ruthenium(IV) complexes oxidize organic substrates faster than the analogous bis(bipyridine) complexes, with fewer side reactions. The increased hydrophobic character of the biquinoline ligand, relative to that of bipyridine, enhances the rate of oxidation of hydrophobic substrates in aqueous solution. In addition, side reactions such as conproportionation are decreased, presumably through the increased steric bulk of the biquinoline ligand, relative to that of bipyridine. Thus, in the design of substrate oxidants, it is important to differentiate between hydrophobic and steric ligand effects, where it is possible to enhance reactivity and minimize side reactions.

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Supplementary Material Available: Table X, listing carbon and hydrogen elemental analysis data for the synthesized complexes (1 page). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of the Acid-Catalyzed Aquation and Base Hydrolysis of Nitropentacyanoferrate(III) in Aqueous Solution. Evidence for a Pseudo-Zero-Order Hydrolysis Process

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The title reactions were studied spectrophotometrically and kinetically in the pH ranges 0.3–2.0 and 11–13.7, respectively. For the acid-catalyzed aquation, a dependence of the observed rate constant on the square of the acid concentration was found. A mechanism consisting of acid-catalyzed aquation of a protonated nitro complex is proposed to account for these observations and the kinetic parameters (ΔH^*, ΔS^*, and ΔV^*). Base hydrolysis was found to be catalyzed by iron(II) species and exhibits pseudo-zero-order kinetics. In the presence of $Fe^{II}(CN)_5NO_2^{4-}$ as catalyst, aquation of this complex is the rate-determining step of the process, followed by a rapid ligand-exchange reaction between the Fe(II) and Fe(III) species. The observed mechanistic results are discussed in reference to related systems reported in the literature.

Introduction

Substitution reactions of pentacyanoiron(II/III) follow the overall reaction (1) and have received considerable attention from both a kinetic and a thermodynamic point of view.[1-11] Most of

$$Fe(CN)_5X + Y \rightleftharpoons Fe(CN)_5Y + X \qquad (1)$$

the studies were performed on the iron(II) complexes and only a few[10-14] on the less reactive and more stable iron(III) species. Noteworthy is the fact that some of the latter reactions are catalyzed by traces of $Fe^{II}(CN)_5X^{n-}$ complexes.[11] We recently studied the substitution reactions of $Fe(CN)_5NO_2^{3-}$[15] and found the complex to be relatively stable in aqueous solutions in the range $5 \leq pH \leq 10$. In more acidic medium, acid-catalyzed aquation occurs and the reaction product is $Fe(CN)_5H_2O^{2-}$. In basic medium (pH >10), hydrolysis to $Fe(CN)_5OH^{3-}$ occurs and the rate of the process depends on $[OH^-]$. These reported observations were of preliminary nature, and in this paper we report a detailed kinetic analysis of numerous rate parameters, viz. $[H^+]$, $[OH^-]$, [Fe(II) species], temperature, and pressure, in order to reveal the intimate nature of the substitution mechanisms.

Experimental Section

Potassium nitropentacyanoferrate(III), $K_3[Fe(CN)_5NO_2]$, was prepared as described before,[15] and its purity was checked by elemental analyses and IR and UV–vis spectroscopy. Solutions containing $Fe(CN)_5NO_2^{4-}$ were prepared by dissolving $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ in 0.2 M NaOH. Conversion of the nitrosyl complex to the nitro species (for which ϵ = 3000 M^{-1} cm^{-1} at 400 nm) was observed by monitoring spectral changes. Solutions of HCl and NaOH were used to adjust the pH in acidic and basic media, respectively, and buffers were not employed to avoid further complications. Chemicals of analytical reagent grade and doubly distilled water were used throughout this study.

