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The kinetics and mechanism of the oxidation of inorganic oxysulfur compounds by potassium ferrate. Part I. Sulfite, thiosulfate and dithionite ions

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Abstract

The kinetics and mechanism of the oxidation of the sulfite (SO_3^{2-}) , thiosulfate $(S_2O_3^{2-})$ and dithionite $(S_2O_4^{2-})$ ions by ferrate (FeO_4^{2-}) ions was studied under pseudo-first-order conditions and, in addition, the reaction with thiosulfate ions was studied under non-pseudo-first-order conditions. Previous work on sulfite and thiosulfate was repeated and extended, specifically over a larger pH range, and using non-pseudo-first-order kinetics. Dithionite was only studied at high pH values because of rapid hydrolysis below a pH of about 10. The kinetics for sulfite and thiosulfate showed a first-order dependence on hydrogen, oxysulfur and ferrate ion concentrations at high pH values, but became independent of the hydrogen ion concentration below a pH of about 8.5. The kinetics for dithionite involved two terms, one being first-order in the hydrogen, dithionite and ferrate ion concentrations, and the other being first-order in only the dithionite and ferrate ions. For all three reductants the proposed mechanism has a rate-determining step involving reaction between unprotonated ferrate and thiosulfur ions. For dithionite there is also a product. Sulfite produced sulfate, whereas thiosulfate and dithionite gave sulfite. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Potassium ferrate (K_2FeO_4) is a powerful oxidizing agent, where iron is in the +6 oxidation state, which is readily reduced to the more stable +2 and +3 states with a high potential (2.20 V in acidic conditions). The kinetics and mechanisms of reactions with a number of reducing agents have been studied. In particular, there have been detailed investigations of the oxidation of organic sulfur compounds such as diethyl sulfide, 2,2'thiodiethanol and dimethyl sulfoxide [1]; various thiols in pentane [2]; benzene sulfinate, methionine and dimethyl sulfoxide [3]; thioxane [4]; mercaptopropionic acid, mercaptoethane sulfonic acid and mercaptobenzoic acid [5]; and methyl cysteine, cystine and cysteine [6]. Most of these reactions show a kinetic dependence on the concentration of the ferrate, hydrogen and reductant ions. The kinetic expressions often involve two or three terms indicating rate-determining steps between the reductant and both protonated and deprotonated ferrate ions, plus a direct reaction between ferrate ions and water. The equations for the thiols are more involved, resulting from the formation of complexes between the reductant and Fe^{3+} ions.

There have been preliminary studies of the oxidation of inorganic oxysulfur ions. Goff and Murmann [7] studied the oxidation of sulfite ions $(SO_3^2^-)$, finding a first-order dependence on the concentration of ferrate ions and a second-order dependence on the concentration of sulfite ions; limited hydrogen ion dependent experiments indicated an increase in the rate with an increase in the hydrogen ion concentration. This study was extended by Johnson and Bernard [8] where they found a first-order dependence on the concentration of each of the hydrogen, sulfite and ferrate ions. The pH range studied was much broader than that used by Goff

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and Murmann, but was still somewhat limited (8.9-11.0). They proposed a mechanism involving the reaction between ferrate ions and hydrogen sulfite ions as the rate-determining step. Johnson and Read [3] found similar results for the oxidation of thiosulfate ions $(S_2O_3^{2-})$, though a fairly narrow pH range was again used (8.8-10.6). In this case the proposed mechanism involved a rate-determining step between the thiosulfate and the protonated ferrate ions.

The present study introduces an exhaustive investigation into the oxidation of inorganic oxysulfur ions by ferrate ions. Part I extends the study of the oxidation of the sulfite and thiosulfate ions over a wider pH range and investigates the oxidation of disulfite ($S_2O_5^{2-}$) and dithionite ($S_2O_4^{2-}$) ions. Subsequent parts cover the thiosalts, $S_nO_6^{2-}$, n = 2-6.

A major problem when studying the kinetics of the inorganic oxysulfur ions is that many of them decompose rapidly in aqueous solution. This is accompanied by a decrease in pH, which is a major concern when these compounds appear in industrial effluents (for example, [9]).

Sulfite and thiosulfate ions are relatively stable in aqueous media. Dithionite ions disproportionate into hydrogen sulfite and thiosulfate ions in acid solutions, but are somewhat more stable under basic conditions, producing sulfite and sulfide ions.

Disulfite ions rapidly decompose, immediately forming hydrogen sulfite ions under acidic conditions [10]. For this reason it was impossible to study the kinetics of the reaction with ferrate ions.

2. Experimental

2.1. Instrumentation

The reactions were monitored spectrophotometrically with a Durrum D110 stopped-flow which was completely computer interfaced using OLIS software. The kinetics were analyzed using SigmaPlot 4.0. A Hewlett– Packard 8452A diode-array spectrophotometer was used to follow some of the kinetics and to obtain reactant and product spectra. A Beckman System Gold high performance liquid chromatograph, completely

Table 1

Experimental data for runs at constant pH values under pseudo-first-order conditions

computer interfaced, was used for reactant and product determinations and stoichiometric confirmation.

