Decay of Ferrate(V) in Neutral and Acidic Solutions. A Premix Pulse Radiolysis Study

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Iron in the +5 oxidation state was generated by the reduction of aqueous potassium ferrate(VI), K_2FeO_4, using pulse radiolytically generated free radicals. The predominant mode of decay is first-order, in the pH range 3.6 to 7, with the rate constant decreasing from 7×10^4 s^{-1} to about 100 s^{-1}. The instability of K_2FeO_4 under the conditions used required the use of the premix pulse radiolysis technique in which the pulse is delivered 100−200 ms after mixing of K_2FeO_4 solution with buffers. The rate law and the observation of small pH-dependent spectral shifts indicate that ferrate(V) exists in at least three protonated forms that, formulated as tetrahedral species, form the following equilibria: $H_3FeO_4 \rightleftharpoons H_2FeO_4^- + H^+$, $5.5 \le pK_1 \le 6.5$; $H_2FeO_4^- \rightleftharpoons HFeO_4^{2-} + H^+$, $pK_2 \approx 7.2$; $HFeO_4^{2-} \rightleftharpoons FeO_4^{3-} + H^+$, $pK_3 = 10.1$. The rate-limiting process in the first-order decay is the aquation of a tetrahedral ferrate(V) species into a species which is probably six-coordinate. The subsequent first order decay of the octahedral species is so fast that a second-order decay mode for H_3FeO_4 and $H_2FeO_4^-$ is not observed. The species present in alkaline solution, FeO_4^{3-} and $HFeO_4^{2-}$, aquate very slowly (≤ 10 s^{-1}) decay predominatly by a second-order process.

Introduction

Pentavalent and tetravalent iron are frequently postulated as intermediates in enzymatic processes and also in mechanisms of iron-catalyzed oxidation such as the Fenton reaction.[1−4] However little is known of the basic properties of these unstable oxidation states. Potassium ferrate (K_2FeO_4), is well characterized[5−8] and has been used by us as a precursor for the generation of ferrate(V) by pulse radiolysis.[9−13] Previous studies of the optical spectra,[9,10] decay rates and associated pK_a's[11] of ferrate(V) species under alkaline conditions were successful owing to the stability of the precursor in alkali. This basic information permitted subsequent studies of the reactivity of ferrate(V) toward a number of organic and biological compounds.[12,13] An extension of these studies into the neutral and acidic range has required the development of rapid premixing techniques in which ferrate(VI) survives 0.1−0.2 s after the potassium ferrate solution is brought to the desired pH.

Optical spectra of ferrate(V) obtained upon reduction of $FeO_4^{2-}/HFeO_4^-$ with radiation generated free radicals showed only a slight sensitivity to pH. Extension of these spectral studies into the more alkaline pH range showed that the spectrum of ferrate(V) species does not provide a good method of determining the pKa's of this oxidation state except in the UV (270 nm) where $pK_3 = 10.1$ was determined from a plot of absorbance *vs.* pH.[11] An increase in the decay rate near pH 7 indicated a further protonation of ferrate(V) but this reaction was not completely characterized owing to limits on the mixing time of the premixing apparatus and the instability of ferrate(VI) below pH 7. An improved premixing apparatus (See Experimental Section) enabled the investigation to be extended to lower pH's which led, as will be shown, not only to confirmation of the earlier reported value of $pK_2 \approx 7.5$[11] but also to an estimate of pK_1.

The earlier studies in alkaline solutions showed that ferrate(V) species decay by bimolecular reactions which are strongly pH dependent. The k_{obs} second-order rate constant increases with [H$^+$] from pH 12−10 and levels off below the $pK_3 = 10.1$. The overall decay in this pH range was found to fit a mechanism that is consistent with equilibria (2,−2), (3,−3) and reactions (4) ($k_4 = 1.0 \times 10^7$ M^{-1} s^{-1})[11] and (5) ($k_5 = 1.5 \times 10^7$ M^{-1} s^{-1})[11]:

