

Kinetic Studies of the Reactions of Pentacyanoferrate(II) Complexes with Peroxydisulfate

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Reactions of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ (L = 4-aminopyridine (4-ampy), pyridine (py), 4,4'-bipyridine (4,4'-bpy), and pyrazine (pz)) with peroxydisulfate, $\text{Fe}(\text{CN})_5\text{L}^{3-} + \text{S}_2\text{O}_8^{2-} \rightleftharpoons \text{Fe}(\text{CN})_5\text{L}^{2-} + \text{SO}_4^- + \text{SO}_4^{2-}$, have been found to follow an outer-sphere electron transfer mechanism. The specific rate constants of oxidation are 1.45 ± 0.01 , $(9.00 \pm 0.02) \times 10^{-2}$, $(5.60 \pm 0.01) \times 10^{-2}$, and $(2.89 \pm 0.01) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, for L = 4-ampy, py, 4,4'-bpy, and pz, respectively, at $\mu = 0.50 \text{ M LiClO}_4$, $T = 25 \text{ }^\circ\text{C}$, $\text{pH} = 4.4\text{--}8.8$. The rate constants of oxidation for the corresponding $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ complexes were also measured and were found to be faster than those of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complexes by a factor of $\sim 10^2$ even after the corrections for the differences in reduction potentials and in the charges of the complexes. The difference in reactivity may arise from the hydrogen bonding between peroxydisulfate and the ammonia ligands of $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ and nonadiabaticity observed in the $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complexes.

Introduction

In previous studies of the binuclear complexes of $(\text{CN})_5\text{FeLRu}(\text{NH}_3)_n$ ($n = -1, 0$), peroxydisulfate was widely used as an oxidizing agent.^{1–4} One of the advantages of this oxidant lies in its stability in a wide range of pH values. It was also found that the oxidation of the Ru(II) center is much faster than that of the Fe(II) center.¹ Recently the oxidation of ruthenium(II) ammine complexes by peroxydisulfate has been carefully investigated,⁵ and the results have been interpreted with the aid of Marcus theory for outer-sphere electron transfer. The electron transfer step was viewed⁵ as involving the reductive cleavage of the peroxide bond in $\text{S}_2\text{O}_8^{2-}$. In the present work, we extend the study to the oxidation of pentacyanoferrate(II) complexes, and for the purpose of comparison, the kinetics of the oxidation of the corresponding pentaammineruthenium(II) complexes were also investigated.

Experimental Section

Materials. Solutions of pentacyanoferrate(II) complexes were prepared under nitrogen atmosphere by dissolving $\text{Na}_3\text{Fe}(\text{CN})_5\text{NH}_3 \cdot 3\text{H}_2\text{O}$ ^{6,7} in predeaerated solutions containing a large excess of ligands. $[\text{Ru}(\text{NH}_3)_5\text{L}](\text{PF}_6)_2$ (L = 4-aminopyridine (4-ampy),⁸ pyridine (py),⁹ pyrazine (pz),¹⁰ and 4,4'-bipyridine (4,4'-bpy)¹¹) were prepared as described in the literature except that the complexes were precipitated as PF_6^- salts. The doubly deionized distilled water was obtained by passing house-line distilled water through an Osmonics P-12 water purification system. All other chemicals were of reagent grade and were used without further purification.

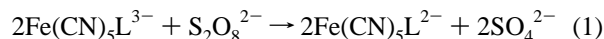
Kinetic Measurements. All kinetic measurements were carried out either on a Hitachi U-2000 spectrophotometer or on a Phtal RA-401 stopped-flow apparatus (Union Giken), depending on the rate of the reaction. The measurements were performed at an ionic strength of

0.50 under pseudo-first-order conditions with peroxydisulfate in excess. Reactions were monitored by following either the disappearances of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complexes or the formation of the Fe(III) complex (4-aminopyridine complex only). The observed rate constants were obtained from the slopes of linear least square fits of $\ln(A_\infty - A_t)$ vs time plots.

