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Reduction of Oxyiron(V) by Sulfite and Thiosulfate in Aqueous Solution

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The reduction of oxyiron(V), $Fe^{V}O_4^{3-}$ by inorganic oxysulfur species (SO_3^{2-} and $S_2O_3^{2-}$) has been studied anaerobically in alkaline medium by using a premix pulse radiolysis technique. Studies on the reactions of $Fe^{VI}O_4^{2-}$ with the two sulfur radicals were also carried out. The spectroscopic results demonstrated that sulfur radicals reduced $Fe^{VI}O_4^{2-}$ to $Fe^{V}O_4^{3-}$ which is subsequently reduced by oxysulfur species by a two-electron reduction step to Fe(III). The rate constants for reduction of $Fe^{VI}O_4^{2-}$ to $Fe^{V}O_4^{3-}$ by sulfite and thiosulfate radicals ($^{\bullet}SO_3^{-}$ and $S_4O_6^{\bullet 3-}$) were found to be $(1.9 \pm 0.3) \times 10^8$ and $(7.5 \pm 0.8) \times 10^7$ M^{-1} s^{-1}, respectively. However, the reactions of $Fe^{V}O_4^{3-}$ with the SO_3^{2-} and $S_2O_3^{2-}$ ions were separated by an order of magnitude, with SO_3^{2-} reacting at $(3.9 \pm 0.3) \times 10^4$ M^{-1} s^{-1} while $S_2O_3^{2-}$ reacted with Fe(V) at $(2.1 \pm 0.1) \times 10^3$ M^{-1} s^{-1} at pH 11.4.

1. Introduction

The importance of iron redox chemistry involving high-valent iron−oxo intermediates in several biological, industrial, and environmental processes is well established and is a topic of both past and current interest.[1−18] Fe^{V} and Fe^{IV} are frequently postulated as reactive intermediates in biochemical catalytic processes involving heme peroxidases, cytochrome P450, and methane monooxygenase.[7,17−19] Ferryl ($Fe^{IV}{=}O$) and perferryl ($Fe^{V}{=}O$) units have been implicated in iron−dioxygen systems, Fenton reactions, and oxidations catalyzed by Fe(II)/Fe(II) complexes.[20−25] Recently, structural evidence for the reactive intermediate having a $Fe^{IV}{=}O$ unit in the activation of nonheme iron enzymes was given.[26,27] Despite involvement of these oxidation states of iron in numerous reactions, only sporadic information on the fundamental properties of Fe^{V} and Fe^{IV} in the absence of a specialized ligand system in aqueous solution is available. Limited attempts have been made to understand the characteristics of Fe^{V} in its simple state as an oxyanion ($Fe^{V}O_4^{3-}$) in aqueous solution.[28,29]

Studies on the kinetics of $Fe^{V}O_4^{3-}$ reactions remain relatively unexplored. To perform Fe(V) kinetic studies, Bielski and co-workers[28,29] generated $Fe^{V}O_4^{3-}$ by reducing $Fe^{VI}O_4^{2-}$ with radicals such as e_{aq}^{-}, $^{\bullet}CO_2$, and $^{\bullet}CH_2OH$ at near diffusion-controlled rates (e.g., $Fe^{VI}O_4^{2-} + e_{aq}^{-} \rightarrow Fe^{V}O_4^{3-}$, $k = 2 \times 10^{10}$ M^{-1} s^{-1}). Decay of Fe^{V}_{aq} was studied as a function of pH in aqueous solutions.[30] In alkaline pH, the decay of Fe^{V} was second-order ($2k_{obs} \approx 10^7$ M^{-1} s^{-1}). However, the observed decay of Fe^{V} became first-order in the pH range 3.6 to 7.0, with the rate constant decreasing from 7×10^4 s^{-1} to about 100 s^{-1}. These workers also studied reactions of $Fe^{V}O_4^{3-}$ with amino acids and carboxylic acids,[31−34] which suggested that the rates are affected by the replacement of the α−C-H atom by functional groups such as −OH and $-NH_2/{}^{-}NH_3^{+}$. In our studies[35] of the Fe^{V}_{aq} reaction with cyanide in alkaline solutions, we observed for the first time the spectroscopic evidence for one-electron reduction of Fe^{V} to Fe^{IV}, which is subsequently reduced to Fe^{III}.

