

## Stoichiometry and Kinetics of the Substitution-Controlled Oxidation of Pentacyanoaquoiron(II) Species by Hydrogen Peroxide and by *tert*-Butyl Hydroperoxide in Aqueous Sodium Perchlorate Solution<sup>1</sup>

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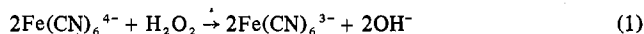
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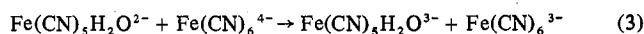
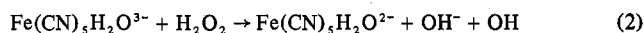
The stoichiometries and kinetics of oxidation of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  (generated in situ by aquation of  $\text{Fe}(\text{CN})_5\text{NH}_3^{3-}$ ) by hydrogen peroxide and *tert*-butyl hydroperoxide (ROOH) at ionic strength 1.0 M are reported. The stoichiometric measurements were consistent with  $\Delta[\text{Fe}^{\text{III}}]/\Delta[\text{ROOH}] = 2$ . The kinetics were monitored spectrophotometrically in a stopped-flow apparatus over wide  $[\text{Fe}^{\text{II}}]$ , [oxidant], and pH ranges. The empirical rate law for both reactions is given by  $d[\text{Fe}^{\text{III}}]/dt = (2(k_1 + k_2K_a/[\text{H}^+])/(1 + K_a/[\text{H}^+]))[\text{ROOH}]_T$ , where  $K_a$  is the acid dissociation constant for ROOH,  $k_1$  and  $k_2$  are the rate constants for reactions of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  with ROOH and  $\text{ROO}^-$ , respectively, and  $[\text{ROOH}]_T$  is the analytical peroxide concentration. It was found that kinetic data for iron(II) monomer reactions could be obtained using reactant solutions which contained time-dependent proportions of other iron(II) species by maintaining a large excess of ligand. Comparison of the kinetic data for oxidation with those for complexation by pyrazine, thiourea, isonicotinamide, acetonitrile, cyanide, and nitrite under similar experimental conditions indicates that the oxidation processes are limited by substitution at the iron(II) center. Available kinetic data support earlier mechanisms for the photocatalyzed oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  by  $\text{H}_2\text{O}_2$ .

### Introduction

It has long been assumed that photocatalysis of the oxidation of hexacyanoferrate(II) by hydrogen peroxide is due to the photoaquation of  $\text{Fe}(\text{CN})_6^{4-}$  to give  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ , which catalyzes the overall reaction



through the rapid steps of the cycle<sup>2-4</sup>



However, despite the fact that the stoichiometry of the pentacyanoaquoiron(II)-hydrogen peroxide reaction is known to be  $\Delta[\text{Fe}^{\text{II}}(\text{CN})_5(\text{aq})]/\Delta[\text{H}_2\text{O}_2] = 2$ ,<sup>5</sup> the rate constant for reaction 2 has not been established by direct kinetic measurement.

Our study of this latter process and of the corresponding oxidation of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$  by *tert*-butyl hydroperoxide was also prompted by an interest in the nature of water molecules attached to low-spin iron centers, particularly those in biochemical systems.<sup>7,8</sup> Since the initiation of this work, Malin and his coworkers<sup>9,10</sup> have demonstrated that  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$  can be reproducibly generated in situ by aquation of  $\text{Fe}(\text{CN})_5\text{NH}_3^{3-}$ , which obviates the necessity of working with the complicated mixture<sup>11</sup> obtained by reduction of  $\text{Fe}(\text{CN})_5\text{NO}^{2-}(\text{aq})$  by hydroxylamine in strongly basic solution.<sup>12</sup> In addition, the subsequent publication<sup>13,14</sup> of kinetic data for substitution of a wide range of ligands at the  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$  center has allowed the assignment of the mechanism of reaction 2, which appears to be limited by substitution of the oxidant at the iron(II) center.

### Experimental Section

**Reagents.** All water was deionized and distilled from alkaline potassium permanganate in an all-glass still. Water for kinetic experiments was flushed for 15 min with nitrogen that had been passed through an acidic chromium(II) solution. Stock solutions of sodium perchlorate were prepared by neutralization of reagent grade anhydrous sodium carbonate with reagent grade perchloric acid and were standardized gravimetrically.<sup>15</sup>

Sodium pentacyanoammineferrate(II) (Fisher Certified) was recrystallized from concentrated ammonia solution and dried overnight in a vacuum desiccator over a phosphorus pentoxide-sodium sulfate mixture. The recovered trihydrate was analyzed.<sup>16</sup> Anal. Calcd for

$\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ : C, 18.42; N, 25.78; H, 2.78. Found: C, 18.95; N, 25.93; H, 2.65. Sodium pentacyanoaquoferate(II) was generated in situ from sodium pentacyanoammineferrate(II) by dissolving the purified solid in deoxygenated sodium perchlorate solutions.<sup>9</sup> The synthetic methods of Hofmann and Asperger<sup>12</sup> were abandoned because a pure product could not be obtained.

Sodium hydroxide was prepared carbonate free as described by Belcher and Nutten<sup>17</sup> and standardized by titration with potassium hydrogen phthalate to a phenolphthalein end point. Cerium(IV) sulfate (ca. 0.1 M) was prepared from reagent grade ceric ammonium nitrate and sulfuric acid and standardized as described in Belcher and Nutten.<sup>18</sup> Reagent grade ferrous ammonium sulfate was used in cerium(IV) standardization. Sodium thiosulfate solution (1 M from Will Scientific Co.) was standardized against potassium iodate.<sup>19</sup>

Pyrazine and isonicotinamide of high purity were used as supplied by Aldrich. The pyrazine was stored at 0 °C. Spectroquality acetonitrile (Eastman) was used as supplied. Sodium nitrite and sodium cyanide were reagent grade and were dried at 100 °C in a vacuum oven for 1 h before use. Hydrogen peroxide (ACS Certified, 30% from Fisher Scientific Co.) was standardized after dilution by titration with cerium(IV) using ferroin indicator. *tert*-Butyl hydroperoxide (90%, Wallace and Tiernan) was vacuum distilled and standardized iodometrically with sodium thiosulfate, as described by Cass,<sup>20</sup> and stored at 0 °C. Buffer solutions were prepared from Fisher Certified dry buffer salts.

An Orion 801 Digital pH-mV meter was used in determining the acid concentrations of all solutions used in kinetic experiments and in determining the acid dissociation constant of *tert*-butyl hydroperoxide by titration with sodium hydroxide. The Orion single-junction reference electrode (Model 90-01) and pH electrode (silver-silver chloride internal standard, Model 91-01-00) were employed.

The stopped-flow apparatus has been described previously.<sup>21</sup> The present apparatus is interfaced to Northeastern's CDC 6600 system through a Digital Equipment PDP-11A computer and provides direct, on-line processing of kinetic data.<sup>22</sup> Temperature was maintained to  $\pm 0.05$  °C. A Beckman DK ratio-recording spectrophotometer was used for determining reactant and product spectra.

