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Kinetics and Mechanism of the Ferrate Oxidation of Thiosulfate and Other Sulfur-Containing Species

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The kinetics of the reaction of ferrate, FeO_4^{2-}, with several sulfur-containing species in aqueous media have been investigated, and the results are reported. It was found that, when the reductant is in excess, ferrate rapidly oxidizes thiosulfate to sulfite, benzenesulfinate to benzenesulfonate, methionine to its corresponding sulfoxide, and dimethyl sulfoxide to dimethyl sulfone. The rate law for each reaction is first order with respect to each reactant and first order with respect to the hydrogen ion concentration. A mechanism for each oxidation reaction is discussed.

Introduction

Although the ferrate ion, FeO_4^{2-}, has been known for over a century, its chemistry remains relatively unexplored. In view of its potential utility in environmental and synthetic applications, one goal of this laboratory is to develop the chemistry of this unusual oxidation state of iron. We have begun a series of studies on the redox kinetics of ferrate with a variety of substrates.[1]

Ferrate is a tetrahedral ion, is isostructural with chromate or manganate,[2] and is a strong oxidant as well (0.9 and 1.9 V (vs NHE) in basic and acidic media, respectively).[3] The oxidations of a few organic substrates have been reported, all from a synthetic perspective. Although from its redox potentials and structure one might anticipate its chemistry to be essentially identical with that of permanganate or chromate, there are significant differences in its reactivity. Aqueous potassium ferrate oxidizes alcohols to aldehydes or ketones,[4] thiols to disulfides or sulfonic acids,[5] aromatic amines to azo compounds,[6] and 1° aliphatic amines deaminate to form aldehydes.[4] The products and yields of all these reactions depend upon reaction times and conditions. Surprisingly, however, ferrate is unreactive toward addition across double or triple bonds. Such distinct reaction preferences should make ferrate an important and selective oxidant for synthetic organic studies.

To date, only a handful of kinetic studies of ferrate oxidations have appeared in the literature.[7−11] Goff and Murmann[7] reported the first kinetic investigation in 1974 for the ferrate oxidation of hydrogen peroxide and sulfite. Their sulfite work has been recently reinvestigated by Johnson,[8] and his results were different from those originally reported. In addition, Johnson reported the oxidation of selenite and found evidence for a quasi-stable ferrate/selenite-bridged intermediate. Bielski and co-workers have reported the ferrate oxidation of amino acids[11] and a pulse-radiolytic study[10] of the ferrate reduction by the hydrated electron to form Fe^{V}_{aq}. Most recently Johnson and Hornstein have reported the oxidation of hydrazine and monomethylhydrazine to molecular nitrogen:[9,12]

$$FeO_4^{2-} + N_2H_4 \rightarrow N_2 + Fe^{II} \qquad (1)$$

$$FeO_4^{2-} + CH_3N_2H_3 \rightarrow N_2 + CH_3OH + Fe^{II} \qquad (2)$$

For these reactions, diazene intermediates were postulated on the basis of the reduction of an unsaturated carboxylic acid using ferrate and hydrazine.

This paper reports the kinetics for the oxidation of thiosulfate, benzenesulfinate, dimethyl sulfoxide, and methionine with ferrate in basic media. Mechanisms for these oxidation reactions are also presented.

Experimental Section

Materials. Sodium thiosulfate, sodium benzenesulfinate, dimethyl sulfoxide, and methionine were purchased from Aldrich Chemicals and used without further purification. The thiosulfate was standardized by iodometric titration. All other chemicals were of reagent grade.

Potassium ferrate was prepared by the method reported by Thompson, Ockermann, and Schreyer.[13] The crude product was recrystallized and the purity checked by spectrophotometric analysis at 505 nm (ϵ = 1100 M^{-1} cm^{-1}).[14] Purities up to 95% were obtained, and the measured rates were found to be independent of the sample purity.

Stock solutions of the reductants were prepared using deionized water. Ionic strength was maintained with sodium perchlorate, and sodium phosphate buffers were used to control pH. The phosphate ion also prevented precipitation of iron hydroxides, which are produced

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during the reduction process. Solutions were bubbled with argon gas for 15 min to remove dissolved oxygen from solution prior to kinetic measurements.

