Inorg. Chem. **1992**, *31*, 5140–5142

Kinetics and Mechanism of the Ferrate Oxidation of Sulfite and Selenite in Aqueous Media

Michael D. Johnson*,† **and Jonathan Bernard**

Department of Chemistry, Mount Allison University,
Sackville, New Brunswick E0A 3C0, Canada

Received May 27, 1992

Introduction

With the emergence of bioinorganic investigations into the reaction mechanisms of catalase, peroxidase, and cytP450, the importance of iron in its high oxidation states has become apparent.[1] For example, in catalase and peroxidase the formation of an iron(IV) intermediate, $(\mathrm{Porp})\mathrm{Fe}^{\mathrm{IV}}{=}\mathrm{O}$, has been postulated as a key step in their enzymatic activity.[2] For cytP450, the generation of an iron(IV) or iron(V) heme complex appears to be important in its catalytic cycle.[3] As a result of these biochemical studies, an interest in high-oxidation-state iron complexes has arisen in an attempt to model these metalloproteins.[4] In order to provide a basis for planning and interpreting these studies, a knowledge of the fundamental solution chemistry of iron in these oxidation states is necessary.

At present, the only high-oxidation-state complexes of iron which may be isolated as solids are ferrate salts, e.g., K_2FeO_4, where iron is present as iron(VI).[5] Potassium ferrate is prepared by the hypochlorite oxidation of ferric nitrate in strongly alkaline solution[6] and the potassium salt is stable indefinitely when kept dry. The ferrate ion has been shown to exist in aqueous media as the tetrahedral species FeO_4^{2-}.[7] Numerous spectroscopic studies of ferrate have been understaken to characterize this unusual ion and include ESR,[8] Mossbauer,[9] infrared,[10] and visible spectroscopy.[11] Redox potentials for this strong oxidant have been estimated in both acidic and basic media, 2.20 and 0.72 V, respectively.[12]

Surprisingly, the kinetics of ferrate reactions remain relatively unexplored. Bielski and co-workers have studied the reaction of ferrate with the hydrate electron and most recently with a series of amino acids.[13] Goff and Murmann determined the ^{18}O-exchange kinetics between ferrate and solvent water and demonstrated its structural integrity as a simple tetrahedral oxometalate in aqueous media.[7] In addition, they reported the first kinetic investigation of ferrate oxidation. The reductants studied were hydrogen peroxide and sulfite. Our recent reinvestigation into the sulfite reduction kinetics, however, have shown the early sulfite work to be incorrect. This is a report of our findings for the ferrate/sulfite system and an extension to the ferrate oxidation of selenite.

Experimental Section

Potassium ferrate, K_2FeO_4, was prepared by hypochlorite oxidation of ferric hydroxide according to the method of Thompson, Schreyer, and ockerman[6] and stored in a desiccator until needed. Typical purities of 94–97% were obtained upon recrystallization of the crude reaction product. Analyses were performed using the chromite method.[14]

Stock solutions of sulfite and selenite were prepared from recrystallized sodium sulfite and sodium selenite (Aldrich). Ionic strength was maintained with sodium perchlorate, and sodium phosphate buffers were used to control pH. The phosphate ion also prevented precipitation of ferric hydroxide, which is produced during the reduction process. Millipore water was used throughout. Bubbling with argon gas was used to remove dissolved oxygen from solution where indicated.

Kinetic Measurements. Kinetic measurements were made using a Durrum Model D-110 stopped-flow apparatus interfaced with a computerized data acquisition system. The observed rate constants were obtained from an exponential fit of the raw data utilizing a data-processing routine developed by the OLIS Corp. (Jefferson, GA). In all cases, at least a 10-fold molar excess of reductant over the ferrate was used to maintain pseudo-first-order conditions. The observation wavelength was 505 nm. Each rate constant is an average of three to five trials.

