Oxidation of the thiosulfate ion with a (μ-oxo)diiron(III) complex: kinetic evidence for self reaction of the thiosulfate radical ion
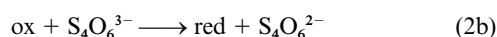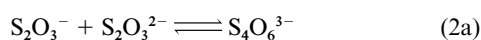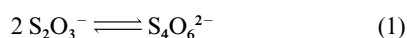
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In aqueous Hphen⁺–phen buffer media (pH 3.9–5.2), the complex ion $[Fe^{III}_2(\mu\text{-O})(phen)_4(H_2O)_2]^{4+}$ **1** (phen = 1,10-phenanthroline) has been shown to oxidise the thiosulfate ion to the tetrathionate ion. In the presence of excess phenanthroline, **1** itself was reduced to $[Fe(phen)_3]^{2+}$ **3²⁺**, an inhibitor for the reaction. According to the proposed mechanism, an inner-sphere, one-electron reduction of **1** by $S_2O_3^{2-}$ generates $[Fe(phen)_3]^{3+}$ **3³⁺**, $[Fe(phen)_3]^{2+}$ **3²⁺** and the thiosulfate radical ion $S_2O_3^-$; **3³⁺** is then further reduced to **3²⁺** by another $S_2O_3^{2-}$ ion. The radical ion $S_2O_3^-$ either re-oxidises **3²⁺** to **3³⁺** and thus inhibits the reaction, or produces the tetrathionate ion through a self reaction. Kinetic activity of **1** swamps that for its hydrolysed derivatives.

Thiosulfate is an important, industrial reducing agent. Mild oxidising agents oxidise it to tetrathionate[1] *via* the transient radical ion $S_2O_3^-$, detected by induced polymerisation of acrylonitrile in aqueous solution.[2] The radical ion produces tetrathionate either by self reaction [eqn. (1)], or by coupling with $S_2O_3^{2-}$ [eqn. (2a)] followed by oxidation of the $S_4O_6^{3-}$ radical ion [eqn. (2b)].

$$2\,S_2O_3^- \rightleftharpoons S_4O_6^{2-} \qquad (1)$$

$$S_2O_3^- + S_2O_3^{2-} \rightleftharpoons S_4O_6^{3-} \qquad (2a)$$

$$ox + S_4O_6^{3-} \longrightarrow red + S_4O_6^{2-} \qquad (2b)$$

Many workers assumed self reaction in schemes proposed for the oxidation reactions of $S_2O_3^{2-}$. Nevertheless, a major objection to the self reaction (1) is that such a mechanism, which involves a second-order decay of the intermediate $S_2O_3^-$ ion would have a relatively high steady-state concentration of the intermediate. Re-oxidation of product by $S_2O_3^-$ would therefore be significant and product inhibition observed. So far, no such inhibition has been reported.
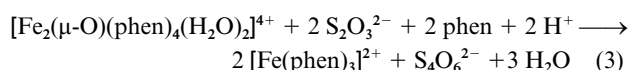
While investigating the preliminary kinetics of oxidation of $S_2O_3^{2-}$ by the (μ-oxo)diiron(III) complex ion $[Fe_2(\mu\text{-O})(phen)_4(H_2O)_2]^{4+}$ **1** (phen = 1,10-phenanthroline) in slightly acidic aqueous media, we recently observed product inhibition by $[Fe(phen)_3]^{2+}$ **3²⁺**. The results appeared interesting compared with the reactions discussed above and we conducted the more detailed studies presented here. The crystal structure of **1** $[NO_3]_4 \cdot 5H_2O$ is known[3] and some time ago we investigated the kinetics and equilibria of its reaction with hydroxylamine.[4] Besides this, kinetic studies of oxidation by multinuclear iron complexes are in general rare.[5]

Results and discussion

Stoichiometry

In the presence of $[\text{complex}] \ll c_{phen}$ $(= [\text{phen}] + [\text{Hphen}^+])$ each mol of **1** oxidises 1.85 ± 0.05 mol of thiosulfate, and is reduced to 1.90 ± 0.06 mol of $[Fe(phen)_3]^{2+}$. No sulfate ion could be detected in the product solution under conditions where the lower limit of detection is 1×10^{-5} mol dm⁻³, but the expected yield of SO_4^{2-} is 2×10^{-2} mol dm⁻³ provided that **1** oxidises $S_2O_3^{2-}$ to SO_4^{2-} quantitatively. The results suggest that $\leqslant 0.05\%$ of the total $S_2O_3^{2-}$ consumed changed into SO_4^{2-}.

