Trace Metal Ion Catalysis in the Oxidation of $Fe(CN)_6^{4-}$ by H_2O_2

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The rate constants for the oxidation of pentacyano(*N*-methylpyrazinium)ferrate(II) by hydrogen peroxide and the substitution by dimethyl sulfoxide under saturation conditions are the same ($k = (3.8 \pm 0.1) \times 10^{-4}$ s^{-1} at pH 7.1 (MOPS buffer), 25 °C, and $I = 1.0$ M by use of $LiClO_4$). The peroxide reaction is not catalyzed by Mo(VI) or W(VI). The kinetics of the oxidation of hexacyanoferrate(II) by hydrogen peroxide were monitored under conditions where catalysis by pentacyanoaquoferrate(II) was neglible. The kinetic traces were approximately pseudo-zero-order under typical conditions (2.00×10^{-3} M $Fe(CN)_6^{4-}$, 1.00×10^{-2} M H_2O_2, 5.0×10^{-3} M $Mpyz^+$, pH 4.0 (acetate buffer), and 25 °C). The slopes (a) were not very reproducible, (b) varied with the initial concentration and source of the hexacyanoferrate(II), (c) were linearly dependent on the concentration of added Mo(VI) or W(VI), (d) were too large for the values expected for an outer-sphere direct reaction between the reductant and hydrogen peroxide, and (e) were substantially decreased by the presence of metal ion chelators. It was found through studies with added iron(III) or iron(II) that the reaction rates are catalyzed and largely driven by trace metal ion contaminants in the absence of chelating agents. Attempts to measure the true rate of oxidation of hexacyanoferrate(II) by hydrogen peroxide were unsuccessful, but it was shown that the upper limit established is more in line with that expected for the outer-sphere pathway. Some preliminary studies of the very slow oxidation of hexacyanoruthenate(II) by hydrogen peroxide are presented.

Introduction

The oxidation of hexacyanoferrate(II) by hydrogen peroxide in acidic and neutral solution has been studied periodically throughout this century. Kinetic studies have been reported by several research groups.[1-4] It is clear that if modest concentrations of $Fe(CN)_5OH_2^{3-}$ are present, a catalytic cycle involving peroxide oxidation of this species followed by reduction of the pentacyanoaquoferrate(III) product by hexacyanoferrate(II) is important. However, it is possible to study the $Fe(CN)_6^{4-}$ reaction under conditions where the "impurity" is present at kinetically insignificant levels. Under these conditions little is known about the mechanism although various rate laws have been proposed.[1,2] The rate appears to be unusually high for an outer-sphere oxidation by hydrogen peroxide,[5,6] but it is difficult to suggest a plausible inner-sphere pathway that has experimental support.

We have reexamined this system and tested for catalysis by molybdenum(VI) and tungsten(VI). These d^0 metal ions are often excellent catalysts for inner-sphere oxidations by hydrogen peroxide. The active forms of the catalysts in neutral and acidic aqueous solution are the rapidly formed and robust oxodiperoxo complexes $MO(O-O)_2(H_2O)_2$ and their conjugate bases $MO(O-O)_2(OH)(H_2O)^-$ (pK_a = 1.85 and 0.12 for M = Mo and W, respectively).[7-9] We have proposed that inner-sphere attack by the reducing agent at the η^2-peroxo group is required for effective catalysis.[10] We have effectively eliminated catalysis by $Fe(CN)_5OH_2^{3-}$ in the $Fe(CN)_6^{4-}$ system through the use of experimental conditions where its formation rate is minimized, and further by the addition of *N*-methylpyrazinium cation ($Mpyz^+$) to convert efficiently trace amounts of $Fe(CN)_5OH_2^{3-}$ to the inactive complex $Fe(CN)_5(Mpyz)^{2-}$ (*vide infra*). We have independently measured the rate of oxidation of $Fe(CN)_5(Mpyz)^{2-}$ by H_2O_2, in both the absence and the presence of Mo(VI) and W(VI). In addition, some preliminary kinetic results on the oxidation of $Ru(CN)_6^{4-}$ by hydrogen peroxide are presented.