In the present study, we have investigated the reaction between oxyiron(V), $Fe^{V}O_4^{3-}$ and inorganic oxysulfur species, sulfite (SO_3^{2-}) and thiosulfate ($S_2O_3^{2-}$), in alkaline medium. The kinetic measurements of the oxidation of these and other inorganic oxysulfur species by Fe^{VI} have been previously carried out by other workers.[36−39] However, similar studies with transient Fe^{V} have not been made, and thus we are unable to fully understand the overall mechanism of the oxidation chemistry involving high oxidation states of iron with sulfur species. The present work is the first study to examine $Fe^{V}O_4^{3-}$ reactivity with SO_3^{2-} and $S_2O_3^{2-}$. In both systems, a two-electron reduction of Fe^{V} to Fe^{III} was observed. We have also examined the reactions of $Fe^{VI}O_4^{2-}$ with inorganic oxysulfur radicals that resulted in the formation of $Fe^{V}O_4^{3-}$.

2. Experimental Section

The kinetic studies were carried out using the pulse-radiolytic technique and experiments were conducted on a BNL 2 MeV van de Graff accelerator. The rates for the reactivity of Fe(VI) with inorganic oxysulfur species were too fast to allow the study of the reaction of $Fe^{V}O_4^{3-}$ with SO_3^{2-} and $S_2O_3^{2-}$ using traditional pulse radiolysis,[36−39] where the reactants are stored for a long time period in a reservoir from which the pulsing cell is automatically filled. Therefore, the accelerator was interfaced with a premix apparatus consisting of three Hamilton Precision Liquid Dispenser (PDL II) units. This premixing apparatus had an effective dead time of ≈1.5 s under our conditions and we were able to follow UV/vis absorbance changes out to many seconds.

The Fe(VI) solution (0.001 M borate/0.005 M phosphate; pH = 9.0) was mixed with either a SO_3^{2-} or a $S_2O_3^{2-}$ solution (0.10 M phosphate buffer; 0.5 M ethanol) and was pulse irradiated. Both solutions were saturated with nitrous oxide; $[N_2O] = 0.026$ M. The sequence of reactions following the electron pulse (eq I) occurred within a fraction of a microsecond[28,29] and led to formation of $Fe^{V}O_4^{3-}$, as shown in eqs 1−4. The numbers in parentheses in eq I are G values, that is, the number of radicals

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formed per 100 eV of energy dissipated in the aqueous solution.[40]

$$H_2O \rightsquigarrow H(0.55),\ e_{aq}^-(2.65),\ OH(2.75),\ H_3O^+(2.65),\ H_2O_2(0.72),\ H_2(0.45) \quad (I)$$

$$N_2O + e_{aq}^- + H_2O \rightarrow OH + OH^- + N_2 \quad (1)$$

$$H + OH^- \leftrightarrow e_{aq}^- + H_2O \quad (2)$$

$$OH/O^- + S \rightarrow H_2O/OH^- + {}^{\bullet}S \qquad (S = \text{substrate}) \quad (3)$$

$$Fe^{VI}O_4^{2-} + {}^{\bullet}S \rightarrow Fe^{V}O_4^{3-} + \text{product} \quad (4)$$

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 $\varepsilon_{472nm} = 7580$.[41] The measurements were made in a 2.0 cm light path.

It should be noted here that when S is an alcohol such as ethanol, the carbon-centered alcohol radical formed from OH radical attack has been shown to very rapidly reduce Fe(VI) to Fe(V) and this is the preferred method of producing Fe(V) either to measure the spontaneous rate of Fe(V) disappearance as a control or to measure the reactivity of Fe(V) with a stable substrate. Reaction 4 was monitored by observing the disappearance of Fe(VI) at 510 nm and formation of Fe(V) at 380 nm. The concentration of Fe(VI) was in excess and was varied to obtain the pseudo-first-order rate of the reaction 4. The reaction of Fe(V) with the sulfur-containing substrates studied here was measured using 0.5 M ethanol and 100−200 μM Fe(VI), from which Fe(V) is generated according to reactions 5 and 6.

$$OH/O^- + CH_3CH_2OH \rightarrow H_2O/OH^- + CH_3{}^{\bullet}CHOH \quad (5)$$

$$Fe^{VI}O_4^{2-} + CH_3{}^{\bullet}CHOH \rightarrow Fe^{V}O_4^{3-} + CH_3CHO + H^+ \qquad k = 9 \times 10^9\ M^{-1}\ s^{-1} \quad (6)$$

$$Fe^{V}O_4^{3-} + S \rightarrow Fe(III) + \text{product} \quad (7)$$

Reaction 7 was measured by monitoring the decay of Fe(V) under pseudo-first-order conditions in which the substrate concentration was kept in much higher concentration than Fe(V) produced in the reaction 6 but much lower than the ethanol concentration.