Results and Discussion

Oxidation of Sulfite. The reaction stoichiometry was determined and found to be 3:2 for sulfite to ferrate, respectively. This supports the overall reaction

$$2FeO_4^{2-} + 3SO_3^{2-} \rightarrow 2Fe(III) + 3SO_4^{2-}$$

as originally reported by Murmann and Goff.[7] No differences were found when atmospheric oxygen was excluded from the solutions. A redetermination of oxygen transfer was not undertaken, and the original measurements are assumed correct; i.e., two of the three sulfate ions produced during oxidation possess an oxygen originating from the ferrate ion.[7]

The kinetics of the sulfite/ferrate redox reaction were measured under pseudo-first-order conditions with sulfite in excess. As shown in Figure 1, at constant pH, a plot of k_{obs} versus $[SO_3^{2-}]$ was linear with a small positive y-intercept; see supplemental data for observed rate constants. The linear sulfite dependence indicates a first-order sulfite term in the rate law. Ferrate decomposition rates measured under identical solution conditions, without sulfite, agree with the value found for the y-intercept in the reduction studies. The intercept was therefore assigned to the rate constant for ferrate oxidation of solvent water in the absence of sulfite. No differences in rate constants were found when atmospheric oxygen was excluded.

The second-order sulfite rate constants measured at varying hydrogen ion concentrations are shown in Figure 2. A first-order dependence on hydrogen ion is observed with the zero y-intercept, indicating no hydrogen ion independent term present. A rate law may be written as follows:

$$\frac{-d[\mathrm{Fe(VI)}]}{dt} = k_{\mathrm{SO_3}}[FeO_4^{2-}][SO_3^{2-}][H^+]$$

The value for $k_{\mathrm{SO_3}}$ is $(1.8 \pm 0.2) \times 10^{12}\ \mathrm{M^{-2}\ s^{-1}}$. A mechanism consistent with this rate law is shown in Scheme I. In this scheme, reaction I-2 is the rate-determining step and all others are assumed to be rapid. Due to its transient nature, no determination of the preequilibrium constant for the ferrate/sulfite dimerization reaction was feasible; therefore, no direct evaluation of k_2 ($k_{\mathrm{SO_3}} = k_1k_2/k_{-1}$) is possible. Dimeric intermediates similar to the one proposed in reaction I-1 have been demonstrated in analogous

---

[†] Present address: Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88001.

(1) Dunford, H. B. *Advances in Inorganic Biochemistry*; Elsevier: Amsterdam, 1982; Vol. 4, pp 41–68.

(2) Weiss, R. *J. Chem. Soc., Chem. Commun.* **1986**, 93.

(3) Groves, J. T. *J. Chem. Educ.* **1985**, *62*, 928.

(4) Hashemoto, S.; Talsumo, Y.; Kitogawa, T. *J. Am. Chem. Soc.* **1987**, *109*, 8096. Di Nello, R. K.; Dolphin, D. *Biochem. Biophys. Res. Commun.* **1979**, *86*, 190.

(5) Audette, R. J.; Quail, J. W. *Inorg. Chem.* **1972**, *11*, 1904.

(6) Thompson, G. W.; Ockerman, L. T.; Schreyer, J. M. *J. Am. Chem. Soc.* **1951**, *73*, 1379.

(7) Goff, H.; Murmann, R. K. *J. Am. Chem. Soc.* **1971**, *93*, 6058. Hoppe, M. L.; Schlemper, E. O.; Murmann, R. K. *Acta Crystallogr.* **1982**, *B38*, 2237.

(8) Carrington, A.; Ingram, D. J. E.; Schonlard, D. S.; Symons, M. C. R. *Proc. R. Soc. London, A* **1960**, *254*, 101.

(9) Ito, A.; Ono, K. *J. Phys. Soc. Jpn.* **1969**, *26*, 1548; *Chem. Abstr.* **1969**, *71*, 54882.

(10) Griffith, W. *J. Chem. Soc. A* **1966**, 1467.

(11) Carrington, A.; Schonlard, D. S.; Symons, M. C. R. *J. Chem. Soc.* **1957**, 659.

(12) Wood, R. H. *J. Am. Chem. Soc.* **1958**, *80*, 2038.

