Oxidation of Inorganic Compounds by Ferrate(VI) and Ferrate(V): One-Electron and Two-Electron Transfer Steps

V I R E N D E R   K .   S H A R M A *

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Ferrate(VI) ($Fe^{VI}O_4^-$, Fe(VI)) and ferrate(V) ($Fe^VO_4^{3-}$, Fe(V)) have a high oxidizing power and upon decomposition form a nontoxic byproduct, Fe(III), which makes them environmentally friendly oxidants in water and wastewater treatment. The kinetics of the reaction between Fe(VI) and I^- was determined using a stopped-flow technique. The second-order rate constants (k, M^{-1} s^{-1}) for the oxidation of I^- and other inorganic compounds by protonated ferrate(VI) ($HFe^{VI}O_4^-$) and ferrate(V) ($Fe^VO_4^{3-}$) ions were correlated with thermodynamic reduction potentials to understand the reaction mechanisms. A linear relationship was found between log k and 1-e^- reduction potentials for iodide, cyanides, and superoxide while oxy-compounds of nitrogen, sulfur, selenium, and arsenic demonstrated a linear relationship for 2-e^- reduction potentials. The estimated limits for the reduction potentials of the couple are $E^o(Fe^{VI}/Fe^V) \geq 0.76$ V and $E^o(Fe^{VI}/Fe^{IV}) \geq -0.18$ V. Conclusions drawn from the correlations are consistent with the mechanisms postulated from stoichiometries, intermediates, and products of the reactions. Implication of the kinetic results in treatment using ferrate(VI) is briefly discussed.

Introduction

High-valent iron-oxo species are well-known to be involved in iron enzymes, environmentally benign "super iron" batteries, green chemistry syntheses, Fenton-like chemistry, and applications for pollutant remediation (*1–7*). In recent years, iron in the +6 oxidation state, ferrate(VI) ($Fe^{VI}O_4^{2-}$, Fe(VI)) has been suggested as an alternative water-treatment oxidant. Examples include oxidation of endocrine disruptors and pharmaceuticals (*8–12*). Fe(VI) may address the concerns associated with currently used chemicals such as free chlorine, chloramines, and ozone. Like ozone, Fe(VI) does not react with the bromide ion; so carcinogenic bromate ion is not produced in the treatment of bromide-containing water (*13*). Another halide ion, I^-, can also react with either chlorine or ozone to ultimately produce iodinated disinfection byproducts (IDPBs) (*14*). However, kinetics studies have not been carried out to determine whether Fe(VI) contributes to IDPBs in iodide-containing waters. This paper thus presents the kinetics of the reaction between Fe(VI) and I^- ion.

Other high oxidation states of iron, ferrate(V) ($Fe^VO_4^{3-}$, Fe(V)) and ferrate(IV) (Fe(IV)), have been postulated as intermediates in the oxidation of inorganic and organic pollutants by Fe(VI) (*15–25*), but concrete evidence has not been given for the preference of the reactions for either of the intermediate iron species. In this paper, the values of rate constants, k (M^{-1} s^{-1}) for the oxidation of inorganic compounds (S) by protonated Fe(VI) species ($HFe^{VI}O_4^-$) were obtained by analyzing the second-order rate constants as a function of pH in the alkaline region. The correlations of k with 1-e^- and 2-e^- reduction potentials were sought to gain information on whether the reactions take place by either 1-e^- transfer (Fe(VI) → Fe(V)) to form a free radical intermediate or a 2-e^- transfer (Fe(VI) → Fe(IV)) in the rate determining steps.

A limited number of oxidation studies with Fe(V) have been conducted (*21, 26–29*). Fe(V) has much higher reactivity than Fe(VI) does and may oxidize pollutants that react sluggishly with Fe(VI). The correlations of rate constants with reduction potentials were also conducted on the reactivity of ferrate(V) with S to determine the electron transfer reactions of Fe(V) species. From the correlations with Fe(VI) and Fe(V), the limited potentials for redox couples ($HFe^{VI}O_4^-/Fe^{IV}$, $HFe^{VI}O_4^-/Fe^V$, Fe^V/Fe^{IV}, and Fe^V/Fe^{III}) were estimated for the first time. The given values are useful in understanding the mechanistic aspects of the ferrate(VI) and ferrate(V) reactions with pollutants.

