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Inorganica Chimica Acta 361 (2008) 1041–1046

Inorganica Chimica Acta

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Reactivity of ferrate(V) ($Fe^VO_4^{3-}$) with aminopolycarboxylates in alkaline medium: A premix pulse radiolysis

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Received 19 April 2007; received in revised form 9 July 2007; accepted 25 July 2007
Available online 3 August 2007

Dedicated to Professor Edward I. Solomon on the occasion of his 60th birthday.

Abstract

A premix pulse radiolysis technique was used to study the reaction between Fe(V) and APCs. Fe(V) reactions with glycine, IDA, NTA, EDTA and DTPA were measured at pH 12.5. Spectral results showed that Fe(V) is reduced to Fe(III); therefore, the reaction of Fe(V) with APCs proceeds *via* a concerted two-electron oxidation, which converts Fe(V) to Fe(III). The rate law for the oxidation of these APCs by Fe(V) is first-order with respect to each reactant at this pH. Fe(V) reactivity with APCs at pH 12.5 was found to increase in the order of tertiary < secondary < primary and vary from $1.6 \times 10^2\ M^{-1}\ s^{-1}$ to $1.4 \times 10^4\ M^{-1}\ s^{-1}$. Both EDTA and DTPA reacted faster than NTA with Fe(V) and Fe(VI). The order of reactivity of amines with Fe(V) suggests that FeO_4^{3-} attacks at the nitrogen atom sites of the APCs, which leads to large differences in the rate constants. In addition, Fe(V) is approximately three- to five-orders of magnitude more reactive than Fe(VI). The reaction of Fe(V) with EDTA was studied as a function of pH (9.0–12.5). The rate constants increased as the pH decreased. The speciation of EDTA and Fe(V) were used to fit the data.

Keywords: Ferrate(V); Oxidation; Aminopolycarboxylates; EDTA; Pulse radiolysis

1. Introduction

High oxidation states of iron play an important role in oxidation and hydroxylation reactions mediated by iron-containing enzymes [1–5]. Iron in +4 and +5 oxidation states has been implicated in the most difficult C–H hydroxylations of saturated carbon centers in a wide range of organic compounds by proteins such as methane monooxygenase and cytochrome P450 [6–14]. The ferryl species, Fe(IV)=O rather than hydroxyl radicals has been postulated in Fenton-type reactions [15–18]. Oxo-Fe(IV) and oxo-Fe(V) as active species have been proposed in the GIF oxygenation system [19,20]. Fe(IV) and Fe(V) species are also frequently invoked as intermediates in oxidation of inorganic and organic substrates by $Fe^{VI}O_4^{2-}$ [21–26]. Despite the involvement of iron(V) in numerous chemical and biological oxidations, not much progress has been made on its reactivity in aqueous solution.

Formation of salts of oxyanion iron(V) ($Fe^VO_4^{3-}$) has been shown in high-temperature melts [27–31]. Single crystals of K_3FeO_4 were found to be black orthorhombic having space group *Pnma* with $a = 770.16$ pm, $b = 909.20$ pm, and 783.70 pm. Six-coordinated iron(V) has been stabilized in oxide lattice in order to characterize it spectroscopically [32]. A stable solution of iron(V), prepared by dissolving K_3FeO_4 in cold alkaline solutions has been reported, but pulse radiolytically generated FeO_4^{3-} in 5 M NaOH decays with a rate constant equal to $4\ s^{-1}$ at 15 °C [33,34]. The spectrum of FeO_4^{3-} has a peak at 380 nm with a molar extinction coefficient of

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doi:10.1016/j.ica.2007.07.019

1460 $M^{-1}cm^{-1}$ [34]. Limited work on the reactivity of FeO_4^{3-} has been conducted [22,34–41]. The oxidation of carboxylic acids by Fe(V) occurs through a two-electron reduction of Fe(V) to Fe(III). Rates depend on the nature of substituent group at the α-carbon atom of the acids and decrease in the order of $\alpha\text{-C–NH}_2 > \alpha\text{-C–OH} > \alpha\text{-C–H}$ [35]. Fe(V) deaminates amino acids to give corresponding α-keto derivatives [35]. The reaction of thiocyanate ion (SCN^-) proceeds by a two-electron oxidation [40] while the oxidation of cyanide (CN^-) proceeds by sequential one-electron reductions of Fe(V) to Fe(IV) to Fe(III) in alkaline solution [39].