(13) Bielski, B. H. J.; Thomas, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 7761. Bielski, B. H. J.; Thomas, M. J. *Inorg. Chem.* **1989**, *28*, 3947. Bielski, B. H. J.; Sharma, V. K. *Inorg. Chem.* **1991**, *30*, 4306.

(14) Schreyer, J. M.; Thompson, G. W.; Ockerman, L. T. *Anal. Chem.* **1950**, *22*, 1426.

0020-1669/92/1331-5140$03.00/0

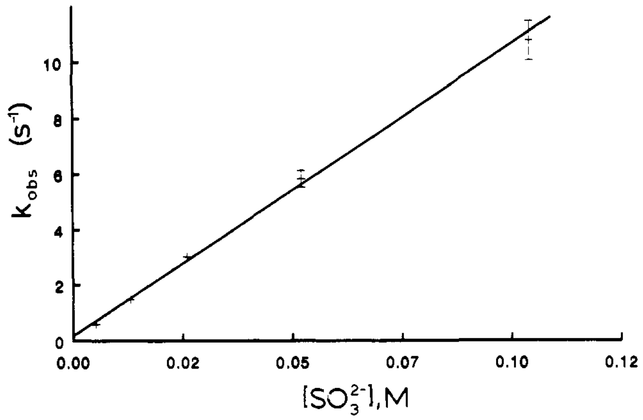

Figure 1. Plot of k_{obs} (M^{-1} s^{-1}) versus $[SO_3^{2-}]$ for ferrate oxidation of sulfite. Conditions: $T = 25.0$ °C, $I = 1.0$ M ($NaClO_4$).

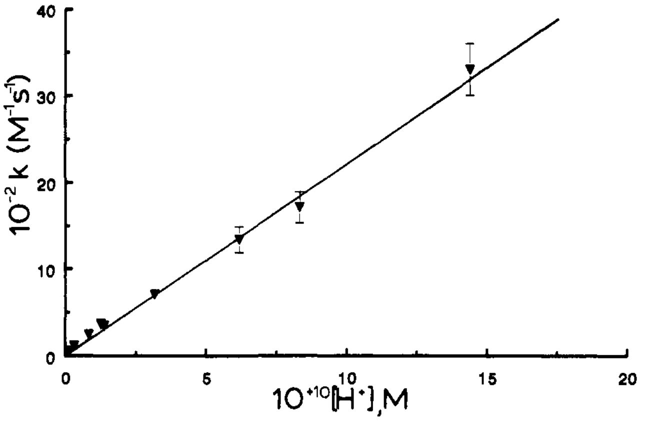

Figure 2. Plot of k versus $[H^+]$ for ferrate oxidation of sulfite. Conditions: $T = 25.0$ °C, $I = 1.0$ M ($NaClO_4$).

chromate oxidation reactions.[15,16] Attempts to observe this intermediate using rapid-scanning spectrophotometry were unsuccessful.

Scheme I

$$HSO_3^- + FeO_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_3Fe{-}O{-}SO_3H^{3-} \qquad (I\text{-}1)$$

$$O_3Fe{-}O{-}SO_3H^{3-} \xrightarrow{k_2} Fe(IV) + SO_4^{2-} \qquad (I\text{-}2)$$

$$Fe(IV) + HSO_3^- \xrightarrow{k_3} Fe(II) + SO_4^{2-} \qquad (I\text{-}3)$$

$$Fe(IV) + Fe(II) \xrightarrow{k_4} 2Fe(III) \qquad (I\text{-}4)$$

The ^{18}O-enriched-ferrate tracer studies reported by Murmann and Goff are consistent with Scheme I. The dimerization and redox reaction in steps I-1 and I-2 provide for direct transfer of an oxygen from ferrate(VI) to the sulfur center. Reaction I-3 must proceed via either an outer-sphere mechanism to produce sulfate with oxygens incorporated from the solvent water or an inner-sphere mechanism where ferrate(IV) is extremely labile and normalizes its oxygen prior to oxidation of another sulfite. Overall, this scheme requires that two sulfates must be produced via eq I-2 and one via eq I-3 to give the two-thirds ^{18}O enrichment found by Murmann and Goff.