Kinetic Measurements. The reaction rates were measured spectrophotometrically using a D110 Durrum spectrophotometer with an OLIS computer interface. The reactions were monitored at 505 nm under pseudo-first-order conditions with the reductant in at least 10-fold excess. Typical reductant ranges were between 0.05 and 0.002 M. Absorbance changes were fitted using an OLIS data fitting routine. Each rate constant is an average of three to five trials. The temperature was controlled to within 0.1 °C. For determination of the activation parameters, five to seven temperatures ranging from 12 to 34.0 °C were used. All studies were conducted using 0.05 M phosphate buffers ($I = 1.0$ M $NaClO_4$) to control pH and to prevent any precipitation of iron hydroxide/oxides by complexation of the iron final product. No effect on the observed rate constants was found between the phosphate concentrations of 0.01 and 0.05 M. The ferrate concentrations were between 1×10^{-4} and 5×10^{-4} M.

The rapid-scan spectrophotometer used was a Harrick rapid-scan monochromator interfaced with a Durrum stopped-flow spectrometer. The data collection and manipulation system was designed by the OLIS Corporation.

IR measurements were made using a Perkin-Elmer 1720X FT-IR spectrometer. UV−vis measurements were made on an HP diode array spectrophotometer.

Results and Discussion

Oxidation of Thiosulfate. Stoichiometry. Thiosulfate rapidly reduces ferrate in aqueous media, and when the reduction is carried out under phosphate-buffered (basic) aerobic conditions, no ferric oxy hydroxides precipitate from solution. The presence of Fe(III) was demonstrated by the addition of potassium thiocyanate to the spent solutions to form the red ferric thiocyanate complex. When oxygen was excluded, Fe(III) was again the only iron species found.

As a check for the production of sulfate as the final product, barium chloride was added to the spent, filtered solutions where thiosulfate was kept in excess (no phosphate buffer used). Under the experimental concentrations where barium sulfite would remain in solution but barium sulfate would precipitate, no precipitate of barium sulfate was observed upon oxidation of thiosulfate with ferrate. On the basis of earlier work,[8] the reaction with sulfite will be slower than the thiosulfate reaction under the conditions of this study; therefore, conversion of the sulfite to sulfate would not be observed. When ferrate is used in slight excess, however, a white precipitate is immediately formed upon treatment of the spent solution with aqueous barium chloride. This suggests the subsequent oxidation of sulfite to sulfate.

To confirm the presence of sulfite, malachite green was added to the reaction mixtures. Sulfite preferentially decolorizes malachite green by formation of an addition compound.[15] Tests of spent ferrate/thiosulfate reaction mixtures immediately gave a positive spot test for the presence of sulfite. As a check for possible interferences, ferric ion, thiosulfate, sulfate, nor tetrathionate decolorized malachite green.

A [1.3(±0.2)]:1 stoichiometry was determined for ferrate to thiosulfate by rapid mixing of known ratios of thiosulfate and ferrate until the purple color of ferrate no longer rapidly disappears and sulfate does not appear, since sulfite is also oxidized by ferrate. Such strictures provide difficulties in obtaining a good end point in the "titration" method; therefore, attempts to quantify the amount of sulfite produced by this reaction were undertaken. Spectrophotometric quantification of the malachite green reaction with the sulfite produced also supports complete conversion of thiosulfate to sulfite. The stoichiometry is pH independent between 7.5 and 11.0. On the basis of the above information, the following reaction may be written:

$$14H^+ + 4FeO_4^{2-} + 3S_2O_3^{2-} \rightarrow 4Fe^{3+} + 6SO_3^{2-} + 7H_2O \quad (3)$$

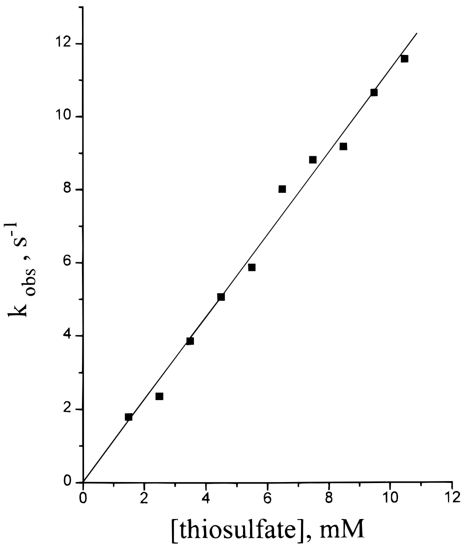

Figure 1. Typical plot of k_{obs} versus [thiosulfate]. Conditions: pH 8.5, $T = 25.0$ °C, $I = 1.0$ M ($NaClO_4$), 0.05 M (Na phosphate) buffer.