Electrochemistry. The cyclic voltammetric measurements were performed on a PAR Model 273A potentiostat/galvanostat system which is interfaced with a SNC 486-33 computer. The standard three-electrode electrochemical cell was used for measurements. Carbon paste was used as the working electrode and a platinum wire as the counter electrode. A saturated calomel electrode was used as the reference electrode.

Results and Discussion

Stoichiometry of the Oxidation. First, we investigate the stoichiometry of the oxidation. For this purpose, we studied the absorption spectra of the oxidation of the $\text{Fe}(\text{CN})_5\text{4-ampy}^{3-}$ complex in the presence of excess peroxydisulfate ion ($[\text{Fe}(\text{II})] = 2.0 \times 10^{-4} \text{ M}$, $[\text{S}_2\text{O}_8^{2-}] = 2.5 \times 10^{-2} \text{ M}$) at $\text{pH} = 8.75$ (tris). We found that the disappearance of the $\text{Fe}(\text{CN})_5\text{4-ampy}^{3-}$ complex ($\lambda_{\text{max}} = 320 \text{ nm}$) corresponds to the formation of the $\text{Fe}(\text{CN})_5\text{4-ampy}^{2-}$ complex ($\lambda_{\text{max}} = 560 \text{ nm}$) with an isosbestic point at $\lambda = 428 \text{ nm}$. The molar absorptivity of $2.83 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at band maximum for the product solution agrees with the literature reported value for the Fe(III) complex.¹² The results suggest that the peroxydisulfate oxidation of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complexes in neutral solutions is a simple electron transfer process as shown in eq 1 and no other side reactions are involved in the oxidation.



Kinetics of the Oxidation of Pentacyanoferrate(II) and Pentaammineruthenium(II) Complexes. Since the dissociation of the $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complexes occurs at low pH, the kinetic studies of the oxidation reaction were carried out at $\text{pH} > 4$, where the dissociation does not interfere. The observed rate constants of oxidation of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ (L = 4-ampy, py, pz, 4,4'-bpy) complexes at $\text{pH} = 4.39\text{--}8.75$ are listed in Table 1.

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Table 1. Pseudo-First-Order Rate Constants for the Oxidation of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ and $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ with $\text{S}_2\text{O}_8^{2-}$ ^a

ligand	Fe(II)			Ru(II)		
	pH	$10^3[\text{S}_2\text{O}_8^{2-}]$, M^{-1}	10^3k_{obs} , s^{-1}	pH	$10^4[\text{S}_2\text{O}_8^{2-}]$, M^{-1}	k_{obs} , s^{-1}
4-ampy	8.75 (tris)	5.00	14.4	5.03 (acetate)	4.20	47.3
		10.0	29.5		5.04	62.0
		15.5	44.1			
		20.0	57.5			
		25.0	73.3			
py	5.23 (acetate)	2.50	0.56	5.03 (acetate)	2.00	6.40
		7.50	1.44		3.00	9.22
		12.5	2.33		4.00	15.8
		17.5	3.16		6.00	21.8
		25.0	4.4			
pz	4.39 (acetate)	5.00	0.299	5.03 (acetate)	10.0	2.48
		10.0	0.590		30.0	7.18
		15.0	0.884		50.0	10.9
		20.0	1.19		70.0	14.5
		25.0	1.46		90.0	19.3
4,4'-bpy	6.90 (phosphate)	2.50	0.259	8.01 (tris)	5.00	6.08
		5.00	0.485		10.1	11.4
		10.0	1.10		15.1	16.1
		15.0	1.61		20.3	20.0
		20.0	2.27		25.3	24.1
25.0	2.84					

^a $\mu = 0.50\text{ M LiClO}_4$, $T = 25\text{ }^\circ\text{C}$, $[\text{Fe}(\text{II})] = (1-2) \times 10^{-4}\text{ M}$, $[\text{L}] = 2.0 \times 10^{-2}\text{ M}$, $[\text{Ru}(\text{II})] = (2-5) \times 10^{-5}\text{ M}$.