**Determination of the Acid Dissociation Constant of *tert*-Butyl Hydroperoxide.** A pH calibration curve for 1 M sodium perchlorate was obtained by titration with a standard hydroxide solution. Solutions containing  $(3.3-9.9) \times 10^{-2}$  M *tert*-butyl hydroperoxide in 1 M sodium perchlorate were then titrated with base at  $25.0 \pm 0.1$  °C. Titrations were performed in a stoppered beaker to protect solutions from carbon dioxide. Equation 4 was used to determine the acid dissociation

$$[\text{OH}^-]_T = [\text{OH}^-] + \frac{[\text{OH}^-][\text{ROOH}]_T}{K_w/K_a + [\text{OH}^-]} \quad (4)$$

constant;  $K_w$  is the acid dissociation constant of water at 25.0 °C in

1 M sodium perchlorate,<sup>23</sup>  $K_a$  is the acid dissociation constant of *tert*-butyl hydroperoxide at 25.0 °C in 1 M sodium perchlorate, and  $[ROOH]_T$ ,  $[OH^-]_T$ , and  $[OH^-]$  are the total analytical concentrations of peroxide and base and the free hydroxide concentration, respectively.

**Spectral Measurements on Solutions of  $Na_3Fe(CN)_5NH_3 \cdot 3H_2O$ .** The spectra of solutions of  $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$  at room temperature (ca. 21 °C) or at 25.0 °C were measured as a function of time. Analytical iron(II) concentrations were in the range (1–100)  $\times 10^{-5}$  M and the acidity was varied from pH ca. 3 to 1 M NaOH. The spectrum was either scanned over the range 700–350 nm or measurements were made at constant wavelength (usually 390 nm). The samples were kept in the dark between measurements to avoid any possible photochemical complications.<sup>24</sup>

**Stoichiometric Measurements.** The stoichiometry of the rapid reaction of pentacyanoaquoiron(II) with hydrogen peroxide has been previously determined by titration<sup>5</sup> and the same stoichiometry can be anticipated in the analogous reaction with *tert*-butyl hydroperoxide. In the latter case the stoichiometry was checked as follows. A  $1.0 \times 10^{-4}$  M iron(II) solution was prepared in 1.0 M NaClO<sub>4</sub>. To half of this solution a measured aliquot of *tert*-butyl hydroperoxide was added to give a  $2.5 \times 10^{-5}$  M solution of this reactant, and the reacted solution was then used as the source of iron(II) in a typical stopped-flow experiment in which it was treated with a 0.05 M *tert*-butyl hydroperoxide solution. The original, untreated iron(II) reactant solution portion was employed in a separate stopped-flow run with 0.05 M *tert*-butyl peroxide. The total transmittance changes in the two kinetic runs were then compared in order to determine how much iron(II) had been oxidized by addition of the aliquot of peroxide to the first reactant portion.

The spectra of reaction products were compared with those of known pentacyanoaquoferrate(III) species under the same conditions.<sup>6</sup>

**Kinetic Measurements.** All experiments were conducted at ionic strength 1.0 M (NaClO<sub>4</sub>–NaOH). Deoxygenated water was used in all experiments since preliminary studies indicated rapid shifts of the iron(II) spectral peak (440 nm) to the iron(III) region (390 nm) in  $10^{-5}$  M iron(II) solutions (no added NaClO<sub>4</sub>) when oxygenated water was used. The iron(II) peak was stable for 2 h if the water was first deoxygenated, even though a nitrogen atmosphere was not maintained. Ligand concentrations were always sufficiently large to ensure pseudo-first-order conditions.

Prethermostated aqueous sodium perchlorate solutions of appropriate ionic strength and acid concentration were used in low-temperature studies. Ligand and iron(II) were then added and the samples introduced into the thermostating coils of the stopped-flow machine.<sup>21</sup> Solutions were always used within 20 min of preparation to minimize possible decomposition of reactants.

The kinetics of the reactions with pyrazine, isonicotinamide, nitrite, hydrogen peroxide, and *tert*-butyl hydroperoxide were investigated by monitoring the appearance of products in the wavelength range 390–525 nm, while the corresponding reactions with acetonitrile, thiourea, and cyanide were followed by monitoring the disappearance of the iron(II) reactant at 434–470 nm. Iron(II) reactant concentrations were in the range (0.25–40)  $\times 10^{-5}$  M and the pH was varied between ca. 5 and 12.8. The iron(II) concentration was limited to  $5 \times 10^{-5}$  M at pH  $\leq 8$  because it was found that the addition of acid to adjust the pH of solutions of  $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$  to less than pH  $\sim 8$  gave iron(II) solutions with irreproducible kinetic properties. The origin of this effect is unknown. The conditions used for reaction with each ligand are shown in the appropriate tables (see Results). In the peroxide reactions, the oxidant was maintained at pH 7–8.5 to avoid base-catalyzed decomposition before mixing.

In all other experiments, the pH's of both the iron(II) and the ligand solutions were separately adjusted to be as close to each other as possible by appropriate addition of aqueous acid (HClO<sub>4</sub>) or base (NaOH).

Kinetic data obtained under pseudo-first-order conditions were treated by a combination of conventional, analog,<sup>25</sup> and on-line data processing.<sup>22</sup> Agreement between these three methods was better than  $\pm 2\%$  for any particular kinetic run. All first-order rate constants quoted are the average of from three to ten runs with the standard deviation included.<sup>26</sup> Second-order rate constants were calculated using a linear least-squares Wang program<sup>26</sup> and are reported to  $\pm 2\%$ . A nonlinear least-squares program<sup>27</sup> was used to fit the hydrogen peroxide and *tert*-butyl hydroperoxide data to their empirical rate laws (see below). Activation parameters were determined by the method of Bodek et al.<sup>28</sup>

## Results

**Preliminary Observations on the Visible Spectra of Aqueous Solutions of  $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$ .** Malin and his coworkers<sup>9,10</sup> have shown that dissolution of  $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$  in aqueous solution at  $[Fe^{II}] \approx 10^{-5}$  M and pH 6.5–8 results in aquation to give  $Fe(CN)_5H_2O^{3-}(aq)$ . The half-life for this reaction is ca. 40 s at 25.0 °C<sup>10</sup> and the resultant solutions of  $Fe(CN)_5H_2O^{3-}(aq)$  obey Beer's law over the range (1–10)  $\times 10^{-5}$  M. It was necessary in the present work to investigate the nature of the aquation products at relatively high concentration levels since the path length of the stopped-flow apparatus<sup>21</sup> is relatively small (2.9 mm) and the oxidation of  $Fe^{II}(CN)_5H_2O^{3-}(aq)$  to  $Fe^{III}(CN)_5OH$ ,  $(H_2O)^{3-,(2-)}$  by hydrogen peroxide and *tert*-butyl hydroperoxide involves much smaller absorbance changes in the visible region than is the case with the complexing ligands of this and previous studies.<sup>9,10,13,14</sup> Experimental conditions for the oxidation studies thus called for higher  $[Fe^{II}]$  (up to  $4 \times 10^{-4}$  M) than previously employed (typically  $10^{-5}$  M or less<sup>9,13,14</sup>).