Materials and Methods

The kinetic studies were performed using chemicals (Sigma, Aldrich) of reagent grade or better and were used without further purification. Water used in preparing solutions was distilled and then passed through an 18 MΩ cm Milli-Q water purification system. A solid potassium ferrate(VI) (K_2FeO_4) of high purity (+98%) was prepared using a Thompson et al. method (*30*). The solutions of Fe(VI) were prepared by adding solid samples of K_2FeO_4 to 0.005 M Na_2HPO_4/0.001 M borate at pH 9.0. A molar absorption coefficient of $\varepsilon_{510\ nm} = 1150$ M^{-1} cm^{-1} was used for the calculation of $[FeO_4^{2-}]$ at pH 9.0. A sodium iodide salt was dissolved in 0.01 M Na_2HPO_4 buffer solution to prepare iodide solution. Fe(V) was generated in the oxidation study, previously conducted, using a pulse radiolysis system (*31*).

A stopped-flow spectrophotometer (SX.18 MV, Applied Photophysics, U.K.) equipped with a photomultiplier (PM) detector was used to carry out the kinetics study. The concentrations of I^- in the experiments were in the range 0.01–0.10 M, while the concentration of Fe(VI) was kept at 5.0×10^{-5} M. Reactions were monitored by measuring the absorbance of Fe(VI) at 600 nm wavelength as a function of time. The kinetics curves were analyzed using the nonlinear least-squares algorithm within the SX.18 MV software. The temperature of the reaction was controlled at 25 ± 0.1 °C with a Fischer Scientific Isotemp 3016 circulating water bath. Nonlinear regression analysis of pH dependence of observed constants was performed using SigmaPlot 2001 software.

Results and Discussion

Kinetics. The kinetics study of the reaction between Fe(VI) and I^- was done under pseudo-first-order conditions in which concentration of I^- ion was in excess compared to ferrate(VI). The kinetics results are presented in Figure 1. The results on the reaction of Fe(VI) with Br^- are also given in Figure 1. The Br^- ion did not react with ferrate(VI) and is in agreement with an earlier report (*13*). However, I^- had an appreciable reactivity with ferrate(VI) (inset Figure 1). The rate of the reaction can be expressed as

$$-d[Fe(VI)]/dt = k[Fe(VI)]^m[I^-]^n \qquad (1)$$

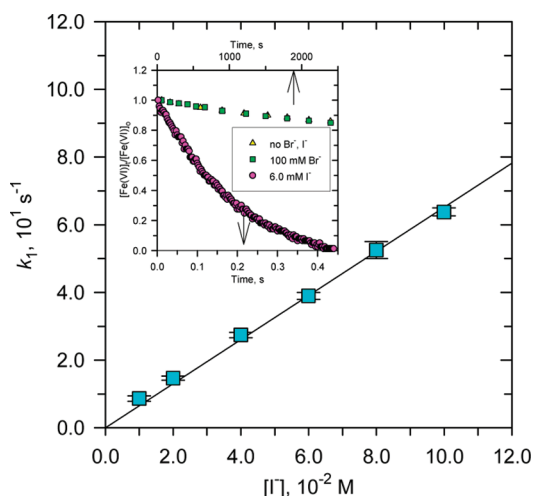* Phone: 321-674-7310; fax: 321-674-8951; e-mail: vsharma@fit.edu.

