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Reaction of Ferrate(VI)/Ferrate(V) with Hydrogen Peroxide and Superoxide Anion – a Stopped-Flow and Premix Pulse Radiolysis Study

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The reduction of ferrate(VI) to ferrate(V) by superoxide ions was studied over the pH range 2.6–13.0 using the premix pulse radiolysis technique. The pH dependence indicates that only the unstable protonated forms of ferrate, H_2FeO_4 (pK_a 3.5) and $HFeO_4^-$ (pK_a 7.3) are reactive, $k(HFeO_4^- + O_2^-) = (1.7 \pm 0.2) \times 10^7\ M^{-1}s^{-1}$. The stable ferrate ion, FeO_4^{2-}, showed no significant reactivity towards either hydrogen peroxide or superoxide anion. The rate constants for the spontaneous dimerization and decomposition of the protonated ferrates, e.g. $k(HFeO_4^- + HFeO_4^-) \approx 250\ M^{-1}s^{-1}$, are orders of magnitude slower than their corresponding reduction by superoxide indicating an outer-sphere mode of electron transfer for the latter process. In contrast the ferrate(VI) species $H_3FeO_4^+$ ($pK_a = 1.6 \pm 0.2$), H_2FeO_4, and $HFeO_4^-$ oxidize hydrogen peroxide, e.g. $k(HFeO_4^- + H_2O_2) = 170\ M^{-1}s^{-1}$), at rates which correspond closely to their dimerization rates suggesting an inner-sphere controlled mechanism.

Key words: ferrate(VI), ferrate(V), hydrogen peroxide, superoxide radical, kinetics, pulse radiolysis

INTRODUCTION

Potassium ferrate (K_2FeO_4) is a strong oxidant and hydroxylating agent that was shown to have potential uses as a bactericide and as a waste-water treatment agent.[1–4] Although the tetrahedral ferrate(VI) ion, FeO_4^{2-}, has been well characterized with respect to structure[5] and spectral properties,[3,6,7] its aqueous chemistry is not yet well established. Earlier studies by Wood established that ferrate(VI) decomposed rapidly and exothermally to iron(III) and dioxygen in strong acids,[8] while those of Goff and Murmann established that the oxygen ligands of ferrate(VI) exchange very slowly with solvent water at pH 10.[9] Carr *et al.*,[3] who studied the spectral and kinetic properties of ferrate(VI) as a function of pH by the stopped-flow technique, reported the existence of at least two unstable protonated forms, H_2FeO_4 and $HFeO_4^-$, which under their experimental conditions decayed by mixed first and second-order kinetics. Various ferrate(VI) oxidations of organic compounds have been reported.[1–4,10–15] Amino acids, in particular, are readily deaminated and oxidized by ferrate(VI) in neutral solutions.[12–14] The latter

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reactions are strongly proton catalyzed. In contrast, the oxidation of hydrogen peroxide in alkaline solution is reportedly catalyzed by hydroxide ions.[9]

There appear to have been few studies of ferrate(VI) reactions, conducted over a wide pH range, that address specifically the reactivities of the different protonated ferrate(VI) forms. In the present work we examine the reactions of ferrate(VI) with the active oxygen species, superoxide and hydrogen peroxide, over the widest accessible pH ranges. The results show that the reactivities of the ferrate(VI) species are highly dependent on their degree of protonation. We have also re-examined the earlier work by Carr *et al.*,[3] that is the spontaneous decay rates of ferrate(VI) as a function of pH, under our experimental conditions. The results are interpreted in terms of the susceptibility of protonated ferrates to undergo substitution reactions and we believe it may thus be possible to discriminate between inner- and outer-sphere electron transfer pathways in the O_2^- and H_2O_2 systems.

The ferrate(V) oxidation state is very unstable and has proven to be a much more facile oxidant than ferrate(VI).[16–18] It is conveniently generated by pulse radiolysis where such radicals as e_{aq}^-, $\bullet CO_2^-$ and $\bullet CH_2OH$ reduce ferrate(VI) to ferrate(V) at near diffusion controlled rates.[16–18] As in the case of ferrate(VI), the reactivity and stability of ferrate(V) are dependent upon the degree of protonation.[13,18] We have observed that the protonated species $HFeO_4^{2-}$ reacts with amino acid anions at rates in excess of $10^6\ M^{-1}s^{-1}$,[12,15] which is comparable to the rate constant for the second order decay of this protonated ferrate ion species.[18] In contrast, the fully deprotonated form (FeO_4^{3-}) is relatively unreactive in these bimolecular reactions. Thus to further elucidate our understanding of the chemistry of ferrate(V), the rate constants of the ferrate(V) reactions with H_2O_2 and O_2^- were measured over as wide a pH range as was experimentally feasible. As will be shown the reactions of the protonated forms of ferrate(V) with O_2^- and H_2O_2 play an important role in the overall reduction of ferrate(VI) by these active oxygen species.

EXPERIMENTAL

Chemicals

K_2FeO_4 of 98.6% purity was prepared as has been previously described.[18,19] High purity O_2 and Ar (99.999%; MG Gases Ltd.) were used for purging and/or saturating solutions. Hydrogen peroxide (30% Ultrapure Vycor-Distilled; Apache Chem. Co.) was standardized by the $KMnO_4$ method. Ferricytochrome C (Type VI) was purchased from Sigma. Other chemicals used were of reagent grade. All solutions were prepared with water which, after distillation, had been passed through a Millipore ultrapurification system. 100–300 μM solutions of ferrate(VI) were prepared by dissolving K_2FeO_4 in water followed by filtration though a 0.22 μm filter which removes small traces of colloidal iron(III). These solutions which are stable for several hours have a natural pH $\approx$ 9.0. Their concentrations were determined spectrophotometrically at the absorption peak using $\varepsilon_{510nm} = 1150\ M^{-1}cm^{-1}$.[17,18]

In stopped-flow and premix pulse-radiolysis studies these ferrate(VI) solutions were mixed in a 1:1 volume ratio with buffers of desired pH. Unless stated otherwise all final solution-mixtures contained 0.025 M phosphate and either perchloric acid (pH<3.6), 0.025 M acetate (pH 3.6–5.5) or 0.005 M borate (pH>8.0). The pH of the reaction mixture was always measured after completion of an experimental run. All experiments were carried out at 23.0 ± 0.1°C.