The most likely oxidation product of $S_2O_3^{2-}$ is therefore $S_4O_6^{2-}$ [eqn. (3)]. Formation of the tetrathionate ion was further con-

$$[Fe_2(\mu\text{-O})(phen)_4(H_2O)_2]^{4+} + 2\,S_2O_3^{2-} + 2\,phen + 2\,H^+ \longrightarrow$$
$$2\,[Fe(phen)_3]^{2+} + S_4O_6^{2-} + 3\,H_2O \quad (3)$$

firmed by the method of Kolthoff and Belcher[6] using reaction (4).

$$S_4O_6^{2-} + 3\,CN^- + H_2O \longrightarrow$$
$$S_2O_3^{2-} + SO_4^{2-} + SCN^- + 2\,HCN \quad (4)$$
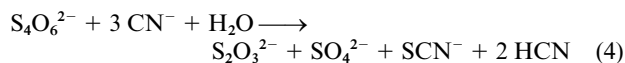
Solution equilibria

In slightly acidic solutions, the oxo-bridge in **1** is thermodynamically stable.[4] Unidentate ligands such as SCN^- rapidly substitute the aqua ligands in **1,** thus indicating their labile nature.[7] Under the experimental conditions used, **1** and its hydrolytic derivative **2** coexist in rapid equilibrium[4] [eqn. (5)]

$$\textbf{1} \rightleftharpoons [Fe_2(\mu\text{-O})(phen)_4(H_2O)(OH)]^{3+} + H^+ \qquad (5)$$
$$\textbf{2}$$
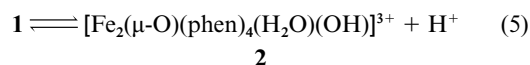
$[K_{a1} = (4.03 \pm 0.05) \times 10^{-6}$ mol dm⁻³ at 25.0 °C, $I = 1.0$ mol dm⁻³] with no evidence for oxo-bridge protonation and bridge breaking. At pH < 2, however, **1** slowly cleaves to $[Fe(phen)_3]^{2+}$ **3²⁺** identified spectrophotometrically.

Kinetics and reaction scheme

Fig. 1 demonstrates a typical example of spectral changes observed for an aqueous solution of **1** mixed with 20–300-fold thiosulfate and excess c_{phen}. Typical absorbance *versus* time data at 510 nm are displayed in Fig. 2(b). Noticeably, the reaction lags behind a hypothetical one-step, first-order reaction [Fig. 2(a)] and demonstrates product inhibition. The highest absorbance recorded in 2(b) is also less than that expected for complete conversion of **1** into **3²⁺**. The observed inhibition increases with increasing amount of added $[Fe(phen)_3]^{2+}$ **3²⁺** [Fig. 2(c) and 2(d)]. Presence or absence of dissolved dioxygen had no effect on the observed absorbance–time profiles.

The $S_2O_3^{2-}$ ion is a well-known one-electron reducing agent[1,8,9] and most probably reduces the diiron(III) species by one-electron steps. It is however, known that $Fe^{III}Fe^{II}$ and Fe^{II}_2 dimers are putative outside a protein environment and quickly dissociate to monomers.[5a,10] According to available kinetic and
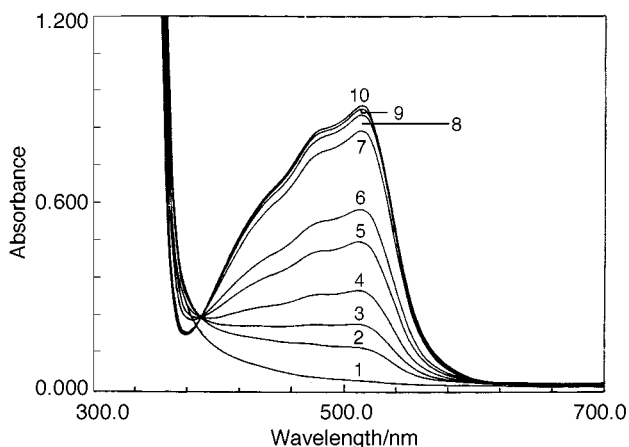
Fig. 1 The UV/VIS spectrum for complex **1** (1). Spectra for a mixture of **1** with 15 mmol dm⁻³ thiosulfate at different times: immediately after mixing (2) and after 1 (3), 3 (4), 5 (5), 7 (6), 15 (7), 20 (8), 25 (9) and 30 (10) min; [complex] 0.05 mmol dm⁻³; c_{phen} 3.0 mmol dm⁻³ ; pH 4.50; T 25.0 °C; I 1.0 mol dm⁻³ (NaNO₃). The isosbestic point is at 389 nm; another isosbestic point can be seen at 623 nm on an expanded scale (not shown).
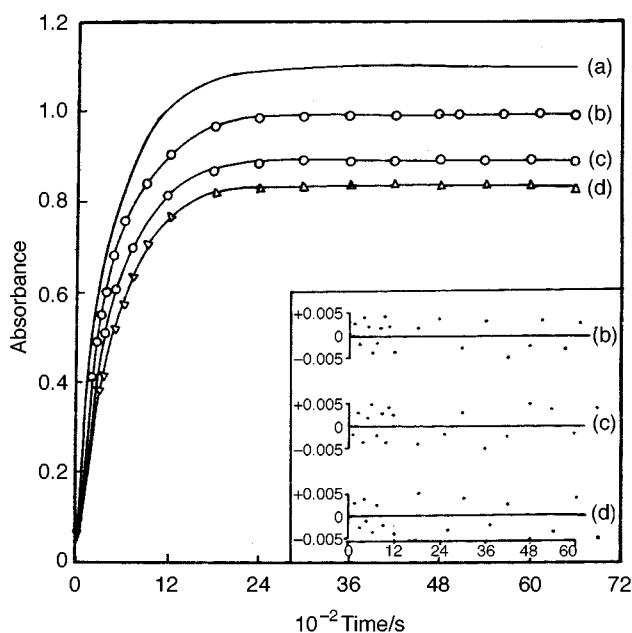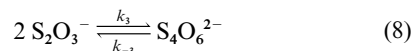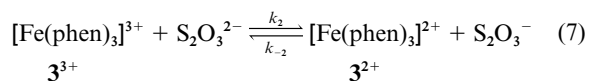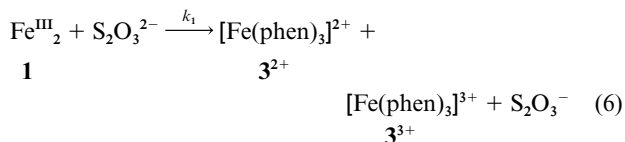