2.2. Materials

Potassium ferrate was synthesized by the method described by Delaude and Laszlo [2], giving a purity over 90% for the recrystallized product. The purity was determined at the maximum of the ferrate peak of 505 nm using a molar absorption coefficient of 1175 M^{-1} cm⁻¹ [4]. The oxysulfur compounds were obtained from BDH Laboratory Supplies at 98% or better purity, except for dithionite which was 90% pure.

2.3. General conditions

All reactions were studied in solutions buffered with 0.05 M disodium hydrogen phosphate. Sodium perchlorate was added to maintain the ionic strength at 1.00. Deionized water was used at all times and anaerobic conditions were employed to ensure that dissolved oxygen was not interfering with the reaction. All experiments were studied at 25°C., except for the temperature-dependent runs conducted to determine the activation parameters.

2.4. Kinetic measurements

The reaction rates were measured by following the decay of the ferrate peak at 505 nm on the stopped-flow or diode-array spectrophotometer. The initial ferrate concentration was kept approximately constant at 2×10^{-4} M.

Table 1 summarizes the experimental conditions for the pseudo-first-order runs conducted over a range of oxysulfur ion concentrations at constant pH values. For completeness, the experimental conditions used by Goff and Murmann [7], Johnson and Bernard [8], and Johnson and Read [3] are included. The present work involved keeping the pH constant and varying the excess reductant concentration in the range 1–12 mM, with each set containing at least 11 data points, each one being the average of approximately five trials. This was repeated at different, constant, pH values. Table 2 summarizes the experimental conditions for the pseudo-

Ion pH Number of different pH runs Oxysulfur ion concentration range (mM Sulfite 10.9, 11.9 [7] 2 2–12				
Sulfite 10.9, 11.9 [7] 2 2–12	Ion	pH	Number of different pH runs	Oxysulfur ion concentration range (mM)
8.9–11.0 [8] 10 5–12	Sulfite	10.9, 11.9 [7] 8.9–11.0 [8]	2 10	2–12 5–12
Thiosulfate 8.8–10.6 [3] 6 1–12	Thiosulfate	8.8-10.6 [3]	6	1–12
Dithionite 9.8–11.0 ^a 9 1–12	Dithionite	9.8–11.0 ^a	9	1–12

^a Signifies present work; references quoted to previous studies.

Table 2

Experimental data for runs at constant oxysulfur ion concentrations under pseudo-first-order conditons

Ion	Oxysulfur ion concentration (mM)	pH range
Sulfite	5.5	8.5-10.9
	5.5	8.2-10.9
Thiosulfate	1.5	7.8–10.1 ^a
	5.5	7.4-9.9
	8.5	7.0–9.7 $^{\rm a}$
Dithionite	2.5	10.2-11.2
	3.5	10.1 - 11.1
	4.5	10.3-11.5
	5.5	10.1 - 12.4
	6.5	9.9–11.4
	5.5	9.7-11.1
	5.5	9.8-10.8

^a Signifies experiments conducted on the diode-array spectrophotometer; all other experiments conducted on the stopped-flow spectrophotometer.

Table 3

Experimental data for runs at constant thiosulfate ion concentration under non-pseudo-first-order conditions. ($[FeO_4^{2-}]_0 = 0.2 \text{ mM}$)

Initial thiosulfate ion concentration	(mM) pH range
2.1	7.6–9.9
1.0	7.6–9.9
0.9	7.9–10.2
0.6	8.1-10.0
0.4	7.3–10.0
0.2	7.5–9.9
0.2	7.9–9.6
0.2	8.0-9.7
0.2	8.2–10.0

first-order runs conducted over a range of pH values at constant oxysulfur ion concentrations using the same approach as previously described. Table 3 summarizes the conditions for the non-pseudo-first-order reactions with thiosulfate ions.

The reaction reached completion within a second for dithionite and between 30 and 50 s for sulfite and thiosulfate.

Under all the experimental conditions, "blank" runs without the reducant present were conducted to ensure that the ferrate ions did not decompose.

2.5. Stoichiometry and reaction products

Stoichiometry was determined by three methods. First, simple visual tests were used to determine the ferrate-oxysulfur molar ratio by determining the point at which the ferrate colour remained after the reaction should have been complete. Then the reaction was followed on the stopped-flow spectrophotometer using ratios of ferrate-oxysulfur from 1:4 to 4:1. A graph was plotted to determine the point at which a constant amount of ferrate was consumed as the amount of oxysulfur increased. This indicated the point at which the oxysulfur became in excess. Finally, various ratios were examined on the diode-array spectrophotometer to determine the amount of ferrate consumed by various amounts of oxysulfur.

The reaction products were identified using the diode-array spectrophotometer and spot tests. The presence of sulfite was determined by the decrease in absorbance of malachite green at 624 nm. Dithionate was detected by its stability under normal oxidizing condition but its conversion to sulfate in a hot solution of potassium chlorate in nitric acid. Sulfate was detected by the formation of a barium sulfate precipitate in warm acid solutions. The final oxidation state of iron was determined using the thiocyanate, *o*-phenanthroline, ferricyanide and ferrocyanide tests.