Experimental Section

Reagents. Solutions of $Fe(CN)_5OH_2^{3-}$ were prepared by dissolving sodium pentacyanoammineferrate(II) in deoxygenated buffer solutions.[11] The pentacyanoammineferrate(II) salt (Fischer Certified) was recrystallized from concentrated ammonia and carefully dried to the trihydrate form. Solutions of *N*-methylpyrazinium chloride were obtained from the iodide salt, prepared by the method of Bahner and Norton[12], by use of anion exchange resin. The [$Mpyz^+$] was assayed spectrophotometrically[13] by complexation with excess $Fe(CN)_5(OH_2)^{3-}$ and the [Cl^-] was determined gravimetrically; the concentration ratio was 1.00. Iron(III) perchlorate was prepared by repeated fuming of reagent grade iron(III) chloride in perchloric acid; solutions in 0.5 M $HClO_4$ were assayed spectrophotometrically at 240 nm (ϵ = 4160 M^{-1}cm^{-1})[14] or as the thiocyano complex.[15] Dimethyl sulfoxide was distilled under vacuum before use. Samples of highly purified EDTMP (ethylenediaminetetramethylphosphonic acid) and DTPMP (diethylenetriaminepentamethylphosphonic acid) were generously donated by Dow Chemical. Lithium perchlorate was prepared by neutralization of the reagent grade carbonate followed by three recrystallizations. The salts $Na_4Fe(CN)_6 \cdot 10H_2O$ (EM Science, ≥99%) and $K_4Fe(CN)_6 \cdot 3H_2O$ (Fisher, Certified ACS) were recrystallized from water. The biological buffer MOPS {3-morpholinopropanesulfonic acid} was obtained from Aldrich. All other chemicals were of reagent grade and were used as supplied. Deionized water was distilled twice before use; the last distillation was from alkaline permanganate.

Kinetic Studies. A Durrum D-110 stopped-flow instrument was used for the rapid reactions, and either a Zeiss PMQII or a HP8452A diode array spectrophotometer, each equipped with a thermostated, rapid-mixing (ca. 1 s) sample compartment, was used to monitor the slower reactions. Reactions of $Fe(CN)_5OH_2^{3-}$ were examined in the presence of $Mpyz^+$, and were monitored at the intense absorption maximum ($\epsilon = 1.2 \times 10^4$ M^{-1} cm^{-1}) for $Fe(CN)_5(Mpyz)^{2-}$ at 655 nm.[13]

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Table 1. Kinetic Results for the Reaction of Pentacyano(*N*-methylpyrazinium)ferrate(II) with Hydrogen Peroxide, the Hydrolyzed Oxodiperoxo Complexes of Mo(VI) and W(VI), and Dimethyl Sulfoxide at 25 °C[a]

$10^2[H_2O_2]_0$, M	$10^4[Mo(VI)]_0$, M	$10^4[W(VI)]_0$, M	$[DMSO]_0$, M	10^4k_{obs}, s^{-1} [b]
1.00				3.9
2.00				3.7
2.00[c]				3.4
6.00				3.7
			0.10	3.9
			0.20	4.0
1.00	5.00			3.4
5.00	250[d]			3.8
1.00		5.00		3.5

[a] Conditions: $[Fe(CN)_5(Mpyz)^{2-}]_0 = (2.50–3.70) \times 10^{-5}$ M, $[Mpyz^+]_0 = (0.15–3.4) \times 10^{-6}$ M, ionic strength maintained at 1.0 M by use of $LiClO_4$, pH = 7.1 (0.01 M MOPS), and $\lambda = 655$ nm unless otherwise indicated. [b] Values are the slopes of plots (linear for at least three half-lives) of $-\ln\{A - A_\infty\}$ vs t. [c] pH = 4.0 (0.0050 M acetate buffer). [d] pH = 7.0 (0.10 M MOPS).

Reactions of hexacyanoferrate(II) with peroxide oxidants were initiated by injection of an aliquot of a solution containing the reductant and *N*-methylpyrazinium ion in water. These solutions were prepared under N_2 (although there was no clear indication that this is necessary, and the reactions were normally not run under anaerobic conditions) and allowed to stand for ca. 30 min before use. More severe problems with irreproducible kinetics were found if the solutions were used immediately; however, prolonged storage (up to a day) was without effect other than allowing traces of $Fe(CN)_5(Mpyz)^{2-}$ to form. The reactions were normally monitored at the 420-nm absorption maximum for $Fe(CN)_6^{3-}$ ($\epsilon = 968$ M^{-1} cm^{-1}).

The oxidation of Fe^{2+} by excess H_2O_2 was monitored by following the formation of Fe(III) at 280 nm. Kinetic data for the oxidation of $Fe(CN)_6^{4-}$ by Fe(III) were collected at 420 nm. The slow oxidation of $Ru(CN)_6^{4-}$ by H_2O_2 was monitored at 326 and 356 nm; values for the extinction coefficients of $Ru(CN)_6^{3-}$ at these wavelengths were taken from the literature.[16] Attempts to test for iron catalysis were thwarted by the formation of a precipitate upon addition of even very small amounts of Fe(III).