FIGURE 1. Observed pseudo-first-order rate constants as a function of [I⁻] at pH 8.5 and 25 °C. Inset: Decay of Fe(VI) concentration with and without the presence of halide ions.

where [Fe(VI)] and [I⁻] are the concentrations of Fe(VI) and I⁻, respectively; m and n are the orders of the reaction; and k is the reaction rate constant. Under pseudo-order condition, the eq 1 becomes

$$-d[\text{Fe(VI)}]/dt = k_1[\text{I}^-]^n \quad (2)$$

$$\text{where } k_1 = k[\text{Fe(VI)}]^m \quad (3)$$

The concentration of Fe(VI) versus time profile fits reasonably to a single-exponential decay curve, suggesting the reaction was first-order with respect to the concentration of Fe(VI) ($m = 1$). The pseudo-first-order rate constant (k_1) for the reaction was determined at different concentrations of I⁻ (Figure 1). The plot of k_1 with [I⁻] was linear. The slope of the log−log plot was determined as 0.91 ± 0.08; indicating that the rate law for the reaction is also first-order with respect to [I⁻] ($n = 1$). The observed rate law of the reaction of Fe(VI) and I⁻ may thus be written as

$$-d[\text{Fe(VI)}]/dt = k[\text{Fe(VI)}][\text{I}^-] \quad (4)$$

The second-order rate constant (k) was determined as $6.51 \pm 0.30 \times 10^2$ M⁻¹ s⁻¹ at pH 9.0 and 25 °C. The second-order rate law for oxidation of I⁻ by Fe(VI) is the same as has been found for a series of inorganic compounds, cyanides, superoxide, sulfide, ammonia, azide, and oxy-compounds of nitrogen, sulfur, selenium, and arsenic ($-d[\text{Fe(VI)}]/dt = k_{\text{obs}}[\text{Fe(VI)}][\text{S}]$) (16, 18, 19, 21, 23, 25, 32−34). Only in a few instances has deviation from the second-order kinetics been observed (25).

The rate of the reaction of Fe(VI) with I⁻ was determined as a function of pH (7.88−10.31) at 25 °C. The second-order rate constants (k_{obs}) decrease with increase in pH (Figure 2A). The values of k_{obs} as a function of pH for oxidation of other inorganic compounds have also been characterized by an increase with decrease in pH (Figure 2). The pH dependence of k for the reactions of Fe(VI) with S was quantitatively modeled by eq 5.

$$k[\text{Fe(VI)}][\text{S}]_{\text{tot}} = \Sigma k_{ij}\alpha_i\beta_j[\text{Fe(VI)}][\text{S}]$$
$$i = 1,2 \text{ and } j = 1,2 \quad (5)$$

α_i and β_j represent the respective species distribution coefficients for Fe(VI) and substrate; i and j represent each of two species of Fe(VI) and each of the two species of compound, and k_{ij} is the species-specific second-order rate constant for the reaction between the Fe(VI) species i with
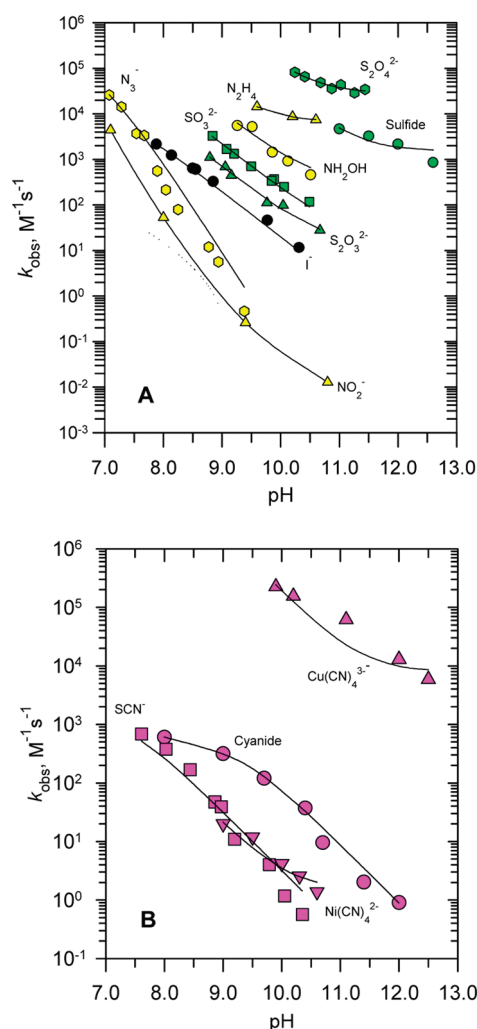