All chemicals used (Sigma, Aldrich) were of reagent grade or better 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. Potassium ferrate (K_2FeO_4) of high purity (98% plus) was prepared by the method of Thompson et al.[42] The Fe(VI) solutions were prepared by addition of solid samples of K_2FeO_4 to 0.005 M Na_2HPO_4/0.001 M borate, pH 9.0, where solutions are most stable.[43] Phosphate serves as a complexing agent for Fe(III), which otherwise precipitates rapidly as a hydroxide that instantly interferes with the optical monitoring of the reaction and also accelerates the spontaneous decomposition of Fe(VI). A molar absorption coefficient $\epsilon_{510\ nm} = 1150\ M^{-1}\ cm^{-1}$ was used for the calculation of $[FeO_4^{2-}]$ at pH = 9.0.[28]

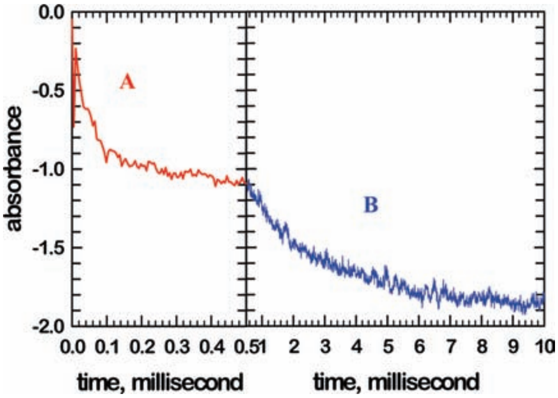

Figure 1. Change in absorbance with time measured at pH 11.4 and at $\lambda = 550$ nm.

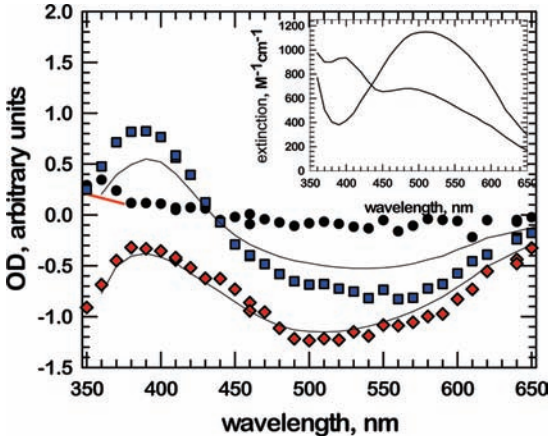

Figure 2. Spectra of $Fe^{V}O_4^{3-}$ obtained from pulse radiolysis of $Fe^{VI}O_4^{2-}-SO_3^{2-}$ solution in 0.0075 M phosphate solution at pH 11.4: black circle, initial; blue square, intermediate (after 0.5 ms); red diamond, final (after 10 ms) along with the calculated spectra (solid black line) that would be observed if Fe(VI) is reduced to Fe(V) (−Fe(VI) + Fe(V)) (0.5 ms) and the observed spectrum once Fe(V) has disappeared. Inset: spectra of Fe(VI) and Fe(V) (from ref 29).

3. Results

Initially, a N_2O saturated solution containing 1.33×10^{-4} M Fe(VI) and 3.30×10^{-2} M sulfite at pH 11.4 was mixed and pulse irradiated. The changes in absorbance as a function of time were measured at 10 nm intervals from 350 to 650 nm. A characteristic example is given in Figure 1, where the initial trace shows the change in absorbance at 550 nm measured immediately after the pulse to 0.5 ms and the subsequent trace shows 0.5 ms after the pulse to 10 ms after the pulse, where the change was constant until much longer times (many seconds) where the reaction between Fe(VI) and sulfite became observable.

Figure 2 shows the spectra that were measured immediately after the pulse, at 0.5 ms after the pulse, and at 10 ms after the pulse. The initial spectrum corresponds to the sulfite radical (${}^{\bullet}SO_3^-$), which formed from the reaction of hydroxyl radical with sulfite,[44] $k = 4.6 \times 10^9\ M^{-1}\ s^{-1}$. This spectrum is similar to the previously reported spectrum[44] of a sulfite radical at this pH, given by the solid red line. Unfortunately, the large absorbance of the ferrate at lower wavelengths precludes a more detailed spectral signature of ${}^{\bullet}SO_3^-$. $Fe^{VI}O_4^{2-}$ subsequently