Complex Formation Studies. Spectral evidence was obtained for the rapid formation of a complex between hexacyanoruthenate(II) and oxohydroxodiperoxomolybdenum(VI) in acetate buffer at pH 4.0. Provided the [Mo(VI)] was $\leq 1.0 \times 10^{-3}$ M, a new band with $\lambda_{max} = 340$ nm was observed. The spectral data, collected by use of a quartz split compartment cell, were consistent with a 1:1 complex for which $K_f = 1.7 \times 10^2$ M^{-1} and $\lambda_{max} = 3 \times 10^3$ M^{-1} cm^{-1} at 25 °C over the concentration range (0.70–5.60) × 10^{-2} M $Ru(CN)_6^{4-}$, (0.50–1.0) × 10^{-3} M $MoO(O–O)_2(OH)(H_2O)^-$, and 0.020 M H_2O_2.

Results

Oxidation of $Fe(CN)_5(Mpyz)^{2-}$ by H_2O_2, $MoO(O\text{-}O)_2(OH)(H_2O)^-$, and $WO(O\text{-}O)_2(OH)(H_2O)^-$. The half-life for dissociation of $Mpyz^+$ from the pentacyanoiron(II) center is approximately 40 min at 25 °C.[18] We have tested for Mo(VI) and W(VI) catalysis of the peroxide oxidation of this relatively stable complex. The experimental conditions and kinetics results are summarized in Table 1. The principal findings are as follows: (a) the first-order rate constant for oxidation of the methylpyrazinium complex by hydrogen peroxide is independent of the oxidant concentration at the levels tested, (b) that rate constant is the same as is observed for ligand exchange with dimethyl sulfoxide under saturation conditions, and (c) there is no detectable catalysis of the peroxide oxidation by either Mo(VI) or W(VI).

Table 2. Effect of Chelating Agents on the Initial Rate of the Reaction of Ferrocyanide with Hydrogen Peroxide[a]

chelating agent	pH	10^8 initial rate, M s^{-1} [b]
none	4.0	350 ± 40
EDTMP	4.0	11 ± 2
DTPMP	4.0	10 ± 2
EDTA	4.0	3.8 ± 0.2
EDTA[c]	4.0	5.0
oxalate	4.0	2.2 ± 0.3
oxalate[d]	4.0	3.0
none	7.0	70
EDTA	7.0	0.7

[a] Conditions: $[K_4Fe(CN)_6]_0 = 2.00 \times 10^{-3}$ M, $[H_2O_2]_0 = 1.00 \times 10^{-2}$ M, $[Mpyz^+]_0 = 5.0 \times 10^{-3}$ M, [chelating agent] = (1.0–5.0) × 10^{-3} M, $[buffer]_{total} = 5.0 \times 10^{-2}$ M ($NaC_2H_3O_2$ or MOPS), $\lambda = 420$ nm, and $T = 25$ °C unless otherwise indicated. [b] As $d[Fe(CN)_6^{3-}]/dt$; entries (with uncertainties) are average values of two to six independent determinations. [c] Added $[Cu^{2+}] = 1.0 \times 10^{-5}$ M. [d] Added $[FeOH^{2+}] = 1.0 \times 10^{-5}$ M.

Bowers et al.[19] found much more complicated kinetics in a careful study of the oxidation of imidazolepentacyanoferrate(II) by hydrogen peroxide. Much of this difficulty derived from the proposed participation of reaction 1. The pentacyanoaquoferrate(III) ion, formed by the substitution-limited peroxide oxidation of the imidazole complex, is reversibly reduced by the same complex; the resulting pentacyanoferrate(II) is then rapidly oxidized by hydrogen peroxide. The participation of $Fe(CN)_5(Mpyz)^{2-}$ in the analogous reaction in our system is much less likely due to its weaker reducing strength relative to $Fe(CN)_5(imz)^{3-}$ (ca. 0.38 V). Nevertheless, we tested for the possibility in a rather intricate way. A reaction was initiated under identical conditions to the fourth entry in Table 1. The reaction was monitored for 20 min, during which time the observed first-order rate constant was 4.1×10^{-4} s^{-1}. Then an aliquot of $Fe(CN)_5OH_2^{2-}$ was added such that its concentration was 1.07×10^{-4} M, and the ongoing reaction was monitored for another 20 min. The rate constant was identical to that measured for the first 20 min in the absence of the added pentacyanoaquoferrate(III). We conclude that the reaction of $Fe(CN)_5OH_2^{2-}$ by $Fe(CN)_5(Mpyz)^{2-}$ is very slow and negligible in our experiments.

$$Fe(CN)_5OH_2^{2-} + Fe(CN)_5(imz)^{3-} \Rightarrow Fe(CN)_5OH_2^{3-} + Fe(CN)_5(imz)^{2-} \quad (1)$$