Equipment

Stopped-flow experiments were carried out using a DX17-MV Sequential Stopped-Flow Spectrofluorimeter (Applied Photophysics, UK) which has a dead-time of 1 ms.

Premix pulse-radiolysis experiments were conducted on a 2 MeV van de Graaff accelerator which is computer interfaced with a premixing apparatus consisting of three Hamilton Precision Liquid Dispenser (PDL II) units, electronic controls and an optical cell (2 cm light path) which is located in the path of the electron beam. An electron pulse is delivered to the reaction mixture shortly after mixing is complete (≈ 50–100 ms) and the ensuing radical induced reactions are monitored spectrophotometrically.[20]

Pulse lengths were varied from 100–900 ns with doses ranging from 2–30 Gy. The thiocyanate dosimeter (0.01 M KSCN, 0.026 M N_2O, pH 5.5) was used as a calibrant taking $G((SCN)_2^-) = 6.13$ (radicals/100 eV) and $\varepsilon_{472nm} = (7950 \pm 2\%)\ M^{-1}cm^{-1}$.

Kinetics

Spontaneous Decay of Ferrate(VI) as a Function of pH

The objective of this stopped-flow study was to determine the kinetic parameters of the spontaneous decay of ferrate(VI) as a function of pH under our experimental conditions as they are indispensable as corrections factors in the study of the H_2O_2 and O_2^- systems. Ferrate(VI) solutions (100 μM) were mixed with appropriate buffers and the loss of absorbance was monitored at 510 nm. The decay kinetics were monitored over at least 3 half-lives and found to be consistent with a purely second-order decay mode. Observations of the $Fe_2(OH)_2(aq)^{4+}$ dimer were made at 300 nm. The dissociation rate of the species (at pH 1.8) was consistent with the kinetic parameters reported by Birus *et al.*[21,22] The first protonation constant of ferrate(VI) and the spectrum of the biferrate ion were determined in a 25 mM phosphate buffer using the kinetic scan capability of the DX-17MV instrument.

The Reaction of Fe(VI) + H_2O_2

The reaction of hydrogen peroxide with ferrate(VI) was studied at 510 nm by the stopped-flow method. In a typical experiment solutions containing ≈ 200 μM ferrate(VI) at pH 9 were mixed with a 0.2 M phosphate buffer (of desired pH) containing 2 M $NaClO_4$ (to maintain a relatively constant ionic strength) and variable amounts of H_2O_2. The reported rate constants are averages of 10 repetitive runs and second order rate constants were usually obtained over a tenfold concentration range of H_2O_2. The highest observed rates measured were $k_{obs} \approx 1000\ sec^{-1}$. The nearly noise free operation of the instrument and of the xenon-arc light source made accurate measurements of halflives less than 1 ms possible.

The Reaction of O_2^- with Ferrate(VI)

The reactions of superoxide anion with ferrate(VI) species were studied by the premix pulse-radiolysis method. In these experiments ferrate(VI) solutions were mixed with a buffer of desired pH containing sodium formate (0.1 M). Both ferrate and buffer/formate solutions were maintained saturated (1.26 mM) with O_2 prior to their mixing. The electron pulse generates the primary radicals listed in reaction (I), where the numbers in parenthesis are G values, that is the number of free radicals formed per 100 eV of energy absorbed by the water[23]:

$$H_2O \text{ -/\textbackslash/-> } OH\,(2.65),\ e_{aq}^-(2.75),\ H(0.65) \qquad (I)$$

Under our experimental conditions the primary radicals are converted to superoxide/perhydroxyl radicals in less than 1 μsec after the pulse[24,25]:

$$e_{aq}^- + O_2 \rightarrow O_2^-;\ k_1 = 2.0 \times 10^{10}\ M^{-1}s^{-1} \qquad (1)$$

$$OH + HCO_2^- \rightarrow H_2O + CO_2^-;\ k_2 = 3.2 \times 10^9\ M^{-1}s^{-1} \qquad (2)$$

$$CO_2^- + O_2 \rightarrow CO_2 + O_2^-;\ k_3 = 2.0 \times 10^9\ M^{-1}s^{-1} \qquad (3)$$

$$H + O_2 \rightarrow HO_2;\ k_4 = 2.0 \times 10^{10}\ M^{-1}s^{-1} \qquad (4)$$

It should be noted that although e_{aq}^- reacts with ferrate(VI) at a diffusion-controlled rate (k(Fe(VI) + e_{aq}^-) = 2×10^{10} $M^{-1}s^{-1}$)[16] this reaction caused little interference as in most runs $[O_2]_o/[Fe(VI)]_o \geq 10$. Typically, doses which generated 5–15 μM of O_2^- were used and the solutions contained 50–140 μM of K_2FeO_4.

The superoxide/perhydroxyl radicals equilibrate instantly and have a $pK_a(HO_2/O_2^-) = 4.8$.[26] As they have absorption peaks at 225 nm and 245 nm respectively they cannot be monitored directly because of the opacity of ferrate(VI) solutions in the UV. While the reduction of ferrate(VI) was observed at 510 nm, the formation and decay of ferrate(V) were monitored at 380 nm ($\varepsilon_{380nm} \approx 1000\ M^{-1}cm^{-1}$).[18] Most kinetic traces were analyzed by an on-line non-linear least squares fitting routine. In some instances, where complex kinetics were found, the absorbance/time data were fitted by a kinetic simulation package (INTKIN) developed by Dr. H.A. Schwarz of BNL.