The visible spectra of iron(II) solutions obtained by dissolving weighed amounts of  $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$  in aqueous alkali metal salt solutions were found to be time dependent and also depended on the analytical iron(II) concentration, acidity, the solution medium, light, and the presence of oxygen. In view of the high rate of aquation of  $Fe(CN)_5NH_3^{3-}$ ,<sup>10</sup> the spectral changes observed over periods of up to 20 h may be taken to reflect the solution properties of  $Fe(CN)_5H_2O^{3-}$ , the initial aquation product.<sup>10</sup> In general, all deoxygenated solutions in the basic region, pH 8 to 1 M NaOH, exhibited initial spectral absorption maxima in the region 400–440 nm, with a variable maximum absorptivity ( $\epsilon_{440} \sim 700$  M<sup>-1</sup> cm<sup>-1</sup> for  $[Fe(II)] \approx 10^{-5}$  M,  $\epsilon_{400} \sim 500$  M<sup>-1</sup> cm<sup>-1</sup> for  $[Fe^{II}] \approx 10^{-4}$  M). This behavior reflects the postulated two-component nature of this system (see below).<sup>11</sup> Neutral conditions and low  $[Fe^{II}]$  favored maxima at the longer wavelengths. The absorption maxima shifted with time to the 385–390-nm region (the region of maximum absorbance for  $Fe_2(CN)_{10}^{6-}$ <sup>29</sup>) through an acid-dependent isosbestic point at 430–440 nm.

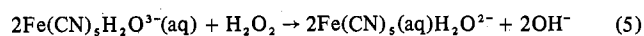
This shift was always accompanied by an increase in maximum molar absorptivity. The rate of development of the 385–390-nm absorption was very low at pH  $\geq 8$ , the observed molar absorptivity reaching 700–1100 M<sup>-1</sup> cm<sup>-1</sup> after ca. 20 h. However, solutions kept for this period were cloudy and the establishment of equilibrium was uncertain. Kinetic experiments involving reaction of excess isonicotinamide with such aged iron(II) solutions indicated a significant decrease in  $[Fe(CN)_5H_2O^{3-}(aq)]$  and  $[Fe_2(CN)_{10}^{6-}(aq)]$  and the rate constants at fixed, excess [isonicotinamide] (see below and Table I) were only about 70% of those obtained when freshly prepared iron(II) solutions were employed.

At pH 3, spectral equilibrium was established in ca. 2 h, the initial maximum absorption at  $[Fe^{II}] \approx 10^{-4}$  M shifting from ca. 440 to 390 nm via an isosbestic point at 415 nm. Shifts toward the dimer spectral region were still observed at pH 5, although the rate of change was significantly lower than at pH 3. However, as observed by Malin,<sup>9</sup> the spectra of deoxygenated solutions containing  $[Fe^{II}] \approx 10^{-5}$  M were invariant for at least 1 h at pH 6–9. Dimerization of  $Fe(CN)_5H_2O^{3-}$  to give  $Fe_2(CN)_{10}^{6-}$  is evidently much more favorable at higher  $[Fe^{II}]$  and acidities outside the range pH 6–9. First-order plots for these spectral changes were nonlinear in the absence of oxygen, and the kinetics were not investigated in detail in view of the uncertainty of attainment of equilibrium in the absence of decomposition. Similar spectral changes were observed in 1 M NaCl, NaBr, and NaI, with no evidence for pentacyanohaloiron(II) complex formation (see ref 14).

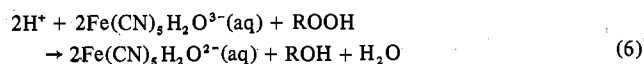
Solutions of pentacyanoaquoiron(II) species and solid  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 3\text{H}_2\text{O}$  samples were found to be light sensitive and were subsequently used and stored in subdued light.

The product of dissolution of  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 3\text{H}_2\text{O}$  in oxygen-saturated 0.5–1 M  $\text{NaClO}_4$  at pH 3 was spectrally identified as  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{2-}$ .<sup>6</sup> First-order plots for appearance of this product were linear for 2–3 half-lives at 380 nm, the pseudo-first-order rate constant being  $(1.7 \pm 0.05) \times 10^{-3} \text{ s}^{-1}$  at  $24 \pm 1^\circ \text{C}$ . At pH  $\geq 8.4$ , the rate of oxidation by oxygen was found to be extremely low. First-order plots at 390 nm were nonlinear under these conditions and the spectra of the products did not correspond to that of the anticipated  $\text{Fe}(\text{CN})_5\text{OH}^{3-}(\text{aq})$  product<sup>6</sup> but instead resembled those obtained under deoxygenated conditions at identical concentration levels.

**Stoichiometries of Oxidation by Hydrogen Peroxide and *tert*-Butyl Hydroperoxide.** As mentioned above, the stoichiometry of the reaction with hydrogen peroxide is given by eq 5,<sup>5,30</sup> and our measurements are consistent with the oc-

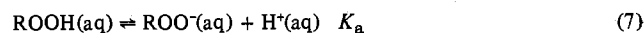


currence of reaction 6 with *tert*-butyl hydroperoxide ( $R =$



$\text{C}(\text{CH}_3)_3$ ) with an upper limit of uncertainty of  $\pm 2\%$  under the experimental conditions of this study.<sup>30</sup>

**Acid Dissociation Constant of *tert*-Butyl Hydroperoxide.** The equilibrium constant for reaction 7 ( $R = \text{C}(\text{CH}_3)_3$ ) was



found to be  $(4.09 \pm 0.42) \times 10^{-13} \text{ M}$  (four determinations) at  $25.0^\circ \text{C}$  and ionic strength 1 M ( $\text{NaClO}_4$ ). The calculated value of  $K_a$  from a nonlinear least-squares fit of titration data to eq 4 was independent of  $[\text{ROOH}]_T$  in the range (3.28–9.94)  $\times 10^{-2} \text{ M}$ .

**Kinetics of Substitution Reactions of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$ .** Kinetic data for complex formation between  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  and pyrazine, thiourea, isonicotinamide, acetonitrile, cyanide, and nitrite at ionic strength 1.0 M ( $\text{NaClO}_4$ ) are collected in Table I.<sup>31</sup> The iron(II) and acid concentration ranges employed were larger than those used in previous work<sup>9,13,14</sup> since the present studies were aimed at investigating the acid-base properties of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$ . Two reactions were observed at  $[\text{Fe}^{II}]_0 \approx 10^{-4} \text{ M}$  and pH  $\geq 8.5$ . Spectral changes associated with these two reactions could not be adequately resolved in the pH region 8.5–9.5. However, the rates of the first of these reactions could be accurately measured at pH  $\geq 9.5$  by maintaining a large excess of the complexing ligand.<sup>32</sup> Under these conditions, the rate of the first reaction is given by

$$-\frac{d \ln [\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}]}{dt} = \frac{d \ln [\text{complex}]}{dt} = k_{\text{obsd}}[\text{L}] \quad (8)$$

where L is the complexing ligand. The observed second-order rate constants,  $k_{\text{obsd}}$ , for complex formation are collected together with pertinent literature data in Table II.

