Fe(CN)_5NCS^{3-}(aq)$. The most likely identity for the intermediate is $(CN)_5FeSCN^{3-}(aq)$, produced by outer-sphere oxidation of the thiocyanatoiron(II) species.[22,23] This assignment is further supported by the conclusion that $K_{N_3^-} << K_{SCN^-}$ in eq 8.[1,17]

The kinetic data of Ašperger[4] can be used to estimate pseudo-first-order rate constants for reaction of $Fe(CN)_5H_2O^{3-}(aq)$ with SCN^- under our experimental conditions. For example, at $[SCN^-] = 0.05$ M, where rate saturation is observed in the dimer reaction at 25 °C (Figure 1), the monomer reaction would give rise to a first-order process with $k_{obsd} = 3.2\ s^{-1}$, which is close to that actually observed at saturation. This similarity of rates, coupled with the similarity of reactant and product spectra, is probably the major factor leading to the observed spectral complications at low $[SCN^-]$.

Finally, the complicated spectral behavior at pH <11 with the other ligands should briefly be considered. The mechanism in eq 2 requires rapid scavenging of a monocyano-bridged iron(II) dimer species, presumably $[(H_2O)(CN)_4Fe(CN)Fe(CN)_5]^{6-}(aq)$, by X. It is conceivable that such an intermediate could behave as a proton acid and be present as $[(OH)(CN)_4Fe(CN)Fe(CN)_5]^{7-}(aq)$ at high pH. Formation of $Fe(CN)_5X^{n-}$ requires breaking of the remaining CN bridge, which may be catalyzed through formation of $[(X)(CN)_4Fe(CN)Fe(CN)_5]^{n-}(aq)$. However, if a water molecule is more difficult to displace than OH^- in the formation of this intermediate, then scavenging efficiency will be decreased at pH < pK_a for coordinated water, and dissociation of $Fe_2(CN)_{10}^{6-}(aq)$ could become kinetically coupled to $Fe(CN)_5X^{n-}(aq)$ formation. Mild support for this suggestion is provided by our observation of an increase in the initial rate of $Fe_2(CN)_{10}^{6-}(aq)$ formation with increasing pH $\gtrsim 9$.[1]

Registry No. $Fe_2(CN)_{10}^{6-}$, 28850-28-4; isonicotinamide, 1453-82-3; pyrazine, 290-37-9; DMSO, 67-68-5; thiourea, 62-56-6; NO_2^-, 14797-65-0; CN^-, 57-12-5; SO_3^{2-}, 14265-45-3; SCN^-, 302-04-5; HS^-, 15035-72-0.

References and Notes

(1) G. Davies and A. R. Garafalo, *Inorg. Chem.*, **15**, 1101 (1976).

(2) J. M. Malin and H. E. Toma, *Inorg. Chem.*, **12**, 2080 (1973).

(3) J. M. Malin and H. E. Toma, *Inorg. Chem.*, **13**, 1772 (1974).

(4) Z. Bradic, M. Pribanic, and S. Ašperger, *J. Chem. Soc., Dalton Trans.*, 353 (1975).

(5) (a) G. Emschwiller, *C. R. Hebd. Seances Acad. Sci.*, **238**, 341 (1954); (b) *ibid*, **239**, 1213 (1954); (c) *ibid.*, **259**, 4281 (1964); (d) *ibid.*, **260**, 4333 (1965); (e) *ibid.*, **265**, 281 (1967).

(6) J. E. Crooks, M. Zetter, and P. A. Tregloan, *J. Sci. Instrum.*, **3**, 73 (1970).

(7) M. Schure, to be submitted for publication.

(8) E. F. Caldin, "Fast Reactions in Solution", Blackwell, Oxford, 1964, p 43.

(9) J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, **5**, 573 (1966).

(10) Z. Bradic, D. Pavlovic, I. Murati, and S. Ašperger, *J. Chem. Soc., Dalton Trans.*, 344 (1974).

(11) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973).

(12) The spectra with $X = SCN^-$ were measured at $[SCN^-] = 0.20$ M and room temperature. The ratio $[Fe(CN)_5SCN^{4-}]/[Fe(CN)_5H_2O^{3-}]$ is ca. 20 under these conditions. The pH dependence of the spectra of thiocyanato complexes is presumably connected with protonation of $Fe(CN)_5SCN^{4-}$ at low pH.[2]

(13) The experiments with $X = SO_3^{2-}$ and tu were conducted in order to establish whether or not other sulfur-containing ligands catalyze the dissociation of $Fe_2(CN)_{10}^{6-}(aq)$ (see Discussion). The lower values of k_{obsd} for these two ligands may reflect differences in the stability of reaction precursors as compared to those for other X's in Table I, although this suggestion can only be tentative in view of the limited data available for reactions with SO_3^{2-} and tu.

(14) G. Emschwiller and S. K. Jorgensen, *Chem. Phys. Lett.*, **5**, 561 (1970).

(15) Similar monobridged cyanoiron(II) dimer species have been described previously.[16]

(16) G. Emschwiller, *C. R. Hebd. Seances Acad. Sci.*, **268**, 692 (1969).

(17) A. D. James and R. S. Murray, *J. Chem. Soc., Dalton Trans.*, 1530 (1975).

(18) K. A. Hofmann, *Justus Liebigs Ann. Chem.*, **312**, 1 (1900).

(19) The enthalpy and entropy changes for eq 9 in ref 5d were obtained over a narrow temperature range (10–20 °C) and complete equilibrium data are not cited. However, it is interesting to note that if $\Delta H \approx -10$ kcal mol^{-1}, then, with $\Delta S_9 = -35$ cal $deg^{-1}\ mol^{-1}$, reaction 9 would be almost thermoneutral.

(20) D. Pavlovic, I. Murati, and S. Ašperger, *J. Chem. Soc., Dalton Trans.*, 602 (1973).

(21) H. E. Toma, J. M. Malin, and E. Giesbrecht, *Inorg. Chem.*, **12**, 2084 (1973).

(22) D. F. Gutterman and H. B. Gray, *Inorg. Chem.*, **11**, 1727 (1972).

(23) R. Stasiw and R. G. Wilkins, *Inorg. Chem.*, **8**, 156 (1969).