FIGURE 2. (A) Fe(VI) oxidation of sulfur and nitrogen-containing substrates (25 °C) and (B) Fe(VI) oxidation of cyanide (22 °C), Ni(II) cyanide (25 °C), thiocyanate (15 °C), and Cu(I) cyanide (15 °C). (Experimental data were taken from refs *16, 18, 19, 21, 23, 25,* and *32−34*.

the compound species j. In alkaline solutions, two types of Fe(VI) coexist (HFeO₄⁻ ⟷ H⁺ + FeO₄²⁻; pK_{a3} = 7.23 (35), therefore [Fe(VI)] = [HFeO₄⁻] + [FeO₄²⁻]. Most of the inorganic compounds used as substrates in this study exist as only one species (no equilibrium species), hence only two reactions of inorganic compounds with HFeO₄⁻ and FeO₄²⁻ were considered when modeling the reactions. Compounds with equilibrium species in the pH range of this study include hydrogen sulfide (H₂S ⟷ H⁺ + HS⁻; pK_a = 7.0), hydrogen cyanide (HCN ⟷ H⁺ + CN⁻; pK_a = 9.3), and hydrogen peroxide (H₂O₂ ⟷ H⁺ + HO₂⁻; pK_a = 11.4) (18, 19, 26). Of the possible four reactions, two of the reactions were eliminated by examining ionic strength dependence measurements for the oxidation of hydrogen sulfide and hydrogen cyanide (18, 19). The rate constants did not vary with the ionic strength, which suggests that one of the reactive species had no charge (H₂S and HCN). Based on this, the kinetic modeling was performed by considering the reactions of only neutral species with two species of Fe(VI).

In modeling the reactions, it was determined that the reactions between HFeO₄⁻ and S predominantly control the rates. This relates to the faster reaction of HFeO₄⁻ than FeO₄²⁻ with compounds. HFeO₄⁻ has a larger spin density on the oxo-ligands than does FeO₄²⁻, which increases the oxidation ability of protonated Fe(VI) (36). The rate constants, k(HFeO₄⁻ + S), were calculated based on the best fit of the experimental
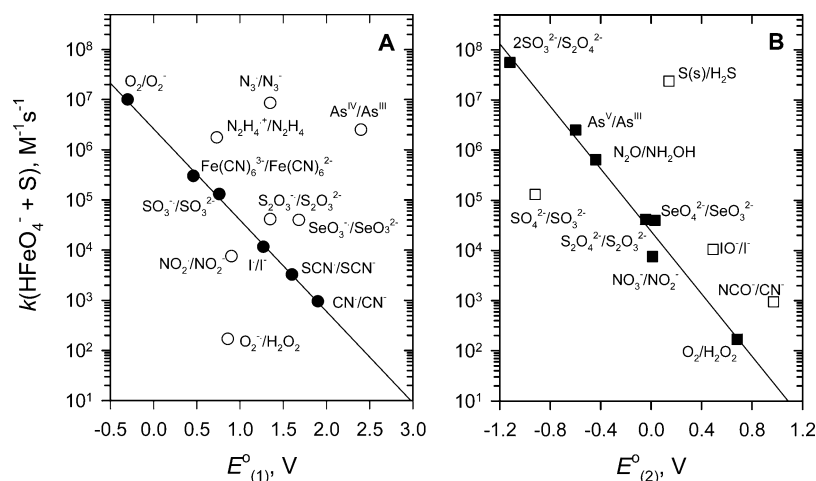
FIGURE 3. log *k* as a function of the standard one-electron reduction potential ($E_{(1)}^o$) (A) and standard two-electron reduction potential ($E_{(2)}^o$) (B) for the reaction of Fe(VI) with inorganic substrates at 25 °C.
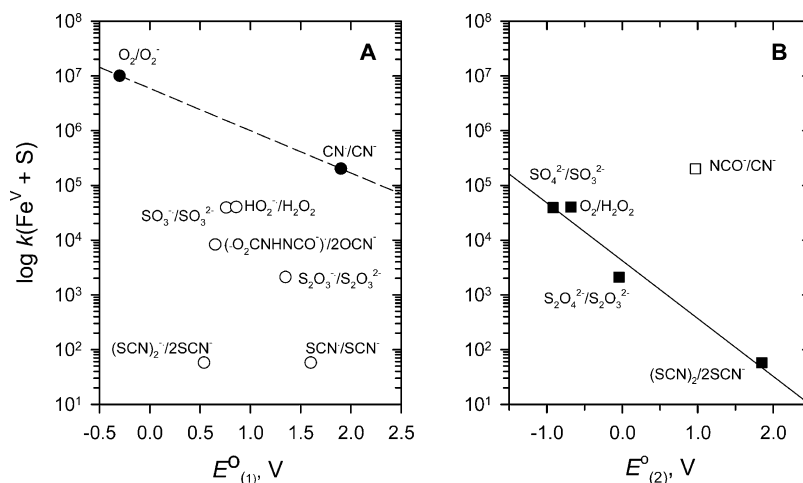