In the present investigation, the reactivity of FeO_4^{3-} with aminopolycarboxylates (APCs) was studied in alkaline medium using a premix pulse radiolysis technique. Aminopolycarboxylates (APCs) contain varying numbers of carboxylate groups bound to nitrogen atoms and can control the action of different metal ions through complexation [41]. For example, many metalloenzymes contain active sites that are similar to the APC molecule, which binds to a metal through the carboxylate or amine groups [42]. The interaction between transition metals and APCs is known to promote the formation and stabilization of higher oxidation states of the corresponding metals [43]. Interestingly, formation of complexes of APCs with metals and radioactive elements interfere with the removal of target species from wastes [41,44]. Such complexes also influence metal bioavailability in the environment [41,45]. The APCs studied in this work were glycine ($NH_2(CH_2COO^-)$), iminodiacetate (IDA, $NH(CH_2COO^-)_2$) and nitrilotriacetate, (NTA, $N(CH_2COO^-)_3$), containing a single nitrogen with one, two and three carboxylate groups, respectively, and ethylenediaminetetraacetate (EDTA ($CH_2N(CH_2COO^-)_2$) and diethylenetriaminepentaacetate, (DTPA ($(^-OOCCH_2)_2$-$NCH_2CH_2N(CH_2COO^-)$ $CH_2CH_2N(CH_2COO^-)_2$), aminocarboxylates linked by one and two ethylene groups, respectively). The spectroscopic and kinetics measurements of the reactions between FeO_4^{3-} and APCs were performed in order to determine whether these reactions proceed by one-electron or two-electrons transfer processes and to learn the nature of Fe(V) attack on APCs. The reactivity of Fe(V) with EDTA was also studied as a function of pH to see how equilibrium species of Fe(V) and EDTA influence the rates.

2. Experimental

2.1. Materials

All chemicals (reagent grade or better) were purchased (Sigma/Aldrich) and were used without further purification. Solutions were prepared with water that had been distilled and then passed through an 18 MΩ cm Milli-Q water purification system. Solid crystals of potassium ferrate (K_2FeO_4) were prepared by the method of Thompson et al. [46], with purity of >98% confirmed by Mossbauer spectroscopic measurements. Solutions of Fe(VI) were prepared by adding solid K_2FeO_4 crystals into 0.005 M Na_2HPO_4/0.001 M borate, pH 9.0, where Fe(VI) is most stable [34]. Phosphate serves as a complexing agent for Fe(III), which otherwise precipitates rapidly as a hydroxide that interferes with the optical monitoring of the reaction and also accelerates the spontaneous decomposition of Fe(VI) [47]. A molar absorption coefficient $\varepsilon_{510\text{ nm}} = 1150\ M^{-1}\ cm^{-1}$ was used for the calculation of $[FeO_4^{2-}]$ at pH 9.0 [34]. Absorbance measurements were done on a Cary 210 spectrophotometer.

2.2. Apparatus

The kinetic measurements of the reactivity of Fe(V) with APCs were carried out on 2 MeV van de Graff accelerator. A premixing apparatus consisting of three Hamilton Precision Liquid Dispenser (PDL H) units was computer interfaced and could be operated by remote control. In routine pulse radiolysis, the reactants are stored for a longer time period in a reservoir from which the pulsing cell is automatically filled. However, due to the relatively rapid reaction of Fe(VI) with APCs, some decomposition of Fe(VI) would occur before pulsing; therefore, a premixing apparatus interface with accelerator was needed. The apparatus had a dead time of ca 1 s. Solutions of Fe(VI) were premixed (1:1v/v) with APCs and pulsed before substantial decay of Fe(VI) could happen. The solutions contained 0.1 M ethanol and were purged with N_2O so pulsing of the solution resulted in the sequence of reactions shown below within a fraction of a microsecond.