2.6. Temperature dependence

The activation parameters were determined by following the reaction at an intermediate oxysulfur ion concentration (5.5 mM) and pH (9.0) at seven different temperatures from 17 to 28°C. This was not done for thiosulfate since the activation parameters have already been reported [3].

2.7. Monitoring the reaction

The spectrum for potassium ferrate under the experimental conditions used in this study shows a significant maximum at 505 nm. No other reactant or product absorbs in this region of the spectrum and therefore the reactions can be monitored quantitatively by recording the ferrate absorption. The molar absorption coefficient is sensitive to reaction conditions, especially pH, hence the value was determined independently using the method described by Carr et al. [11] and found to be 1175 M^{-1} cm⁻¹.

3. Results and discussion

The oxysulfur ions studied were sulfite, disulfite, thiosulfate and dithionite. The disulfite ion is not sufficiently stable to allow for kinetic or activation parameter studies as it is immediately hydrolyzed to the hydrogen sulfite ion:

$S_2O_5^2 - H_2O \rightarrow 2HSO_3^-$

The pseudo-first-order results are summarized in Table 4. Studies at a constant pH over a limited pH range have already been published for sulfite [7,8] and thiosulfate [3], but they are included in this table for completeness. The non-pseudo-first-order results for thiosulfate are summarized in Table 5.

Table 4 Summary of the pseudo-first-order results

Ion	pH range	Orc	ler of react	ion in	Rate constant	Plateau	Maximum time for	ΔН		Products
(Sulfur oxidation number)		[H*]	[S] ^(a)	[FeO ₄ ²⁻]		pH below	reaction (s)	kJmol ⁻¹	Fe	Oxysulfur Ion
Sulfite	10.9, 11.977	-	2	1	-	-	180	-	3+	SO4 ²⁻
SO ₃ 2	8.9 - 11.0 ⁽⁸⁾	1	1	1	2 x 10 ¹² M ⁻² s ⁻¹	-	30	-	3+	SO4 ²⁻
(+4)	8.5 - 9.1 9.1 - 10.9	0 1	1 1	1 1	1 x 10 ⁴ M ⁻¹ s ⁻¹ 7 x 10 ¹² M ⁻² s ⁻¹	9.1	20	32	3+	SQ. ^{2.}
	8.2 - 9.0 9.0 - 10.9	0 1	1 1	1	1 x 10 ⁴ M ⁻¹ s ⁻¹ 3 x 10 ¹² M ⁻² s ⁻¹	9.0	ſ			4
Thiosulfate	8.8 - 10.6 ⁽³⁾	1	1	1	7 x 10 ¹¹ M ⁻² s ⁻¹	-	50	18	3+	SO3 ²⁻
S ₂ O ₃ ²⁻	7.8 - 8.5 8.5 - 10.1	0 1	1 1	1 1	$3 \times 10^{11} M^{-2} s^{-1}$	8.7)			
(O and +4)	7.4 - 8.0 8.0 - 9.9	0 1	1 1	1 1	$\frac{1 \text{ x } 10^{4} \text{M}^{-1} \text{s}^{-1}}{7 \text{ x } 10^{11} \text{M}^{-2} \text{s}^{-1}}$	8.0	40		3+	SO3 ²⁻
	7.0 - 8.0 8.0 - 9.7	0 1	1 1	1 1	8 x 10 ¹¹ M ⁻² s ⁻¹	8.0	J			
Dithionite	9.8 - 11.0	1	1	1	$\sim 10^{14} M^{-2} s^{-1}$					
S_2O_4		0	1	1	3 x 10 ⁴ M ⁻¹ s ⁻¹					
(+3)	10,2 - 11.2									
	10.1 – 11.1	1	1	1	$8 \times 10^{14} \text{ M}^{-2} \text{s}^{-1}$					50 ³ *
	10.3 – 11.5 }		plus			> -	1	-	3+	503-
	10.1 - 12.4	0	1	1	$3 \times 10^4 M^{-1} s^{-1}$					
	9.9 – 11.4									
	9.7 – 11.1	1	1	1	6 x 10 ¹⁴ M ⁻² s ⁻¹]				
	9.8 - 10.8	0	pius 1	1	2 x 10 ⁴ M ⁻¹ s ⁻¹					

(a) [S] indicates the concentration of the oxysulfur ion.

3.1. Reaction products and stoichiometry

3.1.1. The final oxidation state for iron

The problem with determining the final oxidation state of iron at the end of the kinetic run is that if

Table 5 Summary of the non-pseudo-first-order results for thiosulfate

Fe(II) is formed it is readily oxidized to Fe(III), especially in the presence of even small amounts of oxygen. However, under anaerobic conditions, no Fe(II) was detected for any of the reductants and, therefore, Fe(III) is the final kinetic product.