$$H_3FeO_4 \rightleftharpoons H_2FeO_4^- + H^+ \quad 5.5 \le pK_1 \le 6.5 \qquad (1,-1)$$

$$H_2FeO_4^- \rightleftharpoons HFeO_4^{2-} + H^+ \quad pK_2 \approx 7.2 \qquad (2,-2)$$

$$HFeO_4^{2-} \rightleftharpoons FeO_4^{3-} + H^+ \quad pK_3 = 10.1^{11} \qquad (3,-3)$$

$$FeO_4^{3-} + HFeO_4^{2-} \rightarrow Fe(III) + (O_2/H_2O_2) \qquad (4)$$

$$HFeO_4^{2-} + HFeO_4^{2-} \rightarrow Fe(III) + (O_2/H_2O_2) \qquad (5)$$

The product hydrogen peroxide was detected in ^{60}Co radiolysis studies at pH 9[11]. It was postulated that at low concentrations of ferrate(V), there is an oxidative elimination of oxo/hydroxo ligands as peroxide with the resulting two-electron reduction of the ferrate(V) to iron(III).

Experimental Section

Pulse radiolysis experiments were performed on a 2 MeV van de Graaff accelerator which is computer interfaced with a new premixing apparatus consisting of three Hamilton Precision Liquid Dispenser (PDL II) units. The new apparatus, which has a dead time of ≈ 100−200 ms and is computer operated by remote control, was constructed for

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the study of unstable reaction mixtures by pulse radiolysis. Measurements of the rates of decay of ferrate(V) were performed by mixing solutions of potassium ferrate with phosphate (0.025 M) / acetate (0.025 M) buffered sodium formate (0.01 M) solutions under an argon atmosphere. The primary oxidizing radicals formed under these conditions are converted into reducing radicals within a fraction of a microsecond, depending upon the concentrations of the parent compound. In eq I, the numbers in parentheses represent *G*-values, or the

$$H_2O \rightsquigarrow e^-_{aq}\ (2.65),\ OH\ (2.75),\ H\ (0.65),\ H_2O_2\ (0.72),\ H_2\ (0.45) \quad (I)$$

$$OH + HCO_2^- \rightarrow H_2O + CO_2^- \quad (6)$$

$$H + HCO_2^- \rightarrow H_2 + CO_2^- \quad (7)$$

number of molecules/radicals formed per 100 eV of energy absorbed by water.[14]

Both CO_2^- and e^-_{aq} react at near diffusion-controlled rates with $FeO_4^{2-}/HFeO_4^-$ ($pK_a(HFeO_4^-/FeO_4^{2-}) \approx 7.8$;[15] 7.9[16]) yielding the corresponding ferrate(V) species which absorb broadly in the visible range and in the UV:

$$FeO_4^{2-} + CO_2^- \rightarrow FeO_4^{3-} + CO_2 \qquad k_8 = 3.5 \times 10^8\ M^{-1}\ s^{-1} \ ^{10} \quad (8)$$

$$FeO_4^{2-} + e_{aq}^- \rightarrow FeO_4^{3-} \qquad k_9 = 2.0 \times 10^{10}\ M^{-1}\ s^{-1} \ ^{11} \quad (9)$$

The decay of ferrate(V) to iron(III) is most easily monitored near 380 nm; ($\epsilon(Fe(V))_{380nm} = 1000\ M^{-1}\ cm^{-1}$).[9,11] The absorption spectra shown in Figure 1, which have been corrected for the absorbance of ferrate(VI), were calculated assuming a $G(Fe^V) = 6.1$.

The premixing experiment involves rapid lowering of the pH of a K_2FeO_4 solution (which becomes unstable at pH < 9) by mixing it with buffers and allowing a time interval for clearing of turbulence and Schlieren. Preliminary stopped-flow experiments indicated that the spontaneous second-order decay of ferrate(VI) to iron(III) is negligible compared to the dead-time of the new premix apparatus. Initial ferrate(VI) concentrations were ≈ 100 μM which is sufficient for complete scavenging of CO_2^- and e^-_{aq} but not too high as to create significant iron(III) concentrations prior to the pulse. As the spontaneous rate of ferrate(VI) decay is strongly proton dependent the study was limited to pH > 3.5. Stopped-flow spectrometry (Model DX17-MV; Applied Photophysics, U.K.) was also used to obtain ferrate(VI) reference spectra for the calculation of ferrate(V) molar absorptivities.