Tetrathionate and dithionate are also logical oxidation products on the basis of other reactions of thiosulfate with strong oxidants. If tetrathionate were produced, however, the stoichiometry would be 3:1, and if dithionate were formed, a stoichiometry of 1:2 would be observed, both of which are well outside the experimental error of this study. In fact, the 1.3:1 stoichiometry indicates that these are not produced to any significant extent in side reactions. Qualitative tests show that tetrathionate is only slowly oxidized by ferrate (minutes) and dithionate is not oxidized at all. As far as we are aware, this represents the only example of direct thiosulfate oxidation to sulfite.

Kinetics. The reaction kinetics were studied anaerobically, under pseudo-first-order conditions. Absorbance decreases for the loss of ferrate fit nicely to a single-exponential decay. Figure 1 shows a typical plot of the observed rate constants versus the thiosulfate concentration at pH 8.5. The linear dependence indicates a first-order term in thiosulfate for the rate law, and the slope is the observed second-order rate constant. Unlike other ferrate oxidations, no positive intercept (approximately 0.1−0.2 s^{-1} due to ferrate decomposition in the absence of reductant at this pH) was observed. This is because the thiosulfate reaction is very rapid compared with the rate of ferrate decomposition. The plots of k_{obs} versus [reductant], however, do show significant y intercepts at pHs approaching the pK_a of ferrate. This is due to the competitive pathway for the oxidation of water and makes measurement of reaction rates through the pK_a of ferrate difficult, particularly for slow redox reactions.[7,8] Hydrogen ion concentrations were kept constant with the use of phosphate buffers. No significant differences in rate were observed upon changing phosphate buffer concentrations.

Figure 2 shows a plot of the observed second-order rate constants versus the hydrogen ion concentration. The linear dependence on H^+ with a zero y intercept indicates a first-order

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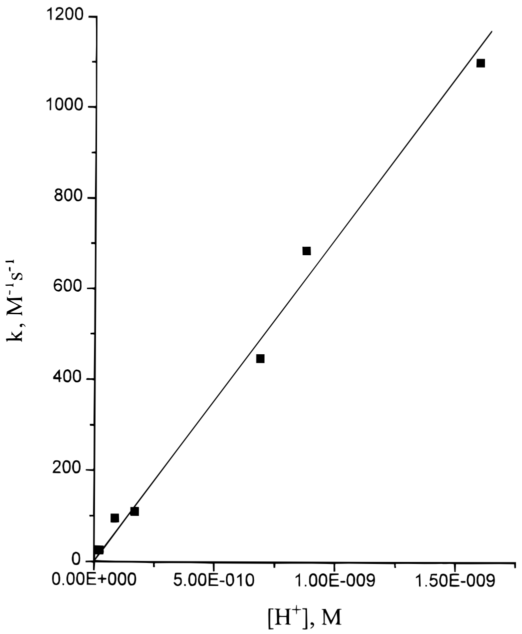

Figure 2. Hydrogen ion dependence on the rate of the thiosulfate/ferrate reaction. Conditions: $T = 25.0$ °C, $I = 1.0$ M ($NaClO_4$), 0.05 M (Na phosphate) buffer.

term in H^+ and no acid-independent term. An observed rate law may be written as

$$-d[Fe(VI)]/dt = k_0[H^+][FeO_4^{2-}][S_2O_3^{2-}] \quad (4)$$

The value for k_0 is $(7.1 \pm 0.2) \times 10^{11}$ M^{-2} s^{-1} at 25 °C and $I = 1.0$ M ($NaClO_4$). This value is similar to that for the ferrate oxidation of sulfite, 1.8×10^{12} M^{-2} s^{-1}.[8] A study of the temperature dependence provides the activation parameters 18.0 ± 3.5 kJ mol^{-1} and 42 ± 20 J mol^{-1} K^{-1} for ΔH^* and ΔS^*, respectively.

Mechanism. The rate law shows a single proton-dependent pathway for the oxidation of thiosulfate by ferrate ion. Since the protonation of thiosulfate does not occur in the pH range studied, it is safe to assume the dependence is due to the protonation of ferrate itself. Since ferrate is a stronger oxidant upon protonation, the reaction rate would be expected to increase.