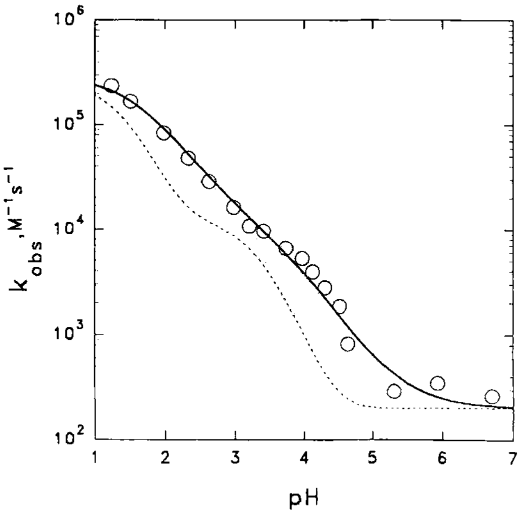

FIGURE 1 The pH dependence of second-order rate constants for the decay of ferrate(VI) to iron(III) in 5 mM(phosphate/acetate) buffers. The fitted curve is obtained using the ferrate(VI) pK_a's and the reaction scheme described in the text. The dashed curve was calculated using the same parameters as the solid curve except that rates of the cross-reactions (10) and (12) were set to zero.

The Reaction of Ferrate(V) with Hydrogen Peroxide

The ferrate(V)/hydrogen peroxide system was studied by the premix pulse-radiolysis method and carried out under conditions similar to those of the $Fe(VI)/O_2^-$ system, except that the K_2FeO_4 and formate/buffer/hydrogen peroxide solutions were purged with argon. These experiments were limited to pH>6.5. Under these conditions the CO_2^- radical and e_{aq}^- reduce Fe(VI) to Fe(V) which reacts with H_2O_2; k(Fe(VI) + CO_2^-) = 3.5×10^8 $M^{-1}s^{-1}$;[17] (Fe(VI) + e_{aq}^-) = 2.0×10^{10} $M^{-1}s^{-1}$.[16] The final reaction mixture after the electron pulse contained 5–15 μM ferrate(V) and 0.5 to 3.0 mM H_2O_2. The reaction of ferrate(V) with hydrogen peroxide was monitored at 380 nm.

RESULTS

Proton Catalyzed Decay and pK_a's of Ferrate(VI)

A stopped-flow study of the stability of ferrate(VI) as a function of pH was carried out under our experimental conditions in order to determine the corresponding kinetic parameters that were needed as correction factors for studies of the oxidation of O_2^- and H_2O_2 by ferrate(VI) and ferrate(V). The results shown in Figure 1, differ from those of Carr *et al.*[3] in that we observed only second-order decay kinetics and, in the pH range 5–7, our data indicate that ferrate(VI) decays an order of magnitude slower. Ernst *et al.*[27] reported similar second-order decays in this pH range. The difference between Carr's and our results may be due to the fact that we kept the concentration of buffer as low as possible in order to avoid the catalytic effects reported in the earlier study.[3]

The data indicate two acid pK_a's, one below pH 2 and the other in the vicinity of pH 4. Carr *et al.* used spectral data to determine the equilibria (6) and (7):

$$H_3FeO_4^+ \rightleftarrows H^+ + H_2FeO_4$$

$$pK_5 = 1.6 \pm 0.2 \qquad (5,-5)$$

$$H_2FeO_4 \rightleftarrows H^+ + HFeO_4^- \quad pK_6 = 3.5^3 \quad (6,-6)$$

$$HFeO_4^- \rightleftarrows H^+ + FeO_4^{2-} \quad pK_7 = 7.3 \pm 0.1 \quad (7,-7)$$

The decay rate profile is consistent with these values but requires a further protonation (5,-5) to account for the increase in the decay rate below pH 3. The fitted line in Figure 1 represents a model in which the species $H_3FeO_4^+$, H_2FeO_4 and $HFeO_4^-$ decompose to iron(III) and O_2 by reactions (8–13) where formation of a diferrate(VI) intermediate, in steady-state amounts, is rate determining ($k_8 = (3.5 \pm 1) \times 10^5\ M^{-1}s^{-1}$; k_9 = fast; $k_{10} \approx k_8$; $k_{11} = (1.5 \pm 0.5) \times 10^4\ M^{-1}s^{-1}$; $k_{12} \approx k_{11}$; $k_{13} = (250 \pm 50)\ M^{-1}s^{-1}$):

$$2\,H_3FeO_4^+ \rightleftarrows [H_4Fe_2O_7]^{2+} + H_2O \quad (8,-8)$$

$$[H_4Fe_2O_7]^{2+} + 2H^+ + 6\,H_2O \rightarrow Fe_2(OH)_2(H_2O)_8^{4+} + 3/2\,O_2 \quad (9)$$

$$H_3FeO_4^+ + H_2FeO_4 \rightleftarrows [\text{diferrate}] \quad (10,-10)$$

$$2\,H_2FeO_4 \rightleftarrows [\text{diferrate}] \quad (11,-11)$$

$$H_2FeO_4 + HFeO_4^- \rightleftarrows [\text{diferrate}] \quad (12,-12)$$

$$2\,HFeO_4^- \rightleftarrows [Fe_2O_7]^{2-} + H_2O \quad (13,-13)$$

The stoichiometries and formulations of the species in reactions (8) and (9), although hypothetical, illustrate this process. The observed rate of ferrate decay will approximate the forward rates of reactions (8–13) if the rate of dissociation of diferrate is less than the rate of intramolecular decomposition e.g. $k_{-8} < k_9$.

The dimeric species $Fe_2(OH)_2(aq)^{4+}$ was detected as the main iron(III) product of $H_3FeO_4^+$ decay by observing its subsequent hydrolysis to $Fe(H_2O)_6^{3+}$ near pH 1.5 at 300 nm.[21,22] This is consistent with the intermediate formation of unstable diferrates in all of the above processes as was earlier suggested by Carr *et al.*[3] The overall decay of $H_3FeO_4^+$ in (8,-8) and (9) is described by the rate law (II).

$$\frac{-d[H_3FeO_4^+]}{dt} = \frac{k_9}{k_{-8} + k_9} k_8 [H_3FeO_4^+]^2 \quad (II)$$

The degree of protonation in steady-state concentrations of diferrates cannot be known but if $k_9 >> k_{-8}$ then the observed rate of decomposition, k_{obs}, is only the rate of diferrate formation, k_8. It is also reasonable to assume that the rates of cross reactions (10) and (12) are the same as the rates of the interaction between the most unstable (i.e. substitutionally labile) of the species involved. The calculated rate of decomposition in Figure 1 is thus the fit of only three independent rate parameters to the experimentally observed second-order decay rates between $1.2 \leq pH \leq 7$.