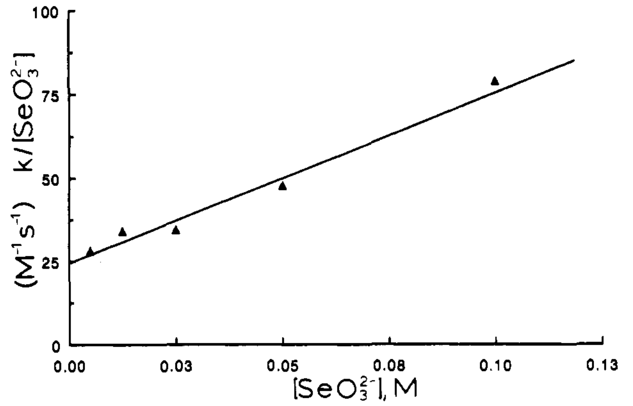

Figure 3. Typical plot of $k/[SeO_3^{2-}]$ versus $[SeO_3^{2-}]$. Conditions: $T = 25.0$ °C, $I = 1.0$ M ($NaClO_4$), pH = 8.44.

This rate law and mechanism, however, disagree with those originally proposed by Murmann and Goff. Their kinetic data indicated the following rate law

$$\text{rate} = k[FeO_4^{2-}][SO_3^{2-}]^2$$

Unfortunately, they reported no detailed hydrogen ion dependence in their study although, qualitatively, larger rate constants were obtained at lower pH's.

In the present study, dilute ferrate and sulfite solutions were mixed together in a stopped-flow apparatus to initiate the reaction. Murmann used small amounts of very concentrated ferrate solutions which were rapidly injected with a syringe into a spectrophotometer cuvette containing a buffered sulfite solution.[17] Perhaps another iron(VI) species was present in their concentrated ferrate stock solution, such as an iron(VI) dimer,[18] which oxidized the sulfite before dissociation could occur. Also, small amounts of periodate were added to stabilize their ferrate solutions and this could have affected their kinetic data. All attempts at reproducing their observations using the above modifications however were unsuccessful in our hands. In each attempt, a first-order sulfite dependence was obtained.

Although it remains uncertain why these two studies differ, one possible explanation is that their hydrogen ion concentrations were not maintained constant for each sulfite concentration in a series. This would lead to an incorrect form of the rate law if the pH dropped upon increasing sulfite concentrations. Although this variation would lead to an incorrect rate law, it should not invalidate their oxygen-transfer study.

Oxidation of Selenite. In order to further explore the reaction kinetics of the ferrate ion, the oxidation of selenite was also investigated. In the presence of excess selenite, a 3:2 ratio of selenite to ferrate was found over the pH range studied. The following reaction may be written:

$$2FeO_4^{2-} + 3SeO_3^{2-} \rightarrow 2Fe(III) + 3SeO_4^{2-}$$

This is consistent with oxidation of selenite by other strong oxidants such as hydrogen peroxide, permanganate, and chlorate, which all give selenate as the only reaction product.[19]

The reaction rates were measured under conditions similar to those for sulfite. Plots of k_{obs} versus the selenite concentration were linear at high pH's but showed significant upward curvature at pH's less than 9; see supplemental data for observed rate constants. Plotting $k_{obs}/[SeO_3^{2-}]$ versus $[SeO_3^{2-}]$ for these data sets gives a straight line (see Figure 3), indicating a first- and a

---

(15) Mason, E. G.; Kowalak, A. D. *Inorg. Chem.* **1963**, *2*, 1218.

(16) Haight, G. P.; Richardson, D. C.; Coburn, N. H. *Inorg. Chem.* **1964**, *3*, 1777.

(17) Murmann, R. K. Personal communication.

(18) Carr, J. D.; Kelter, P. B.; Tabatabai, A.; Spichal, D.; Erickeson, J.; McLaughlin, C. W. *Proc. Conf. Water Chlorination Chem. Environ. Impact Health Eff.* **1985**, 1285.