Oxidation of $Fe(CN)_6^{4-}$ by H_2O_2, $MoO(O\text{-}O)_2(OH)(H_2O)^-$, and $WO(O\text{-}O)_2(OH)(H_2O)^-$. Rabai et al. have studied reaction 2 under a fairly narrow range of conditions that obtain in the hydrogen peroxide-sulfite-ferrocyanide system, a beautiful example of a pH oscillator.[1] Under their conditions ($[Fe(CN)_6^{4-}]_0 = (1.0–2.0) \times 10^{-3}$ M, $[H_2O_2]_0 = (1.0–6.0) \times 10^{-3}$ M, added sulfuric acid such that $[H^+]_{0,total} = (0.25–1.0) \times 10^{-3}$ M, and 25 °C) the rate of formation of ferricyanide obeys nearly zero-order kinetics, and they report the rate law given in eq 3. While this rate law does not hold under concentrations very far removed from those listed, it provides a reference point to test for Mo(VI) and W(VI) catalysis. Another crucial advantage is that the experimental conditions allow measurements free, or nearly so, of catalysis by traces of $Fe(CN)_5OH_2^{3-}$ (*vide infra*).

$$2Fe(CN)_6^{4-} + H_2O_2 + 2H^+ \Rightarrow 2Fe(CN)_6^{3-} + 2H_2O \quad (2)$$

$$-d[H_2O_2]/dt = 1.6 \times 10^{-4}\ s^{-1}[H_2O_2] \quad (3)$$

We have confirmed the experimental findings of Rabai et al., although the kinetic profiles were not highly reproducible from day to day. We found that very similar results were obtained if buffers were used, even though the limiting reagent then became ferrocyanide rather than hydronium ion. Pseudo-zero-order rate

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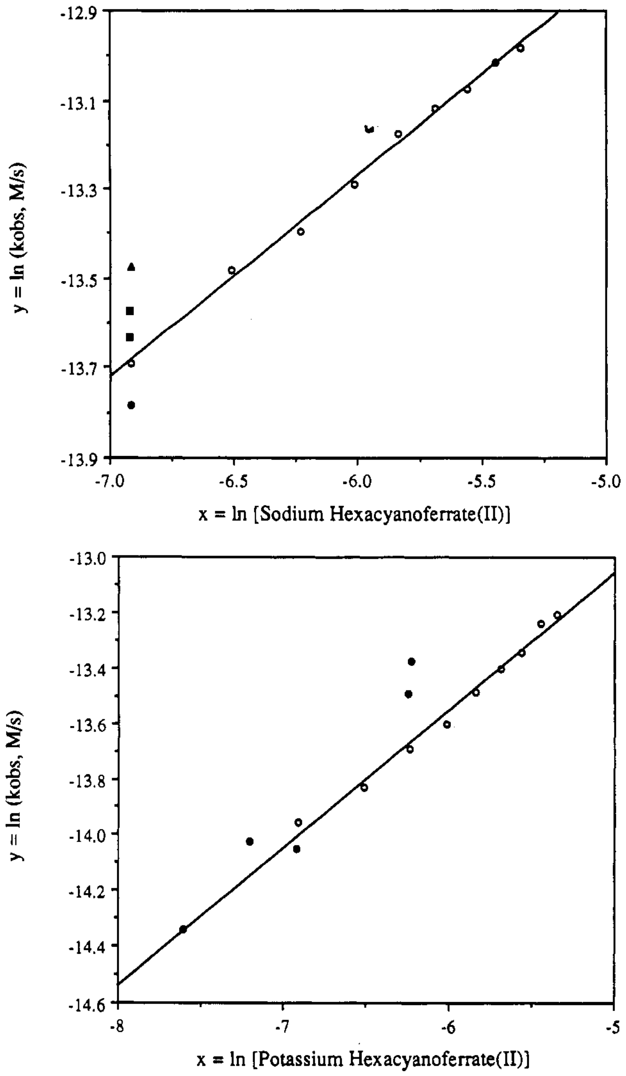

Figure 1. Plots of ln (k_{obs}, M/s) vs. ln [hexacyanoferrate(II)] for the oxidation of sodium (a, top) or potassium (b, bottom) hexacyanoferrate(II) by hydrogen peroxide. Open circles represent data taken on the same day. (a) $y = -10.6 + 0.45x$, $R^2 = 0.996$. (b) $y = -10.6 + 0.50x$, $R^2 = 0.986$. Closed symbols represent data taken on different days, giving indication of typical reproducibility. Conditions: 0.010 M H_2O_2; 5.0 × 10^{-4} M $HClO_4$; 0.010 M $LiClO_4$; (1.0–5.0) × 10^{-3} M $M_4Fe(CN)_6$; T = 25.0 °C.

constants k_{obs} were obtained from the slopes of approximately linear plots of $[Fe(CN)_6{}^{3-}]$ vs. t. Values of this rate parameter varied with the excess $[Fe(CN)_6{}^{4-}]_0$ and whether the recrystallized sodium or potassium salt was used, as shown in Figure 1. Catalysis by both Mo(VI) and W(VI) was found, as illustrated in Figure 2.