Table I. Rate and Activation Parameters for the Acid-Catalyzed Aquation of $Fe(CN)_5NO_2^{3-}$ in Aqueous Solution[a]

temp, °C	pH	k_{obsd},[b] s^{-1}	k,[c] M^{-1} s^{-1}	K,[c] M^{-1}
17	2.0	5.60×10^{-4}	7.5 ± 1.9	0.75 ± 0.21
	1.0	5.30×10^{-2}		
	0.6	0.317		
	0.3	0.910		
25	2.0	1.41×10^{-3}	12.9 ± 1.9	1.11 ± 0.17
	1.3	3.55×10^{-2}		
	1.0	0.124		
	0.70	0.445		
	0.60	0.700		
	0.46	1.29		
	0.40	1.60		
	0.35	1.89		
	0.30	2.10		
32	2.0	2.10×10^{-3}	17.4 ± 2.6	1.22 ± 0.26
	1.0	0.182		
	0.6	1.10		
	0.3	3.30		
40	2.0	4.56×10^{-3}	31.2 ± 2.0	1.48 ± 0.10
	1.0	0.410		
	0.6	2.10		
	0.3	6.41		
ΔH^*, kJ mol^{-1}			43 ± 3	
ΔS^*, J K^{-1} mol^{-1}			−80 ± 10	

[a] Conditions: [Fe(III)] = 1×10^{-3} M; ionic strength 0.5 M ($LiClO_4$). [b] Mean value of at least five kinetic runs. [c] Calculated according to eq 4—see Discussion.

The acid-catalyzed aquation of $Fe(CN)_5NO_2^{3-}$ was monitored at 555 nm by using a Shimadzu UV-250 spectrophotometer for the slow reactions and a Durrum D110 stopped-flow spectrophotometer for the fast reactions (pH <2). The latter instrument was connected to a Tektronix 5111A oscilloscope for visual display of the reaction trace and an Apple

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Table II. Effect of Pressure on the Acid-Catalyzed Aquation of $Fe(CN)_5NO_2^{3-}$ [a]

$[H^+]$, M	pressure, MPa	k_{obsd},[b] s^{-1}	$\Delta V^{\neq}$,[c] $cm^3\ mol^{-1}$
0.2	5	0.461	+2.2 ± 0.1
	25	0.453	
	50	0.445	
	75	0.432	
	100	0.424	
0.5	5	1.84	+1.9 ± 0.1
	25	1.79	
	50	1.76	
	75	1.73	
	100	1.71	

[a] Conditions: $[Fe(III)] = 1 \times 10^{-3}$ M; ionic strength 0.5 M ($LiClO_4$); temperature 25 °C. [b] Mean value of at least five kinetic runs. [c] Calculated from the relationship $(\partial \ln k_{obsd}/\partial p)_T = -\Delta V^{\neq}/RT$.

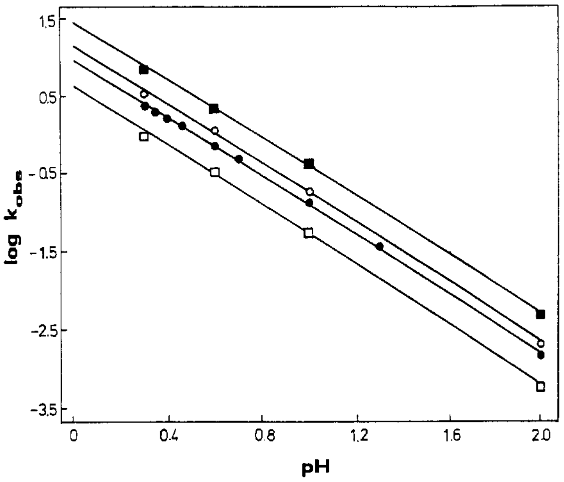

Figure 1. Plots of log k_{obsd} versus pH for the acid-catalyzed aquation of $Fe(CN)_5NO_2^{3-}$ at (□) 17, (●) 25, (○) 32, and (■) 40 °C and 0.5 M ionic strength.

II computer for the evaluation of the pseudo-first-order rate constant by an advanced data acquisition and analysis program.[16] Both instruments were thermostated within ±0.1 °C in the range 17–40 °C. The pressure dependence of the observed rate constant was measured with the aid of a locally manufactured high-pressure stopped-flow system.[17] First-order kinetics (up to 3 half-lives) was observed for all kinetic runs in acidic medium.