Kinetic analysis was performed by an on-line non-linear least squares fitting routine. Under some conditions ferrate(V) decay occurs by both first- and second-order processes, *i.e.* there exists a strong positive dose dependence of the observed rate of decay. The first-order component (k_d), can be evaluated from plots of k_{obs} vs dose plots (k_{obs} vs [Fe(V)]), where the slope yields second order rate constants and the intercept is k_d. This method was required only for experiments at pH > 7. Typically, dose independence over the above range was used to ascertain true first-order behavior.

Potassium ferrate of high purity was made by a method previously described.[6,17] A molar absorptivity of 1150 $M^{-1}\ cm^{-1}$ at 510 nm (pH > 9)[10,11] was used to determine ferrate(VI) concentrations. All other chemicals were of reagent grade. The water was doubly-distilled and Milli-Q filtered. The argon blanket gas was of 99.999% purity (Liquid Carbonic Specialty Gas Corp., Chicago).

Results

The objective of these studies was to determine the characteristics of ferrate(V) in neutral and acidic solutions. As noted above, the most reliable means of determining protonation constants of transients generated by pulse radiolysis is by accurate measurements of the changes in the optical absorption spectrum of the species. In this case the measurements are complicated by the fact that the spectrum of the ferrate(VI) parent species is itself pH dependent and exhibits p*K*a's at ≈ 3.5 and 7.8.[15] We initially measured the point-by-point absorption spectrum of ferrate(VI) in the stopped-flow apparatus at specified pH's between 3.8 and 7.6 and then, using the same buffer mixtures, reproduced these pH's in the premix pulse radiolysis set up. Using the ferrate(VI) spectra as references, the ferrate(V) spectra were calculated from the absorption change following the reaction of e_{aq}^-/CO_2^- with ferrate(VI). The ferrate(V) and ferrate(VI) spectra are shown in Figure 1. As is apparent the ferrate(V) spectrum is pH dependent and suggests the presence of at least one p*K*a in this range. However the small differences in molar absorptivities and the accumulated uncertainties in the measurement were insufficient for reliable spectral computation of p*K*a's. Measurements after the pulse of the change in absorption at 417 nm (where the spectra of ferrate(VI) species approximate an isosbestic point) indicated an overall change of only about 200 $M^{-1}\ cm^{-1}$ in the molar absorptivity of ferrate(V) on going from pH 7.6 to pH 3.8.