The existence of the species, nominally $H_3FeO_4^+$, with a $pK_a \approx 1.6$ is inferred from the pH dependences of the decay rates and the reaction with hydrogen peroxide (vide infra). The rate constants proposed for Reactions (8)–(13) otherwise depend only on the assumptions that $k_8 = k_{10}$ and $k_{11} = k_{12}$. A computed fit, in which these cross-reactions are neglected is also shown in Figure 1.

The first protonation of the ferrate ion occurs between pH 8 and 7 and causes not only a large decrease in its stability but also a substantial change in the absorption spectrum of FeO_4^{2-}, as noted by Carr *et al.*[3] who report a value of $pK_6(HFeO_4^-/FeO_4^{2-}) = 7.8$.[3] We examined this protonation in 0.025 M phosphate buffer and find that, under our conditions, the pK_a is approximately 7.3 and that the spectra of $HFeO_4^-$ and FeO_4^{2-} ions have an isosbestic point near 417 nm as shown in Figure 2.

The ferric products of reactions (8)–(13) could not be determined with confidence except at the lowest pH's where the kinetic and spectral parameters for the species $Fe(OH)^{2+}_{aq}$, $Fe(H_2O)_6^{3+}$, and $Fe_2(OH)_2(H_2O)_8^{4+}$ are known. The decomposition rate of Fe(VI) decreases rapidly with increasing

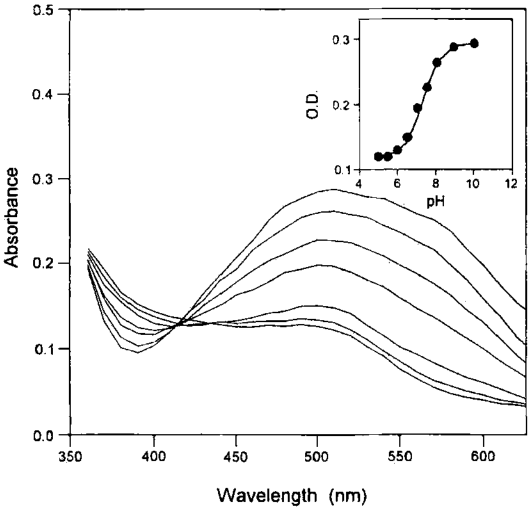

FIGURE 2 The point-by-point (10 nm) spectra of 2.6×10^{-4} M ferrate(VI) in 0.025 M phosphate buffer at pH's (5–10). The upper-most curve is the spectrum of FeO_4^{2-}. The lowest curve is the spectrum of $HFeO_4^-$. The inset shows the change in O.D.(510 nm) as a function of pH, which yields a value of 7.3 for the pK_a ($HFeO_4^-$ eO_4^{2-}).

pH and the immediate products are obscured by secondary reactions (oligomerization of iron(III) or complexation by phosphate buffer) in less acid solution. The time window for observing unpolymerized iron(III) in neutral solution, even when initially produced in micromolar amounts, is of the order of 100–150 ms.[28] Although the decomposed ferrate(VI) solutions show strong absorbances below 400 nm that are typical of hydrolyzed iron(III), initially these solutions were free of precipitates.

The total decay of a diferrate(VI) intermediate to dinuclear iron(III) should yield six oxidizing equivalents. Wood[8] noted long ago that in acid solutions these oxidizing equivalents oxidize water yielding dioxygen. Any added or formed H_2O_2 in this system would be catalytically decomposed to dioxygen by iron(III), a complex process which may account for the formation of ferrous ions during ferrate(VI) decay in dilute alkali.[3] Because ferrate(VI) oxidizes H_2O_2 at rates which are at most pH's competitive with its spontaneous decomposition and since it reacts with its oxidation product O_2^- orders of magnitude faster (vide infra), no intermediates were observed.

The Reaction of Ferrate(VI) with Superoxide

The reactions of ferrate(VI) ions with superoxide and perhydroxyl radicals were investigated between pH 2.6 and 13. A summary of observed second order rate constants is shown in Figure 3. As is apparent k_{obs} increases with a first order proton dependence between pH 13–8, plateaus between ≈ pH 7.5–4.5, and decreases below pH 4.

In the alkaline and neutral pH range the rate law can be simply ascribed to reactions (14) and (15):

$$O_2^- + FeO_4^{2-} \rightarrow FeO_4^{3-} + O_2 \qquad k_{14} \leq 100\ M^{-1}s^{-1} \tag{14}$$

$$O_2^- + HFeO_4^- \rightarrow HFeO_4^{2-} + O_2 \qquad k_{15} = 1.7 \times 10^7\ M^{-1}s^{-1} \tag{15}$$