The base hydrolysis of $Fe(CN)_5NO_2^{3-}$ was monitored at 392 or 555 nm, where $Fe(CN)_5OH^{3-}$ and $Fe(CN)_5NO_2^{3-}$ exhibit characteristic absorptions, respectively, by using an Shimadzu UV-250 spectrophotometer in the range $11 \leq pH \leq 13.7$. In the presence of $Fe^{II}(CN)_5NO_2^{4-}$ kinetic runs for base hydrolysis were only performed at 555 nm due to the strong absorption of $Fe^{II}(CN)_5NO_2^{4-}$ at 392 nm.

Results and Discussion

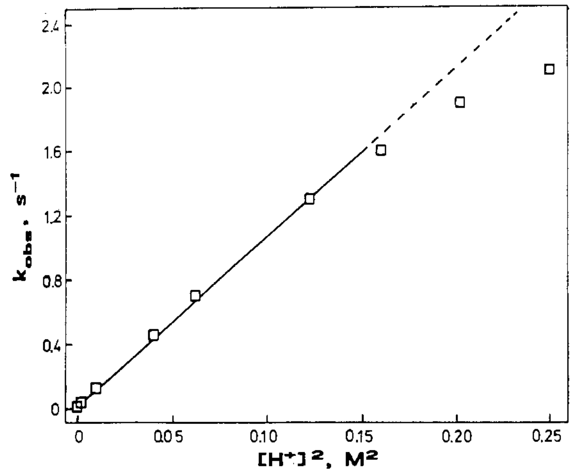

Figure 2. Plot of k_{obsd} versus $[H^+]^2$ for the acid-catalyzed aquation of $Fe(CN)_5NO_2^{3-}$ at 25 °C and 0.5 M ionic strength.

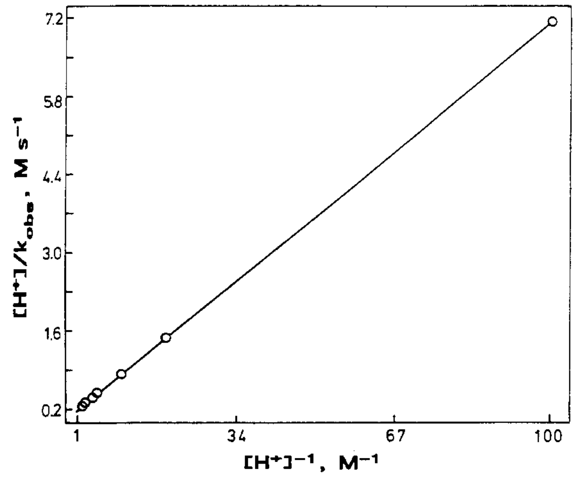

Figure 3. Plot of $[H^+]/k_{obsd}$ versus $[H^+]^{-1}$ for the acid-catalyzed aquation of $Fe(CN)_5NO_2^{3-}$ at 25 °C and 0.5 M ionic strength.

The kinetics of the aquation reaction of $Fe(CN)_5NO_2^{3-}$ in acidic medium was studied as a function of temperature, $[H^+]$, and pressure, for which the results are summarized in Tables I and II. For all the studied acid dependencies, plots of log k_{obsd} versus pH are linear (Figure 1) with slopes varying between 1.87 and 1.91. From this we conclude an approximate dependence of k_{obsd} on the square of the acid concentration. A plot of k_{obsd} versus $[H^+]^2$ for the extended series of data at 25 °C (Figure 2) demonstrates a linear dependence of k_{obsd} on $[H^+]^2$ at low values of $[H^+]$, with a slight curved behavior at higher $[H^+]$ values. Such curved relationships are very typical for precursor complex formation mechanisms involving the formation of a protonated complex as outlined in reaction 2.

$$Fe(CN)_5NO_2^{3-} + H^+ \overset{K}{\rightleftharpoons} Fe(CN)_5NO_2H^{2-}$$

$$Fe(CN)_5NO_2H^{2-} + H^+ \xrightarrow{k} Fe(CN)_5NO^- + H_2O \qquad (2)$$

$$Fe(CN)_5NO^- + H_2O \xrightarrow{fast} Fe(CN)_5H_2O^{2-} + NO^+$$

These are followed by

$$NO^+ + H_2O \rightarrow NO_2^- + 2H^+$$

In this suggested mechanism the nitro complex is protonated in a preequilibrium step with formation constant K, which is followed by the rate-determining acid-catalyzed formation of the nitrosyl–iron(III) species with rate constant k. The final step in the mechanism involves rapid aquation to produce the aqua–iron(III) species. The rate-determining step may involve the formation of a $Fe(CN)_5NO_2H_2^-$ species, which then aquates directly to the final products. The overall rate law for such a mechanism is given by eq 3, according to which k_{obsd} versus $[H^+]^2$