The number in parentheses in Eq. (I) are *G* values, which are the number of radicals formed per 100 eV of energy absorbed in the aqueous solution. Any H atoms are converted to hydrated electrons (reaction 2), which react with nitrous oxide to form hydroxyl radicals (reaction 1). The OH radicals react with ethanol to form reducing radicals (Eq. 3), which in turn reduces Fe(VI) to Fe(V) (reaction 4). In N_2 saturated solutions, the electron reacts directly to reduce $Fe^{VI}O_4^{2-}$ to $Fe^{V}O_4^{3-}$ at a diffusion controlled rate.

$$\mathrm{H_2O} \overset{\rightsquigarrow}{-} \rightarrow \mathrm{H}(0.55), e^-_{\mathrm{aq}}(2.65), \mathrm{OH}(2.75), \mathrm{H_3O^+}(2.65), \\ \mathrm{H_2O_2}(0.72), \mathrm{H_2}(0.45) \tag{I}$$

$$\mathrm{N_2O} + e^-_{\mathrm{aq}} + \mathrm{H_2O} \rightarrow \mathrm{OH} + \mathrm{OH^-} + \mathrm{N_2} \tag{1}$$

$$\mathrm{H} + \mathrm{OH^-} \Longleftrightarrow e^-_{\mathrm{aq}} + \mathrm{H_2O} \tag{2}$$

$$\mathrm{OH/O^-} + \mathrm{CH_3CH_2OH} \rightarrow \mathrm{H_2O/OH^-} + \mathrm{CH_3^{\cdot}CHOH} \tag{3}$$

$$\mathrm{Fe^{VI}O_4^{2-}} + \mathrm{CH_3^{\cdot}CHOH} \rightarrow \mathrm{Fe^{V}O_4^{3-}} + \mathrm{CH_3CHO} + \mathrm{H^+} \\ k = 9 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}[34] \tag{4}$$

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 $\varepsilon_{472\text{ nm}} = (7950 \pm 3\%)$ [48,49]. The majority of the studies were carried out at pH 12.5, where the decomposition of Fe(V) is first-order and relatively slow ($k \sim 8.0\ s^{-1}$). Conditions were chosen such that this reaction is a minor component in the presence of APCs, where Fe(V) disappearance is dependent on the APC concentration.

3. Results and discussion

Initially, reactions between Fe(V) and APCs were measured at pH = 12.5. Solutions of approximately 0.2 mM Fe(VI) and 5.0×10^{-2} M APCs (premixing concentration) were mixed and pulse irradiated. Spectra obtained for reaction of Fe(V) with IDA and EDTA after the pulse are shown in Fig. 1. The initial spectrum shows the change in absorbance for the disappearance of Fe(VI) and the formation of Fe(V) normalized for extinction coefficients assuming a mechanism consisting of reactions (1–4). The second spectrum is the change in absorbance after Fe(V) disappears, again assuming the mechanism from reactions (1–4) and that the disappearance of Fe(V) is to a non-absorbing entity. Analogous results were obtained upon reaction of Fe(V) with DTPA. NTA did not react sufficiently rapidly with Fe(V) within the parameters of our experimental conditions.