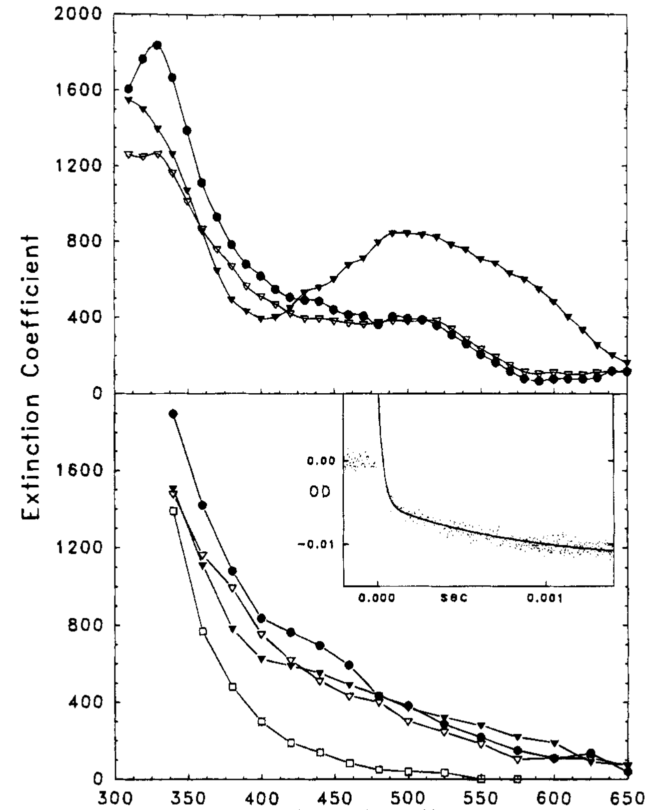

Figure 1. Point-by-point absorption spectra of ferrate(VI) {upper} and ferrate(V) {lower} in 0.025 M phosphate/acetate buffer. The ferrate(VI) spectra (● pH = 3.8; ▽ pH = 5.6; ▼ pH 7.6 respectively) were obtained by mixing buffer solution with potassium ferrate solutions in a stopped-flow spectrophotometer. The ferrate(V) spectra (● pH 3.8; ▽ pH 5.6; ▼ pH 7.6 respectively) were obtained from premix pulse radiolysis of the corresponding ferrate(VI) solutions. The absorption changes after the pulse (380 nm, pH = 5.6) are shown in the inset of the lower figure. The initial absorbance rise represents the conversion of ferrate(VI) to ferrate(V). The measured extinction coefficients of ferrate(V) were corrected for the disappearance of ferrate(VI) at the relevant pH. The spectra of ferrate(V) (lower) illustrate the change in absorbancies with pH between 3.8 and 7.6. The final product(s) of ferrate(V) decay absorb only in the UV. Their spectra are indicated in the lower figure (□).

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The spectral data were therefore consistent with one or more p*K*a's in this pH range. Under the circumstances, an analysis of the decay rates of ferrate(V) provided a more reliable method of determining the location of these p*K*a's. Ferrate (V) decays by second order kinetics, reaction (5), at high pH but the mode of decay becomes first order as the pH is decreases from 10 to 7. For our maximum concentration ($\approx 15\ \mu$M), the decay of ferrate(V) is almost exclusively by a first-order pathway at pH < 6.5. As the pH is decreased further, the first-order decay rate increases very rapidly until it reaches a limiting rate of about 6×10^4 s^{-1} near pH 4.5. These first-order decay rates k_d are summarized in Figure 2. The values of k_d were found to be independent of both formate concentration and of the phosphate/acetate buffer concentrations. The absence of buffer catalysis was also confirmed in experiments in which phosphate or acetate were used separately as buffers without any effect upon the observed rates of spontaneous decay.

Inspection of the decay data shows two regimes of first-order decay. From pH 9 to pH 7.0, k_d increases slowly to about 100 s^{-1} from an initial rate of $k_d \leq 5$ s^{-1}. As pH is further reduced there is a regime of higher order proton dependence since the rate increases by nearly three orders of magnitude within a pH range of ≈ 6.5 to 5.0. These two regimes indicate that the $HFeO_4^{2-}$ undergoes two further protonations. The resulting forms H_3FeO_4 and $H_2FeO_4^-$ decay exclusively by first-order pathways.

The resolution of the p*K*a's requires a kinetic model to account for the complex proton dependence of k_d. We hypothesize that the tetrahedral (T_d) (triply-protonated form, H_3FeO_4, must undergo a spontaneous conversion to a form of ferrate(V) with an expanded coordination sphere. A reasonably satisfactory fit of the data is possible if H_3FeO_4 with expanded coordination shell $(Fe(OH)_5)_{aq})O_h)$ protonates again (13) prior to decomposition. The decay of $H_2FeO_4^-$ can be accounted for by a single first-order process. The reactions necessary to describe the pH dependence of first-order ferrate(V) decay are summarized as follows:

protonations of iron(V)

$$H_3FeO_4 \rightleftharpoons H_2FeO_4^- + H^+ \qquad 5.5 \leq pK_1 \leq 6.5$$

$$H_2FeO_4^- \rightleftharpoons HFeO_4^{2-} + H^+ \quad pK_2 \approx 7.2$$

$$HFeO_4^{2-} \rightleftharpoons FeO_4^{3-} + H^+ \qquad pK_3 = 10.1\ ^{11}$$

first-order decay processes

$$HFeO_4^{2-} + 2H^+ + 4H_2O \rightarrow Fe(OH)_3(H_2O)_3 + H_2O_2 \quad k_{10} \approx 5\ s^{-1} \quad (10)$$