On the basis of its reactions with sulfite, where ferrate acts as a two-electron oxidant and as an oxygen transfer agent, the reaction mechanism given in Scheme 1 for the oxidation of thiosulfate is proposed. The charges are not balanced, since the nature of the Fe(IV) moiety has yet to be characterized, although its existence in aqueous media has been established by Bielski and co-workers.[10a]

Scheme 1

$$HFeO_4^- \underset{}{\overset{K_a}{\rightleftharpoons}} FeO_4^{2-} + H^+ \quad (I.1)$$

$$HFeO_4^- + S_2O_3^{2-} \xrightarrow{k_H} Fe^{IV} + OSSO_3^{2-} + H^+ \quad (I.2)$$

$$HFeO_4^- + OSSO_3^{2-} \rightarrow Fe^{IV} + S_2O_5^{2-} + H^+ \quad (I.3)$$

$$FeO_4^{2-} + OSSO_3^{2-} \rightarrow Fe^{IV} + S_2O_5^{2-} \quad (I.4)$$

$$Fe^{IV} + S_2O_3^{2-} \rightarrow Fe^{II} + OSSO_3^{2-} \quad (I.5)$$

$$Fe^{IV} + OSSO_3^{2-} \rightarrow Fe^{II} + S_2O_5^{2-} \quad (I.6)$$

$$Fe^{IV} + Fe^{II} \rightarrow 2Fe^{III} \quad (I.7)$$

$$H_2O + S_2O_5^{2-} \overset{K_d}{\rightleftharpoons} 2SO_3^{2-} + 2H^+ \quad (I.8)$$

From the above mechanism the following expression may be written for k:

$$k = k_H[H^+]/([H^+] + K_a) \quad (5)$$

Under the conditions that the rates were measured (between pH 8 and 11), $[H^+]$ is less than the ferrate K_a ($pK_a = 7.3$)[11]) and eq 5 reduces to

$$k = k_H K_a^{-1}[H^+] \quad (6)$$

The slope, k_0, of the plot of k versus $[H^+]$ is a composite of k_H and K_a

$$k_0 = k_H K_a^{-1} \quad (7)$$

and the bimolecular rate constant k_H at 25 °C may be calculated as 36 000 M^{-1} s^{-1}.

This two-electron mechanism is in contrast with the ferrate oxidation of cysteine, where Bielski proposed that the oxidation occurs via a one-electron pathway to produce Fe(V) and cysteine radicals.[10b] The latter subsequently dimerize to produce cystine. If thiosulfate were oxidized initially via a one-electron process to produce $S_2O_3^-$, dimerization to produce tetrathionate might be anticipated. Since our studies indicate that tetrathionate is a minor product at best, a one-electron pathway appears unlikely. The proposed two-electron oxidation does conform with other ferrate oxidations that we have studied. Apparently, when provided a choice, ferrate will take the two-electron pathway preferentially over a one-electron pathway.

Using pulse radiolysis, Bielski has established that Fe(IV) is a strong oxidant and appears to react at least 1 order of magnitude faster than ferrate with reductants. This supports the assumption that the steps in the mechanism involving the oxidations by Fe(IV) are not rate-determining.[10] The steps involving oxidation of $OSSO_3^{2-}$ by Fe(IV) (eqs I.5 and I.6 in Scheme 1) may be of minimal importance since they represent two highly reactive intermediates. They are included, however, for completeness.

The sulfur oxidation intermediate, $OSSO_3^{2-}$, proposed in this mechanism has been suggested in the monoperoxysulfate oxidation of coordinated thiosulfate:[17]

$$[Co(NH_3)_5S_2O_3]^+ \xrightarrow{HSO_5^-} [Co(NH_3)_5SOSO_3]^+ \xrightarrow{HSO_5^-} [Co(NH_3)_5SO_2SO_3]^+ \quad (8)$$

This "isodithionite" species is rapidly oxidized to metabisulfite by monoperoxysulfate. Qualitative experiments with ferrate show a similar reaction pattern with coordinated thiosulfate.