There was no detectable reaction between FeO_4^{2-}

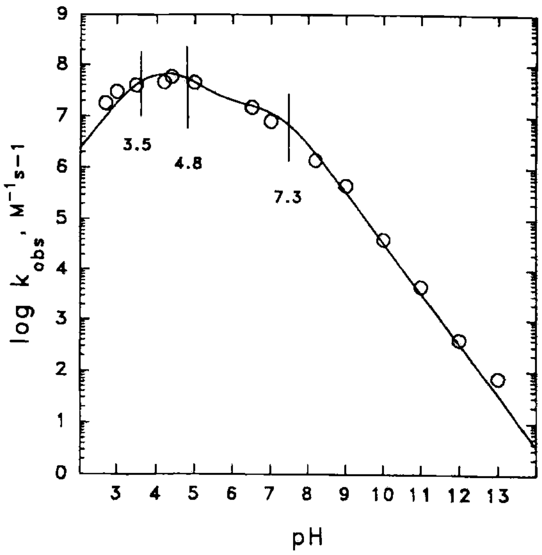

FIGURE 3 The pH dependence of the reaction of ferrate(VI) and superoxide ion. The line is calculated from the rate constants $k_{15}(HFeO_4^- + O_2^-) = 1.7 \times 10^7\ M^{-1}s^{-1}$ and k_{19} ($H_2FeO_4 + O_2^-$) = $7 \times 10^8\ M^{-1}s^{-1}$. The pK_a's ($H_2FeO_4/HFeO_4^-$) = 3.5, (HO_2/O_2^-) = 4.8, and ($HFeO_4^-/FeO_4^{2-}$) = 7.3 are indicated.

and the superoxide radical and the value of k_{14} is an approximated upper limit. In the alkaline range (pH 10) the observed loss of the ferrate(VI) is $-G(\mathrm{Fe(VI)}) = 0.5\ G(O_2^-)$, which suggests that O_2^- reacts rapidly with a product of the initial ferrate(VI) reduction. This is presumably an unobserved ferrate(V) species which is usually much more reactive than ferrate(VI). However, the decay of the ferrate(VI) absorbance was exponential and no transients were observed. The observed second-order rate constants reported in Figure 3 are corrected for the above given stoichiometric factor.

As alkalinity decreases to the pH range 8–9, new features are observed. The stoichiometry of reaction between ferrate(VI) and O_2^- becomes 1:1, and the bleaching of the ferrate(VI) absorbance at 510 nm is no longer exponential. Furthermore, a transient absorbance at 350–400 nm due to ferrate(V)[18] is observed. Typical kinetic traces at pH 8.2 are shown in Figure 4. The data were simulated by numerical integration of the differential equations arising from reactions (16)–(17):

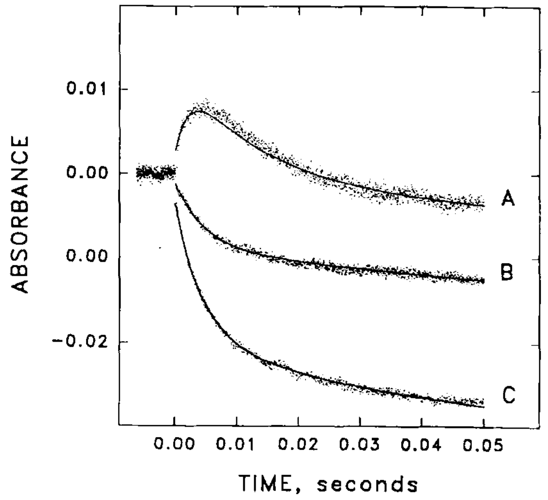

FIGURE 4 Kinetic traces from pre-mix pulse radiolysis experiments (pH 8.2): (A) ferrate(V) formation and decay at 380 nm; 146 μM ferrate(VI), 20 μM O_2^-, (B) ferrate(VI) reduction at 510 μm; 146 μM ferrate(VI), 8 μM O_2^-, (C) 510 nm; 146 μM ferrate(VI), 20 μM O_2^-. The solid line through the 2000 data points were calculated from the reaction scheme, rate constants (k_{16}–k_{18}) and spectral characteristics given in the text.

$$O_2^- + \mathrm{Fe(VI)} \rightarrow \mathrm{Fe(V)} + O_2 \qquad k_{obs} = 1.2 \times 10^6\ M^{-1}s^{-1} \qquad (16)$$

$$2\ \mathrm{Fe(V)} \rightarrow 2\ \mathrm{Fe(III)} + 2\ H_2O_2 \qquad k_{17} = 1.0 \times 10^7\ M^{-1}s^{-1} \qquad (17)$$

$$O_2^- + \mathrm{Fe(V)} \rightarrow \mathrm{Fe(IV)} + O_2 \qquad k_{18} = (1.0 \pm 0.3) \times 10^7\ M^{-1}s^{-1} \qquad (18)$$

The rate of reaction (17) and the spectrum of ferrate(V) at this pH are known from a previous study[18]. The rates of reaction (16) and reaction (18) were evaluated over a three-fold range of $[\mathrm{ferrate(VI)}]_o$ using the kinetic model. At pH<8, the rate of reaction (16) increases and the ferrate(V) produced decays almost exclusively by reaction (17). The decomposition product, Fe(III), reacts with superoxide at a rate $k(O_2^- + \mathrm{FeOH}^{2+}) = 1.5 \times 10^8\ M^{-1}s^{-1}$, the interference of this reaction is insignificant (≤2%) at pH 7 and decreases with decreasing pH as $k(HO_2 + \mathrm{Fe}^{3+}) \leq 500\ M^{-1}s^{-1}$.[29] The likely product of reaction (18), iron(IV), was not detected as it most likely absorbs strongly only in the UV range at this pH.

Figure 3 shows that k_{obs} has a plateau region between pH 4.8 and 3.5 and decreases as the solution becomes more acidic (pH<3.5). In this system the experiments were not extended below pH 2.6 because of the high spontaneous rate at which ferrate(VI) decays at this pH. Studies were extended to the lowest possible pH in order to determine whether the HO_2 radical (pK_a 4.8) reacts with either H_2FeO_4 or $HFeO_4^-$. The computed fit suggests that while O_2^- reacts rapidly with H_2FeO_4 (19), HO_2 is relatively unreactive:

$$O_2^- + H_2FeO_4 \rightarrow H_2FeO_4^- + O_2 \qquad k_{19} = 7 \times 10^8\ M^{-1}s^{-1} \qquad (19)$$

Alternative schemes in which HO_2 might participate as an important factor would necessarily involve proton ambiguities. However, we presume that this does not happen as the fit of all the data in Figure 3 can be accounted for by reactions