Table 2. Specific Rate Constants of Oxidation of Fe(II) and Ru(II) Complexes by Peroxydisulfate^a

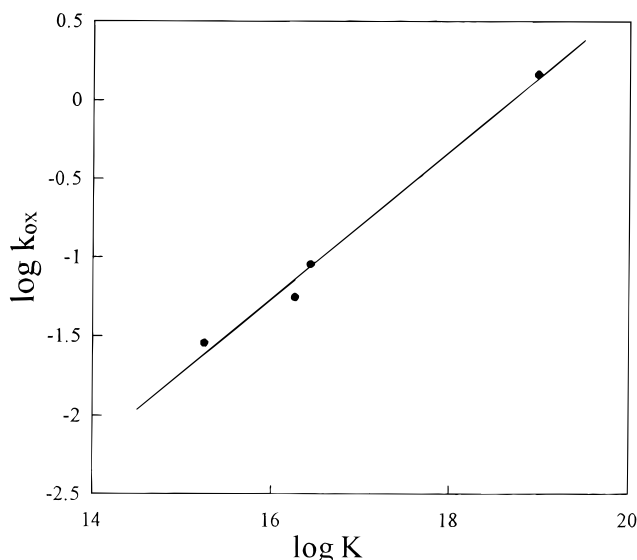
ligand	Fe(II)			Ru(II)			
	k_{ox} , $\text{M}^{-1}\text{ s}^{-1}$	$E_{1/2}$, V(vs NHE)	$k_{\text{ox}}^{\text{corr}, b}$, $\text{M}^{-1/2}\text{ s}^{-1}$	k_{ox} , $\text{M}^{-1}\text{ s}^{-1}$	$E_{1/2}$, V(vs NHE)	$k_{\text{ox}}^{\text{corr}, b}$, $\text{M}^{-1/2}\text{ s}^{-1}$	$k_{\text{ox}}^{\text{corr}}(\text{Ru})/k_{\text{ox}}^{\text{corr}}(\text{Fe})$
4-ampy	1.45 ± 0.01	0.33 ^c	1.8×10^{-9}	$(5.9 \pm 0.3) \times 10^4$	0.15 ^e	1.4×10^{-7}	7.8×10^1
py	$(9.00 \pm 0.02) \times 10^{-2}$	0.48 ^d	2.0×10^{-9}	$(1.80 \pm 0.07) \times 10^4$	0.30 ^f	7.8×10^{-7}	3.9×10^2
pz	$(2.89 \pm 0.01) \times 10^{-2}$	0.55 ^d	2.6×10^{-9}	$(1.07 \pm 0.02) \times 10^3$	0.49 ^f	1.9×10^{-6}	7.3×10^2
4,4'-bpy	$(5.60 \pm 0.01) \times 10^{-2}$	0.49	1.5×10^{-9}	$(4.08 \pm 0.07) \times 10^3$	0.34 ^g	3.8×10^{-7}	2.5×10^2

^a $\mu = 0.50\text{ M LiClO}_4$, $T = 25\text{ }^\circ\text{C}$, $\text{pH} = 4.4-8.8$. ^b $k_{\text{ox}}^{\text{corr}} = k_{\text{ox}}/Q_{\text{IP}}\sqrt{K}$. ^c Reference 12. ^d Reference 13. ^e Reference 8. ^f Reference 14. ^g Reference 15.