FIGURE 4. log *k'* as a function of $E_{(1)}^o$ (A) and $E_{(2)}^o$ (B) for reactions of Fe(V) (dashed line represents currently known 1-e⁻ intermediate, Fe(IV)).

data (Figure 2 and Table S1). In the case of hydrogen sulfide (Figure 2A) and Cu(CN)$_4$$^{3-}$ (Figure 2B), the fitted line deviated from some experimental data. It appears that second-order rate constants obtained at high pH and a low temperature (15 °C) had large errors to cause the deviations from the fitted lines (*18, 34*). In the case of hydrogen peroxide, a detailed pH study in the acidic to alkaline range has been performed and the species-specific rate constant for the oxidation of H$_2$O$_2$ by HFeO$_4$$^-$ was determined from a detailed kinetic analysis of the data (*26*).

Correlations of Rate Constants with Reduction Potentials. Electron transfer reactions should show a linear relationship between log *k* and the reduction potentials (*38*). These correlations are under thermodynamic limitations. Plots between log *k* and the standard 1-e⁻ and 2-e⁻ reduction potentials, $E_{(1)}^o$ and $E_{(2)}^o$ are linear for the compounds which have shown experimentally their preference of either 1-e⁻ or 2-e⁻ transfer steps (Figure 3, Table S1). The values of reduction potentials are relative to the standard reduction potential for hydrogen half reactions. The formation of Fe(V) in the reaction of Fe(VI) with O$_2$$^-$ was seen spectroscopically (*27*). Experimental results for oxidation of cyanides by Fe(VI) also demonstrated 1-e⁻ transfer step (*21, 39*). A linear relationship of log *k* with $E_{(1)}^o$ in Figure 3A is strong ($r^2 = 0.998$; $n = 6$; filled symbols). The oxy compounds of selenium, nitrogen, and sulfur have shown 2-e⁻ transfer processes, which agree with reaction stoichiometries and products (*16, 22−24*). The line drawn using $E_{(2)}^o$ for these compounds also had a strong

relationship with log *k* ($r^2 = 0.982$; $n = 7$). This is shown in Figure 3B in which filled symbols represent the relationship. Significantly, substrates with 2-e⁻ transfer process do not fall on the line when 1-e⁻ E^o for their redox pair was used (open symbols in Figure 3A), confirming their preference of oxidation by a 2-e⁻ transfer mechanism (e.g., Fe^{VI} + S → Fe^{IV} + S(O)). Similarly, substrates that undergo 1-e⁻ transfer reactions deviated from the linearity (open symbols in Figure 3B), which indicates their oxidation preference via a 1-e⁻ transfer process (e.g., Fe^{VI} + S → Fe^V + S•). These linear relationships clearly shown in Figure 3 are mathematically expressed as log k(1-e⁻) = 6.39 (±0.05) − 1.83(±0.04) $E_{(1)}^o$ and log k(2-e⁻) = 4.44 (±0.11) − 3.09(±0.19) $E_{(2)}^o$.