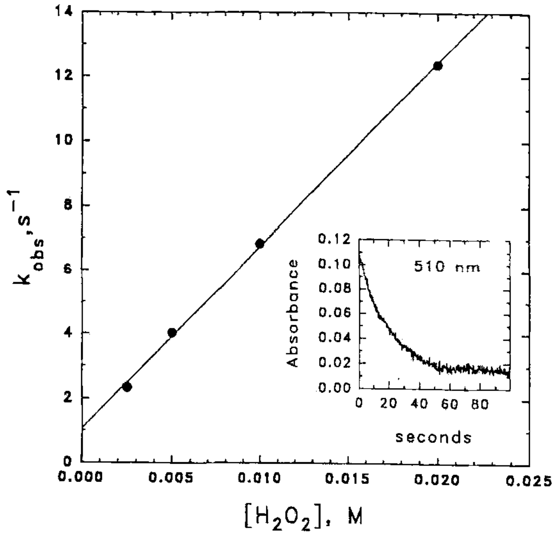

FIGURE 5 Plot of the observed first-order decay rates of ferrate(VI) (0.17 mM) at 510 nm vs $[H_2O_2]_o$ at pH 4.3 in 0.1 M phosphate buffer containing 1.0 M sodium perchlorate; 23.0 ± 0.1°C. **Inset:** Observed first-order decay of ferrate(VI) at 510 nm for the reaction of $[Fe(VI)]_o = 0.1$ mM with $[H_2O_2]_o = 1.0$ mM at pH 7.9 in 0.1 M phosphate buffer containing 1.0 M sodium perchlorate.

(15) and (19). Since in acid solution (pH<6) $H_2FeO_4^-$ decays spontaneously at a rate of 6×10^4 s^{-1}, it does not perturb the kinetics of reaction (19).[30]

The Reaction of Ferrate(VI) with Hydrogen Peroxide

The reactivity of ferrate(VI) with hydrogen peroxide was investigated in the pH range 1.6 to 13.0 by a stopped-flow method as described in the Experimental Section. A typical plot (at pH 4.3) of k_{obs} vs $[H_2O_2]_o$ is shown in Figure 5. The intercept derives from the spontaneous decay (k_{spont}) of ferrate(VI). Except in the strongest acid solutions (pH<2.5), the spontaneous process was less than ≈20% of the maximum observed rates. Some representative observed rate constants which were obtained under acidic conditions are listed in Table 1. The stoichiometry at pH 9 was determined by bleaching of the FeO_4^{2-} absorbance with carefully measured quantities of H_2O_2 added to an excess of ferrate(VI). The ratio of Δ [Ferrate(VI)]: Δ $[H_2O_2]$ = (1.0:1.50 ± 0.2), is consistent with the overall reaction (20):

$$2FeO_4^{2-} + 3H_2O_2 + 8H_2O \rightarrow 2Fe(OH)_3(aq) + 3O_2 + 4OH^- \qquad (20)$$

Stoichiometric measurements were not attempted at lower pH's because of the instability of ferrate(VI) and of H_2O_2 in the presence of Fe(III). The expected intermediates, either ferrate(IV)[31] (two-electron reduction product) or ferrate(V) were not detected as both react rapidly with hydrogen peroxide (See below). However at pH 9, in solutions containing added ferricytochrome c, $[Cyt_c(Fe^{3+})]_o$:$[ferrate(VI)]_o \approx 10$–$15$, the reaction of ferrate(VI) induced the formation of ferrocytochrome c. Under these conditions O_2^- reacts faster with the ferricytochrome c ($k = 2.6 \times 10^5\ M^{-1}s^{-1}$)[24] than with ferrate(VI) ($k \approx 5.0 \times 10^5\ M^{-1}s^{-1}$).

The pH dependence of the calculated second-order rate constants, $k_{calc} = (k_{obs} - k_{spont})$, are shown in Figure 6. It was not possible to extend the study below pH 1.6, in search of a plateau region, owing to the limited time resolution of the stopped-flow instrument. As in the study of the spontaneous ferrate(VI) decay, the data require to postulate a $pK_5 \approx 1.6$ for a species '$H_3FeO_4^+$', which is consistent with the requirements of the decay rate study.

The curve fitted to the experimental data in Figure 6 was obtained by a non-linear least squares fit using Expressions III and IV:

$$-d[Fe(VI)]/dt = k_{calc}[Fe(VI)]\,[H_2O_2] \qquad (III)$$

where k_{calc} = Expression IV.

The rate constants $k_a - k_e$ were assigned to the

$$\frac{k_a + k_bK_5/[H^+] + k_cK_5K_6/[H^+]^2 + k_dK_5K_6K_x/[H^+]^3 + k_eK_5K_7K_x/[H^+]^4}{(1 + K_x/[H^+])(1 + K_5/[H^+] + K_5K_b/[H^+]^2 + K_5K_6K_7/[H^+]^3)} \qquad (IV)$$

TABLE 1 Representative observed rate constants for the reduction of ferrate(VI).

pH	$[H_2O_2]$, mM	k_{obs} (sec^{-1})	k_{calc} ($M^{-1}s^{-1}$)
1.7	0.00	500 (intercept)	6.2×10^4
	1.25	(580 ± 30)	
	2.50	(640 ± 30)	
	5.00	(814 ± 22)	
	10.00	(1130 ± 110)	
2.13	0.00	90 (intercept)	5.6×10^4
	2.50	(224 ± 18)	
	5.00	(371 ± 17)	
	10.00	(640 ± 40)	
	20.00	(1140 ± 100)	
2.9	0.00	4 (intercept)	1.25×10^4
	2.50	(35 ± 8)	
	5.00	(70 ± 9)	
	10.00	(135 ± 14)	
	20.00	(256 ± 15)	
4.26	0.00	1 (intercept)	5.8×10^2
	2.50	(2.3 ± 0.07)	
	5.00	(4.0 ± 0.3)	
	10.00	(6.9 ± 0.6)	
	20.00	(12.4 ± 1.3)	

Rate constants were the mean of 5–10 runs. The highest observed rates were measured after the reaction was 75% complete within the mixing time of the instrument. Intercepts reflect the spontaneous decay rate of Fe(VI). Its value depends on the pH and the initial [Fe(VI)], typically 10^{-4}M.

reactions as listed in Table 2a. The rise in k_{calc} above pH 9 (as earlier reported by Goff and Murmann)[9] to a plateau above pH 12 corresponds to the ionization of hydrogen peroxide ($pK_x = pK(H_2O_2) = 11.65, \mu = 0.0$). A value of $pK_x = 11.4$ is used in the computation (IV) assuming that the $pK_a(H_2O_2)$ shifts about − 0.2 units, similar to that reported for $pK_a(H_2O)$ when the ionic strength increases from 0.0 to 1.0 M.[32] Other aspects of the pH dependence are explained by the previously reported pK_a's of ferrate(VI).