$$k_{obsd} = kK[H^+]^2/(1 + K[H^+]) \qquad (3)$$

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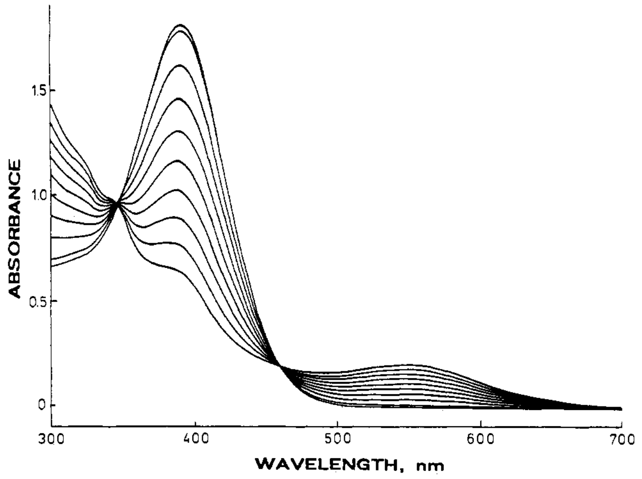

Figure 4. Repetitive-scan UV-vis spectra for base hydrolysis of $Fe(CN)_5NO_2^{3-}$. Conditions: [Fe(III)] = 1 × 10^{-3} M; [NaOH] = 0.5 M; Δt = 10 min; optical pathlength 1 cm.

should be linear at low [H^+] and curved at higher [H^+] as demonstrated in Figure 2. At low [H^+], i.e. where $1 + K[H^+] \approx 1$, the slope of k_{obsd} versus $[H^+]^2$ should equal kK and has a value of 10.3 M^{-1} s^{-1}. A more accurate fit of the data can be obtained by rewriting eq 3 as in (4) and plotting $[H^+]/k_{obsd}$ versus $1/[H^+]$.

$$[H^+]/k_{obsd} = 1/k + 1/kK[H^+] \tag{4}$$

All the data points in Figure 2 then fall on a straight line with intercept $1/k$ and slope $1/kK$, from which k and K could be evaluated. The corresponding values of k and K are summarized as a function of temperature in Table I, the validity of these fits being demonstrated by the plots in Figure 3.

The plot in Figure 1 clearly demonstrates that there is no significant intercept, i.e. no significant acid-independent pathway under the present conditions. Furthermore, this also indicates that there is no significant contribution from a reverse reaction, which would also show up as an intercept in such a case. The slight curvature in Figure 2 is in good agreement with the relatively small preprotonation constant of between 0.7 and 1.5 M^{-1}. This constant has the magnitude of an ion-pair formation constant between a 3− and a 1+ charged species at an ionic strength of 0.5 M.[18] The rate constant k is second order and represents the acid-catalyzed formation of the intermediate nitrosyl complex. This process is characterized by a relatively low activation enthalpy, characteristic for the breakage of a secondary N–O bond and very similar to that found for the cleavage of O–C bonds in the acid-catalyzed decarboxylation of carbonato complexes. The significantly negative value for $\Delta S^{\ddagger}$ presumably results from the formation of a highly ordered transition state involving bond formation with the proton prior to loss of H_2O.

The pressure dependence of this reaction was studied at two acid concentrations, and in both cases the observed rate constant only decreases slightly with increasing pressure (Table II), resulting in a slightly positive $\Delta V^{\ddagger}$. Since the observed rate constant is a composite function, it follows that $\Delta V^{\ddagger} = \Delta \bar{V}(K) + \Delta V^{\ddagger}(k)$. However, since $\Delta V^{\ddagger}$ shows no remarkable acid dependence, it can be concluded that $\Delta \bar{V}(K)$ is either very small or independent of pH. Ion-pair formation or protonation in the preequilibration step involves charge neutralization, which could result in an overall increase in volume due to a decrease in electrostriction.[19] However, experience has shown us that such reaction volumes are in many cases not predictable and usually very small.[20,21] Similarly, it is difficult to predict the magnitude of $\Delta V^{\ddagger}(k)$, since this step involves bond formation, charge neutralization, and cleavage of the O–N bond. The overall almost zero value for $\Delta V^{\ddagger}$ indicates that this component is most probably also close to zero and that intrinsic and solvational volume contributions cancel each other. We conclude that the suggested mechanism in (2) is in agreement with all the observed kinetic results and now turn to the base hydrolysis process.