Thiosulfate-ferrate ratio	$k (M^{-2} s^{-1})$	Intercept (M ⁻¹ s ⁻¹)	R^2	Linear pH range
10:1	11×10^{11}	-31	0.99	>8.7
5:1	8.7×10^{11}	-290	0.90	> 8.7
4:1	5.2×10^{11}	30	0.99	>8.3
3:1	8.1×10^{11}	41	0.84	>8.6
2:1	5.5×10^{11}	9	0.88	>8.8
1:1	8.0×10^{11}	34	0.98	>8.8
3:4	8.3×10^{11}	85	0.97	>8.5
3:4	12×10^{11}	310	0.96	>8.3
3:4	9.7×10^{11}	130	0.95	>8.2
Average	8×10^{11}	35	0.94	>8.5



Fig. 1. The observed rate constant, k_{obs} , versus the hydrogen ion concentration for sulfite ([FeO₄²⁻]₀ = 0.2 mM, [SO₃²⁻]₀ = 5.5 mM).

3.1.2. The oxysulfur ion product

It has already been reported that the final product in the oxidation of the sulfite and the thiosulfate ions is sulfate and sulfite, respectively. In the present study the final product in the oxidation of dithionite is sulfite. It should be noted that, of course, the sulfite product can itself be further oxidized, but this is a much slower reaction and, especially under pseudo-first-order conditions, the ferrate ions are rapidly consumed.

3.1.3. The stoichiometry

The stoichiometry for the sulfite and thiosulfate ions has already been determined and the stoichiometry for the dithionite ions was determined by the methods described in Section 2, giving the following equations:

$$2FeO_4^{2-} + 3SO_3^{2-} + 10H^+ \rightarrow 2Fe^{3+} + 3SO_4^{2-} + 5H_2O$$

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

$$2FeO_4^{2-} + 3S_2O_4^{2-} + 4H^+ \rightarrow 2Fe^{3+} + 6SO_3^{2-} + 2H_2O$$

3.2. Rate law analysis

Previous results for the oxidation of sulfite ions [7,8] and thiosulfate ions [3] show that the kinetics depend on the concentrations of the hydrogen, the reductant and the ferrate ions. Therefore, the data were initially analyzed using a kinetic expression of the form

$$-\frac{d[FeO_4^{2^-}]}{dt} = k[H^+]^x[S]^y[FeO_4^{2^-}]^z$$
(1)

where $[H^+]$ represents the hydrogen ion concentration and [S] represents the oxysulfur ion concentration; x, y and z are their respective orders and k the overall rate constant. Under pseudo-first-order conditions, with $[H^+]$ constant and [S] in large excess

$$-\frac{d[\text{FeO}_4^{2^-}]}{dt} = k_{\text{obs}}[\text{FeO}_4^{2^-}]^z$$
(2)

where

 $k_{\rm obs} = k[\mathrm{H}^+]^x[\mathrm{S}]^y \tag{3}$

At constant pH values

$$k_{\rm obs} = k_1 [S]^{\nu} \tag{4}$$

where

$$k_1 = k[\mathrm{H}^+]^x \tag{5}$$

And at constant reductant concentrations

$$k_{\rm obs} = k_2 [\mathrm{H}^+]^x \tag{6}$$

where

$$k_2 = k[\mathbf{S}]^{\nu} \tag{7}$$

Under non-pseudo-first-order conditions the data were analyzed by the method described previously [6].

3.3. The rate laws

In all cases the order with respect to ferrate ions was one.

3.3.1. The rate law for the sulfite ions

The results for the previous studies [7,8] are shown in Table 4. There is a discrepancy shown for the order in both hydrogen ion and sulfite ion concentration.

In the present study the kinetics were determined at a constant sulfite ion concentration of 5.5 mM over a wider pH range than previous studies, from 8.2 to 10.9. The results in the pH range from 9.0 to 10.9 confirmed the conclusion reached by Johnson and Bernard [8] that the kinetics obey the equation

$$-\frac{d[\text{FeO}_4^{2^-}]}{dt} = k[\text{H}^+][\text{SO}_3^{2^-}][\text{FeO}_4^{2^-}]$$
(8)

The two separate studies (see Tables 2 and 4) gave values for k of 7×10^{12} and 3×10^{12} M⁻² s⁻¹, respectively, compared to the value of 2×10^{12} M⁻² s⁻¹ obtained earlier [8]. An average value of 5×10^{12} M⁻² s⁻¹ is used for later calculations.

At lower pH values (8.2–9.1) the reaction did not obey Eq. (8) but was independent of the hydrogen ion concentration. This change in dependence is illustrated in Fig. 1 where the plot of k_{obs} versus [H⁺] according to Eq. (6) shows a linear dependence up to a hydrogen ion concentration of about 10^{-9} M, and no dependence at higher values for the hydrogen ion concentration. The values of the observed rate constant, k', when the rate is independent of the hydrogen ion concentration is approximately 1×10^4 M⁻¹ s⁻¹. This phenomenon was not observed by previous workers since the kinetics were only studied at relatively high pH values.



Fig. 2. The absorbance versus wavelength at 1 s intervals for the reaction between ferrate and thiosulfate.