The k_{obs} vary linearly with the concentration of $\text{S}_2\text{O}_8^{2-}$, and the second-order rate constants of oxidation were obtained from the slopes of the one-parameter linear least square fits of the k_{obs} vs $[\text{S}_2\text{O}_8^{2-}]$ plots according to eq 2. The second order rate

$$k_{\text{obs}} = 2k_{\text{ox}}[\text{S}_2\text{O}_8^{2-}] \quad (2)$$

constants are listed in column 2 of Table 2. Pseudo-first-order rate constants of the oxidation of the corresponding pentaammineruthenium(II) complexes are also listed in Table 1. The k_{obs} also vary linearly with $[\text{S}_2\text{O}_8^{2-}]$, and the second-order rate constants according to eq 2 are listed in column 5 of Table 2. The oxidation of the $\text{Fe}(\text{CN})_5\text{pz}^{3-}$ complex by $\text{S}_2\text{O}_8^{2-}$ has been investigated before, and the rate constant was $2.5\text{ M}^{-1}\text{ s}^{-1}$ at $\mu = 0.10\text{ M}$ and $\text{pH} = 4.28$,¹ greater than our measured value by 2 orders of magnitude. Since it was found that the dissociation of the complex might accompany the oxidation in the previous study, the difference in rate may arise from interferences of the dissociation reaction and the oxidation of the dissociation product, namely $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$. We have measured the rate of oxidation of $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ by $\text{S}_2\text{O}_8^{2-}$, and the rate constant is $6.6 \pm 0.3\text{ M}^{-1}\text{ s}^{-1}$, at $\mu = 0.10\text{ M LiClO}_4$ and $\text{pH} = 4$. We have no satisfactory explanation for the fast rate of oxidation of $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ compared to other $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complexes, but it will not be surprising that the lability of the aquo ligand¹⁶ may cause $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ to undergo, at least to a certain extent, an electron transfer reaction with $\text{S}_2\text{O}_8^{2-}$ through an inner-sphere mechanism.

**Figure 1.** Log k_{ox} vs log K for $\text{Fe}(\text{CN})_5\text{L}^{3-}-\text{S}_2\text{O}_8^{2-}$ reactions.

The reactions of $\text{S}_2\text{O}_8^{2-}$ with $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complexes at $\text{pH} \geq 5$ proceed predominantly by the electron-transfer process. When we plot log k_{ox} against log K (Figure 1), where K is the equilibrium constant for the one-electron oxidation of the complex by $\text{S}_2\text{O}_8^{2-}$ (taking $E_{1/2} = 1.45\text{ V}$ for $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$, SO_4^- couple¹⁷), a linear relationship is observed with a slope of 0.47 ± 0.04 , which agrees well with the value of 0.5 predicted by the Marcus–Hush theory for outer-sphere electron transfer

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reaction.¹⁸ The mechanism of the reaction therefore is similar to that of the $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}-\text{S}_2\text{O}_8^{2-}$ system.⁵ As shown in Table 2, the specific rate constants of oxidation of $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ complexes are much greater than those of the corresponding $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complexes. However, before any comparison can be made between the two metal centers, the rate constants must be corrected for the differences in reduction potentials and in the charges of the complexes. In order to do this, we divide the measured rate constants by Q_{IP} , the ion pair formation constant between the complex and $\text{S}_2\text{O}_8^{2-}$, as expressed in eqs 3–5¹⁹ and by \sqrt{K} , where K was previously defined. a is the