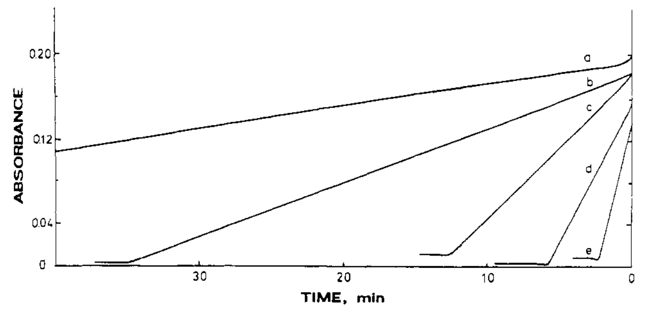

Figure 5. Plots of optical density versus time for the base hydrolysis of $Fe(CN)_5NO_2^{3-}$. Conditions: temperature 25 °C; ionic strength 0.5 M; wavelength 555 nm; [OH^-] = 0.1 M; [added Fe(II)] = 0 (a), 2.67 × 10^{-5} (b), 9.45 × 10^{-5} (c), 1.88 × 10^{-4} (d), and 4.44 × 10^{-4} M (e).

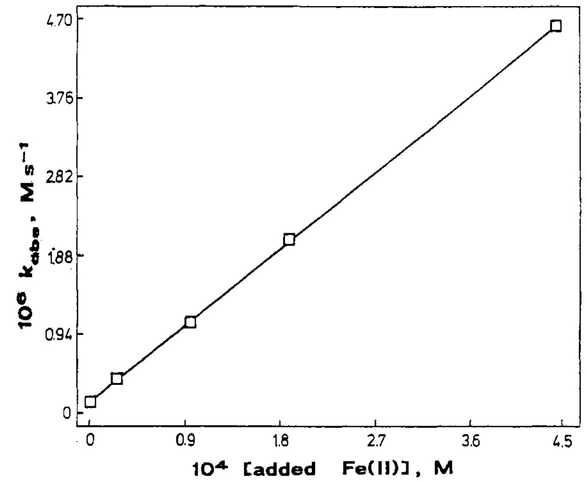

Figure 6. Plot of k_{obsd} versus concentration of added $Fe^{II}(CN)_5NO_2^{4-}$.

In alkaline solution the substitution process follows the overall reaction in (5), which is accompanied by characteristic spectral changes as shown in Figure 4. Very surprising was our observation that absorbance–time plots at 392 and 555 nm are linear and exhibit zero-order behavior. A typical example for such a curve is shown in Figure 5a. The slope of the line was used to estimate the zero-order rate constant $k_{obsd} = -d[Fe(CN)_5NO_2^{3-}]/dt$, which exhibits a distinct dependence on [OH^-] as shown by the data in Table III. These reactions are indeed very slow and reach a limiting rate at [OH^-] ≥ 0.05 M. Some preliminary experiments revealed that the process is catalyzed by trace quantities of Fe(II) species. In the presence of added $Fe^{II}(CN)_5NO_2^{4-}$ the rate plots exhibit perfect zero-order behavior (see Figure 5) and the observed rate constant increases linearly with [Fe(II)] as shown by the data in Figure 6. The small intercept in Figure 6 corresponds to the presence of some Fe(II) complex in the starting material. The slight deviations from zero order observed in the rate plots in the absence of added Fe(II) are presumably due to the slow formation of sufficient quantities of Fe(II) via the reduction of $Fe(CN)_5NO_2^{3-}$ by NO_2^-[15] or OH^-,[11] which will account for the initial increase in the rate of the reaction. The catalysis by Fe(II) species found in this study is in good agreement with earlier reports on related systems.