3.3.2. The rate law for the thiosulfate ions

3.3.2.1. Pseudo-first-order kinetics. The results from previous work over the pH range from 8.8 to 10.6 are included in Table 4 giving the rate expression [3]

0.12

$$-\frac{d[\text{FeO}_4^{2^-}]}{dt} = k[\text{H}^+][\text{S}_2\text{O}_3^{2^-}][\text{FeO}_4^{2^-}]$$
(9)

with a value for k of 7×10^{11} M⁻² s⁻¹. This has been confirmed in the present study for this pH range. Also a rapid scan was conducted to ascertain that the disappearance of the absorption peak at 505 nm was due to the reaction of ferrate and that no other compound was absorbing in this region; the scan is shown in Fig. 2.

In addition, the kinetics have been determined over a wider range of pH values from 7.0 to 10.1, at constant thiosulfate ion concentrations of 1.5, 5.5 and 8.5 mM as shown in Tables 1, 2 and 4. The results of the experiments at thiosulfate ion concentrations of 1.5 and 8.5 mM are shown in Figs. 3 and 4. There is a linear dependence between k_{obs} and $[H^+]$ up to a pH value between 8 and 8.7 as indicated in Table 4. The rate constants from the three sets of data are 3×10^{11} , 7×10^{11} and 8×10^{11} M⁻² s⁻¹ giving an average value of 6×10^{11} M⁻² s⁻¹ which agrees closely with the previously calculated value of 7×10^{11} M⁻² s⁻¹[3].

However, at pH values lower than the plateau indicated in Table 4, Eq. (9) is no longer obeyed since there is no dependence on the hydrogen ion concentration. In this case an observed rate constant k', of approximately 1×10^4 M⁻¹ s⁻¹, is obtained which is identical to that calculated for the sulfite ion oxidation. This was not observed in earlier studies as the lowest pH studied was 8.8. 3.3.2.2. Non-pseudo-first-order kinetics. Nine nonpseudo-first-order runs were conducted at different initial thiosulfate-ferrate ratios as shown in Tables 3 and 5. A typical plot of k_1 versus the hydrogen ion concentration is shown in Fig. 5. The average value for k is 8×10^{11} M⁻² s⁻¹ and the kinetics become independent of the hydrogen ion concentration below a pH value of approximately 8.5. This agrees with the pseudo-first-order results.

Ferrate

3.3.3. The rate law for the dithionite ions

A major complication when studying the kinetics of the dithionite ions is their instability in aqueous solutions. Dithionite ions readily form thiosulfate and hy-



Fig. 3. The observed rate constant, k_{obs} , versus the hydrogen ion concentration for thiosulfate ([FeO₄²⁻]₀ = 0.2 mM, [S₂O₃²⁻]₀ = 1.5 mM).



Regression Output	
y-intercept	0.2
slope	6.9 e + 09
r^2	0.98

Fig. 4. The observed rate constant, k_{obs} , versus the hydrogen ion concentration for thiosulfate ([FeO₄²⁻]₀ = 0.2 mM, [S₂O₃²⁻]₀ = 8.5 mM).





Fig. 5. The rate constant, k_1 , versus the hydrogen ion concentration for thissulfate ([FeO_4^2-]_0 = 0.2 mM, [S_2O_3^2-]_0 = 0.2 mM).

drogen sulfite ions in acidic solutions, or sulfite and sulfide ions in base [10]:

 $2S_2O_4^{2-} + H_2O \rightarrow S_2O_3^{2-} + 2HSO_3^{-}$ $3S_2O_4^{2-} + 6OH^{-} \rightarrow 5SO_3^{2-} + S^{2-} + 3H_2O$

The decomposition occurs quite rapidly, especially at lower pH values. For this reason, fresh, buffered, samples were prepared for each individual run, and the reactions were followed at high pH values (9.7–12.4). Under these conditions the oxidation was complete in 1 s, and decomposition was not a major problem. Only pseudo-first-order reactions were studied as the hydrolysis interfered with the slower rate of reaction for non-pseudo-first-order kinetics.

The results are summarized in Table 4.

All nine runs performed at a constant pH showed a

linear dependence according to Eq. (4), although the R^2 values were below 1, with an average value of 0.92. None of the plots showed a positive intercept. A typical plot is shown in Fig. 6. It was not possible to obtain an accurate value for the order in terms of the hydrogen ion concentration, or for the rate constant, k, according to Eq. (5), because of the very narrow pH range that was able to be studied. However, the evidence supports that the concentration of hydrogen ions is first order with a rate constant, k, of $10^{14} \text{ M}^{-2} \text{ s}^{-1}$. The plot according to Eq. (5) had an intercept of $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Since there was no intercept in the plot of k_{obs} versus the dithionite concentration, Eq. (3) should be re-written.





Fig. 6. The observed rate constant, k_{obs} , versus the dithionite concentration at a pH of 10.1 ($[FeO_4^2^-]_0 = 0.2 \text{ mM}$).



Fig. 7. The observed rate constant, k_{obs} , versus the hydrogen ion concentration for dithionite ([FeO₄²⁻]₀ = 0.2 mM, [S₂O₄²⁻]₀ = 4.5 mM).