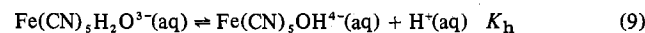
**Reaction with Pyrazine.** The product of reaction with excess pyrazine, pyr, was found to be  $\text{Fe}(\text{CN})_5\text{pyr}^{3-}$  ( $\epsilon_{452} 5260 \text{ M}^{-1} \text{ cm}^{-1}$  at pH  $> 5$ ,  $\epsilon_{452} 4700 \text{ M}^{-1} \text{ cm}^{-1}$  at pH 3.7 (see ref 9)). Its first-order rate of formation from  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$  and pyr at fixed [pyr] was independent of  $[\text{Fe}^{II}] \leq 2 \times 10^{-4} \text{ M}$  at pH  $> 9.5$  and of variations in monitoring wavelength in the range 390–535 nm. However, the first reaction at pH  $< 9.5$  could not be adequately resolved from spectral changes associated with concurrently processes except when a neutral or slightly

Table II. Kinetic Data for Substitution and Oxidation Reactions of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$  in 1 M  $\text{NaClO}_4$

Reactant	$k_{\text{forward}}^a$	$\Delta H_{\text{forward}}^\ddagger$ <sup>b</sup>	$\Delta S_{\text{forward}}^\ddagger$ <sup>c</sup>
(a) Complexation			
CN <sup>-</sup>	$29.9 \pm 0.5^d$	$18.4 \pm 0.1$	$10 \pm 0.3$
	$38^e$		
NO <sub>2</sub> <sup>-</sup>	$29.2 \pm 3.4^f$		
	$38.8 \pm 0.8^d$	$18.5 \pm 0.3$	$11 \pm 1$
Pyrazine	$300 \pm 6^d$	$16.5 \pm 0.2$	$8.1 \pm 0.5$
	$380^g$	$15.4 \pm 0.5$	5
Isonicotinamide	$196 \pm 5^d$		
	$296^g$	$15.8 \pm 0.5$	6
Thiourea	$153 \pm 3^d$		
Acetonitrile	$128 \pm 7^d$		
(b) Oxidation <sup>h</sup>			
H <sub>2</sub> O <sub>2</sub>	$107 \pm 1^d$	$19.8 \pm 0.3$	$17 \pm 1$
HO <sub>2</sub> <sup>-</sup>	$3 \pm 1^d$		
(CH <sub>3</sub> ) <sub>2</sub> COOH	$69.5 \pm 0.5^d$	$16.7 \pm 0.4$	$6 \pm 1$
(CH <sub>3</sub> ) <sub>2</sub> COO <sup>-</sup>	$0.2 \pm 0.5^d$		

<sup>a</sup> Units are  $\text{M}^{-1} \text{ s}^{-1}$  at  $25.0^\circ \text{C}$ . <sup>b</sup> Units are  $\text{kcal mol}^{-1}$ . <sup>c</sup> Units are  $\text{cal deg}^{-1} \text{ mol}^{-1}$  at  $25^\circ \text{C}$ . <sup>d</sup> Present work. <sup>e</sup> Reference 13. <sup>f</sup> Reference 14. <sup>g</sup> Reference 9 (0.5 M  $\text{LiClO}_4$ ). <sup>h</sup> Observed second-order rate constants have been divided by 2 throughout the data analysis to conform with the observed stoichiometries of the redox reactions (eq 5, 6, and 16).

basic iron(II) solution was mixed with pyrazine solution containing sufficient perchloric acid to give the desired pH on mixing. The anomalous effects observed when acidified iron(II) solutions were mixed with acidified or neutral pyrazine solutions may be connected with the bifunctional nature of pyrazine<sup>33</sup> since reactions with isonicotinamide and hydrogen peroxide were well behaved under these conditions. When the first of the above methods of reactant preparation was employed at pH  $< 9.5$ , the second-order rate constants for complex formation were ca. 15% lower than those obtained at higher pH. The involvement of  $\text{pyrH}^+$  is unlikely to account for this rate decrease in complex formation at low pH,<sup>9</sup> and the acid dissociation constant  $K_h \approx 2 \times 10^{-7} \text{ M}$  for equilibrium 9



derived from a fit of the data to a mechanism involving reaction of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  and  $\text{Fe}(\text{CN})_5\text{OH}^{4-}$  with pyr is too large to be compatible with the corresponding parameter for  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{2-}(\text{aq})$  ( $\text{p}K_h' = 8.4$  at  $25^\circ \text{C}$ ). In addition, inclusion of reaction 9 is unnecessary in the description of the kinetic data for all other ligands studied (see below). Activation parameters in Table II were determined from data at pH 11.77 (Table I) where the reaction rate is acid independent and first order in [pyr].

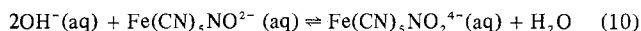
The spectral relaxation phenomena observed<sup>32</sup> on mixing iron(II) reactant solutions at pH  $> 9$  with aqueous sodium perchlorate are at least 500 times slower than are those associated with formation of  $\text{Fe}(\text{CN})_5\text{pyr}^{3-}$  in the experimental acidity range. Since the spectrum of  $\text{Fe}(\text{CN})_5\text{pyr}^{3-}$  varies only slightly with pH (see above), its absorption can be used to estimate the proportions of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  and  $\text{Fe}_2(\text{CN})_{10}^{6-}(\text{aq})$  in iron(II) reactant solutions prepared by dissolution of  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 3\text{H}_2\text{O}$  in 1 M aqueous sodium perchlorate. Reagent solutions containing  $[\text{Fe}^{II}] = 2 \times 10^{-4} \text{ M}$  which had been allowed to stand for 15 min after dissolution at pH 10.5, 11.5, and 12.7 were found to contain ca. 62%  $\text{Fe}_2(\text{CN})_{10}^{6-}(\text{aq})$  by this method, while solutions with  $[\text{Fe}^{II}] = 2 \times 10^{-5} \text{ M}$  formed only 24, 35, and 35%  $\text{Fe}_2(\text{CN})_{10}^{6-}(\text{aq})$  in the same time at pH 9.5, 12.2, and 12.7, respectively. Extension of this technique to periods greater than 1 h was precluded by evidence for loss of pentacyanoiron(II) species.

**Reaction with Thiourea.** The product of reaction of pentacyanoaquoiron(II) species with excess thiourea, tu, exhibited spectral maxima at 406 nm ( $\epsilon$  470 M<sup>-1</sup> cm<sup>-1</sup>, pH independent) and 584 nm ( $\epsilon$  130 M<sup>-1</sup> cm<sup>-1</sup> at pH 3.7, no distinct peak at pH 12.7). At pH 7.8, the rate of complex formation followed eq 8, but at pH 12.1 a plot of the observed pseudo-first-order rate constant vs. [tu] was curved upward.<sup>34</sup> However, the apparent second-order rate constant at low [tu] and pH 12.1 obtained from the slope of this plot was only ca. 10% greater than that at pH 7.8, indicating only a very minor dependence of  $k_{\text{obsd}}$  on reaction acidity.

**Reactions with Isonicotinamide and Acetonitrile.** The kinetics of formation of Fe(CN)<sub>5</sub>IN<sup>3-</sup> (IN = isonicotinamide) and Fe(CN)<sub>5</sub>AN<sup>3-</sup> (AN = acetonitrile) were monitored under pseudo-first-order conditions at 434 and 440 nm, respectively, with [iron(II)] = (1–2) × 10<sup>-5</sup> M and pH 6–12.2 at ionic strength 1 M and 25.0 °C.