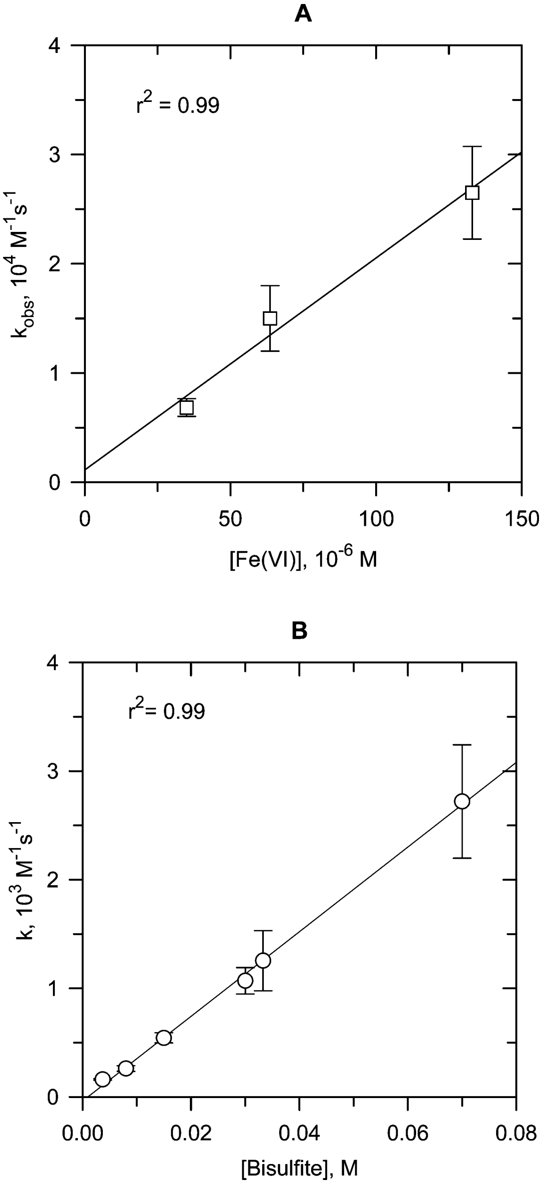

Figure 3. Observed pseudo-first-order rate constants in 0.0075 M phosphate at pH 11.4: (A) $Fe^{VI}O_4^{2-} + {}^{\bullet}SO_3^-$; (B) $Fe^{V}O_4^{3-} + SO_3^{2-}$.

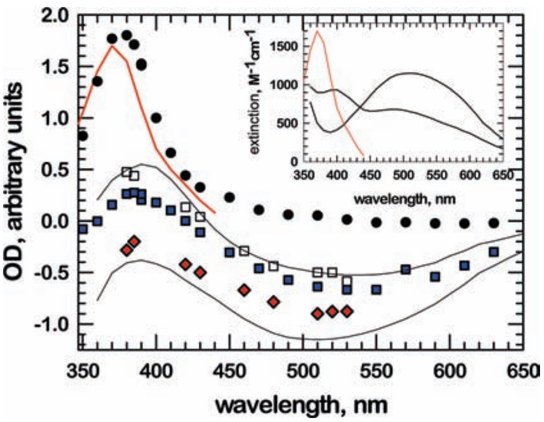

Figure 4. Spectra obtained in pulse-radiolysis of $Fe^{VI}O_4^{2-}-S_2O_3^{2-}$ solution in 0.0075 M phosphate solution at pH 11.4: black circle, initial; blue square, intermediate (after 0.5 ms); red diamond, final (after 100 ms)) along with the known spectrum of $S_4O_6^{3-}$ (solid red line), the calculated spectrum (solid black line) that would be observed if Fe(VI) is reduced to Fe(V) (−Fe(VI) + Fe(V)) (0.5 ms), and the calculated spectrum once Fe(V) has disappeared (10 ms). Inset: spectra of Fe(VI) and Fe(V) (from ref 29).

reacted with ${}^{\bullet}SO_3^-$ to give an intermediate spectrum (0.5 ms after the pulse), which was attributed to the disappearance of some $Fe^{VI}O_4^{2-}$ and the concomitant formation of $Fe^{V}O_4^{3-}$. The absorbance decrease at 510 nm and increase at 380 nm is consistent with the $Fe^{VI}O_4^{2-}$ versus $Fe^{V}O_4^{3-}$ spectra in the inset. $Fe^{V}O_4^{3-}$ further reacted with the substrate SO_3^{2-} on the millisecond time scale to result in the final spectrum. This reaction was completed in 10 ms leading to a spectrum that was attributed to the disappearance of the $Fe^{V}O_4^{3-}$ formed in the previous reaction. Note the overall decrease in absorbance. This postulated mechanism assumes a stoichiometric conversion of a radiation generated radical to an observable intermediate and the stoichiometric conversion of the intermediate to the final product, with the concomitant loss of the parent Fe(VI) that absorbs in the region of interest. The solid black lines represent the calculated spectra that would be observed if Fe(VI) is reduced to Fe(V) (−Fe(VI) + Fe(V)) and if Fe(VI) is consumed. The spectrum obtained for the intermediate species resembled the $Fe^{V}O_4^{3-}$ spectrum (λ_{max} = 380 nm) in an alkaline medium.[28,29] The molar absorbances after correction for the loss of $Fe^{VI}O_4^{2-}$ were also similar to earlier reported[28,29] values for $Fe^{V}O_4^{3-}$. In the reaction of $Fe^{V}O_4^{3-}$ with SO_3^{2-}, Fe(IV) as an intermediate was not observed (Figure 2). Fe^{IV} has a distinct spectrum[45] with $\lambda_{max} \approx 430$ nm and one-electron reduction of Fe(V) would have resulted in this spectrum. The final product in the present study is presumably Fe^{III}, as evidenced by a small absorbance that grew in below 400 nm. This indicates that reduction of $Fe^{V}O_4^{3-}$ by SO_3^{2-} is a two-electron process.