$$H_2FeO_4^- + H^+\ 4H_2O \rightarrow Fe(OH)_3(H_2O)_3 + H_2O_2 \quad k_{11} \approx 150\ s^{-1} \quad (11)$$

$$H_3FeO_4(T_d) + H_2O \rightleftharpoons (Fe(OH)_5)_{aq}(O_h) \qquad K_{12} \qquad (12,-12)$$

$$(Fe(OH)_5)_{aq} + H^+ \rightleftharpoons (Fe(OH)_4)^+_{aq} \qquad K_{13} \qquad (13,-13)$$

$$(Fe(OH)_4)^+_{aq} + H^+ \rightarrow Fe^{III}(aq) + H_2O_2 \qquad (14)$$

The above reactions can be treated by assuming rapid equilibrium between the tetrahedral forms of Fe (V) and by applying the steady-state approximation to the octahedral species in reactions (12−14). This analysis gives expression (II) and

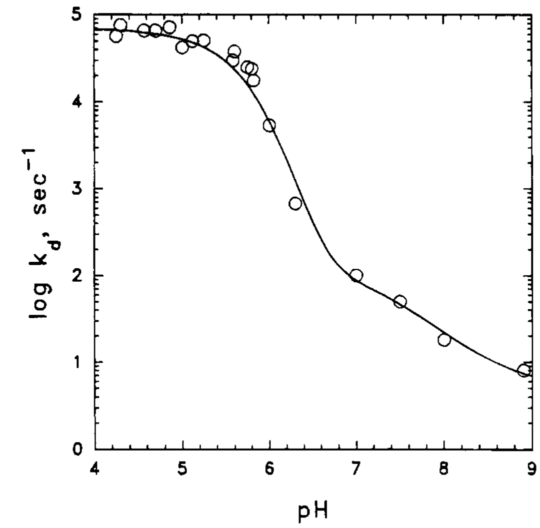

Figure 2. The pH dependence of observed first-order decay rates, k_d, of ferrate(V) in 0.025 M phosphate/acetate buffers at 25 °C. The solid line is fitted using the kinetic model from which expression III is derived. Rate and equilibrium constants are from eqs 1, 2, and 12−14.

(III) for the overall decay rate constant k_d:

$$-d[Fe^V]/dt = k_d[Fe^V] \qquad (II)$$

$$k_d = k_{11}f\{H_2FeO_4^-\} + \frac{f\{H_3FeO_4\}A[H^+]^2}{B + C[H^+] + D[H^+]^2} \qquad (III)$$

The fractions of iron(V), $f\{\}$, are calculated from the equilibria (1)−(3). The parameters A−D which arise from the steady-state treatment, are $A = \{k_{12}k_{13}k_{14}\}$, $B = \{k_{-12}k_{-13}\}$, $C = \{k_{-13}k_{13} + k_{-12}k_{14}\}$, and $D = \{k_{13}k_{14}\}$. A good fit is obtained by assuming $pK_1 = 6.0$ and $A = 7.0 \times 10^{20}$ M^{-2} s^{-3}, $B = 3.8 \times 10^4$ s^{-2}, $C = 1.8 \times 10^9$ M^{-1} s^{-2} and $D = 1.0 \times 10^6$ M^{-2} s^{-2} (See Figure 2). Since, however other values of pK_1 in the range from 5.5 to 6.5 yield acceptable fits with suitable adjustment of the parameters $A-D$, it is not possible ascribe a single definite value to pK_1. The ratio A/D yields the forward rate of the possible T_d(tetrahedral) → O_h(octahedral) interconversion, $k_{12} = 7 \times 10^4$ s^{-1}, which is indicated in reaction 12. The other rate constants cannot be solved for separately.