Reactions between HO_2^- and either $H_3FeO_4^+$ or H_2FeO_4 can be neglected since either would exceed the diffusion-controlled limit in order to have any effect upon the overall measured rate of reaction. The reaction between FeO_4^{2-} and H_2O_2 is not considered significant for mechanistic reasons which are given in the Discussion.

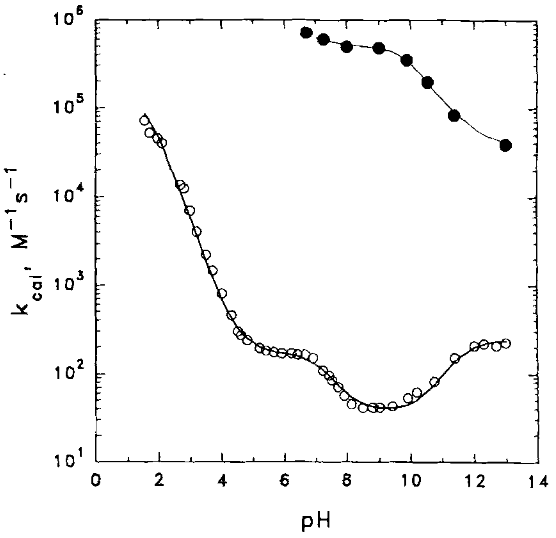

FIGURE 6 Lower Curve. The effect of pH on the rate constant for the reaction of ferrate(VI) with hydrogen peroxide in 0.1 M phosphate buffer, 1.0 M $NaClO_4$ (23.0 ± 0.1 °C). The fitted line was calculated with Expression IV using the rate and equilibrium constants given in the text. **Upper Curve.** The effect of pH on the rate constant for the reaction of ferrate(V) with H_2O_2 in 0.025 M phosphate buffer, 0.1 M $NaCO_2H$, (23.0 ± 0.1 °C). The fitted line was calculated from rate and equilibrium parameters given in the text.

The Reaction of Hydrogen Peroxide with Ferrate(V)

The reactions of $H_2FeO_4^-$ ($pK_a \approx 7.2$), $HFeO_4^{2-}$ ($pK_a = 10.1$) and FeO_4^{3-} with hydrogen peroxide were measured using pre-mix pulse radiolysis. In these experiments the second order decay (17) of ferrate(V) at pH>7 becomes first-order upon addition of millimolar amounts of H_2O_2. The observed rates measured at pH 9.0 are directly proportional to $[H_2O_2]_0$. No transients were observed and there was no detectable chain decomposition of the parent FeO_4^{2-} following the reaction of ferrate(V) with H_2O_2. This indicates that, as in the case of the oxidation of phenol,[14] amino acids,[12,15] and hydroxycarboxylic acids,[13] ferrate(V) reacts with H_2O_2 by a two-electron transfer step ($k_{21} = 5 \times 10^5\ M^{-1}s^{-1}$):

$$\text{HFeO42- + H2O2} \xrightarrow{4H_2O} Fe(OH)_3(aq) + O_2 + 2OH^- \qquad (21)$$

TABLE 2

A. Rate Parameters for the Reaction of Ferrate(VI) and H_2O_2 in 1.0 M $NaClO_4$, 23.0 ± 0.1 °C.

$k_a\ (H_3FeO_4^+ + H_2O_2) = (1.6 \pm 0.2) \times 10^5\ M^{-1}s^{-1}$
$k_b\ (H_2FeO_4 + H_2O_2) = (2.1 \pm 0.2) \times 10^3\ M^{-1}s^{-1}$
$k_c\ (HFeO_4^- + H_2O_2) = (1.7 \pm 0.2) \times 10^2\ M^{-1}s^{-1}$
$k_d\ (HFeO_4^- + HO_2^-) = (4.0 \pm 0.4) \times 10^5\ M^{-1}s^{-1}$
$k_e\ (FeO_4^{2-} + HO_2^-) = (2.5 \pm 0.3) \times 10^2\ M^{-1}s^{-1}$

B. Rate Parameters for the Reaction of Ferrate(V) and H_2O_2 in 0.1 M Sodium Formate, 23.0 ± 0.10 °C.

$k(H_2FeO_4^- + H_2O_2) = (6 \pm 1) \times 10^5\ M^{-1}s^{-1}$
$k(HFeO_4^{2-} + H_2O_2) = (5 \pm 1) \times 10^5\ M^{-1}s^{-1}$
$k(HFeO_4^{2-} + HO_2^-) = (4 \pm 1) \times 10^6\ M^{-1}s^{-1}$
$k(FeO_4^{3-} + HO_2^-) = (4 \pm 1) \times 10^4\ M^{-1}s^{-1}$

The pH dependence of the observed second-order rate constants is shown in Figure 6 (upper curve). In spite of the limited pH range available for this study, the rate constants for the reactions ($H_2FeO_4^-$ + H_2O_2), ($HFeO_4^-$ + H_2O_2), ($HFeO_4^-$ + HO_2^-) and (FeO_4^{3-} + HO_2^-) can be evaluated with reasonable (± 20%) accuracy assuming that the reaction between FeO_4^{3-} and H_2O_2 is not significant. The rate constants used to calculate the fitted curve in Figure 6 are listed in Table 2b.