The bimolecular rate constant for the reaction of $Fe^{VI}O_4^{2-}$ with ${}^{\bullet}SO_3^-$ was determined under pseudo-first-order conditions with an excess of $Fe^{VI}O_4^{3-}$ by varying $[Fe^{VI}O_4^{3-}]$ and measuring its disappearance at a variety of wavelengths; exponential disappearance of $Fe^{VI}O_4^{3-}$ was observed. The reactions in the experiment can be described by eqs 8−10. The initial product of reaction 9 is SO_3, which is subsequently hydrated to SO_4^{2-} ($SO_3 + 2OH^- \rightarrow H_2SO_4 \rightarrow SO_4^{2-} + H_2O$).[46] This hydrated oxygen transfer most likely occurs at a much slower rate than the electron-transfer step (reaction 9). A plot of observed first-order rate constants at various $[Fe^{VI}O_4^{2-}]$ was linear (Figure 3A). Fitting the points to a regression line led to a second-order rate constant for reaction 9 as $k_9 = (1.9 \pm 0.3) \times 10^8$ M^{-1} s^{-1}. The rate constant for the reaction of $Fe^{V}O_4^{3-}$ with SO_3^{2-} ion (reaction 10) was measured under pseudo-first-order conditions with SO_3^{2-} in excess. A first-order reaction with respect to SO_3^{2-} was observed. A linear plot of observed first-order rate constants at various $[SO_3^{2-}]$ (Figure 3B) gave a second-order rate constant, $k_{10} = (3.9 \pm 0.3) \times 10^4$ M^{-1} s^{-1}.

$$OH + SO_3^{2-} \rightarrow {}^{\bullet}SO_3^{-} + OH^- \qquad (8)$$

$$Fe^{VI}O_4^{2-} + {}^{\bullet}SO_3^{-} \rightarrow Fe^{V}O_4^{3-} + SO_3 \qquad (9)$$

$$Fe^{V}O_4^{3-} + SO_3^{2-} + 3H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + 3OH^- \qquad (10)$$

A similar series of experiments were carried out where the substrate was thiosulfate. Here, 1.0×10^{-4} M FeO_4^{2-} and 1.5×10^{-1} M thiosulfate were mixed and pulse irradiated at pH 11.4. Spectra obtained following the pulse are shown in Figure 4. The reaction of ${}^{\bullet}OH$ radicals with the $S_2O_3^{2-}$ ion leads to the formation of a radical adduct, $S_2O_3OH^{2-}$ ($k_{11} = (7.8 \pm 2.1) \times 10^9$ M^{-1} s^{-1}), which reacted with excess $S_2O_3^{2-}$ to form $S_4O_6^{3-}$ ($k_{12} = (6 \pm 2) \times 10^8$ M^{-1} s^{-1}).[47] This thiosulfate radical anion has a maximum at ≈370 nm[45] (the solid red line), which agrees well with the absorbance of the initial transient generated in these pulse radiolysis experiments. This radical, $S_4O_6^{3-}$, then reacted with $Fe^{VI}O_4^{2-}$ to give $Fe^{V}O_4^{3-}$. This step was followed by the reduction of $Fe^{V}O_4^{3-}$ to Fe^{III}_{aq} by thiosulfate itself (Figure 4). This two-electron reduction of Fe(V) to Fe(III) (eq 14) is similar to the Fe(V)−sulfite system. Again, a Fe(V)/thiosulfate adduct was not observed during the reaction of $Fe^{V}O_4^{3-}$ with $S_2O_3^{2-}$.

$$S_2O_3^{2-} + {}^{\bullet}OH \rightarrow S_2O_3OH^{2-} \qquad (11)$$

$$S_2O_3OH^{2-} + S_2O_3^{2-} \rightarrow S_4O_6^{\bullet 3-} + OH^- \qquad (12)$$

$$Fe^{VI}O_4^{2-} + S_4O_6^{\bullet 3-} \rightarrow Fe^{V}O_4^{3-} + S_4O_6^{2-} \qquad (13)$$

$$Fe^{V}O_4^{3-} + S_2O_3^{2-} + 3H_2O \rightarrow Fe(OH)_3 + S_2O_4^{2-} + 3OH^- \qquad (14)$$