$$Fe(CN)_5NO_2^{3-} + OH^- \rightarrow Fe(CN)_5OH^{3-} + NO_2^- \tag{5}$$

Murray and co-workers[11] found that the substitution reactions of $Fe(CN)_5NH_3^{2-}$ and $Fe(CN)_5H_2O^{2-}$ are catalyzed by the corresponding Fe(II) complexes. In later work[10] they observed a similar effect for the bridge-cleavage reaction of $[Fe^{III}Co^{III}(CN)_{11}]^{5-}$. From their original suggestions to account for the observed zero-order behavior, the base hydrolysis mechanism

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Table III. Rate Data for the Base Hydrolysis of $Fe^{III}(CN)_5NO_2^{3-}$ in Aqueous Solution[a]

temp, °C	pressure, MPa	[added Fe(II)],[b] M	$[OH^-]$, M	10^7k_{obsd},[c] $M\ s^{-1}$	k_6,[d] s^{-1}	$\Delta H^{\ddagger}$, $kJ\ mol^{-1}$	$\Delta S^{\ddagger}$, $J\ K^{-1}\ mol^{-1}$	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$
25	0.1	0	0.001	0.022				
			0.010	0.80				
			0.025	1.0				
			0.050	1.3				
			0.10	1.2				
			0.50	1.2				
25	0.1	0	0.10	1.20	10.0×10^{-3}			
		2.67×10^{-5}		4.12				
		9.45×10^{-5}		10.7				
		1.88×10^{-4}		20.5				
		4.44×10^{-4}		45.9				
17	0.1	$0–3.73 \times 10^{-4}$	0.10		4.40×10^{-3}	97 ± 9	+42 ± 30	
20		$0–1.97 \times 10^{-4}$			5.04×10^{-3}			
25		$0–1.82 \times 10^{-4}$			1.00×10^{-2}			
30		$0–6.87 \times 10^{-5}$			2.04×10^{-2}			
33		$0–6.67 \times 10^{-5}$			3.67×10^{-2}			
25	0.1	$0–4.44 \times 10^{-4}$	0.10		10.0×10^{-3}			+20.1 ± 1.0
	5	$0–8.33 \times 10^{-5}$			8.7×10^{-3}			
	50	$0–8.33 \times 10^{-5}$			6.4×10^{-3}			
	100	$0–8.33 \times 10^{-5}$			4.1×10^{-3}			
	125	$0–8.33 \times 10^{-5}$			3.5×10^{-3}			

[a] Conditions: $[Fe(III)] = 1 \times 10^{-3}$ M; ionic strength 0.5 M. [b] Fe^{II} added as $Fe^{II}(CN)_5NO_2^{4-}$. [c] Mean value of between two and four kinetic runs; k_{obsd} is the observed pseudo-zero-order rate constant. [d] Calculated from the slope of k_{obsd} versus [Fe(II)] as demonstrated in Figure 6.

should consist of the aquation of $Fe^{II}(CN)_5NO_2^{4-}$ followed by deprotonation of $Fe^{II}(CN)_5H_2O^{3-}$ to produce $Fe^{II}(CN)_5OH^{4-}$, which subsequently reacts rapidly with $Fe^{III}(CN)_5NO_2^{3-}$ in an electron-transfer process to produce $Fe^{III}(CN)_5OH^{3-}$ and $Fe^{II}(CN)_5NO_2^{4-}$. However, it is generally accepted[22] that the pK_a value of $Fe^{II}(CN)_5H_2O^{3-}$ should be greater than 13, such that deprotonation seems rather unlikely under our conditions. We therefore prefer the following mechanism, in which electron transfer occurs between $Fe^{II}(CN)_5H_2O^{3-}$ and $Fe^{III}(CN)_5NO_2^{3-}$:

$$Fe^{II}(CN)_5NO_2^{4-} + H_2O \xrightarrow{k_6} Fe^{II}(CN)_5H_2O^{3-} + NO_2^- \qquad (6)$$

$$Fe^{II}(CN)_5H_2O^{3-} + Fe^{III}(CN)_5NO_2^{3-} \rightarrow Fe^{III}(CN)_5H_2O^{2-} + Fe^{II}(CN)_5NO_2^{4-} \qquad (7)$$

$$Fe^{III}(CN)_5H_2O^{2-} + OH^- \rightleftharpoons Fe^{III}(CN)_5OH^{3-} + H_2O \qquad (8)$$