These results strongly suggest to us the presence of an adventitious redox catalyst. The following results provide strong evidence that the catalyst is not $Fe(CN)_5OH_2{}^{3-}$. The pseudo zero-order rate constant obtained for a kinetic run with 1.0 × 10^{-2} M H_2O_2, 2.0 × 10^{-3} M $Fe(CN)_6{}^{4-}$, 5.0 × 10^{-4} H^+, and 5.0 × 10^{-3} M $Mpyz^+$ at 25 °C was 2.4 × 10^{-6} M s^{-1}. The $Mpyz^+$ was present in both the ferrocyanide solution and that containing the other reagents prior to mixing and was in sufficient concentration to rapidly and quantitatively complex and thereby effectively sequester any pentacyanoaquoferrate(II) formed prior to and during the reaction. The rate constant for a control experiment without $Mpyz^+$ was 2.7 × 10^{-6} M s^{-1}. Further, we find that detectable levels (3 × 10^{-7} M) of $Fe(CN)_5(Mpyz)^{2-}$ in even concentrated solutions of $Fe(CN)_6{}^{4-}$ containing $Mpyz^+$, protected from light[20] and with no added acid, are formed quite slowly.

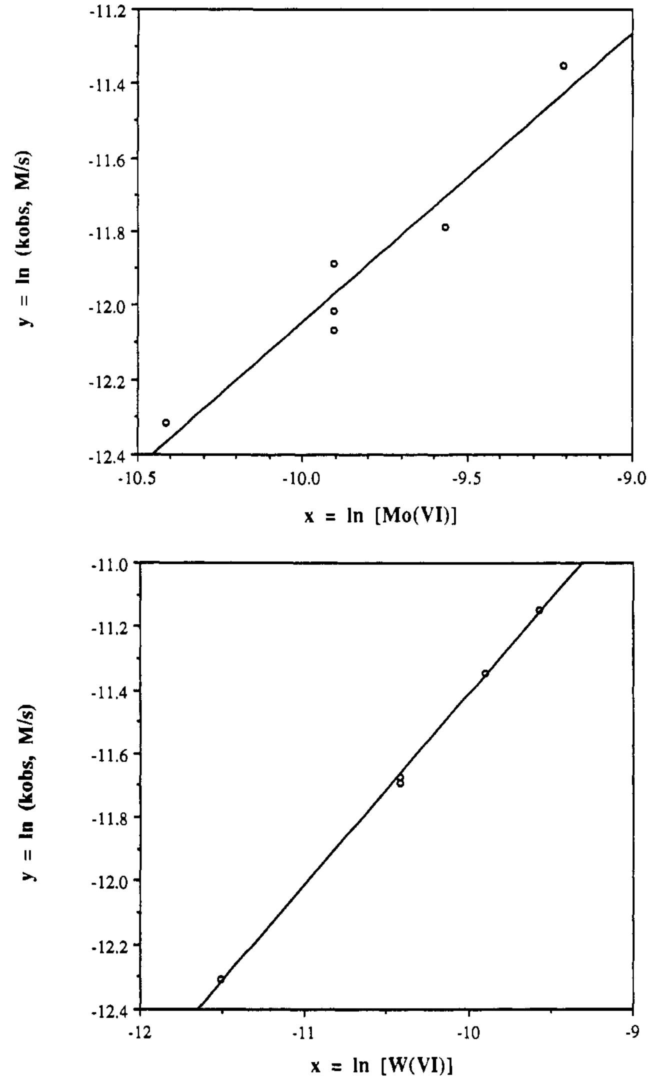

Figure 2. Molybdenum(VI) and tungsten(VI) catalysis of the oxidation of hexacyanoferrate(II) by hydrogen peroxide. (a) $y = -4.23 + 0.78x$, $R^2 = 0.936$. (b) $y = -5.43 + 0.60x$, $R^2 = 0.998$. Conditions: 0.010 M H_2O_2; 1.0 × 10^{-3} M $Na_4Fe(CN)_6$; $[HClO_4]$ = 5.0 × 10^{-4} M + ([Mo(VI)] or [W(VI)]); (0.30–1.0) × 10^{-4} M Mo(VI) in part a or (1.0–7.5) × 10^{-5} M W(VI) in part b; 0.010 M $LiClO_4$, T = 25.0 °C.