Fig. 8. The observed rate constant, k_{obs} , versus the hydrogen ion concentration for two separate sets for dithionite ([FeO₄²⁻]₀ = 0.2 mM, [S₂O₄²⁻]₀ = 5.5 mM).

$$k_{\rm obs} = k[{\rm H}^+][{\rm S}_2{\rm O}_4^{2-}] + k''[{\rm S}_2{\rm O}_4^{2-}]$$
(3a)

and Eq. (5) becomes

 $k_1 = k[H^+] + k''$ (5a) giving a value for k'' of $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. A second set of runs was conducted at five different constant dithionite ion concentrations over various pH ranges from 9.9 to 12.4 as shown in Table 2. The results are summarized in Table 4 and the graph at a dithionite ion concentration of 4.5 mM over the pH range of 10.3–11.5 is shown in Fig. 7. All the results gave a linear dependence on the hydrogen ion concentration according to Eq. (6), indicating an order of one, with R^2 values somewhat below unity with an average value of 0.82. Again, an intercept was obtained for all five sets, and hence Eq. (6) should be re-written.

$$k_{\rm obs} = k_2 [\rm H^+] + k'' [\rm S_2 O_4^{2-}]$$
(6a)

The slopes of these plots give an average value for k of 8×10^{14} M⁻² s⁻¹. The intercept increased with increasing dithionite concentration in agreement with Eq. (6a), giving a value for k'' of 3×10^4 M⁻¹ s⁻¹ which is in complete agreement with the value obtained from the k_1 versus hydrogen ion concentration data.

Therefore, the kinetic expression is

Table 6						
Average	values	for	the	rate	constants	

$$-\frac{d[\text{FeO}_4^{2^-}]}{dt} = k[\text{H}^+][\text{S}_2\text{O}_4^{2^-}][\text{FeO}_4^{2^-}] + k''[\text{S}_2\text{O}_4^{2^-}][\text{FeO}_4^{2^-}]$$
(10)

To determine the effect of hydrolysis on the kinetic results, two independent sets were conducted over a slightly larger pH range without preparing fresh dithionite solutions before each reaction. The results of the runs at various pH values and a constant dithionite ion concentration of 5.5 mM are shown in Fig. 8. Both sets were conducted from low hydrogen ion concentration to high hydrogen ion concentration, and set 2 was conducted over a longer time period than set 1. Although there is some scatter, it can be seen that both sets show similar results at first, giving a value for k of 6×10^{14} M $^{-2}$ s $^{-1}$ and for k'' of 2×10^4 M $^{-1}$ s $^{-1}$ (consistent with the previous results). However, the k_{obs} values are lower than expected later in the runs, with lower values for the longer set. This is consistent with the hydrolysis of the dithionite ions over time, decreasing the concentration of the reductant in solution.

3.3.4. Comparison of the rate laws

For all three reductants the kinetics are first-order in hydrogen, oxysulfur and ferrate ion concentrations at high pH values. For sulfite and thiosulfate ions the hydrogen ion dependence becomes zero below a pH value of approximately 9.1, and 8.0–8.7, respectively. Because of dithionite hydrolysis, the hydrogen ion dependence could not be determined below a pH of 9.7. The average overall rate constant, k, increased from approximately 7×10^{11} to 5×10^{12} to 8×10^{14} M⁻² s⁻¹ for the thiosulfate, sulfite and dithionite ions, respectively, as shown in Table 6. The rate constant, k', for the low pH regions for the sulfite and thiosulfate ions was approximately 1×10^4 M⁻¹ s⁻¹ in both cases.

Within the experimental errors all the plots according to Eqs. (4)–(6) went through the origin except for the plot of k_{obs} versus [H⁺] for dithionite, indicating a second term in the kinetic expression as shown in Eq. (10). The rate constant, k'', for the second term is 3×10^4 M⁻¹ s⁻¹ which is very similar to the value of k'for the low pH region for sulfite and thiosulfate.

Ion	Experimental ra	ite constants		Rate constant for rate-determining step(s) $(M^{-1} s^{-1})$
	$k (M^{-2} s^{-1})$	$k' (M^{-1} s^{-1})$	k'' (M ⁻¹ s ⁻¹)	_
Sulfite	5×10^{12}	1×10^4		$k_{\rm r} = 1.5 \times 10^4$
Thiosulfate	7×10^{11}	1×10^4		$k_{\rm b} = 2 \times 10^3$
Dithionite	8×10^{14}		3×10^4	$ \begin{aligned} k_{\rm d} &= 2 \times 10^6 \\ k_{\rm t} &= 3 \times 10^4 \end{aligned} $

3.4. Activation parameters

The activation enthalpy for thiosulfate has already been reported at 18 kJ mol⁻¹[3]. For sulfite, Goff and Murmann [7] did not detect any change in rate constant with temperature over the range $8-20^{\circ}$ C, however, a change was observed in the present work, giving an activation enthalpy of 32 kJ mol⁻¹. Because of the instability of the dithionite ions it was not possible to determine accurately its activation enthalpy.