During the oxidation of sulfite to sulfate, Murmann used ^{18}O labeling to demonstrate that an oxygen in the first coordination sphere of ferrate is incorporated in the sulfate reaction product.[7] He proposed that an Fe−O−S bond was formed during this process. This observation was also used by Johnson to explain the kinetics for the oxidation of sulfite and selenite.[8] Since an outer-sphere mechanism would likely produce $S_2O_3^-$ radicals, we suggest that a ferrate/thiosulfate ester is a probable intermediate in this reaction:

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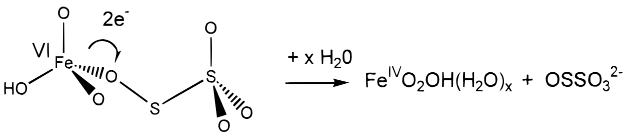

Such an intermediate would be helpful to understand the oxidation of thiosulfate (eq I.2 in Scheme 1) by hydrogen ferrate. Adducts have been proposed for the two-electron oxidation of thiosulfate by Ag(III) and CrO_4^{2-}, except that these species have an M−S bond.[16b,c] Although the thiosulfate complexes were spectrally observable with these oxidants, attempts to observe a ferrate/thiosulfate adduct using rapid-scanning spectroscopy (at pH 9 between 300 and 650 nm within 11 ms of mixing) were unsuccessful. This may be due to a combination of small equilibrium constant coupled with rapid redox reactions.

Oxidation of Other Sulfur Compounds. In order to examine ferrate/sulfur redox reactions further, where dimerization of sulfur products should not be important, and to provide fundamental information regarding the relative rates of sulfur oxidation, the oxidation of benzenesulfinate, methionine, and dimethyl sulfoxide with ferrate was studied. Ferrate solutions are rapidly decolorized upon addition of excess reductant under conditions similar to those for thiosulfate. The reaction stoichiometry for benzenesulfinate, methionine, and dimethyl sulfoxide with ferrate are (1.5 ± 0.1):1, (1.3 ± 0.1):1, and (1.5 ± 0.1):1, respectively, at pH 9.0. Using the same approach as described for thiosulfate, the final iron product was shown to be Fe(III).

The iron(III) in the spent solutions was removed using ion exchange chromatography (SP-Sephadex). For benzenesulfinate, the UV spectrum of the final organic product was recorded in the chromatographed aqueous solution. For methionine and DMSO, the solutions were extracted with methylene chloride, the extracts evaporated to dryness, and IR spectra obtained of the final product. These techniques showed that the final organic oxidation products correspond to addition of an oxygen to the sulfur atom, which agrees with a preliminary study of ferrate oxidation of other sulfur compounds by Carr and Barzatt.[5] On the basis of these two observations, an overall reaction for each reductant may be written as

$$10H^+ + 2FeO_4^{2-} + 3PhSO_2^- \rightarrow 2Fe^{3+} + 3PhSO_3^- + 5H_2O \quad (9)$$

$$10H^+ + 2FeO_4^{2-} + 3CH_3SMet \rightarrow 2Fe^{3+} + 3CH_3S(O)Met + 5H_2O \quad (10)$$

$$10H^+ + 2FeO_4^{2-} + 3CH_3S(O)CH_3 \rightarrow 2Fe^{3+} + 3CH_3S(O)_2CH_3 + 5H_2O \quad (11)$$

The kinetics were studied under conditions identical with those for the thiosulfate and show a simple first-order dependence on H^+ with no acid-independent term (Figure 3). The following general rate law may be written, where S represents the sulfur reductant.

$$-d[Fe(VI)]/dt = k_0[H^+][FeO_4^{2-}][S] \quad (12)$$

Table 1 shows k_0 values for the three reductants at 25 °C and $I = 1.0$ M ($NaClO_4$). The temperature dependence of this reaction was studied to obtain ΔH^* and ΔS^* for k_0, and these values are also presented in Table 1. Since benzenesulfinate, methionine and dimethyl sulfoxide are not protonated in the pH range studied, the acid dependence must be due to the protonation of ferrate itself. The general reaction mechanism given by Scheme 2 is proposed. Step II.2 in Scheme 2 is probably similar to that for thiosulfate and involves an oxygen transfer. Using the same arguments as for thiosulfate, the bimolecular rate constant k_H for each reductant may be calculated (see Table 1).