The rate constants for the reactions of Fe(V) with S (*k'*, M⁻¹ s⁻¹) are available for a few compounds (Table S2) and correlations of *k'* with redox potentials are shown in Figure 4. In the 1-e⁻ reduction of Fe(V), correlation was possible only for O$_2$$^-$ and CN⁻ (Figure 4A) in which experimental results confirmed the formation of transient Fe(IV) (*26, 27*). Significantly, 2-e⁻ transfer substrates, SO$_3$$^{2-}$, S$_2O_3$$^{2-}$, H$_2O_2$, and SCN⁻ did not show any relationship with the line in Figure 4A; however, these compounds had a reasonable linearity with the 2-e⁻ redox potential ($r^2 = 0.96$; $n = 4$) (Figure 4B). No intermediate Fe(IV) spectrum was seen in the reduction of Fe(V) by these compounds (*26, 29, 40*), which further supports the relationship in Figure 4B. The oxidation of CN⁻ by Fe(V) also deviated from a linearity in Figure 4B, which is consistent with the results for a 1-e⁻ transfer step
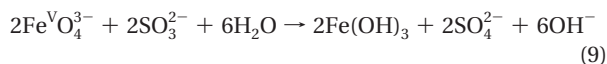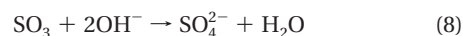
(Figure 4A). The NCO$^-$ had no relationship with 1-e$^-$ transfer oxidation by Fe(V) (Figure 4A) and is in agreement with experimental results. The linear expressions of Figure 4 are described as log k'(1-e$^-$) = 6.77 − 0.77$E_{(1)}$° and log k'(2-e$^-$) = 3.62($\pm$0.16) − 1.05($\pm$0.14) $E_{(2)}$°.

Mechanisms. In studying the reaction of Fe(VI) with O$_2^-$, the spectrum of the 1-e$^-$ reductive transient Fe^{V}O$_4^{2-}$ was observed (26), in agreement with the relationship suggested in Figure 3. The spectroscopic evidence for sequential 1-e$^-$ reduction of Fe(V) to Fe(IV) to Fe(III) by CN$^-$ in alkaline medium was provided earlier (27), which supports the oxidation of CN$^-$ by Fe(VI) and Fe(V) through a 1-e$^-$ transfer step to yield a free radical (Figure 3A and 4A). In the case of the oxidation of H$_2$S, a 1-e$^-$ transfer is the most likely step rather than a 2-e$^-$ oxidation to form sulfur (Figure 3). The radical formation in the oxidation of H$_2$S was proposed in describing the products of the reactions (18).

Using the values of k given in Table S1 for oxidation of Cu(CN)$_4^{3-}$ and Ni(CN)$_4^{2-}$ by Fe(VI), the E° for Cu(CN)$_4^{2-}$/Cu(CN)$_4^{3-}$ and Ni(CN)$_4^-$/Ni(CN)$_4^{2-}$ was calculated as −0.73 and 1.82 V, respectively. The value of E°(Cu(CN)$_4^{2-}$/Cu(CN)$_4^{3-}$) obtained from the k' for oxidation of Cu(CN)$_4^{3-}$ by Fe(V) (Table S2) and the linear equation of Figure 3A was −0.63 V. This is in reasonable agreement with the calculated value (−0.73 V) from the linear line in Figure 3A and is consistent with the linear line in Figure 4A using only two data points. However, the reported values of E° in acidic to neutral pH range conditions for reductions of Cu(CN)$_4^{2-}$ and Ni(CN)$_4^-$ are 0.66 and 1.15 V, respectively (41, 42). The differences in E° may be related to different solution conditions. Another possibility is that the metal center is not involved in the oxidation as was the case in the oxidation of the Fe(II)−cyanide complex (39) (Fe^{VI} + Fe(CN)$_6^{4-}$ → Fe^V + Fe(CN)$_6^{3-}$) (Figure 3A). An electron-transfer is probably occurring through the cyanide ligand, and the values of E°, obtained in the present study, may represent standard potentials of Cu(CN)$_3$CN$^{2-•}$/Cu(CN)$_4^{3-}$ and Ni(CN)$_3$CN$^{-•}$/Ni(CN)$_4^{2-}$ redox pairs.