3.5. Mechanism

3.5.1. Sulfite and thiosulfate ions

General mechanisms have already been proposed by Goff and Murmann [7], and Johnson and Bernard [8] for the oxidation of sulfite. Goff and Murmann proposed an initial fast equilibrium between the ferrate and the sulfite ions to form a complex, followed by the reaction between this complex and sulfite ions. The mechanism is unlikely to be correct as it involves a rate-determining step involving a complex with a 4- charge reacting with the sulfite ions. Also, it leads to kinetics that are second-order in sulfite which has not been observed by other workers. Johnson and Bernard proposed an initial equilibrium between sulfite and hydrogen sulfite ions, followed by the equilibrium between hydrogen sulfite and ferrate ions forming a complex which decomposed as the rate-determining step. Given the fact that the pK_a for HSO₃⁻ is approximately 7 [12], and that the pK_a for HFeO₄⁻ is higher [11,13,14], and the supporting evidence for the value of $K_{\rm a}$ calculated later, it is suggested that a more likely mechanism would involve initial equilibrium between unprotonated and protonated ferrate ions, followed by the rate-determining step of reaction between protonated ferrate and sulfite ions as follows:

$$HFeO_{4}^{-} \rightleftharpoons FeO_{4}^{2-} + H^{+}$$

$$HFeO_{4}^{-} + SO_{3}^{2-} \xrightarrow{k_{r}} Fe(IV) + SO_{4}^{2-} + H^{+}$$

$$Fe(IV) + SO_{3}^{2-} \rightarrow Fe(II) + SO_{4}^{2-}$$

$$Fe(IV) + Fe(II) \rightarrow 2Fe(III)$$

where k_r is the rate constant for the rate-determining step, and Fe(IV) represents an unstable complex which readily reacts with more sulfite to produce Fe(II).

The results in this paper support the mechanism proposed by Johnson and Read [3] for thiosulfate oxidation with the first two steps being similar to the above, namely

$$\text{HFeO}_4^- \rightleftharpoons \text{FeO}_4^{2-} + \text{H}^+$$

$$\begin{split} \mathrm{HFeO}_{4}^{-} + \mathrm{S}_{2}\mathrm{O}_{3}^{2-} &\xrightarrow{k_{\mathrm{h}}} \mathrm{Fe}(\mathrm{IV}) + \mathrm{OSSO}_{3}^{2-} + \mathrm{H}^{+} \\ \mathrm{HFeO}_{4}^{-} + \mathrm{OSSO}_{3}^{2-} &\rightarrow \mathrm{Fe}(\mathrm{IV}) + \mathrm{S}_{2}\mathrm{O}_{5}^{2-} + \mathrm{H}^{+} \\ \mathrm{FeO}_{4}^{2-} + \mathrm{OSSO}_{3}^{2-} &\rightarrow \mathrm{Fe}(\mathrm{IV}) + \mathrm{S}_{2}\mathrm{O}_{5}^{2-} \\ \mathrm{Fe}(\mathrm{IV}) + \mathrm{S}_{2}\mathrm{O}_{3}^{2-} &\rightarrow \mathrm{Fe}(\mathrm{II}) + \mathrm{OSSO}_{3}^{2-} \\ \mathrm{Fe}(\mathrm{IV}) + \mathrm{OSSO}_{3}^{2-} &\rightarrow \mathrm{Fe}(\mathrm{II}) + \mathrm{S}_{2}\mathrm{O}_{3}^{2-} \\ \mathrm{Fe}(\mathrm{IV}) + \mathrm{Fe}(\mathrm{II}) &\rightarrow 2\mathrm{Fe}(\mathrm{III}) \\ \mathrm{H}_{2}\mathrm{O} + \mathrm{S}_{2}\mathrm{O}_{5}^{2-} &\stackrel{K_{\mathrm{d}}}{\rightleftharpoons} 2\mathrm{SO}_{3}^{2-} + 2\mathrm{H}^{+} \end{split}$$

where $k_{\rm h}$ is the rate constant for the rate-determining step.

From both the above mechanisms a rate expression can be derived as follows:

$$-\frac{d[Fe(VI)]}{dt} = \frac{k_{\rm r}[{\rm H}^+][{\rm SO}_3^{-2}^-][Fe(VI)]}{[{\rm H}^+] + K_{\rm a}}$$
(11)

or

$$-\frac{d[Fe(VI)]}{dt} = \frac{k_{h}[H^{+}][S_{2}O_{3}^{2}^{-}][Fe(VI)]}{[H^{+}] + K_{a}}$$
(12)