The reaction of the thiosulfate radical ($S_4O_6^{\bullet 3-}$) with $Fe^{VI}O_4^{2-}$ was measured at 430 nm at various [$Fe^{VI}O_4^{2-}$] (Figure 5A). The second-order rate constant for the reaction was determined as $k_{13} = (7.5 \pm 0.8) \times 10^7$ M^{-1} s^{-1}. The second-order rate constant for the reaction between $Fe^{V}O_4^{3-}$ and $S_2O_3^{2-}$ was also measured by following the kinetics at 380 nm at various concentrations of thiosulfate (Figure 5B). A first-order reaction with respect to $Fe^{V}O_4^{3-}$ was observed and the second-order rate constant for reaction 14 determined was $k_{14} = (2.1 \pm 0.1) \times 10^3$ M^{-1} s^{-1}. It should be noted here that we were able to carry out concentration studies where the thiosulfate concentration was 0.3 M in spite of the 0.02 M N_2O concentration limit as the e_{aq}^- reaction with N_2O is $k = 9 \times 10^9$ M^{-1} s^{-1} while the e_{aq}^- reaction with thiosulfate is $k = (0.7{-}1) \times 10^8$ M^{-1} s^{-1}.[41,47,48]

In our experiments, no adduct formation is observed between $Fe^{V}O_4^{3-}$ and $SO_3^{2-}/S_2O_3^{2-}$ although previous studies[36−38] on the oxidation of SO_3^{2-} by $Fe^{VI}O_4^{2-}$ postulated the formation of an adduct intermediate, $[O_3Fe^{VI}OSO_3]^{4-}$. The kinetic characteristic for a stabilized intermediate is that the plot of observed rate as a function of substrate concentration would give an intercept. As shown in Figures 3B and 5B, the data give no evidence of any positive intercept. The corollary of this is that there might be an observable intermediate and none was seen. This is, however, rather more difficult to confirm; the kinetic evidence is more compelling. In our experiments, the concentrations of oxysulfur species were up to 0.07 and 0.3 M for SO_3^{2-} and $S_2O_3^{2-}$, respectively, and there is a possibility of formation of adducts at much higher concentrations of oxysulfur species than used in the present study.

4. Discussion

The rate and spectroscopic study of the reactions of $Fe^{VI}O_4^{2-}$ and $Fe^{V}O_4^{3-}$ with oxysulfur and their radical species allowed us (i) to learn whether reduction of Fe(V) occurs through a one-electron or two-electron process and (ii) to compare reactivity of Fe(VI) and (V) with SO_3^{2-} and $S_2O_3^{2-}$ and their corresponding radicals, and (iii) to see the difference in reactivity of Fe(V) with oxysulfur species.

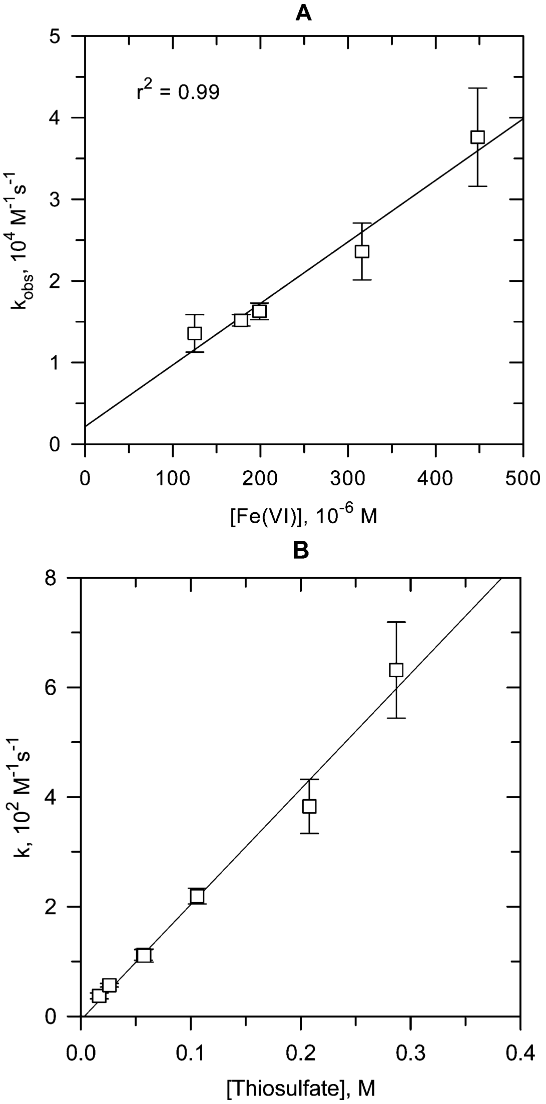

Figure 5. Observed pseudo-first-order rate constants in 0.0075 M phosphate at pH 11.4: (A) $Fe^{VI}O_4^{2-} + S_4O_6^{3-}$; (B) $Fe^{V}O_4^{3-} + S_2O_3^{2-}$.