(19) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

Table I. Ferrate–Selenite Rate Data at Varying pH's[a]

pH	k_a (M^{-1} s^{-1})	k_b (M^{-2} s^{-1})
8.44	25 ± 2	500 ± 50
8.52	15 ± 1	310 ± 20
8.65	14 ± 1	100 ± 10
8.80	9.8 ± 1	96 ± 8
8.93	6.7 ± 0.5	37 ± 4
9.52	1.6 ± 0.1	
9.90	0.55 ± 0.03	
10.25	0.37 ± 0.02	
10.73	0.13 ± 0.01	

[a] Conditions: T = 25 °C, I = 1.0 M ($NaClO_4$), [phosphate buffer] = 0.05 M, $[FeO_4^{2-}] = 2 \times 10^{-4}$ M.

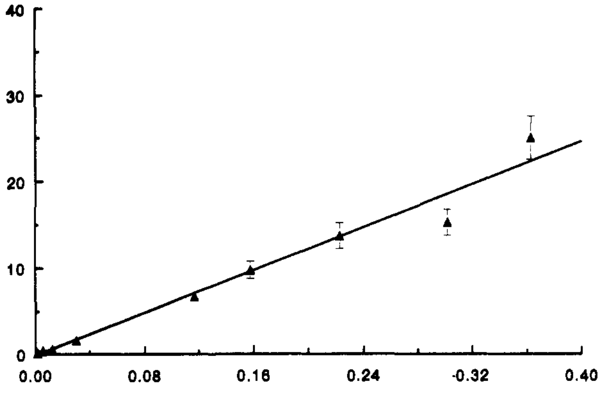

Figure 4. Plot of k_a versus $[H^+]$ for ferrate oxidation of selenite. Conditions: T = 25.0 °C, I = 1.0 M ($NaClO_4$).

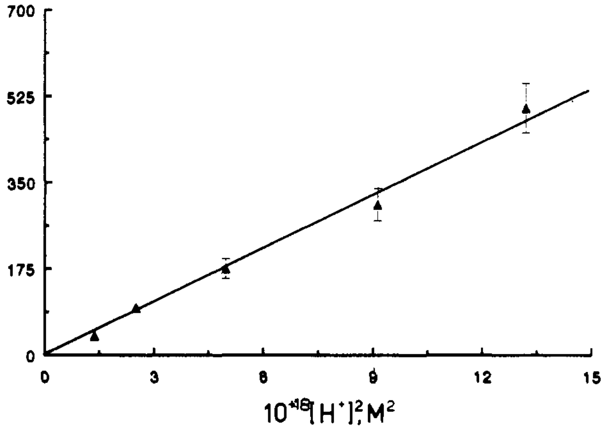

Figure 5. Plot of k_b versus $[H^+]^2$ for ferrate oxidation of selenite. Conditions: T = 25.0 °C, I = 1.0 M ($NaClO_4$).

second-order term in selenite. The following rate law may be written (see Table I for rate constants):

$$\frac{-d[Fe(VI)]}{dt} = k_a[FeO_4^{2-}][SeO_3^{2-}] + k_b[FeO_4^{2-}][SeO_3^{2-}]^2$$

Simple first- and second-order hydrogen ion dependences were found for k_a and k_b, respectively (see Figures 4 and 5). An overall rate law may be written as follows. Values for k_{SeO_3} and k_{SeO_3}' are (6.2 ± 0.1) × 10^9 M^{-2} s^{-1} and (3.8 ± 0.2) × 10^{19} M^{-3} s^{-1}.

$$\frac{-d[Fe(VI)]}{dt} = k_{SeO_3}[FeO_4^{2-}][SeO_3^{2-}][H^+] + k_{SeO_3}'[FeO_4^{2-}][SeO_3^{2-}][H^+]^2$$

In light of the mechanistic details for the sulfite oxidation and the rate law determined for this system, Scheme II is proposed. As for the sulfite study, no determination of the ferrate/selenite preequilibrium constant was possible; therefore, no evaluation of k_2 and k_3 may be made.