It has been shown that complexation of Fe(CN)<sub>5</sub>H<sub>2</sub>O<sup>3-</sup> by IN is first-order in [IN] at pH 6.5–8.<sup>9</sup> Since the corresponding reaction with pyr is first-order in [pyr] at high pH (Table I), it is assumed that the reactions with IN and AN follow eq 8 under our experimental conditions. Second-order (essentially pH-independent) rate constants calculated on this assumption are given in Table II.

**Reactions with Cyanide and Nitrite Ions.** The formation of Fe(CN)<sub>6</sub><sup>4-</sup> was observed in the reaction of pentacyanoaquoiron(II) species with excess CN<sup>-</sup> at [OH<sup>-</sup>] = 0.05–0.1 M and ionic strength 1 M (cf. ref 14). The rate of disappearance of Fe(CN)<sub>5</sub>H<sub>2</sub>O<sup>3-</sup> at 434–470 nm obeyed eq 8 in the range [Fe<sup>II</sup>] = (2.5–11) × 10<sup>-5</sup> M. Different product spectra in the reaction with excess NO<sub>2</sub><sup>-</sup> at high and low pH reflected shifts in equilibrium 10.<sup>36</sup> At [OH<sup>-</sup>] = 0.05 M, the



rate of formation of Fe(CN)<sub>5</sub>NO<sub>2</sub><sup>4-</sup>(aq) (which has an absorption maximum at 390 nm and  $\epsilon_{450}$  750 M<sup>-1</sup> cm<sup>-1</sup>) obeyed eq 8. The initial reaction was followed by slow conversion of Fe<sub>2</sub>(CN)<sub>10</sub><sup>6-</sup>(aq) to Fe(CN)<sub>5</sub>NO<sub>2</sub><sup>4-</sup>. This same phenomenon was observed at pH 11, but before dimer conversion to Fe(CN)<sub>5</sub>NO<sub>2</sub><sup>4-</sup>(aq) was complete, a third spectral change, attributed to formation of Fe(CN)<sub>5</sub>NO<sub>2</sub><sup>2-</sup>, eq 10, was observed. This latter process became the only kinetically observable spectral change at pH < 8 and interfered severely with kinetic measurements for the Fe(CN)<sub>5</sub>H<sub>2</sub>O<sup>3-</sup>-NO<sub>2</sub><sup>-</sup> reaction at pH < 9.<sup>37</sup> Under more alkaline conditions the rate of the latter reaction obeyed eq 8 at 5.0–25.0 °C and ionic strength 1.0 M. The kinetic data are collected in Table II.

**Reactions of Fe(CN)<sub>5</sub>H<sub>2</sub>O<sup>3-</sup> with Hydrogen Peroxide and *tert*-Butyl Hydroperoxide.** In these reactions the pseudo first-order rate constants for iron(III) product formation from excess peroxide obtained at 390 nm were given by eq 11 over

$$k_{\text{obsd}} = \frac{d \ln [\text{Fe}^{\text{III}}]}{dt} = \frac{(A + B/[\text{H}^+])}{1 + K_a/[\text{H}^+]} [\text{ROOH}]_T \quad (11)$$

the range [Fe<sup>II</sup>] = (2.5–40) × 10<sup>-5</sup> M, where R = H or -C(CH<sub>3</sub>)<sub>3</sub>, K<sub>a</sub> is the acid-dissociation constant of H<sub>2</sub>O<sub>2</sub> (2.15 × 10<sup>-12</sup> M at 25.0 °C<sup>38</sup> or (CH<sub>3</sub>)<sub>3</sub>COOH (4.09 × 10<sup>-13</sup> M at 25.0 °C (this work)), [ROOH]<sub>T</sub> is the analytical peroxide concentration, and A and B are empirical parameters with units of M<sup>-1</sup> s<sup>-1</sup> and s<sup>-1</sup>, respectively.<sup>39</sup> A nonlinear least-squares fit<sup>27</sup> of the data from Table III<sup>31</sup> to eq 11 with K<sub>a</sub> fixed at 2.15 × 10<sup>-12</sup> M gave A = (214 ± 1) M<sup>-1</sup> s<sup>-1</sup> and B = (14 ± 4) × 10<sup>-12</sup> s<sup>-1</sup> for the reaction with H<sub>2</sub>O<sub>2</sub> at 25.0 °C and ionic strength 1.0 M. Figure 1a allows visual comparison of observed and calculated second-order rate constants  $k_{\text{obsd}}/[\text{H}_2\text{O}_2]$  for this fit of the data. Activation parameters for

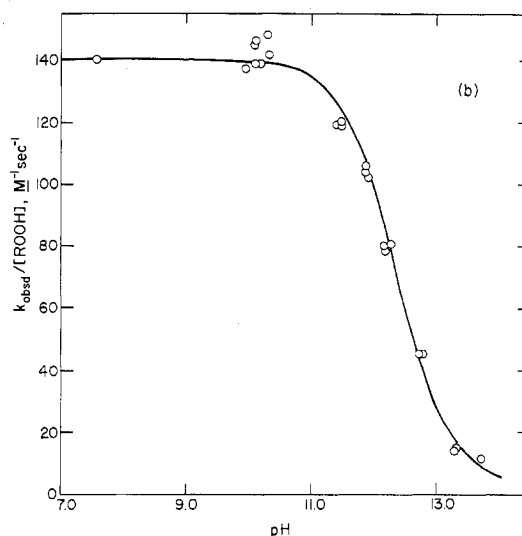
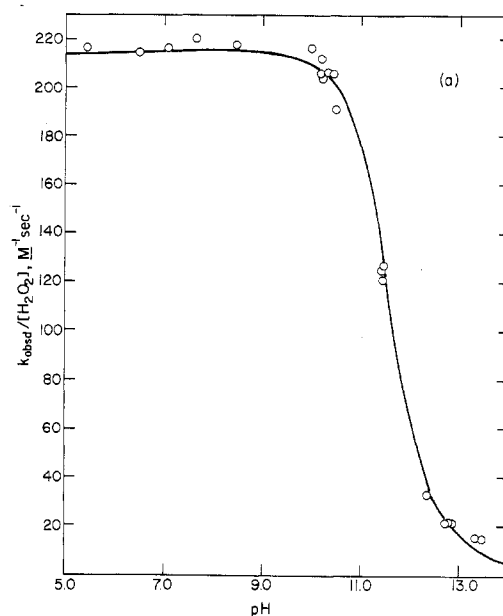


Figure 1. (a) Plot of  $k_{\text{obsd}}/[\text{H}_2\text{O}_2]$  vs. pH at 25.0 °C and 1 M NaClO<sub>4</sub>. (b) Plot of  $k_{\text{obsd}}/[\text{ROOH}]$  vs. pH at 25.0 °C and 1 M NaClO<sub>4</sub>. The points are experimental and the curves are those generated by a computer fit of the data to eq 11.

reaction with H<sub>2</sub>O<sub>2</sub> (Table II) were obtained from a computer fit<sup>28</sup> of the data at pH < 8.5 at 25.0 °C and at pH 7 at 5.0 and 15.0 °C, where the second terms in the numerator and denominator of eq 11 may be neglected (see Table III).