Fig. 2 The absorbance *versus* time curves at 510 nm: [complex] 0.05 mmol dm⁻³; c_{phen} 3.0 mmol dm⁻³; [S₂O₃²⁻] 15.0 mmol dm⁻³; pH 4.50; T 25.0 °C; I 1.0 mol dm⁻³ (NaNO₃); [**3²⁺**] (mmol dm⁻³), 0 (a) and (b); 0.05 (c); 1.0 (d); [**3²⁺**] in aqueous blank was the same as in the experimental mixture. Simulated curve for a hypothetical, one-step reaction with rate constant 2.83×10^{-3} dm³ mol⁻¹ s⁻¹ (a). Real data (b)–(d). Some experimental points in the initial parts of (b)–(d) have not been shown for clarity. The solid lines in (b)–(d) are simulated curves using the reaction sequence (6–8) and rate constants (dm³ mol⁻¹ s⁻¹), $k_1 = 2.83 \times 10^{-3}$, $k_2 = 1.6 \times 10^{6}$, $k_{-2} = 3.5 \times 10^{9}$, $k_3 = 6.7 \times 10^{6}$, $k_{-3} = (3.3 \pm 0.2) \times 10^{-2}$ s⁻¹; ε (dm³ mol⁻¹ cm⁻¹) values: **1** 2400; **3²⁺** 1.1×10^4; **3³⁺** 0. The residual plots for (b), (c) and (d) are shown in the inset.

thermodynamic data [11,12] all such iron(III) and iron(II) monomers must change completely to their respective tris chelates, *viz.*, **3³⁺** or **3²⁺** in the presence of excess phenanthroline. The time-scale for such changes is very much smaller than in the present kinetic experiments. As discussed, the observed product inhibition suggests the self reaction of S₂O₃⁻. Eqns. (6)–(8)

$$\text{Fe}^{III}_2 + \text{S}_2\text{O}_3^{2-} \xrightarrow{k_1} [\text{Fe(phen)}_3]^{2+} +$$
$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{3^{2+}}$$
$$[\text{Fe(phen)}_3]^{3+} + \text{S}_2\text{O}_3^- \quad (6)$$
$$\mathbf{3^{3+}}$$

$$[\text{Fe(phen)}_3]^{3+} + \text{S}_2\text{O}_3^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\text{Fe(phen)}_3]^{2+} + \text{S}_2\text{O}_3^- \quad (7)$$
$$\mathbf{3^{3+}} \qquad\qquad\qquad\qquad\qquad \mathbf{3^{2+}}$$

$$2\,\text{S}_2\text{O}_3^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{S}_4\text{O}_6^{2-} \qquad (8)$$

therefore form a simple and logical sequence for the reaction between **1** and S₂O₃²⁻; the product inhibition arising from re-oxidation of **3²⁺** by S₂O₃⁻.