A reasonable candidate for the proposed adventitious catalyst is iron. The rather rapid oxidation of hexaaquoiron(II) by hydrogen peroxide is markedly catalyzed by both Mo(VI) and W(VI),[9] and the reduction of iron(III) by hexacyanoferrate(II) would be expected to be very rapid.[21] The data plotted in Figure 3 demonstrate that added iron indeed is an effective catalyst in this system, in accordance with the rate expression 4, where $[Fe]_t$ is the concentration of added iron(II).

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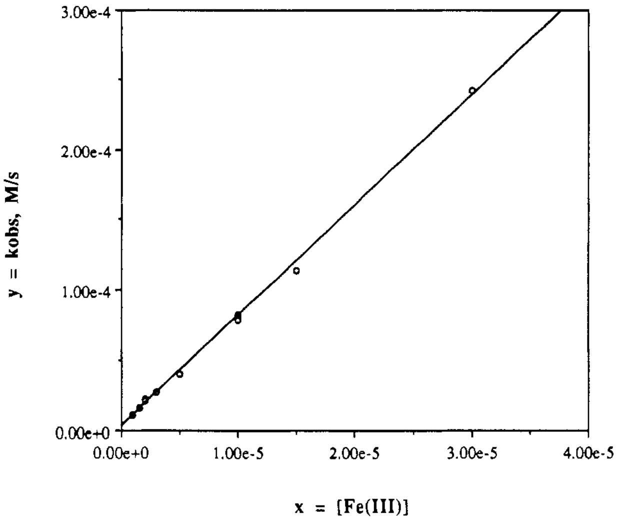

Figure 3. Catalytic effect of added iron on the rate of oxidation of hexacyanoferrate(II) by hydrogen peroxide. Conditions: 0.010 M acetate (pH = 4.0); 0.010 M H_2O_2; 5.0 × 10^{-3} M $Mpyz^+$; 2.0 × 10^{-3} M $K_4Fe(CN)_6$; (0.10–3.0) × 10^{-5} M added Fe(III); $T = 25.0$ °C. $y = 2.85E\text{-}6 + 7.86x$, $R^2 = 0.998$.

$$d[Fe(CN)_6^{3-}]/dt = \{(3 \pm 1) \times 10^{-4}\ s^{-1} + (7.9 \pm 0.1) \times 10^2\ M^{-1}\ s^{-1}\ [Fe]_t\}[H_2O_2] \quad (4)$$

The reproducibility of these kinetic runs was the best seen during the course of the study, presumably because the inadvertent and variable catalyst concentration normally encountered contributed ≤40% to the reaction rate. The first-order dependence with respect to hydrogen peroxide was demonstrated in separate experiments. The intercept of eq 4 is in reasonable agreement with the rate constant determined in the absence of added iron (i.e., eq 3), and would correspond to ca. 4 × 10^{-7} M iron if this were the only catalyst and was responsible for the observed reaction rate.

We confirmed that the iron(III)–hexacyanoferrate(II) reaction is very rapid under our experimental conditions. On the basis of stopped-flow kinetic data collected between 10 and 30 ms at 25 °C, pH 4.0 (0.05 M acetate buffer), 1.0 × 10^{-4} M $FeOH^{2+}$, (0.50–1.0) × 10^{-3} M $Fe(CN)_6^{4-}$, and 2.5 × 10^{-3} M $Mpyz^+$ (to sequester any pentacyanoferrate(II)), the second-order rate constant is 1 × 10^5 M^{-1} s^{-1}. Spectral scans of spent reaction mixtures clearly showed the presence of Prussian blue, but none was formed during the rapid reaction of interest. Pentacyano(*N*-methylpyrazinium)ferrate(II), however, does not appear to undergo a redox reaction with iron(III) at pH 4.0, but instead immediately forms a complex, the details of which were not pursued.

We determined the rate expression given in eq 5 for the oxidation of iron(II) by hydrogen peroxide at pH 4.0 and 25 °C.