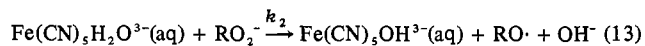
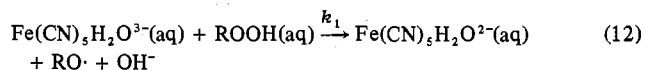
The kinetic data for reaction with *tert*-butyl hydroperoxide<sup>39</sup> (Table IV)<sup>31</sup> were fitted to eq 11 by nonlinear least squares,<sup>27</sup> which gave A = 139 ± 1 M<sup>-1</sup> s<sup>-1</sup> and B = (2 ± 4) × 10<sup>-13</sup> s<sup>-1</sup> at 25.0 °C. The fit of observed and calculated data is illustrated in Figure 1b. The low precision in the computer-generated estimate of B is caused by the small kinetic contribution from reaction 13 and the ca. 10% proportion of RO<sub>2</sub><sup>-</sup> even at the highest experimental pH (13.32); measured rates were comparatively low under these conditions. Activation parameters (Table II) were determined as described above for the hydrogen peroxide reaction.

No kinetic wavelength dependence was observed for the reaction of *tert*-butyl hydroperoxide with Fe(CN)<sub>5</sub>H<sub>2</sub>O<sup>3-</sup> over the wavelength range 380–430 nm. However, studies under similar conditions with hydrogen peroxide gave wavelength-dependent rate constants at fixed [H<sub>2</sub>O<sub>2</sub>] and pH < 10. Although curved first-order plots were obtained at 380

nm, similar plots at 390 and 410 nm were linear but the pseudo-first-order rate constants at 410 nm were ca. 70% lower than those at 390 nm. Since conversion of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$  to  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{2-}$  or  $\text{Fe}(\text{CN})_5\text{OH}^{3-}$  is quantitative and these products have maximum absorbances in the 390-nm region,<sup>40</sup> the latter wavelength was chosen to monitor the reactions. The largest spectral changes were observed for the monomer reaction at this wavelength. It should be emphasized that eq 11 is obeyed over a 16-fold range of [iron(II)] (see above and Table III).

Subsequent slow spectral changes at 380 nm are presumably due to  $\text{Fe}_2(\text{CN})_{10}^{6-}(\text{aq})$  oxidation by peroxide coupled with relaxation of dimeric iron(III) oxidation products to give monomeric species (cyanoiron(III) dimers are generally less stable than their iron(II) analogues at these concentration levels).<sup>6</sup> Attempts to resolve these concurrent kinetic processes were unsuccessful over a wide range of experimental conditions.

The measured stoichiometries and rate law (11) for the reaction with the peroxides are consistent with the mechanism of eq 12–15. Here, reactions 12 and 13 are postulated to be



rate determining, the peroxide species ROOH and  $\text{RO}_2^-$  are linked by rapid equilibria as in (7) and  $\text{RO} \cdot$  is a radical species which undergoes very rapid reduction in step 14.<sup>41</sup> Assumption of a steady state for  $[\text{RO} \cdot]$  leads to eq 16, which is of the same

$$k_{\text{obsd}} = \frac{2(k_1 + k_2 K_a / [\text{H}^+])}{1 + K_a / [\text{H}^+]} [\text{ROOH}]_{\text{T}} \quad (16)$$

form as eq 11 with  $A = 2k_1$  and  $B = 2k_2 K_a$ . Thus  $k_1 = 107 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_2 = 3 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$  for reaction of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$  with  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^-$ , respectively, at 25.0 °C. The corresponding values for *t*-BuOOH and *t*-BuO<sub>2</sub><sup>-</sup> are  $69.5 \pm 0.5 \text{ M}^{-1} \text{ s}^{-1}$  and  $0.2 \pm 0.5 \text{ M}^{-1} \text{ s}^{-1}$  at 25.0 °C, respectively.

Comparison of the rate constants and activation parameters for oxidation of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$  by the two peroxides with corresponding data for complexation with a variety of ligands (Table II) strongly suggests that the oxidation processes are limited by substitution of peroxide species at the iron(II) center. This conclusion is supported by the distinct lack of kinetic or spectral evidence for formation of significant concentrations of iron(II)–peroxide complexes under the experimental conditions.

## Discussion

Comparison of the kinetic data in Table II for complexation of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  by  $\text{CN}^-$ ,  $\text{NO}_2^-$ , pyrazine, and isonicotinamide indicates good agreement between our results and those of recent studies.<sup>9,13,14</sup> This agreement is significant since it illustrates that rate data for reactions of monomeric  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  species can be obtained even under conditions where substantial and time-dependent proportions of dimeric complexes exist (i.e., at high pH and high  $[\text{Fe}^{\text{II}}]$ ); in the present work such data were obtained by maintaining a large excess of complexing ligand.<sup>32</sup>

James and Murray<sup>14</sup> indirectly obtained the rate constant for  $\text{CN}^-$  complexation with  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  at 25 °C from a study of  $\text{CN}^-$  and HCN substitution at  $\text{Fe}(\text{CN})_5\text{py}^{3-}(\text{aq})$ ; agreement between their indirect estimate and the value

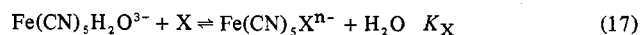
obtained directly in the present work supports their proposed mechanism.<sup>14</sup>

The kinetic data for reaction with pyrazine and isonicotinamide differ in 1 M  $\text{NaClO}_4$  and 0.5 M  $\text{LiClO}_4$  despite the fact that no significant ionic strength dependence of the rate constant was noted in the latter medium.<sup>9</sup> In view of the high formal negative charge of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$ , it may be anticipated that kinetic parameters will, to some extent, depend upon the alkali metal salt used to maintain a constant ionic medium.<sup>42</sup>

Rate constants are now available for complexations of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  by ligands ranging from  $\text{Co}(\text{NH}_3)_5(4,4\text{-bpy})^{3+}(\text{aq})$  ( $k_f = 5.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C<sup>44</sup>) to  $\text{SO}_3^{2-}$  ( $k_f = 3.3 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C<sup>13</sup>) and it is evident that complexation rate constants decrease as the formal charge product of the reactants becomes more positive. The indirect estimate of the rate constant for complexation of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  by HCN ( $344 \pm 25 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\Delta H_f^\ddagger = 17.0 \pm 1.3 \text{ kcal mol}^{-1}$ ,  $\Delta S_f^\ddagger = 11 \pm 5 \text{ cal deg}^{-1} \text{ mol}^{-1}$ )<sup>14</sup> is consistent with those for other neutral ligands (Table II). An increase of the formal negative charge on the complexing ligand is accompanied by a corresponding increase in  $\Delta H_f^\ddagger$  (Table II).<sup>45</sup> However, an unequivocal choice between this and other mechanistic alternatives involving five-coordinate  $\text{Fe}(\text{CN})_5^{3-}$  intermediates<sup>9,13,14</sup> is not possible in the absence of more extensive activation parameter data. It should be noted that  $\Delta H_f^\ddagger$  ( $16.8 \pm 0.5 \text{ kcal mol}^{-1}$  in 1.0 M  $\text{LiClO}_4$ )<sup>9</sup> for *N*-methylpyrazinium complexation is higher than are those for neutral nitrogen heterocycles,<sup>9</sup> which might not be anticipated from the trends suggested by the data in Table II.