This sequence permits excellent simulation (Fig. 2) of the observed kinetics using the package KFSIM40,[13a] which expresses this reaction sequence as a series of differential equations and performs numerical integration to yield the optimised rate constants and the concentrations of the participating species at desired time intervals. The KFSIM40 package consists of two programs, KINSIM40 and FITSIM40. The program KINSIM40 compiles a reaction sequence written with the DOS editor, and simulates concentration (or any linear function of it) at desired time intervals corresponding to a given mechanism and a given set of rate constants. Incorporation of known absorption coefficients (ε) yields calculated values for the absorbance at different time. The simulated absorption–time curve can be visually compared with the real curve. One can change the mechanism, any rate constant and ε value to produce a better fit.

The program FITSIM40 involves regression analysis utilising the Marquardt technique by default. It yields optimised rate constants, associated errors and concentrations (absorbance) for a real data set and a given mechanism. The absorbance–time data simulated by the optimised rate constants may be read from the DOS editor and hence residual plots constructed.

We fitted the observed absorbance–time data in the proposed sequence using eight input parameters: three known ε values (see caption to Fig. 2) and five rate constants, out of which k_2 and k_{-2} were kept fixed. Reasonably good estimates for these two constants are possible. Available redox potentials for the couples [Fe(phen)₃]³⁺/²⁺ (1.06 V)[14] and S₂O₃⁻¹/²⁻ (1.30 V)[1a] are sufficiently precise and may be used to yield a reliable value for the ratio $k_2/k_{-2} = 4.5 \times 10^{-4}$. Again the k_{-2} step should be diffusion controlled since the analogous reaction between [Fe(bipy)₃]³⁺ and S₂O₃²⁻ is known to be so. A good estimate for k_{-2} is therefore 3.5×10^9 dm³ mol⁻¹ s⁻¹.[15] This along with the k_2/k_{-2} ratio, gives $k_2 = 1.6 \times 10^6$ dm³ mol⁻¹ s⁻¹. We therefore optimised only the three unknown rate constants k_1, k_3 and k_{-3} with FITSIM40 and thus obtained unique solutions. The observed fit is quite sensitive to the individual rate constants. For example, decreasing k_2 by more than 5%, keeping other constants unchanged, appreciably decreases the simulated absorbances and evidently worsens the fit, which cannot be improved by altering k_1, k_3 or k_{-3} in either direction. One may increase the simulated A_t by increasing k_1 and thus partially balance the adverse effect of decreasing k_2 on the fit, but then the A_t values at longer times far exceed the real value. The fit is affected less dramatically, though quite appreciably, when k_2 is kept constant whilst k_{-2} is decreased up to 95% of the input value. Further decrease in k_2 has no effect on the fit.

The observed kinetics and its simulation demonstrate that the proposed steps are necessary and sufficient to explain the observed inhibition of the reaction by **3²⁺**. We did test other different sequences. In one of them, for example, steps (6) and (7) were followed by eqn. (2). In another, a sequence of consecutive irreversible steps were considered: **1** ⟶ **3²⁺** + **3³⁺**; **3³⁺** ⟶ **3²⁺**. None reproduced the observed inhibition.

Variations in rate constants

The optimised second-order rate constant k_1 (Table 1) decreases with increasing [S₂O₃²⁻]. The calculated first-order rate constant k_1^0 (= k_1[S₂O₃²⁻]) increases with increasing [S₂O₃²⁻], gradually saturating at high [S₂O₃²⁻] (Fig. 3). A similar variation is

observed for k_1^0 with [H$^+$] (Fig. 3). However, k_1^0 does not change when c_{phen} is increased. The average values of optimised $k_3 = (6.7 \pm 0.3) \times 10^6$ dm^3 mol^{-1} s^{-1} and $k_{-3} = (3.3 \pm 0.2) \times 10^{-2}$ s^{-1} are independent of pH, c_{phen}, [S$_2$O$_3^{2-}$] and [3^{2+}] as expected.

Rate and equilibrium constants of some reactions analogous to eqn. (8) have been listed in Table 2. The equilibrium constants are moderate to high and reflect the strong nucleophilicity of the S-atom in its different oxoanions and oxoanion radicals. The equilibrium constant ($k_3/k_{-3} = 2 \times 10^8$ dm^3 mol^{-1}) for the formation of S$_4$O$_6^{2-}$ [eqn. (8)] is much larger than that (800 dm^3 mol^{-1}) for the formation of S$_4$O$_6^{3-}$ [eqn. (2a)] and reflects the higher stability of the S$_4$O$_6^{2-}$ ion.