In this mechanism reaction 6 is the rate-determining step and is followed by rapid electron transfer and deprotonation. In this way the concentration of $Fe^{II}(CN)_5NO_2^{4-}$ remains constant throughout the base hydrolysis process and reaction 6 attains pseudo-zero-order behavior as observed for the disappearance of $Fe^{III}(CN)_5NO_2^{3-}$. The very slow reaction observed in the absence of added Fe(II) (see intercept in Figure 6) must be due to trace impurities of $Fe^{II}(CN)_5NO_2^{4-}$ in the starting material. Further evidence for the validity of the suggested mechanism comes from a detailed analysis of the available kinetic data in Table III. First, the slope of the line in Figure 6 corresponds to the pseudo-first-order rate constant for reaction 6 and has a value of $10.0 \times 10^{-3}\ s^{-1}$ at 25 °C and 0.1 M ionic strength. This is in very good agreement with the value of $7.7 \times 10^{-3}\ s^{-1}$ at 25 °C and 1.0 M ionic strength reported by Swinehart and Rock.[23] Second, the $[OH^-]$-dependence data exactly account for the drastic pH dependence of this reaction in terms of the equilibrium given in (9).

$$Fe^{II}(CN)_5NO^{2-} + 2OH^- \overset{K_9}{\rightleftharpoons} Fe^{II}(CN)_5NO_2^{4-} + H_2O \qquad (9)$$

In acidic, neutral, and slightly alkaline medium this equilibrium is shifted to the left and the nitrosyl complex is stable and does not catalyze the aquation process under such conditions. However, in basic medium (pH ≥11) this equilibrium produces the nitro complex, which undergoes aquation to initiate the catalytic cycle.[23-25] The rate law for this process, based on reactions 6 and 9, is given in (10), from which it follows that a plot of k_{obsd}^{-1} versus

$$k_{obsd} = k_6K_9[OH^-]^2/(1 + K_9[OH^-]^2) \qquad (10)$$

$[OH^-]^{-2}$ should result in a linear relationship with a slope $(k_6K_9)^{-1}$ and intercept k_6^{-1}. A fit of the data in Table III results in $k_6 = 1.21 \times 10^{-7}\ M\ s^{-1}$ and $K_9 = 1.86 \times 10^4\ M^{-2}$. The value of k_6 must be divided by [Fe(II)] to obtain the pseudo-first-order rate constant for reaction 6. However, this cannot be done since the [Fe(II)] as impurity is not known. Nevertheless, this value is in very close agreement with the directly determined value of 1.20×10^{-7} M s^{-1} (see Table III). The value of K_9 is also in excellent agreement with the value of $1.82 \times 10^4\ M^{-2}$ (at 25 °C and 0.5 M KCl) reported in the literature[25] and underlines the validity of the suggested mechanism.

We have also studied the temperature and pressure dependence of k_6 under conditions where equilibrium 9 is completely shifted to the right. The results (Table III) demonstrate that the aquation process is dissociative and is characterized by significantly positive values for $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$. A comparison with literature values[9,20,27] reveals that the volumes of activation for reaction 6, i.e. for the process outlined in (11), is in good agreement with values of around

$$Fe^{II}(CN)_5NO_2^{4-} \rightarrow [Fe^{II}(CN)_5^{3-} + NO_2^-]^{\ddagger} \qquad (11)$$

20 $cm^3\ mol^{-1}$ reported for the aquation and substitution reactions of a series of Fe(II) complexes of the type $Fe^{II}(CN)_5L$. Charge dilution on going to the transition state will result in a decrease in electrostriction and may contribute to the positive value of $\Delta V^{\ddagger}$. It is encouraging to note how well-detailed aspects of this rather complex catalytic process are in line with data reported for the rate-determining step or, for closely related reactions, with data in the literature. We are presently investigating this system in other solvents and will report our findings in due course.

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Registry No. $Fe(CN)_5NO_2^{3-}$, 20774-48-5; $Fe(CN)_5NO_2^{4-}$, 15003-01-7.

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