The activation enthalpy and entropy for reaction with hydrogen peroxide are also anomalously high, while those for the corresponding reaction with *tert*-butyl hydroperoxide are "normal". Of all the neutral ligands studied, hydrogen peroxide is likely to be the most extensively solvated by water molecules in aqueous sodium perchlorate solution.<sup>46</sup> A requirement for desolvation of  $\text{H}_2\text{O}_2$  on complex formation with  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  would lead to positive contributions to the overall enthalpy and entropy of activation, as observed. The low rates for reaction with the "hard" ligands  $\text{HO}_2^-$  and  $(\text{CH}_3)_3\text{CO}_2^-$  may also reflect a requirement for substantial desolvation of these anions on complexation. The wavelength-dependent kinetic phenomena noted in the reaction with  $\text{H}_2\text{O}_2$  suggest specific interactions of peroxide species with iron(II) reactants or, more likely,<sup>14</sup> iron(III) products (see below).

Recently, Murray<sup>14</sup> considered equilibrium constants for complexation (eq 17) where X varies from  $\text{Cl}^-$  ( $K_X < 1 \text{ M}^{-1}$ )



to  $\text{CN}^-$  ( $K_X = 1.2 \times 10^{10} \text{ M}^{-1}$  at 25 °C). The variations in  $K_X$  suggest<sup>9,14</sup> classification of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$  as a "soft" center, which is consistent with an invariance of its visible spectrum in the presence of large excesses of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{N}_3^-$  and with a lack of any evidence for iron(II)–peroxo complex formation (present work). The highest pH used in our complexation kinetic studies was 12.8. The  $\text{p}K_a$  for eq 9 must be similar to  $\text{p}K_w$  in 1 M  $\text{NaClO}_4$  ( $13.77^{23}$ ) in order to be consistent with the invariance of rate with pH up to this limit in the reactions with pyrazine and  $\text{NO}_2^-$ . In addition, the rate of complexation by isonicotinamide is independent of pH in the range 6–12.2 (Table I). Although it is possible that the rate constants for reaction of these three ligands with  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  and  $\text{Fe}(\text{CN})_5\text{OH}^{4-}(\text{aq})$  are similar, this does not seem likely, particularly since  $\text{NO}_2^-$  is negatively charged.

The apparent low acidity of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  suggests the existence of a weak Fe–O bond<sup>47</sup> and also helps to explain

its marked tendency toward formation of the di- $\mu$ -cyano-iron(II) dimer  $\text{Fe}_2(\text{CN})_{10}^{6-}(\text{aq})$  (this work and ref 29). However, the enthalpies of activation in Table II are noticeably higher than are those typically observed for complexation at labile cationic centers,<sup>48</sup> suggesting that desolvation of  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  (perhaps involving counterions) may be an important factor in determining activation barriers for complex formation in this latter system.

Although the majority of established substitution-controlled redox systems involve  $d^3$  or low-spin  $d^6$  transition metal centers,<sup>45</sup> this may just be the result of their inherently low rates of substitution. Thus, evidence is slowly accumulating for substitution-controlled rate phenomena in redox reactions of  $\text{Ti}^{3+}(\text{aq})$  ( $d^1$ ),<sup>49</sup>  $\text{Cr}^{2+}(\text{aq})$  ( $d^4$ ),<sup>50</sup> and  $\text{MnOH}^{2+}(\text{aq})$  ( $d^4$ ).<sup>51</sup> However, it is still evident that in all cases the transition metal center exhibiting this phenomenon is a strong oxidant or reductant.<sup>45</sup>

The reaction of oxygen with  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$  is much slower than is oxidation by hydrogen peroxide: assuming that the reaction with oxygen is first order in  $[\text{O}_2]$ , with  $[\text{O}_2] = 10^{-3}$  M in oxygen-saturated 1 M  $\text{NaClO}_4$  at 1 atm,<sup>52</sup> the second-order rate constant would be ca.  $2 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C, which is more than 50 times lower than that for  $\text{H}_2\text{O}_2$ . Reactions of  $\text{Fe}^{2+}(\text{aq})$ <sup>53</sup> and  $\text{Fe}(\text{CN})_6^{4-}$ ,<sup>4,12b</sup> with oxygen are also slower than are those with  $\text{H}_2\text{O}_2$ , whereas the opposite order of reactivity has been noted in the reactions of  $\text{Ru}(\text{NH}_3)_6^{2+}$ .<sup>54</sup> Recent comparisons<sup>9,55</sup> of spectral and other properties of  $\text{Fe}^{\text{II}}(\text{CN})_5$ - and  $\text{Ru}^{\text{II}}(\text{NH}_3)_5$ -containing complexes suggest many commonalities but, unfortunately, no kinetic data are available for oxidation of  $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$  by  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  so the kinetic implications of these commonalities cannot be appraised.

Inner-sphere mechanisms have been proposed for oxidation of  $\text{Cr}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  and  $\text{Co}(\text{CN})_5^{3-}(\text{aq})$  by  $\text{H}_2\text{O}_2$ .<sup>56</sup> However, in the absence of complexation data, the possibility of substitution-controlled redox mechanisms in these systems is an open question.

Finally, it should be noted that the rate constants for reaction 2 ( $107 \text{ M}^{-1} \text{ s}^{-1}$  (this work)) and reaction 3 ( $10^3 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>57</sup> are both sufficiently large to support efficient photocatalysis of the  $\text{Fe}(\text{CN})_6^{4-}$ - $\text{H}_2\text{O}_2$  reaction.

**Registry No.**  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ , 18497-51-3;  $\text{H}_2\text{O}_2$ , 7722-84-1;  $(\text{CH}_3)_3\text{COOH}$ , 75-91-2;  $\text{CN}^-$ , 57-12-5;  $\text{NO}_2^-$ , 14797-65-0; pyrazine, 290-37-9; isonicotinamide, 1453-82-3; thiourea, 62-56-6; acetonitrile, 75-05-8.

**Supplementary Material Available:** Tables I, III, and IV listing kinetic data for complexation with pyrazine, thiourea, isonicotinamide, acetonitrile,  $\text{CN}^-$ , and  $\text{NO}_2^-$  and oxidation by  $\text{H}_2\text{O}_2$  and *tert*-butyl hydroperoxide (4 pages). Ordering information is given on any current masthead page.