Scheme II

$$HSeO_3^- + FeO_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_3Fe\text{–}O\text{–}SeO_3H^{3-} \quad \text{(II-1)}$$

$$O_3Fe\text{–}O\text{–}SeO_3H^{3-} \xrightarrow{k_2} Fe(IV) + SeO_4^{2-} \quad \text{(II-2)}$$

$$O_3Fe\text{–}O\text{–}SeOH_3^{3-} + HSeO_3^- \xrightarrow{k_3} Fe(II) + 2SeO_4^{2-} \quad \text{(II-3)}$$

$$Fe(IV) + HSeO_3^- \xrightarrow{k_4} Fe(II) + SeO_4^{2-} \quad \text{(II-4)}$$

$$Fe(IV) + Fe(II) \xrightarrow{k_5} 2Fe(III) \quad \text{(II-5)}$$

The one major difference from the sulfite reaction mechanism (Scheme I) that is present in Scheme II involves the reaction of the Fe(VI)–SeO_3 dimer with another selenite rather than solely undergoing internal redox to form selenate and an Fe(IV) intermediate. Considering the large difference in the reduction potentials of the sulfate/sulfite and selenate/selenite couples, this modification of reaction pathways is not unreasonable. Sulfite is much more easily oxidized ($E°$ = 0.92 V) than selenite ($E°$ = –0.03 V)[20] and should undergo rapid internal redox rather than reacting with another sulfite ion. In contrast however, the poorer reducing ability of selenite would impart sufficient stability to the Fe(VI)–selenite dimer intermediate and allow it to react with another selenite ion rather than exclusively undergoing internal electron transfer (eq II-2). If oxygen transfer occurs in the selenite/ferrate reaction as it does for sulfite, then eq II-3 would be expected to proceed via an outer-sphere mechanism to provide the same ^{18}O-enrichment ratio found in the sulfite study. Reaction II-4 provides an alternative route for the reduction of Fe(IV) to Fe(II) at low pH's, where reaction II-3 is insignificant.

In each of the above reaction schemes, the proton term in the corresponding rate laws may be associated with protonation of either reactant. The K_a's for ferrate, sulfite, and selenite are 5 × 10^{-8},[18] 1.0 × 10^{-7},[21] and 5 × 10^{-8},[22] respectively, and the similarity of these dissociation constants results in typical proton ambiguity. Since protonation of an oxidant, e.g., chromate and permanganate, often increases its reactivity,[20] it might be postulated that $HFeO_4^-$ is the protonated species.

If the same ion is protonated in steps II-1 and II-3, however, the $[H^+]$ and $[H^+]^2$ terms in the selenite rate law favor hydrogen selenite as the reactive species. Possible diprotonation of the ferrate ion is an unlikely explanation for the $[H^+]^2$ term, since the dissociation constant for H_2FeO_4 is 2.5 × 10^{-4},[18b] putting this equilibrium well outside the pH range studied to be a significant contributor. Considering the similarity of the reaction schemes for both sulfite and selenite, it is tempting to also postulate hydrogen sulfite as the reactive sulfur species.

Acknowledgment. The authors wish to acknowledge the Natural Sciences and Engineering Research Council of Canada for an operating grant. J.B. thanks the Mount Allison University Research Committee for providing undergraduate summer support. Dr. R. Kent Murmann is kindly thanked for his helpful commentary during this work.

Supplementary Material Available: Tables listing observed rate constants and stoichiometric results (4 pages). Ordering information is given on any current masthead page.

---

(20) *Handbook of Biochemistry and Molecular Biology*, 3rd ed.; CRC Press: Cleveland, OH, 1976; Physical and Chemical Data Vol. 1, pp 122–129.

(21) Harris, G. M.; van Eldik, R. *Inorg. Chem.* **1980**, *19*, 880.

(22) Gmelin. *Handbuch der Anorganischen Chemie*; Verlag Chemie, GMBH: Weinheim/Bergstr., Germany, 1960; System No. 9, Part B2, p 466.