The products of the reactions between Fe(VI) and oxy-compounds indicate a 2-e$^-$ transfer mechanism, which is also supported by the linearity of rates with 2-e$^-$ redox potentials of compounds (Figure 4). For example, AsO$_4^{3-}$ and SeO$_4^{3-}$ were the products of the reaction of Fe(VI) with AsO$_3^{3-}$ and SeO$_3^{3-}$ (16, 43). Also, the formation of As(IV) from AsO$_3^{2-}$ in a 1-e$^-$ transfer is not supported by the relationship in Figure 3 (open symbol). For the oxidation of NH$_2$OH, the identified oxidized product was N$_2$O (23, 24) and no oxygen transfer from an oxidant occurred, hence the reaction proceeded through the formation of the HNO intermediate (Fe^{VI} + NH$_2$OH → Fe^{IV} + HNO). Azide is also oxidized by a 2-e$^-$ transfer through the same intermediate to yield the observed products of the reaction, N$_2$ and N$_2$O (Fe^{VI} + N$_3^-$ → Fe^{IV} + NO$^-$ + N$_2$; 2 NO$^-$ + H$_2$O → N$_2$O + 2 OH$^-$) (23). The formation of N$_2$H$_2$ as an intermediate from the oxidation of N$_2$H$_4$ by Fe(VI) by 2-e$^-$ transfer was also experimentally confirmed (Fe^{VI} + N$_2$H$_4$ → Fe^{IV} + N$_2$H$_2$ + 2 OH$^-$) (22). The relationship in Figure 3B determined E° for N$_2$,NO$^-$/N$_3^-$ and N$_2$H$_2$/N$_2$H$_4$ as −0.81 and −0.58 V, respectively.

Figure 3 shows that k for the reaction between Fe(VI) and SO$_3^{2-}$ falls on the line for 1-e$^-$ transfer, but deviated from the 2-e$^-$ transfer process. This contradicts the 2-e$^-$ transfer mechanism presented earlier for the oxidation of SO$_3^{2-}$ by Fe(VI) (15, 16). An alternate mechanism involving a 1-e$^-$ rate determining step is described by reactions 6−9.

$$Fe^{VI}O_4^{2-} + SO_3^{2-} \rightarrow Fe^VO_4^{3-} + {}^•SO_3^- \tag{6}$$

$$Fe^{VI}O_4^{2-} + {}^•SO_3^- \rightarrow Fe^VO_4^{3-} + SO_3 \tag{7}$$

$$SO_3 + 2OH^- \rightarrow SO_4^{2-} + H_2O \tag{8}$$

$$2Fe^VO_4^{3-} + 2SO_3^{2-} + 6H_2O \rightarrow 2Fe(OH)_3 + 2SO_4^{2-} + 6OH^- \tag{9}$$

The individual reactions of this mechanism were recently confirmed independently by spectral and kinetic measurements (29). This mechanism suggests that two of the sulfates are produced in the reactions from the 2-e$^-$ transfer from Fe^{V}O$_4^{3-}$ and is therefore consistent with two-thirds ^{18}O enriched sulfate found in the study conducted with ^{18}O-enriched Fe^{VI}O$_4^{2-}$ (15). Moreover, 2-e$^-$ transfer is also supported by the correlation in Figure 4B. Overall, the products and intermediates of the oxidation of substrates by Fe(VI) and Fe(V) are in agreement with the strong linear relationships in Figures 3 and 4.