Both SO_3^{2-} and $S_2O_3^{2-}$ reduced Fe(V) to Fe(III) without forming an observable Fe(IV) species. In our earlier study of the reaction between Fe(V) and cyanide,[35] the one-electron reduction intermediate Fe(IV) could be observed as it subsequently reacted at a slower rate with cyanide to give Fe(III). This fact that in the cyanide reaction Fe(V) is faster than Fe(IV) which is faster than Fe(VI) suggests either that cyanide stabilizes the Fe(IV) oxidation state before forming the final Fe(III) product or that Fe(IV) is intrinsically less oxidizing than Fe(V). As no Fe(IV) transients are observed in our studies involving these oxysulfur species, then either the oxysulfur species exert no stabilizing influence on the Fe(IV) transient or the Fe(IV) is as reactive or even more reactive then Fe(V) is with SO_3^{2-} and $S_2O_3^{2-}$ or the pathway is a two-electron reduction of Fe(V) to Fe(III). The two-electron pathway for sulfite oxidation to sulfate is known ($E^0(SO_4^{2-}/SO_3^{2-}) = -0.092$ V[49]), and if Fe(V) can carry out this process leading to direct formation of Fe(III), then the standard reduction potential for the couple Fe(V)/Fe(III) is likely to be greater than −0.092 V in a basic medium. Independent experiments are needed to determine this value.

The rate constant, k_9, for reduction of $Fe^{VI}O_4^{2-}$ to $Fe^{V}O_4^{3-}$ by ${}^{\bullet}SO_3^-$ was determined to be higher than the rate constant, k_{13}, for reduction by $S_4O_6^{\bullet 3-}$. The redox potential for the couple

TABLE 1: $Fe^{VI}O_4^{2-}$ and $Fe^{V}O_4^{3-}$ Oxidation of Sulfite and Thiosulfate at pH = 11.4 and 22 °C

	k, M^{-1} s^{-1}	
substrate	Fe^{VI}	Fe^{V}
SO_3^{2-}	$(2.0 \pm 0.2) \times 10^1$	$(3.9 \pm 0.3) \times 10^4$
$S_2O_3^{2-}$	$(2.8 \pm 0.3) \times 10^0$	$(2.1 \pm 0.1) \times 10^3$

$SO_4^{2-}/^{\bullet}SO_3^-$ has been estimated in a basic medium ($SO_4^{2-} + H_2O + e^- \rightarrow {}^{\bullet}SO_3^- + 2OH^-$; $E = -2.47$ V[50]). The reported reduction potential may not be representing the reducing power of $^{\bullet}SO_3^-$ because its initial one-electron-transfer product is SO_3, followed by a hydrating step to SO_4^{2-}.[46] The formation of $Fe^{V}O_4^{3-}$ from one-electron reduction of $Fe^{VI}O_4^{2-}$ was clearly seen experimentally, and the variation in rates of reactions 9 and 13 may be correlated with the reduction potential difference in their corresponding products. The reducing character of $^{\bullet}SO_3^-$ has rarely been demonstrated in the literature because of the difficulty of producing $^{\bullet}SO_3^-$ in the presence of oxidants and SO_3^{2-} during normal pulse radiolysis experiments. Oxidants usually react with SO_3^{2-} before the production of $^{\bullet}SO_3^-$ could occur in the experiments. However, use of the premix pulse radiolysis technique in which reagents are mixed just before pulsing avoids such difficulties and the reduction of Fe(VI) by $^{\bullet}SO_3^-$ to Fe(V) (reaction 9) could be measured in the present study. The value of k_{13} is approximately 2 times less than the value of k_9, which indicates that the $S_4O_6^{\bullet 3-}$ radical has less reducing power than the $^{\bullet}SO_3^-$ radical. This is consistent with the reported reduction potentials of −1.07 and −0.63 V for the $S_4O_6^{2-}/S_4O_6^{\bullet 3-}$ and $SO_3^{2-}/^{\bullet}SO_3^-$ couples, respectively.[45,50,51]