$$Q_{\text{IP}} = \frac{4\pi N a^3}{3000} \exp(-U(a)/kT) \quad (3)$$

$$U(a) = \frac{z_A z_B e^2}{D a (1 + \beta a \mu^{1/2})} \quad (4)$$

$$\beta = \left(\frac{8\pi N e^2}{1000 D k T} \right)^{1/2} \quad (5)$$

distance between $\text{S}_2\text{O}_8^{2-}$ and the corresponding metal centers, z_A and z_B are the charges of the ions, D is the static dielectric constant of water, k is the Boltzmann constant, and μ is the ionic strength. The values of radii are 5.0×10^{-8} and 4.0×10^{-8} cm for $\text{Fe}(\text{CN})_5\text{L}^{3-}$ and $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ complexes (assuming them to be equal to those of $\text{Fe}(\text{CN})_5\text{py}^{3-}$ ²⁰ and $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$,²¹ respectively) and 3.4×10^{-8} cm for $\text{S}_2\text{O}_8^{2-}$.⁵ According to this treatment, the corrected rate constants of $\text{Fe}(\text{CN})_5\text{L}^{3-}-\text{S}_2\text{O}_8^{2-}$ and $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}-\text{S}_2\text{O}_8^{2-}$ systems are listed in columns 4 and 7 of Table 2. After these corrections, the rate ratios (Ru to Fe) are still of the order $10-10^2$ as shown in column 8 of Table 2. The intrinsic reactivities of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ and $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ complexes toward oxidation are expected to be similar since the self-exchange rate constant of $\text{Ru}(\text{NH}_3)_5\text{py}^{2+/3+}$ is $4.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ²² as compared to that of the $\text{Fe}(\text{CN})_5\text{py}^{3-/2-}$ couple which is $7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.²³ Therefore, it is not likely that the difference in rate arises from the difference in reactivities between the two metal centers. Although we have no satisfac-

tory explanation, we tend to believe that the discrepancy may arise from the charge interaction between the metal complexes and peroxydisulfate. In the ion pair formation process for the outer-sphere mechanism, we assume that the reactants are brought in close contact and the internuclear distance is the sum of the radii of the reacting species. For the $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}-\text{S}_2\text{O}_8^{2-}$ system, this is appropriate because we are bringing together species of opposite charges. Moreover, the possible hydrogen bonding between ammonia hydrogen and the peroxydisulfate oxygen will further favor their coming together. For the $\text{Fe}(\text{CN})_5\text{L}^{3-}-\text{S}_2\text{O}_8^{2-}$ system, this approach may not be true because of the repulsion between species of like charges. Furthermore, hydrogen bonding between the reactants is not possible in this case. Under these circumstances, a close approach of the reactants could be excluded. As a consequence, the coupling of orbitals may be diminished and the reaction may be occurring in the nonadiabatic regime.²⁴ Haim et al.,²⁵ in their study of the reactivity of the pyrazine-bridged binuclear complex of $\text{Ru}(\text{NH}_3)_5^{2+/3+}$ and $\text{Ru}(\text{edta})^{2-/-}$, have also investigated the oxidations of $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ and $\text{Ru}(\text{edta})\text{pz}^{2-}$ by $\text{S}_2\text{O}_8^{2-}$. The intrinsic reactivities of $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ and $\text{Ru}(\text{edta})\text{pz}^{2-}$ are similar and the self-exchange rate constants after correction for the charge effect are $\sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for both species. Nevertheless, the ratio of the rate constants of oxidation of $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ and $\text{Ru}(\text{edta})\text{pz}^{2-}$ toward $\text{S}_2\text{O}_8^{2-}$ after corrections for the charge effect and reduction potentials is still $\sim 10^3$, similar to what we have observed. A comparison of the intramolecular electron transfer rate constants between binuclear complexes of $(\text{CN})_5\text{Fe}^{\text{II}}\text{LCo}^{\text{III}}(\text{NH}_3)_5$ and $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{LCo}^{\text{III}}(\text{NH}_3)_5$ further supports our argument. In these binuclear complexes, the interaction between charge on the cobalt(III) center with that of the reducing centers will not affect their separation. The ratios of intramolecular electron transfer rate constants ($k_{\text{Ru}}/k_{\text{Fe}}$) for the two systems with L = imidazole, pyrazine and 4,4'-bipyridine range from 5.5 to 36.²⁶ However, after the corrections of reduction potentials of pentacyanoferrate(II) and pentaammineruthenium(II) couples, the ratios fall between 0.41 and 1.7, indicative of the similarity in intrinsic reactivities of $\text{Fe}(\text{CN})_5^{3-}$ and $\text{Ru}(\text{NH}_3)_5^{2+}$ metal centers.

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