The tendency of k_1^0 to saturate at higher [H$^+$] suggests that a protonated species dominates in kinetics over its conjugate base. In the experimental pH range, the near-exclusive form of the reductant is S$_2$O$_3^{2-}$ since at 25 °C pK_{a1} and pK_{a2} for H$_2$S$_2$O$_3$ are low, 0.35 and 1.01 respectively.[18] Some workers proposed that reduction of [IrCl$_6$]$^{2-}$ and I$_2$[9] with S$_2$O$_3^{2-}$ involved an asymmetrical form of S$_2$O$_3^{2-}$. Its conjugate acid (HS)SO$_3^-$ is believed to be a weak acid (p$K_{SH} \approx 10$) and Mehrotra and co-workers[19] assumed the protic equilibria, (HS)SO$_3^-$ $\rightleftharpoons$ H$^+$ + S$_2$O$_3^{2-}$ to explain their observed increase in rate with increasing pH in the reduction of [IrCl$_6$]$^{2-}$ with S$_2$O$_3^{2-}$. In the present system, rate increased with decreasing pH, and kinetically one cannot accommodate any of the possible protic equilibria involving the S$_2$O$_3^{2-}$ ion. Hence, the hydrolysis equilibrium of 1 [eqn. (5)] is the only plausible explanation for the observed dependence of k_1^0 on [H$^+$], provided 1 dominates over 2 kinetically.

Table 1 Optimum k_1 values^a for the reduction of the [Fe^{III}$_2$(μ-O)(phen)$_4$(H$_2$O)$_2$]$^{4+}$ ion with thiosulfate in aqueous solutions

| [S$_2$O$_3^{2-}$]/ mmol dm^{-3}	c_{phen}/ mmol dm^{-3}	pH^b	$10^3 k_1$/dm^3 mol^{-1} s^{-1}
1.0	3.0	4.50	2.83
2.5			2.73
5.0			2.40
8.0			2.06
10.0			1.88
12.5			1.61
15.0^c			1.36
		5.16	1.22
		4.76	1.34
		4.50	1.37
		4.22	1.49
		4.10	1.53
		3.99	1.54
		3.93	1.55
	6.0		1.37
	9.0		1.37
	12.0		1.36

^{a} Temperature 25.0 °C; [complex] 0.05 mmol dm^{-3}; $I = 1.0$ mol dm^{-3} (NaNO$_3$). Reported k_1 are the average of 2–3 determinations, precision of an individual set lies within 2–5%; standard deviation 4–8%. ^{b} Average of initial and final experimental pH. ^{c} A parallel experiment under conditions of this set was carried out after passing N$_2$ gas; rate constant changed only 2.5%. Experiment also repeated in the presence of 0.05 and 1.0 mmol dm^{-3} 3^{2+} added externally; rate constants did not change significantly.

The tendency of k_1^0 to saturate at higher [S$_2$O$_3^{2-}$] suggests adduct formation between the oxidant and reductant. This is expected from the labile nature[4,7] of the terminal H$_2$O in 1 and other oxo-bridged iron(III) complexes.[5,20] Adduct formation is indicated also from the observed increase in the absorbance at the isosbestic point (389 nm) with increase in [S$_2$O$_3^{2-}$]. Measured absorbances at 389 nm are 0.155, 0.226, 0.240 and 0.248 for [S$_2$O$_3^{2-}$] = 0, 5.0, 10.0 and 15.0 mmol dm^{-3} respectively. The standard deviation in three independent measurements for A_{389} at a fixed [S$_2$O$_3^{2-}$] is $\leqslant$0.003, which shows that the changes in A_{389} with [S$_2$O$_3^{2-}$] are reproducible and systematic, albeit small, and do not arise out of experimental uncertainties. It is noticeable in this instance that the spectrum of an aqueous solution of 1 without S$_2$O$_3^{2-}$ does not pass through the isosbestic point (Fig.1). One can conclude that 1 and S$_2$O$_3^{2-}$ together in solution rapidly form some new species, (I, say) which slowly changes to [Fe(phen)$_3$]$^{2+}$ maintaining the isosbestic point [eqn. (9)]. This is a somewhat elaborated form

$$1 + S_2O_3^{2-} \underset{}{\overset{K_1}{\rightleftharpoons}} I \overset{k_i}{\longrightarrow} 3^{3+} + 3^{2+} + S_2O_3^- \qquad (9)$$
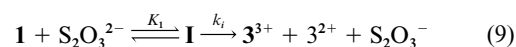
of eqn. (6) and leads to eqn. (10) provided that the hydrolysed Fe^{III}$_2$ species 2 does not react appreciably with S$_2$O$_3^{2-}$.

$$k_1^0 = (k_i K_1[H^+][S_2O_3^{2-}])/\{[H^+](1 + K_1[S_2O_3^{2-}]) + K_{a1}\} \quad (10)$$