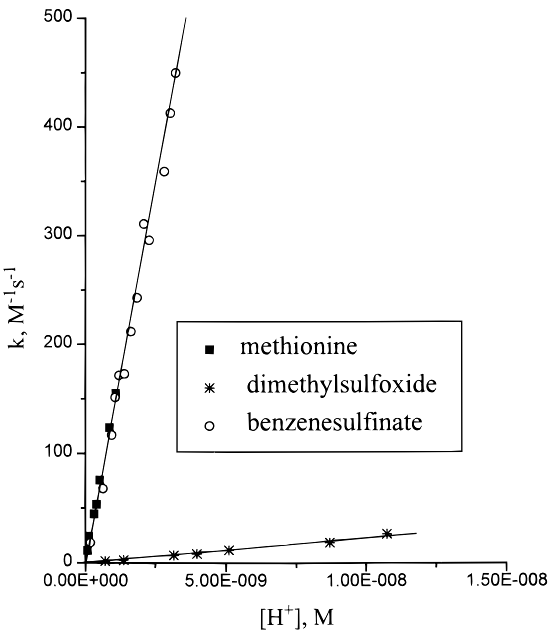

Figure 3. Hydrogen ion dependence on the rate of the S/ferrate reactions. Conditions: $T = 25.0$ °C, $I = 1.0$ M ($NaClO_4$), 0.05 M (Na phosphate) buffer.

Table 1. Kinetic and Thermodynamic Data for Ferrate−Sulfur Oxidations

substrate	k_0 ($M^{-1}\,s^{-1}$)	k_H ($M^{-1}\,s^{-1}$)	ΔH^* (kJ/mol)	ΔS^* (J/(mol K))
thiosulfate	$(7.1 \pm 0.2) \times 10^{11}$	3.6×10^4	18.0 ± 3.5	42 ± 20
benzenesulfinate	$(1.3 \pm 0.2) \times 10^{11}$	7.0×10^3	20.6 ± 2.6	33 ± 15
methionine	$(1.4 \pm 0.1) \pm 10^{11}$	6.5×10^3	34.0 ± 2.7	84 ± 9
dimethyl sulfoxide	$(2.2 \pm 0.1) \times 10^9$	1.1×10^2	41.0 ± 1.8	55 ± 10

Scheme 2

$$HFeO_4^- \overset{K_a}{\rightleftharpoons} FeO_4^{2-} + H^+ \quad (II.1)$$

$$HFeO_4^- + S \xrightarrow{k_H} Fe^{IV} + S(O) + H^+ \quad (II.2)$$

$$Fe^{IV} + S \rightarrow Fe^{II} + S(O) \quad (II.3)$$

$$Fe^{II} + Fe^{IV} \rightarrow 2Fe^{III} \quad (II.4)$$

Conclusions

This is the first complete study of the oxidation of sulfur-containing compounds by ferrate. When the reductant is present in excess, thiosulfate is oxidized to sulfite, benzenesulfinate is oxidized to benzenesulfonate, methionine is converted to its corresponding sulfoxide, and dimethyl sulfoxide is oxidized to dimethyl sulfone. Each oxidation is presumed to occur via a two-electron step and involve oxygen transfer.[7] This is consistent with other ferrate oxidations[1,9,11,18] and supports an emerging theme for ferrate; that is, it preferentially acts as a

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(18) We have studied the oxidation of hydroxylamine and substituted hydroxylamines: Johnson, M. D.; Hornstein, B. J. To be submitted for publication.

two-electron oxidant when either a one- or two-electron oxidation pathway is available.

The order of oxidation is thiosulfate > benzenesulfinate ≈ methionine > dimethyl sulfoxide. For thiosulfate, the terminal S(−II) is presumably the site for oxidation, since it would be expected to be most readily oxidized. This is supported by preliminary ferrate oxidation studies of HS^-, where the rates are too fast to measure with stopped-flow techniques.[19] The slower oxidation of dimethyl sulfoxide compared to methionine is most likely due to the presence of an oxygen on the sulfur atom and its electron-withdrawing effects.[20] In an analogous fashion, the SO_3 moiety attached to the S(−II) atom in thiosulfate also decreases the reaction rate compared to HS^-.

Unfortunately, there appears to be little consistency in the activation parameters for the oxidations reported herein. Due to the paucity of thermodynamic data for ferrate oxidations, little can be concluded about these parameters at this time. This study includes them for completeness and to build up the available information regarding ferrate oxidations.

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