Both Eqs. (11) and (12) reduce to simple first-order equations of the form shown in Eqs. (8) and (9) obtained experimentally at high pH values when $[H^+] < K_a$. For the sulfite ions the experimental rate constant

$$k = \frac{k_{\rm r}}{K_{\rm a}}$$

and for the thiosulfate ions

$$k = \frac{k_{\rm h}}{K_{\rm a}}$$

In order to determine k_r and k_h , the rate constants for the rate-determining steps, an accurate value for K_a is required. From the proposed mechanisms this is the second equilibrium constant for H₂FeO₄. A range of values has been reported in the literature, but previous work in similar systems indicates a value of approximately 3×10^{-9} (p $K_a = 8.5$) [5,11,13,14]. Using this number

$$k_{\rm r} = 1.5 \times 10^4 \,{\rm M}^{-1} \,{\rm s}^{-1}$$

 $k_{\rm h} = 2 \times 10^3 \,{\rm M}^{-1} \,{\rm s}^{-1}$

At low pH values where $[H^+] > K_a$, Eqs. (11) and (12) reduce to equations independent of the hydrogen ion concentration, giving a rate constant equivalent to k'. Under these (low pH) conditions the rate constants for sulfite and thiosulfate oxidation are identical. A region where the reaction is independent of hydrogen ion concentration was observed for both the sulfite and thiosulfate ions. The point at which this occurs is difficult to identify, but from the results shown in Tables 4 and 5, it can be seen that it is in the pH range from 8.0 to 9.1, with an average value of 8.5. This is confirmation for the pK_a of $HFeO_4^$ as, according to Eqs. (11) and (12), the plateau appears in the plot of k_{obs} versus $[H^+]$ when $[H^+] = K_a$. This feature was not observed by previous workers because they did not study the kinetics at pH values below 8.8. The appearance of the plateau at pH values considerably higher than the pK_a value for $HSO_3^$ or $HS_2O_3^-$ is further evidence for a rate-determining step involving protonated ferrate ions rather than protonated sulfite or thiosulfate ions.

3.5.2. Dithionite ions

A general mechanism, consistent with the kinetics, stoichiometry and reaction products is

$$HFeO_{4}^{-} \rightleftharpoons FeO_{4}^{2-} + H^{+}$$

$$HFeO_{4}^{-} + S_{2}O_{4}^{2-} \stackrel{k_{d}}{\rightarrow} Fe(IV) + S_{2}O_{5}^{2-} + H^{+}$$

$$FeO_{4}^{2-} + S_{2}O_{4}^{2-} \stackrel{k_{t}}{\rightarrow} Fe(IV) + S_{2}O_{5}^{2-}$$

$$Fe(IV) + S_{2}O_{4}^{2-} \rightarrow Fe(II) + S_{2}O_{5}^{2-}$$

$$Fe(IV) + Fe(II) \rightarrow 2Fe(III)$$

$$S_{2}O_{5}^{2-} + H_{2}O \rightarrow 2SO_{3}^{2-} + 2H^{+}$$

where $k_{\rm d}$ and $k_{\rm t}$ are the rate constants for the two rate-determining steps.

The above mechanism leads to the following rate expression:

$$-\frac{d[Fe(VI)]}{dt} = \frac{k_{d}[H^{+}][S_{2}O_{4}^{2}^{-}][Fe(VI)]}{[H^{+}] + K_{a}} + \frac{k_{t}K_{a}[S_{2}O_{4}^{2}^{-}][Fe(VI)]}{[H^{+}] + K_{a}}$$
(13)

When $[H^+] < K_a$, which is the case in this study since the lowest pH value studied was 9.7, Eq. (13) reduces to

$$-\frac{d[Fe(VI)]}{dt} = \frac{k_{d}}{K_{a}}[H^{+}][S_{2}O_{4}^{2^{-}}][Fe(VI)] + k_{t}[S_{2}O_{4}^{2^{-}}][Fe(VI)]$$
(14)

This is identical to the rate expression shown as Eq. (10) which was obtained experimentally.

Using the value for $K_{\rm a}$ as before this gives

$$k_{\rm d} = 2 \times 10^6 \,{\rm M}^{-1} \,{\rm s}^{-1}$$

and

$$k_t = 3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$$

3.5.3. Comparison of the mechanisms

All three reductants are oxidized with a rate-determining step involving reaction with protonated ferrate ions. The rate constant for this step increases from 2×10^3 M⁻¹s⁻¹ for thiosulfate, to 1.5×10^4 M⁻¹s⁻¹ for sulfite, to 2×10^6 M⁻¹s⁻¹ for dithionite. The high reactivity of the dithionite ions is mirrored by the fact that this is the only ion that is also directly oxidized by the deprotonated ferrate ions, with a rate constant of $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. This is very similar to the calculated rate constant of $1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for sulfite and thiosulfate ions at low pH values.

4. Conclusion

Potassium ferrate readily oxidizes the sulfite, thiosulfate and dithionite ions giving Fe(III). The sulfite ions are oxidized to sulfate, and both the thiosulfate and dithionite ions are oxidized to sulfite. All reductants have a rate-determining step involving protonated ferrate, with dithionite also having a rate-determining step involving deprotonated ferrate. The sulfite and thiosulfate reductants exhibit kinetics which are first-order in each of the hydrogen, oxysulfur and ferrate ion concentrations at high pH values, but show a lack of dependence on the hydrogen ion concentration at low pH values. Dithionite has two kinetic terms, one being first-order in the concentration of each of the hydrogen, dithionite and ferrate ions and the other being dependent on only the dithionite and ferrate ion concentrations. The rate of reaction increases from thiosulfate, to sulfite to dithionite. The kinetics for dithionite could only be studied at high pH values because of fast hydrolysis at pH values below about 10. Disulfite hydrolyzed too quickly to allow kinetics studies to be made.

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