The disappearance of Fe(V) may be explained by two alternate mechanisms; one-electron (Eq. 5) or two-electron (Eq. 6) transfer processes.

$$\mathrm{Fe(V)} + \mathrm{APC} \rightarrow \mathrm{Fe(IV)} + \mathrm{APC}^{\bullet} \qquad (5)$$

$$\mathrm{Fe(V)} + \mathrm{APC} \rightarrow \mathrm{Fe(III)} + \mathrm{APC(Oxidized)} \qquad (6)$$

Fe(IV) is formed from the one-electron reduction of Fe(V) (Eq. 5), as observed earlier for the cyanide substrate [39]. The characteristic spectrum of Fe(IV) ($\lambda_{\max} = 430$ nm) was not observed in these experiments [50] as the optical density (O.D.) at 380 nm of the Fe(V) reaction with APCs was the same as the O.D. of Fe(V) without APCs. This indicates that the reaction between Fe(V) and APCs was stoichiometric, i.e., no additional Fe(V) was produced, which suggests Fe(V) reaction with APCs proceeds in a single step to Fe(III). This eliminates the formation of Fe(V) from the reaction between Fe(VI) and possible free radical intermediate, $\mathrm{APC}^{\bullet}$. The $\mathrm{APC}^{\bullet}$ can potentially reduce Fe(VI) at a faster rate $k \approx 10^{9}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ [35] to give a chain reaction. The absence of reaction 5 demonstrates that the reaction of Fe(V) with APCs proceeds *via* a concerted two-electron oxidation, which converts Fe(V) to Fe(III).

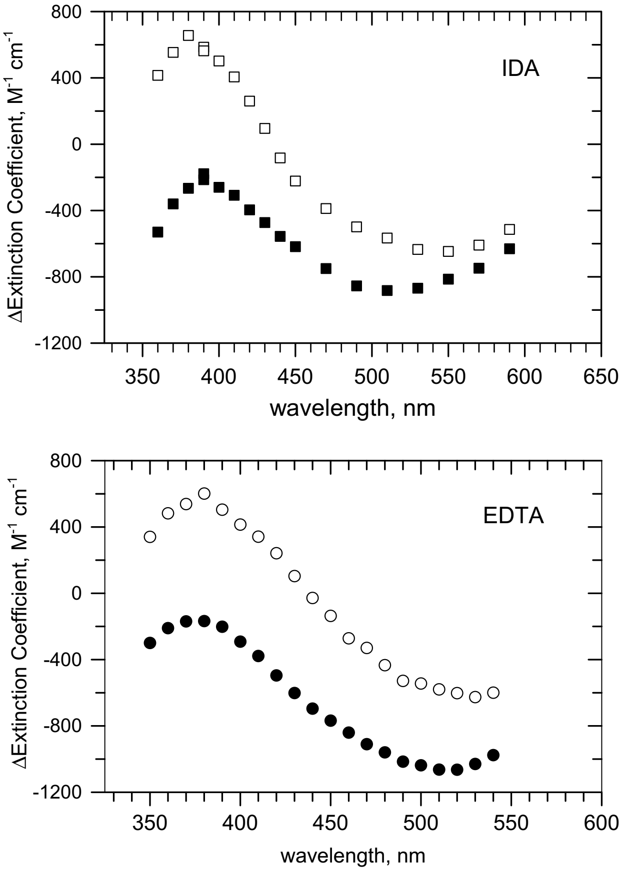

Fig. 1. Δ Extinction coefficient vs. wavelength measured at 0.01 ms (open circles; –Fe(VI) + Fe(V)) and 500 ms (filled circles; –Fe(VI)).

The Fe(V) reaction with APCs was studied under first-order conditions with APCs in excess at pH 12.5. Reactions were measured by following the absorbance changes at 380 nm ($\lambda_{\max}$ of Fe(V)) as a function of time; see Fig. 2. Immediately after the pulse, the Fe(VI) is reduced to