## References and Notes

- Abstracted from the doctoral dissertation of A.R.G. to the Northeastern University Graduate School of Arts and Sciences, 1975.
- B. Lal, *Curr. Sci.*, **16**, 118 (1947).
- J. H. Baxendale, *Advan. Catal.*, **4**, 31 (1952).
- J. Sobkowski, *Rocz. Chem.*, **43**, 1729 (1969).
- B. Jaselskis, *J. Am. Chem. Soc.*, **83**, 1082 (1961); in this paper we show that the products of the title reaction are  $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}(\text{aq})$  and  $\text{Fe}(\text{CN})_5\text{OH}^{4-}(\text{aq})$  (dependent on pH<sup>6</sup>).
- J. H. Espenson and S. Wolenuk, *Inorg. Chem.*, **11**, 1034 (1972).
- H. B. Gray, *Adv. Chem. Ser.*, No. **100**, 365 (1970); L. E. Bennett, *Prog. Inorg. Chem.*, **18**, 1 (1973).
- See, e.g., papers in "Inorganic Biochemistry", G. L. Eichhorn, Ed., Elsevier, New York, N.Y., 1973, especially chapters 24–28.
- J. M. Malin and H. E. Toma, *Inorg. Chem.*, **12**, 2080 (1973).
- J. M. Malin and H. E. Toma, *Inorg. Chem.*, **13**, 1772 (1974).
- G. Emschwiller, *C. R. Hebd. Seances Acad. Sci.*, **238**, 341 (1954).
- (a) K. A. Hofmann, *Justus Liebigs Ann. Chem.*, **312**, 1 (1900); (b) S. Asperger, I. Murati, and D. Pavlovic, *J. Chem. Soc. A*, 2044 (1969).
- Z. Bradic, M. Pribanic, and S. Asperger, *J. Chem. Soc., Dalton Trans.*, 353 (1975).
- A. D. James and R. S. Murray, *J. Chem. Soc., Dalton Trans.*, 1530 (1975).
- E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **5**, 1866 (1966).
- Analyses of solid samples were made by Chemicals, Tempe, Ariz.
- R. Belcher and A. J. Nutten, "Quantitative Inorganic Analysis", 2d ed, Butterworths, London, 1960, p 184.
- Reference 17, p 269.
- Reference 17, p 273.
- W. E. Cass and A. K. Bahl, *J. Org. Chem.*, **39**, 3602 (1974).
- G. Davies, *Inorg. Chem.*, **10**, 1155 (1971).
- M. Schure, to be submitted for publication.
- The  $pK_a$  of water is 13.77 at ionic strength 1 M ( $\text{NaClO}_4$ ) and 25 °C; L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ion Complexes", Chemical Society, London, 1971, p 14.
- S. Asperger, I. Murati, and D. Pavlovic, *J. Chem. Soc.*, 730 (1960).
- J. E. Crooks, M. Zetter, and P. A. Tregloan, *J. Sci. Instrum.*, **3**, 73 (1970).
- Wang desk computer programs were supplied by Dr. C. M. Jankowski.
- The computer program was based on the Los Alamos Scientific Laboratory Reports LA2367 by R. H. Moore and R. K. Zeigler, 1959, and LA2367 and Addenda by P. McWilliams, 1962. The program was modified by S. Terrace for use on the Northeastern University CDC6600 system.
- I. Bodek, G. Davies, and J. H. Ferguson, *Inorg. Chem.*, **14**, 1708 (1975).
- G. Emschwiller, *C. R. Hebd. Seances Acad. Sci.*, **265**, 281 (1967).
- The stoichiometries in eq 5 and 6 are those expected at pH 4. At pH 12.5 the iron(III) product in both reactions is  $\text{Fe}(\text{CN})_5\text{OH}^{3-}$  ( $\epsilon_{389} 1740 \text{ M}^{-1} \text{ cm}^{-1}$ ).
- Supplementary material.
- The kinetics of slower reactions of the pentacyanoaquairon(II) system with complexing ligands will be reported in a later paper.
- A. Haim, *Acc. Chem. Res.*, **8**, 264 (1975).
- Similar behavior has been observed recently in the reduction of (2,9-dimethyl-1,10-phenanthroline)copper(II) complexes by  $\text{Cu}^{\text{I}}$  at pH 7.<sup>35</sup>
- G. Davies and D. J. Loose, *Inorg. Chem.*, **15**, 694 (1976).
- J. Swinehart and P. A. Rock, *Inorg. Chem.*, **5**, 573 (1966).
- The observed rate constant for relaxation of  $\text{Fe}(\text{CN})_5\text{NO}_2^{4-}$  in eq 10 was  $(2.69 \pm 0.06) \times 10^{-2} \text{ s}^{-1}$  at pH 9, ionic strength 1.0 M, and 25.0 °C.
- M. G. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 225 (1949).
- Plots of  $k_{\text{obsd}} (\text{s}^{-1})$  vs.  $[\text{H}_2\text{O}_2]$  in eq 11 had negligible intercepts under all experimental conditions. However, minor intercepts of  $0.41 \text{ s}^{-1}$  at pH <10 and 25.0 °C,  $0.70 \text{ s}^{-1}$  at pH 9.6 and 15.0 °C, and  $0.71 \text{ s}^{-1}$  at pH 9.7 and 5.0 °C were observed in corresponding plots of the *tert*-butyl hydroperoxide data. These intercepts were still observed after repeated fractional redistillation and assay of *tert*-butyl hydroperoxide;<sup>20</sup> however, product spectral studies showed that the reaction with this latter oxidant was  $100 \pm 1\%$  complete under all conditions, indicating that the intercepts are not due to a reversible rate-determining step (additions of  $\text{Fe}(\text{CN})_5\text{OH}^{2-}$  had no kinetic effect and nonexponential traces would be observed if reaction 12 were reversible, since  $[\text{Fe}^{\text{III}}] = 0$  at  $t = 0$ ). The similarity of the intercepts at all temperatures suggests a nonkinetic origin. In any event, their existence does affect the determination of the slopes of plots of  $k_{\text{obsd}}$  vs.  $[\text{ROOH}]$ , which are directly proportional to  $k_1$  for this system.
- This work and ref 6.
- We have no direct observations on reaction 14, but see H. N. Po and N. Sutin, *Inorg. Chem.*, **7**, 621 (1968), and references therein.
- The equilibrium constant for the reaction  $\text{Fe}(\text{CN})_6^{4-} + \text{K}^+ \rightleftharpoons \text{KFe}(\text{CN})_6^{3-}$  is  $60 \text{ M}^{-1}$  at 25 °C and ionic strength 0.03 M.<sup>43</sup>
- W. Eaton, P. George, and G. Hanania, *J. Phys. Chem.*, **71**, 2016 (1967).
- D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **96**, 7845 (1974).
- I. Bodek and G. Davies, *Coord. Chem. Rev.*, **14**, 269 (1974).
- G. Scatchard, G. M. Kavanaugh, and L. B. Ticknor, *J. Am. Chem. Soc.*, **74**, 3715 (1952); W. F. K. Wynne-Jones, *J. Chim. Phys. Phys.-Chim. Biol.*, **46**, 337 (1946); A. G. Mitchell and W. F. K. Wynne-Jones, *Discuss. Faraday Soc.*, **15**, 161 (1953).
- D. Pavlovic, I. Murati, and S. Asperger, *J. Chem. Soc., Dalton Trans.*, 602 (1973).
- D. J. Hewkin and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1970).
- J. P. Birk, *Inorg. Chem.*, **14**, 1724 (1975).
- N. Sutin, *Acc. Chem. Res.*, **1**, 225 (1968).
- G. Davies, *Inorg. Chim. Acta*, **14**, 13L (1975).
- H. W. Harvey, "The Chemistry and Fertility of Sea Waters", 2nd ed, Cambridge University Press, London, 1969, p 184.
- P. George, *J. Chem. Soc.*, 4349 (1954).
- J. R. Pladziewicz, T. J. Meyer, J. A. Broomhead, and H. Taube, *Inorg. Chem.*, **12**, 639 (1973).
- H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973); *J. Am. Chem. Soc.*, **97**, 288 (1975).
- G. Davies, N. Sutin, and K. O. Watkins, *J. Am. Chem. Soc.*, **92**, 1892 (1970).
- R. Stasiw and R. G. Wilkins, *Inorg. Chem.*, **8**, 156 (1969).