As expected from eqn. (10), plots of $1/k_1^0$ vs. $1/[S_2O_3^{2-}]$ at fixed pH and plots of $1/k_1^0$ vs. $1/[H^+]$ at fixed [S$_2$O$_3^{2-}$] are excellent straight lines. Slopes and intercepts of these two straight lines yield $k_i K_1 = (0.41 \pm 0.02)$ dm^3 mol^{-1} s^{-1} [$k_i = (3.7 \pm 0.2) \times 10^{-3}$ s^{-1}], $K_1 = 111 \pm 5$ dm^3 mol^{-1} and $K_{a1} = 5.1 \times 10^{-6}$ mol
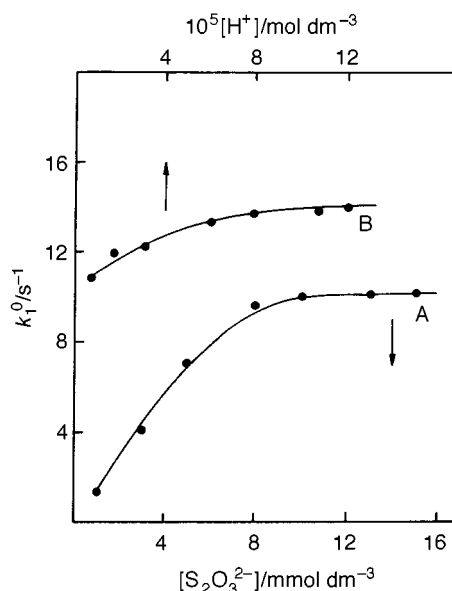

Fig. 3 Variation of the first-order rate constant k_1^0 (= k_1[S$_2$O$_3^{2-}$]) with change in [S$_2$O$_3^{2-}$] at fixed pH (A) and with [H$^+$] at fixed [S$_2$O$_3^{2-}$] (B); [complex] 0.05 mmol dm^{-3}; T 25.0 °C; I 1.0 mol dm^{-3} (NaNO$_3$). The solid lines represent the best visual fits.

Table 2 Rate constants for the self reaction of the S$_2$O$_3^-$ radical ion and some analogous reactions in aqueous solution at 25 °C

Reaction	Forward rate constant^a	Reverse rate constant	Equilibrium constant	Ref.
S$_2$O$_3^{2-}$ + S$_2$O$_3^-$ $\rightleftharpoons$ S$_4$O$_6^{3-}$	2×10^9	$2.5 \times 10^{6\,b}$	800^c	2, 16
SO$_3^-$ + SO$_3^-$ $\rightleftharpoons$ S$_2$O$_6^{2-}$	1.8×10^8	—		17
S$_2$O$_3^-$ + S$_2$O$_3^-$ $\rightleftharpoons$ S$_4$O$_6^{2-}$	6.7×10^6	$3.3 \times 10^{-2\,b}$	$2 \times 10^{8\,c}$	This work
I$_2$ + S$_2$O$_3^{2-}$ $\rightleftharpoons$ I$_2$S$_2$O$_3^{2-}$	7.8×10^9	$2.5 \times 10^{2\,b}$	$3.2 \times 10^{7\,c}$	9
I$_3^-$ + S$_2$O$_3^{2-}$ $\rightleftharpoons$ I$_2$S$_2$O$_3^{2-}$ + I$^-$	4.2×10^8	$9.5 \times 10^{3\,a}$	4.42×10^4	9

^{a} In dm^3 mol^{-1} s^{-1}. ^{b} In s^{-1}. ^{c} In dm^3 mol^{-1}.

dm^{-3} in good agreement with its spectrophotometrically measured value[4], 4.0×10^{-6} mol dm^{-3}. This agreement lends support to eqn. (10) and the proposed inactivity of **2**. It is also indicated that the intermediate adduct **I** contains only one $S_2O_3^{2-}$. The Fuoss equation[21] yields $K_1 = 5.7$ dm^3 mol^{-1} for a purely electrostricted ion pair formed between **1** and $S_2O_3^{2-}$ ions, whose respective radii are 71 nm (ref. 3) and 33 nm (ref. 8). The kinetically measured value for K_1 is much larger than this value and lies close to the first formation constant (126 dm^3 mol^{-1} at 25 °C, $I = 0.47$ mol dm^{-3}) for the Fe^{3+}–$S_2O_3^{2-}$ system.[22] Moreover, $S_2O_3^{2-}$ is a strong nucleophile ($n = 6.36$ on the Swain–Scott scale),[18,23] its co-ordination precedes the redox reactions[1,9] with $[Ag(OH)_4]^-$, $[Fe(H_2O)_6]^{3+}$, Cr(IV), $[Au(NH_3)_4]^{3+}$, $[AuCl_4]^-$, $[OsO_4(OH)_2]^{2-}$, $[Co(NTA)(H_2O)_2]$, $[Cu(NH_3)_4]^{2+}$, I_2 and I_3^-. Deaquation of an iron(III) site in **1** and its inner-sphere interaction with thiosulfate is therefore anticipated. However, oxidation of $S_2O_3^{2-}$ by $[Fe(bipy)_3]^{3+}$, is known to be outer-sphere.[14] The analogous reaction of $[Fe(phen)_3]^{3+}$ with $S_2O_3^{2-}$ should also follow a similar mechanism since ligand substitution in both complexes are slow compared to redox. The outer-sphere mechanism for $[Fe(phen)_3]^{3+}$ is further supported by the Marcus relation, which along with the self exchange rate for the $[Fe(phen)_3]^{3+/2+}$ couple[24] yields $k_2 = 1.8 \times 10^5$ dm^3 mol^{-1} s^{-1}. The value agrees reasonably well with our previous estimate.