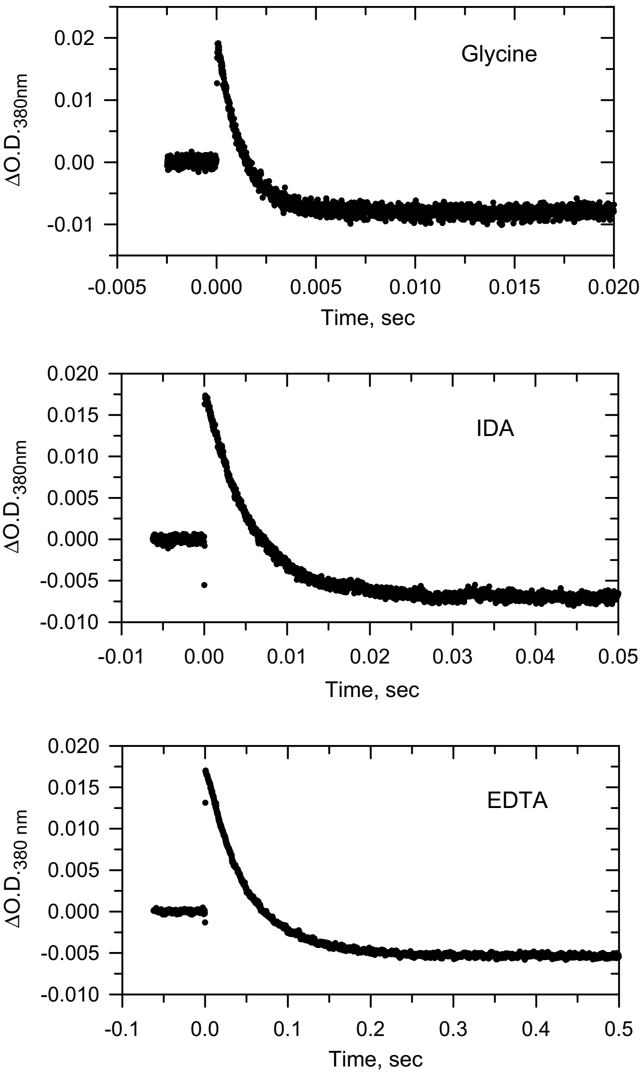

Fig. 2. ΔO.D. vs. time at 380 nm in 0.1 M sodium phosphate at pH 12.5.

Fe(V) so there is a loss of the Fe(VI) absorbance and concomitant gain of the Fe(V) absorbance at 380 nm. Then, the Fe(V) reacts with the PAC so there is a net loss of the Fe(V) absorbance. The reaction of Fe(V) with glycine at pH 12.5 was also studied for a comparison purpose. The absorbance changes in Fig. 2 fit a single-exponential decay, indicating the reaction is first-order with respect to PAC. The pseudo-first-order rates (k', s^{-1}) values were determined at various concentrations of individual APCs. The plots of k' values versus [APC] were linear (Fig. 3). Regression lines were fitted to the data and the slopes were determined as 1.06, 0.91, 1.07, and 1.03 for glycine, IDA, EDTA, and DTPA, respectively. This suggests that the rate law for the reaction is first-order with respect to APC and can be represented as

$$-\mathrm{d}[\mathrm{Fe(V)}]/\mathrm{d}t = k[\mathrm{Fe(V)}][\mathrm{APC}] \tag{7}$$

The values of the observed second-order rate constant, k, for reactions of Fe(V) with APCs are given in Table 1. These values are compared with the reactivity of Fe(VI) with APC under similar conditions. Fe(V) is approximately three- to five-orders of magnitude more reactive than Fe(VI). Fe(V) has a radical character ($\mathrm{Fe^{V}{=}O} \leftrightarrow \mathrm{Fe^{IV} - O^{\bullet}}$), which was deduced from the bimolecular decomposition rate constant of Fe(V), $k \approx 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$ [51]. This radical character of Fe(V) may be responsible for the higher reactivity of Fe(V). Among the studied substrates, glycine is primary amine (1°), IDA is secondary amine (2°), and NTA, EDTA, and DTPA are tertiary amine (3°). The order of reactivity is primary > secondary > tertiary (Table 1). Both EDTA and DTPA reacted faster with Fe(V) and Fe(VI) than NTA. The order of reactivity of amines with Fe(V) suggests that $\mathrm{FeO_4}^{3-}$ attacks at the nitrogen atom of the APCs. Such differences in rates would not have been expected otherwise.