The reactivity of $Fe^{V}O_4^{3-}$ with SO_3^{2-} and $S_2O_3^{2-}$ is compared with $Fe^{VI}O_4^{2-}$ (Table 1). The rate constants for $Fe^{VI}O_4^{2-}$ were estimated at pH 11.4 using reported values in the literature[36−39] and considering a first-order dependence on hydrogen ion concentrations. $Fe^{V}O_4^{3-}$ is approximately 3 orders of magnitude more reactive toward the oxysulfur ion than Fe(VI). The higher reactivity may be due to the partial free-radical character of Fe(V) ($Fe^{V}{=}O \leftrightarrow Fe^{IV}{-}O^{\bullet}$). The reaction of $Fe^{V}O_4^{3-}$ with SO_3^{2-} is an order of magnitude faster than with thiosulfate (Table 1). In studying the oxidation of SO_3^{2-} by $Fe^{VI}O_4^{2-}$, Goff and Murman[39] used a ^{18}O-enriched-$Fe^{VI}O_4^{2-}$ tracer to demonstrate that the oxygen is transferred from $Fe^{VI}O_4^{2-}$ to SO_3^{2-} to yield sulfate (SO_4^{2-}), a reaction product. It is possible that a similar step may also be occurring in the reaction of $Fe^{V}O_4^{3-}$ with SO_3^{2-}. However, direct transfer of oxygen from $Fe^{V}O_4^{3-}$ to the sulfur center of the $S_2O_3^{2-}$ would be hindered because of the extra S atom attached to the SO_3 moiety. This would thus lower the reactivity of $Fe^{V}O_4^{3-}$ with $S_2O_3^{2-}$ compared to SO_3^{2-} as was found in the present study (Table 1).

Overall, the rate study enhanced the understanding of the mechanism for the oxidation of nitrogen- and sulfur-containing substrates by $Fe^{VI}O_4^{2-}$.[16,18,52−54] An earlier proposed mechanism involves the formation of $Fe^{V}O_4^{3-}$ and a substrate radical species ($^{\bullet}$S) in the reaction of $Fe^{VI}O_4^{2-}$ with a substrate (S) (reaction 15). Subsequent steps in the mechanism include the reaction of $Fe^{VI}O_4^{2-}$ with $^{\bullet}$S (reaction 4) and the reaction of $Fe^{V}O_4^{3-}$ with a substrate to give a product (reaction 7). However, the radical species formed in reaction 15 may also self-decompose without reacting with $Fe^{VI}O_4^{2-}$ (reaction 16).

$$Fe^{VI}O_4^{2-} + S \rightarrow Fe^{V}O_4^{3-} + {}^{\bullet}S \qquad (15)$$

$$Fe^{VI}O_4^{2-} + {}^{\bullet}S \rightarrow Fe^{V}O_4^{3-} + \text{product} \qquad (4)$$

$$Fe^{V}O_4^{3-} + S \rightarrow \text{Fe(III)} + \text{product} \qquad (7)$$

$$2{}^{\bullet}S \rightarrow \text{products} \qquad (16)$$

The magnitude of k_4 is of the order of 10^8 M^{-1} s^{-1}, while the rate constant, k_7, is about 3 orders of magnitude higher than the value of k_{15}. The rate constants for reactions 4 and 16 are of similar orders of magnitude, but a large excess of $Fe^{VI}O_4^{2-}$ relative to the concentration of the produced radical ($^{\bullet}$S) ensures the occurrence of reaction 4 in the oxidation of a substrate by $Fe^{VI}O_4^{2-}$. After reaction 4 occurs, $Fe^{V}O_4^{3-}$ can easily react with a substrate to yield a product. Thus reaction 15 is the slow rate-determining step while reactions 4 and 7 are relatively fast steps, consistent with the proposed mechanism.[16,18,52−54] Furthermore, the inclusion of reactions 15, 4, 7, and 16 in the mechanism explains the observed reaction stoichiometry and products of the oxidation by $Fe^{VI}O_4^{2}$. In summary, data on the kinetics and products of the reactions studied in this paper support the mechanism given for the oxidation of substrates by $Fe^{VI}O_4^{2-}$.[16,18,52−54]

5. Conclusions

The spectral measurements on the reactivity of $Fe^{V}O_4^{3-}$ with oxy−sulfur species suggest a two-electron reduction process. However, if the reaction of Fe(IV) is faster than Fe(V), no spectrum of Fe(IV) as an intermediate would be observed. Hence, determination of the rates of Fe(IV) with such substrates are required independently to confirm a two-electron reduction of Fe^{V} to Fe^{III}. A previous study[31] with nitrogen-containing species, cyanide (CN^-), gave one-electron reductions of Fe^{V} to Fe^{IV} to Fe^{III}, which could be demonstrated spectroscopically. The reactivity of $Fe^{V}O_4^{3-}$ with studied oxy−sulfur species differs by an order of magnitude and is three orders of magnitude higher than that of $Fe^{VI}O_4^{3-}$. Future studies would include substrates of biological and environmental interests for better understanding the chemistry of $Fe^{VI}O_4^{2-}$ and $Fe^{V}O_4^{3-}$ with sulfur- and nitrogen-containing substrates.

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