The spontaneous decay rate of $H_2FeO_4^-$ is approximately $k_{11} \approx 150$ s^{-1} from a fit of the values of k_d at higher pH. The range of values indicated for pK_1 give equally satisfactory fits to the data since the value of the coupled protonation, reaction 13 is not known.

Conclusions

We have shown in a previous study that ferrate(V) decays by second-order kinetics in alkaline solution.[11] The transition to a first-order decay mode is ascribed here to the differing properties of the ferrate(V) species which exist in the pH range of 3.8 to 14. These are nominally formulated as H_3FeO_4, $H_2FeO_4^-$, $HFeO_4^{2-}$, and FeO_4^{3-}. The decay of the two alkaline forms requires a bimolecular interaction involving $HFeO_4^{2-}$ in which a diferrate(V) intermediate could be formed. The second-order rate constants of reactions (4) and (5) are of the order of 10^7 M^{-1} s^{-1} indicating that $HFeO_4^{2-}$ is a labile ion if indeed the inner-sphere formation of diferrates is involved. The spontaneous first-order decay of $HFeO_4^{2-}$ is slow however, ($k_{10} \approx 5$ s^{-1}). This is similar to the spontaneous first-order decay rate of FeO_4^{3-}, $k \approx 8$ s^{-1}, as was measured earlier in 2 N NaOH.[9,11] The spontaneous first-order rate increases to approximately 150 s^{-1} for $H_2FeO_4^-$. The process which likely controls first-order decay is the aquation of the tetrahedral ferrate(V) species formed by one-electron reduction of ferrate(VI). The expansion of the coordination sphere of ferrate(V) prior to its unimolecular decomposition is necessary since the products resulting from reductive elimination of hydrogen peroxide are either octahedral $Fe(OH)_3(aq)$ or a peroxo-iron(III) system.[11] We visualize that a peroxide molecule is formed when cis-hydroxide or cis-oxide ligands on octahedral Fe(V) form an O—O bond while remaining coordinated to iron. Protonation of Fe(V) further destabilizes this high oxidation state by reducing the electron donating capacity of the ligands and making the complex susceptible to an intramolecular redox reaction. As in the case of other high valent oxoanions (*e.g.* VO_4^{3-}), protonations also promote the stability of higher coordination numbers.[18-21] The spectral similarities among the ferrate(V) species measured immediately after the pulse also suggest that aquation must be the rate-limiting step in the decay of ferrate(V) and that the species initially formed are likely to be structurally analogous to the ferrate(VI) parent ions.

The unusual proton dependence of the decay of H_3FeO_4 seems to provide the most striking evidence that a structural change precedes the first-order reduction of ferrate(V) to iron(III). Although decay to iron(III) is entirely first order, our analysis of the higher order proton dependence requires that a protonation equilibrium subsequent to the formation of H_3FeO_4 also occurs. Hence the ferrate(V) species which is formed in reaction (13) is less acidic than its precursor. The actual structure is unknown but might be formulated as $[Fe(OH)_4(H_2O)_2]^+$ or $[FeO_2(H_2O)_4]^+$ (the latter may be considered as analogous to the acidic vanadium(V) species (VO_2^+)).[18] The maximum rate of decay is limited by the forward rate at which H_3FeO_4 is aquated ($k_{12} \approx 7 \times 10^4$ s^{-1}) in reaction (12). The second protonation of the octahedral form is postulated to drive the $T_d \rightleftharpoons O_h$ equilibrium to the right and accounts partially for the enhanced proton dependence of the decay of H_3FeO_4.

In summary, we have identified two forms of ferrate(V) that exist in the range $3.8 \leq pH \leq 8.5$ with $5.5 \leq pK_1 \leq 6.5$ and $pK_2 \approx 7.2$. The mode of decay (particularly of H_3FeO_4) strongly suggests that these species aquate before decaying intramolecularly. The d-orbital occupancy of ferrate(V), d^3, also leads us to expect that 4-coordination in ferrate(V) should be inherently unstable relative to 6-coordination.[22]

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