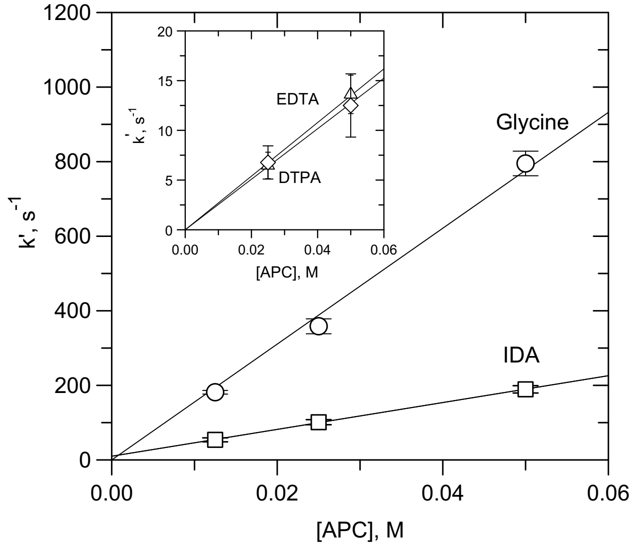

Fig. 3. k' vs. [APC] at pH 12.5.

Table 1
Rate constants for the reaction of Fe(VI) and Fe(V) with APC at pH 12.5

APC	k(FeVI + APC) $\mathrm{M^{-1}\ s^{-1}}$	k(FeV + APC) $\mathrm{M^{-1}\ s^{-1}}$	$\frac{k(\mathrm{Fe(V)}+\mathrm{APC})}{k(\mathrm{Fe(VI)}+\mathrm{APC})}$
Glycine	$(1.6 \pm 0.1) \times 10^{-1}$	$(1.4 \pm 0.1) \times 10^{4}$	9.3×10^{4}
IDA	$(3.8 \pm 0.5) \times 10^{-2}$	$(4.0 \pm 0.3) \times 10^{3}$	1.1×0^{3}
NTA	$\leqslant 4.4 \times 10^{-2}$	$\leqslant 1.6 \times 10^{2}$	
EDTA	$(8.6 \pm 0.8) \times 10^{-2}$	$(2.7 \pm 0.1) \times 10^{2}$	3.1×10^{3}
DTPA	$(1.7 \pm 0.1) \times 10^{-1}$	$(2.6 \pm 0.2) \times 10^{2}$	1.5×10^{3}

Finally, the reaction of Fe(V) with EDTA was studied as a function of pH (9.0–12.5). The disappearance of Fe(V) in the presence of a greater than 10-fold excess of EDTA (pseudo-first-order conditions) fits nicely to a single-exponential decay, indicating the reaction is first-order with respect to Fe(V) in the studied pH range. As shown in Fig. 4, the plot of the first-order rates (k', s^{-1}) determined at various concentrations of EDTA at pH 10.0 was linear, analogous to that seen at pH 12.5 (Fig. 3). This suggests that rate law described above (Eq. 7) was followed over the entire pH range. The second-order rate increases with a decrease in pH (Fig. 5).

The pH dependence is likely related to equilibria involving Fe(V) and EDTA. The acid dissociation equilibria of protonated forms of Fe(V) can be expressed in Eqs. (8)–(10) [51].

$$\mathrm{H_3FeO_4} \Longleftrightarrow \mathrm{H^+} + \mathrm{H_2FeO_4^-} \qquad 5.5 \leqslant \mathrm{p}K_{\mathrm{a1}} \geqslant 6.5 \tag{8}$$

$$\mathrm{H_2FeO_4^-} \Longleftrightarrow \mathrm{H^+} + \mathrm{HFeO_4^{2-}} \qquad \mathrm{p}K_{\mathrm{a2}} = 7.2 \tag{9}$$

$$\mathrm{HFeO_4^{2-}} \Longleftrightarrow \mathrm{H^+} + \mathrm{FeO_4^{3-}} \qquad \mathrm{p}K_{\mathrm{a3}} = 10.1 \tag{10}$$