$$d[Fe(III)]/dt = (106 \pm 9)\ M^{-1}\ s^{-1}[Fe(II)][H_2O_2] \quad (5)$$

The presence of chelating agents known to be especially effective at minimizing metal ion catalysis of certain peroxide reactions[26] substantially slows the rate of oxidation of hexacyanoferrate(II) by hydrogen peroxide. Results obtained with EDTA, EDTMP {ethylenediaminetetra(methylphosphonate)}, and DTPMP {diethylenetriaminepenta(methylphosphonate)} are summarized in Table 2, along with data obtained in oxalate rather than acetate buffer. The kinetic profiles were still roughly pseudo-zero-order, and difficulty in reproducing the slopes was again a problem. The rates were independent of the concentration of the chelating agent over the indicated range, but decreased at higher pH (at least with EDTA). Added copper(II) has only a small kinetic effect provided EDTA is present; in the absence of EDTA a precipitate with hexacyanoferrate(II) is formed. We found that Fe^{III}(EDTA) is a very sluggish oxidant toward hexacyanoferrate(II). For example, starting with 2.0 × 10^{-3} M $Fe(CN)_6^{4-}$, 1.0 × 10^{-4} M Fe(III), 1.0 × 10^{-3} M EDTA, and 5.0 × 10^{-3} M $Mpyz^+$ at pH 4 and 25 °C, only ca. 10% of the stoichiometric amount of $Fe(CN)_6^{3-}$ had been formed after 1 h. On the other hand, Fe^{II}(EDTA) is oxidized rapidly by H_2O_2.[22] The rate suppression measured in oxalate buffer was similar to that observed with the amino carboxylate and amino phosphonate chelates. Catalysis by added iron was largely suppressed in oxalate buffer at pH 4.0, as is the rate of the iron(III)–hexacyanoferrate(II) reaction. For example, no formation of hexacyanoferrate(III) was observed after 1 h starting with 2.0 × 10^{-3} M $Fe(CN)_6^{4-}$, 2.0 × 10^{-4} M Fe(III), and 5.0 × 10^{-3} M $Mpyz^+$ in 0.01 M oxalate at 25 °C. However, the rate of oxidation of iron(II) by hydrogen peroxide is comparable in oxalate and acetate buffers.

Due to protonation and ion pairing, several forms of hexacyanoferrate(II) are present in significant and varying concentrations under our experimental conditions: $Fe(CN)_6^{4-}$, $HFe(CN)_6^{3-}$ (log K_p = 3.6), $KFe(CN)_6^{3-}$ (log K_f = 1.7), and $LiFe(CN)_6^{3-}$ (log K_f = 1.3).[23] However, the observation that similar results were obtained in unbuffered media where hydronium ion was the limiting reagent or in buffered media where hexacyanoferrate(II) was limiting seems to rule out major differences in the reactivity of the various forms, at least where inadvertent catalysis is crucial. Further, we found that experiments performed at pH 4.0 and 25 °C in 0.10 M $La(NO_3)_3$, where $LaFe(CN)_6^-$ is the principal form,[24] were consistent with eq 3 with $k = 2.5 \times 10^{-4}$ s^{-1}. Importantly, catalysis by Mo(VI) was again observed.

Reaction of $Ru(CN)_6^{4-}$ with H_2O_2, $MoO(O\text{-}O)_2(OH)(H_2O)^-$, and $WO(O\text{-}O)_2(OH)(H_2O)^-$. The rate of oxidation of hexacyanoruthenate(II) by hydrogen peroxide is substantially slower than that observed for the more strongly reducing hexacyanoferrate(II) under similar experimental conditions. For example, the initial rate of formation of the Ru(III) product was ca. 1.7 × 10^{-7} M s^{-1} with 4.6 × 10^{-2} M $Ru(CN)_6^{4-}$ and 3.0 × 10^{-2} M H_2O_2 at pH 4.0 (acetate buffer) and 25 °C. Addition of Mo(VI) or W(VI) does not enhance the rate. However, complexation between $MoO(O\text{-}O_2)(OH)(H_2O)^-$ and $Ru(CN)_6^{4-}$ occurs on the stopped-flow time scale; the complex exhibits a maximum at 340 nm, with an extinction coefficient of 3 × 10^3 M^{-1} cm^{-1} and K_f = 1.7 × 10^2 M^{-1} (see experimental section). Complex formation is not observed in oxalate buffer where the principal form of the peroxomolybdenum(VI)[10] is $MoO(O\text{-}O)_2(C_2O_4)^{2-}$. No spectral indication of complexation by $WO(O\text{-}O)_2(OH)(H_2O)^-$ was observed, at least at $\lambda \geq 280$ nm.