Finally, the rate constant, $k \approx 10^5$ M^{-1} s^{-1} for the reduction of FeO$_4^{2-}$ by Fe(II) was used to estimate the lower limits for the standard 1-e$^-$ and 2-e$^-$ reduction potentials using the relationships in Figures 3 and 4 (44). The values were estimated to be E°(Fe^{VI}/Fe^V) $\geq$ 0.76 V and E°(Fe^{VI}/Fe^{IV}) $\geq$ −0.18 V. The lower limit for the Fe^{VI}/Fe^V reaction potential is higher than is E° for Mn^{VII}/Mn^{VI} (0.56 V) in basic medium, which is reasonable because Fe(VI) is known to be a stronger oxidant than Mn(VII). The clear evidence of a 1-e$^-$ transfer reaction for Fe(V) suggests the E° for the Fe^V/Fe^{IV} couple is in the vicinity of 1.8 V (Figure 4A). However, if CN$^-$ forms a complex with Fe^{V}O$_4^{2-}$ prior to electron transfer, a lower E° than 1.8 V for the pair is possible. Similarly, a lower limit for the Fe^V/Fe^{III} redox pair from the oxygen transfer from Fe^{V}O$_4^{2-}$ to S$_2$O$_3^{2-}$ may be estimated as $\geq$ −0.044 V.

Implications. The nonreactivity of Br$^-$ with Fe(VI) may be explained using the relationships derived in Figure 3. The 1-e$^-$ and 2-e$^-$ standard reduction potentials for Br$^-$ are 2.00 (Br$^•$/Br$^-$) and 0.77 V (BrO$^-$/Br$^-$), respectively (45, 46). It seems that Fe(VI) could not overcome such potentials for either 1-e$^-$ or 2-e$^-$ transfer to cause oxidation of Br$^-$ by Fe(VI). The reaction of I$^-$ with Fe(VI) has a second-order rate constant, $k = 1.2 \times 10^4$ M^{-1} s^{-1}, which was calculated, considering HFeO$_4^-$ as the reactive species. Comparatively, second-order rate constants for the oxidation of I$^-$ by HOCl and ozone are 1.4×10^8 and 1.2×10^9 M^{-1} s^{-1}, respectively (45, 46). In chlorination, a 2-e$^-$ transfer produces an oxidized product (45). Ozone also oxidizes I$^-$ via an oxygen atom transfer to form hypoiodite (IO$^-$), which is in equilibrium with hypoiodous acid (HOI) (pK_a = 10.4) (14). The HOI/OI$^-$ species may undergo several reactions including disproportionation to iodate and iodide and the reaction with natural organic matter (NOM) to form iodo-organic compounds (14). Significantly, the oxidation of I$^-$ by Fe(VI) goes through a distinct mechanism of 1-e$^-$ transfer to give I$^•$ (Figure 3). This may have implications in the formation of disinfection byproducts for the oxidation of I$^-$ in water containing organic matter by Fe(VI). A detailed product analysis for the oxidation of I$^-$ by Fe(VI) and the kinetics of the reaction of Fe(V) with I$^-$ is needed to understand the mechanism and implications of the reaction between Fe(VI) and I$^-$.

The relationships given in Figures 3 and 4 provide a strong basis for systematic analysis of reaction mechanisms of electron transfer in the reactions of inorganic pollutants by Fe(VI) and Fe(V). The redox potentials for pairs can be estimated from the rate constants of the reactions or vice versa. The limited reduction potentials for pairs provide the possibility of distinguishing the inner- and outer-sphere oxidation of pollutants using calculations based on the Marcus theory.

Acknowledgments

Supporting Information Available

Tables consisting of reduction potentials and kinetic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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