EDTA has six dissociation constants and its reported pK_a values are 0.25, 0.96, 2.0, 2.7, 6.2, and 10.2 [52], where the two highest pKs correspond to the protonation/deprotonation of the two nitrogen amines. In the pH range studies, two forms of Fe(V), namely, $\mathrm{HFeO_4}^{2-}$ and $\mathrm{FeO_4}^{3-}$ can react with two forms of EDTA ($\mathrm{HEDTA^{3-}} \Longleftrightarrow \mathrm{H^+} + \mathrm{EDTA^{4-}}$, p$K_6 = 10.2$) (Eqs. (11)–(14)).

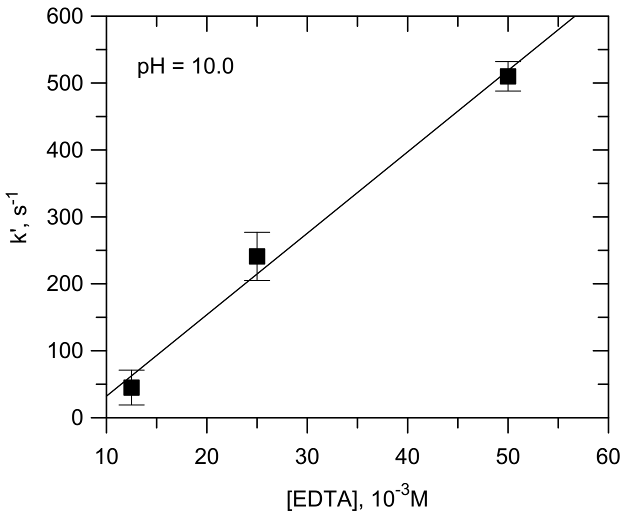

Fig. 4. k' vs. [EDTA] at pH 10.0.

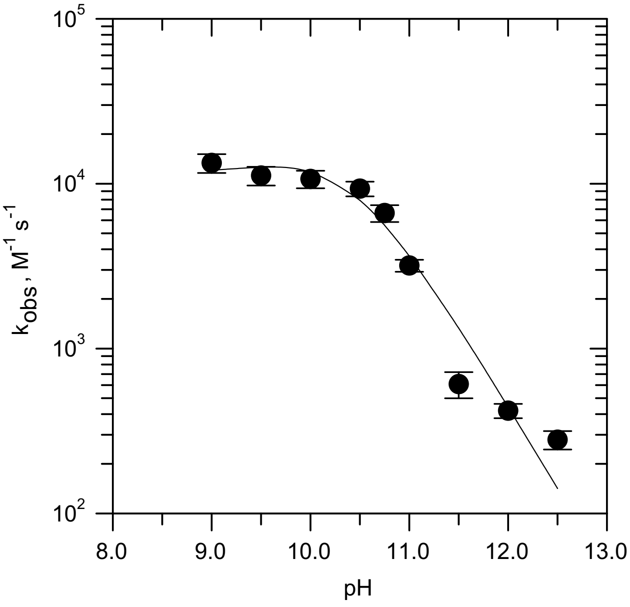

Fig. 5. Rate constant vs. pH for Fe(V) reaction with EDTA.