The assumption regarding non-reactivity of **2** seems justified. Inner-sphere adduct formation with $S_2O_3^{2-}$ by **2** and further by **I** should both be less favourable than **1** due to their lower charges. The lesser number of replaceable water molecules in **I** and **2** than in **1** should also disfavour adduct formation on statistical grounds. Not only should **1** form a better adduct but it should also dominate kinetically over **2** because **1** is more electron deficient and hence can be reduced more easily. It is true for most redox systems involving cationic complexes and anionic reductants that protonation of the oxidant increases its reactivity whereas the opposite is true for protonation of the reductant.[25]

We chose a somewhat restricted set of conditions of pH and c_{phen} for the present experiments to avoid some potential complications. The large excess of c_{phen} over the iron complexes suppresses the loss of phen[4] by **1** and thus minimises the number of kinetically active iron(III) species. Excess c_{phen} lightly buffers the solution to within ± 0.08 (but mostly within ± 0.04) pH units and also sequesters any trace metal ion, known to strongly catalyse[14,26] the dissociation of $S_2O_3^{2-}$ (a potential complication in the study of redox reactions of $S_2O_3^{2-}$). Use of excess c_{phen} was essential also to ensure quantitative formation of the tris(phenanthroline) complexes **3³⁺** and **3²⁺** from any transient bis intermediates. Otherwise, interpretation of kinetic data becomes difficult and oxidation of $[Fe(phen)_3]^{2+}$ to **1** may be an additional complication since Cyfert[27] showed that hydrogen peroxide oxidises $[Fe(phen)_3]^{2+}$ to a $\{Fe_2O\}^{4+}$ species, possibly **1** in the absence of excess phenanthroline.

Substitution or redox

Spectral observations and tendency of k_1^0 to saturate at high $[S_2O_3^{2-}]$ suggested a role for the intermediate **I** in kinetics. Which of the two processes is the slower one, formation of '**I**' or its subsequent decomposition to products, is an interesting question.

Chelation labilises the co-ordinated water molecules. For example, the water exchange rate constant[28] for $[Fe(H_2O)_6]^{3+}$ is 280 s^{-1} at 25 °C, but the value for[29] $[Fe(EDTA)(H_2O)]^-$ is $\approx 10^5$ s^{-1}. Candle and Crumbliss[30] observed a similar labilising influence of hydroxamic acids on water molecules co-ordinated to iron(III) centres while investigating the dissociation reactions of some iron(III) complexes. Labilisation by the ligand Tiron (4,5-dihydroxy-1,3-benzene disulfonic acid, disodium salt monohydrate) was noted also by Zhang and Jordan[31] while studying the kinetics of dissociation reactions of mono-, bis- and tris-

Table 3 Rate constants (k/dm^3 mol^{-1} s^{-1}) for the reduction of some iron(III) complexes in aqueous media, 25.0 °C

Complex	Reducing agent	k	Ref.
$[Fe(phen)_3]^{3+}$	$S_2O_3^{2-}$	$1.8 \times 10^{5\,a}$	This work
	Ascorbate(1−)	$1.5 \times 10^{9\,b}$	32
	ClO_2^-	2.3×10^7	33
$[Fe_2O(phen)_4(H_2O)_4]^{4+\,c}$	$S_2O_3^{2-}$	0.41	This work
	NH_2OH	2.31	4
$[Fe_3O(O_2CMe)_6]^{+\,d}$	NH_2OH	4.6×10^{-2}	5(b)
$[Fe_2O(L)(CH_3CN)_2]^{e}$	Hydroquinone	4.3	5(a)
	Catechol	1.7	5(a)
	Picric acid	0.4	5(a)
	Triphenylphosphine	0.02	5(a)

^{a} Estimated value, see text. ^{b} At 20.0 °C. ^{c} Phenanthroline buffer. ^{d} Acetate buffer, 35.0 °C. ^{e} L is 2dmg·2BF$_2$, CH$_3$CN media.

complexes of this ligand with iron(III) in acidic aqueous solution. Based on these observations, one expects that the water exchange rate constant for **1** should be much higher than 280 s^{-1} and the observed, small value for k_i [$(3.7 \pm 0.2) \times 10^{-3}$ s^{-1}] better fits the intramolecular electron-transfer step in **I**. Accordingly, we conclude that in the present system rapid adduct formation precedes the slow intramolecular electron transfer step.