DISCUSSION

The rate of decomposition of ferrate(VI) in acid media has been resolved into contributions from three protonated forms. The total fit to the data indicates that the rate constants for the reactions (8)–(13) increase regularly with the degree of protonation. Although we have confirmed the existence of $Fe_2(OH)_2(H_2O)_8^{4+}$ as an immediate reaction product at low pH only, it seems likely that a similar species is a product of the bimolecular decay reaction at higher pH as well. Carr *et al.*[3] showed that ferroin ($Fe(phenanthroline)_3^{2+}$) is produced when ferrate(VI) decays in the presence of the ligand at pH 8.75 and proposed that Fe(II) is produced, by a sequence of two-electron decays. In similar (unpublished) observations we have observed that ferroin continues to be slowly produced after ferrate(VI) decay is complete. The addition of H_2O_2 to neutral or slightly alkaline solutions of iron(III)phenanthroline (principally a binuclear species at these pH's) also rapidly produces ferroin. It is therefore possible that the ferrous ions are produced indirectly by reactions of trace H_2O_2 with binuclear iron(III) products, the latter being complexed by phenanthroline. It is difficult to distinguish between the possibilities in alkaline solution because of the many competing reactions that occur on the time-scale of the spontaneous decay of ferrate(VI).

The kinetics of ligand substitution reactions of tetroxyanions have not been extensively investigated but dimerization and oxygen exchange rates can provide indirect measures of the rates at which these are likely to occur. We have taken the decomposition rates of protonated ferrates to reflect a rate-determining step in which these species condense to form unstable diferrates. An argument in favor of rate limiting diferrate formation is that no reference to the hydrolysis rates of variously protonated diferrates is necessary to account for the pH dependence in Figure 1 which is well fit by a simple model. A related system would be the condensation of $HCrO_4^-$ to $Cr_2O_7^{2-}$ which proceeds at 1.8 $M^{-1}s^{-1}$ while hydrolysis occurs at $2.5 \times 10^{-2}\ s^{-1}$.[33] Dissociation may be a slow process in such instances.

The varying rates at which H_2O_2, HO_2^- and O_2^- react suggest that ferrate(VI) oxidizes these species by different mechanisms. Reaction (15) of O_2^- with $HFeO_4^-$ is faster by about five orders of magnitude than the rate at which $HFeO_4^-$ reacts with H_2O_2. This is consistent with an outer-sphere electron transfer mechanism. We have observed that O_2^- reduces the substitutionally inert tetroxyanion permanganate (VII), $E^\circ(MnO_4^-/MnO_4^{2-})$ = 0.56 V,[34] at a rate of ≈ $10^6\ M^{-1}\ s^{-1}$[35] which is comparable to the rate of reaction (15). However the reaction of O_2^- with FeO_4^{2-} (14) is at least five orders-of-magnitude slower than with $HFeO_4^-$ although O_2^- is a good reductant, $E^\circ(O_2/O_2^-) = -0.32$ V.[36] This implies that FeO_4^{2-} is a much weaker one-electron oxidant than $HFeO_4^-$ and/or that the

FeO_4^{2-}/FeO_4^{3-} self-exchange rate is very slow compared to that of $HFeO_4^-/HFeO_4^{2-}$.

The rate constants with which protonated ferrates(VI) react with H_2O_2 (k_a–k_c in Table 2a) parallel fairly closely, but do not exceed, the rate constants k_8, k_{11}, and k_{13} at which we have calculated these species undergo dimerization/decomposition. This is consistent with a rate-determining step which involves prior coordination of peroxide to the metal if the spontaneous decay rates provide an estimate for the maximum rates at which ligand-substitutions are likely to occur. One would not, in any event, expect that H_2O_2 could be oxidized by a simple outer-sphere electron transfer. By the same reasoning, given the slow rate of oxygen exchange for FeO_4^{2-},[9] one can assume that the rate of reaction between FeO_4^{2-} and H_2O_2 is negligibly slow and that the peroxide anion is the effective reductant in alkaline solutions.

Utilizing this assumption, we have calculated from (IV) that $k_d(HFeO_4^- + HO_2^-) = (4.0 \pm 0.4) \times 10^5$ $M^{-1}s^{-1}$. Unlike H_2O_2, HO_2^- might be oxidized to the HO_2 radical (which deprotonates to O_2^-) by a simple electron transfer. However, HO_2^- is a poorer reducing agent (by ≈ 1 V) than O_2^-, yet $k_d(HFeO_4^- + HO_2^-)$ is only about 20-fold smaller than $k_{15}(O_2^- + HFeO_4^-)$. Also, the rate constant for reaction of FeO_4^{2-} with HO_2^- was determined without proton ambiguity (k_e in Table 2a) and its value slightly exceeds the upper limit of $k_{14}(FeO_4^{2-} + O_2^-)$. Since the self-exchange rates of O_2^-/O_2[37,38] and HO_2^-/HO_2[37] are of similar magnitude, according to the Marcus cross-relation[39] we could expect k_{15} to exceed k_d by about eight orders-of-magnitude if both reactions were to proceed by simple outer-sphere electron transfer mechanisms. Clearly this is not the case and it seems probable that the peroxide anion is oxidized by a more complex mechanism, the nature of which is at present uncertain.

The reactions of ferrate(V) with H_2O_2/HO_2^- are fast and preclude observation of this oxidation state as an intermediate in the ferrate(VI)/peroxide system. As we have pointed out in the Results Section, hydrogen peroxide reduces ferrate(V) by a two electron transfer step (21). The calculated rate constants in Table 2b are all somewhat less than the rates for the bimolecular decomposition of protonated ferrates(V)[18] (e.g. Reaction 17). This, and the two-electron nature of the oxidation, are consistent with a rate-determining step in which H_2O_2 ligates to the metal prior to oxidation/reduction. The higher reactivity of ferrate(V) compared to ferrate(VI) in this system, as in some reactions involving organic compounds, may stem from greater substitutional lability in the lower oxidation state.

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