$$HFeO_4^{2-} + HEDTA^{3-} \rightarrow Products \quad (11)$$

$$FeO_4^{3-} + HEDTA^{3-} \rightarrow Products \quad (12)$$

$$HFeO_4^{2-} + EDTA^{4-} \rightarrow Products \quad (13)$$

$$FeO_4^{3-} + EDTA^{4-} \rightarrow Products \quad (14)$$

The rate of disappearance of Fe(V) can be expressed as

$$\begin{aligned}-d[Fe(V)]/dt = {} & k_{10}[HFeO_4^{2-}][HEDTA^{3-}] \\ & + k_{11}[FeO_4^{3-}][HEDTA^{3-}] \\ & + k_{12}[HFeO_4^{2-}][EDTA^{4-}] \\ & + k_{13}[FeO_4^{3-}][EDTA^{4-}] \quad (15)\end{aligned}$$

By using the fraction of speciation of Fe(V) and EDTA (K_{a3} is the equilibrium constant for deprotonation of $HFeO_4{}^{2-}$ and K_6 is the equilibrium constant for deprotonation of $HEDTA^{3-}$), the following equation is obtained:

$$k = \{k_{10}[H^+]^2 + k_{11}K_{a3}[H^+] + k_{12}[H^+]K_6 + k_{13}K_{a3}K_6\}/Z \quad (16)$$

$$\text{where } Z = ([H^+] + K_{a3})([H^+] + K_6) \quad (17)$$

Reactions (12) and (13) introduce the proton ambiguity. Thus, the experimental values of k could be fit reasonably well (a solid line in Fig. 5) by considering either reactions (11) and (12) (model I) or reactions (11) and (13) (model II). Reaction (14) was not needed in fitting the data. Use of model I gave $k_{10} = 1.18 \pm 0.12 \times 10^4\ M^{-1}\ s^{-1}$ and $k_{11} = 2.85 \pm 0.29 \times 10^4\ M^{-1}\ s^{-1}$ while model II gave $k_{10} = 1.18 \pm 0.12 \times 10^4\ M^{-1}\ s^{-1}$ and $k_{13} = 3.58 \pm 0.36 \times 10^4\ M^{-1}\ s^{-1}$.

4. Conclusions

The pH dependence of the reaction rate of Fe(V) with EDTA is opposite to the trend observed for $^{\bullet}OH$ radical as the rate of reaction of $^{\bullet}OH$ radical with EDTA is reduced when EDTA is protonated; therefore, Fe(V) is a much different oxidant than the hydroxyl radical [53]. Using pulse radiolysis, the rate constants were determined as $k(^{\bullet}OH + H_2EDTA^{2-}) = 4 \times 10^8\ M^{-1}\ s^{-1}$, $k(^{\bullet}OH + HEDTA^{3-}) = 2 \times 10^9\ M^{-1}\ s^{-1}$, and $k(^{\bullet}OH + EDTA^{4-}) = 6 \times 10^9\ M^{-1}\ s^{-1}$ [53] and the initial formation of both *N*-centered radical cations and *C*-centered radicals have been suggested [53]. The pattern of reactivity among APCs suggest that the number of nitrogen centers is irrelevant to reaction rate but that the liganding of the nitrogen center (primary > secondary > tertiary) is a factor. This suggests that attack may be at the nitrogen. However, any nitrogen centered radical is much too short-lived to be seen within the timescale of the initial reaction (hundreds of milliseconds) [53].

In the present study, the rate constants were determined from rates of disappearance of Fe(V), which allowed us to postulate the mechanism but did not verify any organic intermediate in the mechanism. Future study on the reaction of Fe(V) and APC should include spectral measurements in which the nature of the radicals formed in the system can be determined. Other studies have shown that a APC ligand complexed with metal ion can be efficiently destroyed by ferrates to free the metal ion, which is subsequently precipitated out from the solution by ferric hydroxide, known to be formed in the reduction of ferrates [54]. The magnitude of the rate constants and the two-electron reduction inferred from the absence of any detectable Fe(IV) suggests that ferrates may be useful in the remediation of metal contamination through the degradation of APCs.

Acknowledgements

Pulse radiolysis studies were carried out at the Center for Radiation Chemical Research at BNL and supported by the US Department of Energy (DE-AC02-98CH10086).

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