The k_i step itself must represent a multistep reaction. Its most likely components are: (a) slow intramolecular electron transfer and formation of a $Fe^{III}Fe^{II}$ dimer (k_i), (b) fast cleavage of the oxo-bridge in the $Fe^{III}Fe^{II}$ dimer, and generation of Fe^{III} and Fe^{II} monomers, (c) rapid and quantitative conversion of the monomers to **3²⁺** and **3³⁺** in the presence of excess phenanthroline.

Rate constants for oxidation by some iron(III) complexes have been gathered in Table 3. Note that the oxo-bridged species react at a slower rate than the comparable monomers.

To our knowledge, the present kinetic investigation is the first example of product inhibition in the oxidation of $S_2O_3^{2-}$ by a metal ion complex and constitutes strong evidence in favour of the self reaction of $S_2O_3^-$ leading to the tetrathionate ion.

Experimental

Materials

Crystals of $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2][NO_3]_4 \cdot 5H_2O$ were prepared by a known[3] method. The prepared samples gave satisfactory electronic spectra[3,4] and elemental analyses (Found: C, 47.2; H, 3.7; Fe, 9.1; N, 13.8. Calc. for $C_{48}H_{32}Fe_2N_{12}O_{13} \cdot 7H_2O$: C, 47.15; H, 3.8; Fe, 9.1; N, 13.75%). Stock solutions of sodium thiosulfate (AR, BDH) were renewed daily and standardised iodometrically against potassium dichromate.[34] Nitrate salts of **3³⁺** and **3²⁺** were prepared according to the literature.[35] 1,10-Phenanthroline monohydrate (Sigma) was used without further purification. Solutions of recrystallised NaNO$_3$ (AR, BDH) were standardised by the ion exchange technique.[36] All other reagents used were of analytical grade. Chromium(II)-scrubbed dinitrogen gas and triply distilled water were used throughout. Reported kinetic data are for 25.0 °C and $I = 1.0$ mol dm^{-3}. The molar absorption coefficient (ε) of an aqueous solution of **1** in the presence of $S_2O_3^{2-}$ was measured immediately after mixing the reagents under the experimental conditions; ε for **3²⁺** was measured under experimental conditions with a fresh solution of the prepared sample (see Table 1, footnote a); **3³⁺** does not absorb at 510 nm, the experimental wavelength.

Kinetics

Kinetics was monitored at 510 nm, the visible maximum of the reaction product $[Fe(phen)_3]^{2+}$, *in situ* in the electrically controlled thermostatted cell housing (CPS-240A) of a Shimadzu spectrophotometer (UV-1601 PC). A large excess of thiosulfate

and c_{phen} over the complex (0.05 mmol dm^{-3}) were used. For some faster reactions, the reductant was rapidly and directly injected into the cell containing other materials in solution and thermally equilibrated in the cell housing. Absorbance data were collected in the 'Kinetic mode' of the spectrophotometer and data collection started almost simultaneously with mixing of the reagents. The pH of experimental solutions was measured with an Orion (710 A) pH-meter using a calibrated [36] combined electrode.

Stoichiometry

A 100 ml portion of 0.10 mmol dm^{-3} complex solution containing three different concentrations (0.40, 0.60, 1.0 mmol dm^{-3}) of $S_2O_3^{2-}$ but a fixed c_{phen} (3.0 mmol dm^{-3}) at pH 4.50 was allowed to equilibrate up to a time after which no absorbance change could be noticed over a period of 3–4 h. The amount of 3^{2+} generated was determined from the solution absorbance measured at 510 nm after appropriate dilution. The whole solution was then eluted through a column of cation exchange resin in the Na$^+$-form. The amount of $S_2O_3^{2-}$ in the eluted solution was quantified iodimetrically using starch indicator.[34] In another sample (P) 100 ml, 4.0 mmol dm^{-3} complex were taken with 20 mmol dm^{-3} $S_2O_3^{2-}$. The solution was eluted similarly after equilibrium was attained and the volume was reduced to $\approx$5 ml by evaporation at 50 °C. A concentrated solution of $Sr(NO_3)_2$ was added to test for the presence of sulfate ion in the product.[37] Under experimental conditions similar to sample P, we tested for the presence of tertrathionate in the eluted solution by the cyanolysis method of Kolthoff and Belcher.[6]

Acknowledgements

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