Discussion

The kinetic results for the oxidation of $Fe(CN)_5Mpyz^{2-}$ by H_2O_2 clearly point to a rate limiting ligand dissociation from the pentacyanoferrate(II) center. Since this dissociation rate is slow and the complex is robust, the presence of $Mpyz^+$ effectively guards against catalysis by $Fe(CN)_5OH_2^{3-}$ in our kinetic studies of the oxidation of $Fe(CN)_6^{4-}$. Beyond this, the $Fe(CN)_5(Mpyz)^{2-}$–H_2O_2 system has some interesting features. Catalysis by traces of iron is not observed, presumably because iron(III) is ineffective as an oxidant toward $Fe(CN)_5(Mpyz)^{2-}$. No detectable outer-sphere oxidation by either H_2O_2 or $MoO(O\text{-}O)_2(OH)(H_2O)^-$ was observed. The rate constants for oxidation of Fe^{2+}, a reductant with comparable reducing strength, are ca. 53 and 5 × 10^4 M^{-1} s^{-1}, respectively. These results strongly support

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[26] The situation is strikingly similar to that encountered in studies of the decomposition of hydrogen peroxide and peroxo acids in basic solution. These reactions are thermodynamically favored but the uncatalyzed reactions must be exceedingly slow. As a result, catalysis is probably observed even in the presence of some of the best metal ion chelating agents known. See, for example: Evans, D. F.; Upton, M. W. *J. Chem. Soc., Dalton Trans.* **1985**, p1151 and p2525.

the proposal[5,6] that there is a very large kinetic advantage for inner-sphere rather than outer-sphere reactions of peroxide.

The direct reaction between hydrogen peroxide and hexacyanoferrate(II) is apparently so slow that catalytic pathways are usually, if not inevitably, dominant. Catalysis by pentacyanoaquoferrate(II) has been demonstrated previously. The present study reveals that if this pathway is eliminated, catalysis by trace quantities of iron becomes important. The rate-determining step for iron catalysis under our experimental conditions is the oxidation of iron(II) by hydrogen peroxide. Therefore, if iron catalysis were the *only* pathway operative in the experiments with added iron (summarized in Figure 3), the predicted slope of eq 4 would be 1.1×10^2 M^{-1} s^{-1}. This is lower than observed by a factor of about 7. This discrepancy is probably not cause for concern, since other kinetic pathways may well contribute—even traces of a molybdenum impurity at the part per thousand level in the iron reagent would be important. The slope and intercept of eq 4 reveal that submicromolar amounts of iron contamination can play a major role in the observed rate of oxidation of hexacyanoferrate(II) by hydrogen peroxide. The rate reduction observed in the presence of chelating agents is in agreement with the presence of trace metal ion catalysts, although it is unlikely that catalysis has been completely eliminated by these sequestering agents.[26] The kinetic profiles are still unusual (approximately pseudo-zero-order), and reproducibility is rather poor. However, the rates are probably slow enough under these conditions to bring the hexacyanoferrate(II)–hydrogen peroxide reaction into line with an outer-sphere mechanism.

There are at least two previously reported examples of trace metal catalysis in slow oxidations of cyanoferrate(II) complexes. The oxidation of hexacyanoferrate(II) by peroxodiphosphate is catalyzed by iron and Cu^{II}(EDTA), but not by Cu^{2+}, Fe^{II}(EDTA), or Fe^{III}(EDTA).[27] The oxidation of $Fe(CN)_5OH_2^{3-}$ by molecular oxygen is strongly catalyzed by ferrous ions.[28]

Some of our results are relevant to the $Fe(CN)_6^{4-}$–H_2O_2–H_2SO_4 system, which exhibits oscillations in a continuous-flow stirred tank reactor.[1,29] To date, iron catalysis has not been included in the reaction schemes used to simulate the kinetic behavior. The required autocatalysis is proposed to involve traces of $Fe(CN)_5H_2O^{3-}$; presumably, addition of $Mpyz^+$ would therefore change the kinetics. In general, our results indicate that the use of $Mpyz^+$ should be considered in studies of $Fe(CN)_6^{4-}$ when traces of $Fe(CN)_5H_2O^{3-}$ may be of significance (provided that the near-IR absorption peak of $Fe(CN)_5Mpyz^{2-}$ does not interfere).

The finding that $Ru(CN)_6^{4-}$ readily replaces a water or hydroxo ligand on $MoO(O\text{-}O)_2(OH)(H_2O)^-$ is of interest. The complex is a "dead-end" one, since catalysis of the peroxide oxidation was not observed. The redox reaction is very slow and comparable to the hexacyanoferrate(II) reaction in the presence of chelating agents. However, the rates are presumably very sensitive to solvent and the countercation—the $[(n\text{-}Bu)_4N]^+$ salts of $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ are readily oxidized by atmospheric oxygen in dimethylformamide solution.[30]

We suggest that testing for catalysis by Mo(VI) and/or W(VI) is a useful mechanistic probe for oxidations by hydrogen peroxide. Both oxygen atom transfer and inner-sphere one-electron transfer reactions are generally and impressively catalyzed. Absence of catalysis is indicative of another type of mechanism, such as the substitution limited rates encountered with $Fe(CN)_5(Mpyz)^{2-}$. Conclusions drawn for reactions that do show catalysis require caution, however, as evidenced by the $Fe(CN)_6^{4-}$ system.

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