Kinetics and Mechanism of the Oxidation of Thiosulphate Ions by Copper(II) Ions in Aqueous Ammonia Solution

By **John J. Byerley, Safaa A. Fouda,** and **Garry L. Rempel,*** Metallurgical Chemistry Research Laboratory, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

Copper(II) ions in aqueous ammonia solution oxidize thiosulphate ions initially to tetrathionate ions; the latter then undergo a subsequent disproportionation reaction to yield trithionate and thiosulphate ions. The detailed kinetics of the reaction suggest a mechanism which involves substitution of thiosulphate ion into the co-ordination sphere of a triamminecopper(II) complex in the rate-determining step. A one-equivalent electron transfer from the thiosulphate to the copper(II) ion, occurring in the intermediate triamminecopper(II)–thiosulphate complex, gives rise to copper(I) and $S_2O_3^-$ ions, the latter dimerizing to tetrathionate ions.

In the extraction of metals from sulphide minerals by ammonia leaching, it has been found that almost invariably thiosulphate ions are a preliminary product of sulphur oxidation.[1-5] The rate of conversion of thiosulphate to thionate, sulphate, and sulphamate ions in aqueous ammonia solution is influenced by the presence of copper(II) ions,[2,6] the latter apparently functioning as an oxidation catalyst. Although considerable evidence has been obtained for the formation and subsequent reaction of thiosulphate ions in aqueous ammonia solution, a detailed kinetic and mechanistic study of the oxidation of these ions in the presence of copper(II) ammine complexes has not been reported. In the presence of oxygen, such a study is difficult since the copper(I) species formed appears to be oxidized rapidly. Also oxidation of thiosulphate ions by molecular oxygen co-ordinated to the copper seems to be involved.[7]

The present investigation reports the kinetics and mechanism of the direct reaction between copper(II) and thiosulphate ions in aqueous ammonia solution in the absence of oxygen. It has previously been suggested that complexes between these ions are formed prior to the oxidation-reduction reaction.[6] The formation of complexes between the ions hexa-amminecobalt(III) [8] or bis(ethylenediamine)copper(II) [9] and thiosulphate is known to occur.

EXPERIMENTAL

Stock solutions of copper(II) ions in aqueous ammonia were prepared from $CuSO_4,5H_2O$ (B.D.H., AnalaR) and concentrated volumetric solutions of ammonium hydroxide (B.D.H.). Stock solutions of thiosulphate ions were prepared from $Na_2S_2O_3,5H_2O$ (B.D.H., AnalaR). All dilutions were made with distilled water. Solutions were degassed and maintained under an atmosphere of argon gas (Linde, ultra high purity) during the reaction. Sodium tetrathionate (anhydrous) was obtained from K & K Laboratories. Potassium trithionate was prepared according to a standard method.[10] All other chemicals used in the analytical determinations were of reagent grade purity.

Determination of Reaction Products.—Determinations of the ions copper(I) and thiosulphate were carried out using a standard iodimetric titration method.[11] Qualitative analyses for sulphur anions were performed according to the methods given by Karchmer.[12] The method of Kelly *et al.*[13] was used in determining trithionate ions quantitatively.

Determination of Reaction Rates.—Reactions were carried out in a divided compartment optical cell (Pyrocell Manufacturing Co.) of known path length. The slotted centre partition of the cell facilitated mixing of the copper(II) and thiosulphate solutions under an atmosphere of argon gas. Kinetic measurements were made by following the decrease in copper(II) concentration, using a Beckman DK-2A ratio recording spectrophotometer set at a wavelength of 612 nm [$\lambda_{max.}$ of the copper(II)–ammonia solutions]. A thermostatted cell holder in conjunction with a Haake constant-temperature circulator allowed temperature control of the reaction solution to within ±0·1 °C. Continuous optical density against time plots were obtained directly by use of a time-drive accessory attached to the spectrophotometer.

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[9] H. Yoneda, *Bull. Chem. Soc. Japan*, 1956, **29**, 68.

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RESULTS AND DISCUSSION

Over the concentration ranges of copper(II) (0·005—0·010M) and ammonia (0·10—1·00M) used in this investigation, the predominant species initially present were thought to be $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (*ca.* 97%) and $[Cu(NH_3)_3(H_2O)_3]^{2+}$ (*ca.* 3%). This conclusion was arrived at by constructing a distribution diagram [14] for the copper complexes as a function of free-ammonia concentration. Values for the formation constants used in constructing this diagram were taken from ref. 15. The spectrum of a solution of copper(II) ions in 0·2M-ammonia (pH 11·2) showed a maximum absorption at 612 nm (ε 45 l mol^{-1} cm^{-1}) and did not change on increasing the ionic strength of the media to 1M by the addition of sodium sulphate. In 2M-ammonium nitrate maxima in the absorption spectra of the tetra-ammine- and triammine-copper(II) complexes have been reported at 590 (ε 52) and 645 nm (ε 40 l mol^{-1} cm^{-1}) respectively.[16] It was found in the present investigation that the maximum absorption of the copper(II)–ammonia solution was essentially unchanged over the range of ammonia concentrations used, *i.e.* the ratio of the tetra-ammine to the triammine complex appears fairly constant as suggested by the distribution diagram.

At pH >10, the copper(II) ammine species are reported as existing in equilibrium with significant concentrations of hydroxo-species.[17] Approximate constants ($K_1 = 250$, $K_2 = 49$ l mol^{-1}) for the stepwise addition of two hydroxide ions to the copper(II) ammine species in ammonia solutions of unit activity at 25 °C have been reported [17] and similar values were also obtained in the present investigation. However, in view of the relatively constant absorption spectra, it appears that the hydroxo-species probably involve co-ordination or association of hydroxide ion at the two axial positions of the copper(II) ammine complexes.

When thiosulphate ions were added to the copper(II)–ammonia solution, an immediate increase in the optical density of the solution was observed prior to commencement of the reaction between the copper(II) ammine species and thiosulphate ions. The position of the absorption maximum at 612 nm, however, did not change and furthermore did not change during the course of the reaction. The optical density increase can be interpreted on the basis of an association between the reducing anion and the copper(II) ammine complex. Such effects have been observed for the addition of reducing anions, including that of thiosulphate, to the bis(ethylenediamine)copper(II) complex, $[Cu(en)_2]^{2+}$.[9] The extent of association is found to differ from one anion to another and is suggested as taking place at one of the axial positions of the copper complex, the association resulting from a strong polarizing effect of the central copper(II) ion on the polarizable anion. Accordingly, the association is presumed to occur without any essential change in the equatorial structure of the copper complex.

In view of the fact that the tetra-ammine- and triammine-copper(II) complexes appear to prevail, apart from axial-position changes brought about by hydroxide and thiosulphate ions present in the solutions, the discussion of the mechanistic aspects of the reaction will be given in terms of four-co-ordinate or equatorial ligand complexes of copper(II). The kinetic results will also be seen to indicate reaction at an equatorial position of the copper(II) species.

Stoicheiometry.—On completion of the reaction between thiosulphate and copper(II) ions, *i.e.* immediately after the optical density at 612 nm became zero, qualitative analyses for the sulphur containing products were performed. The addition of mercury(I) nitrate to a sulphuric acid neutralized reaction solution produced a yellow precipitate which became black on heating, thus indicating the presence of tetrathionate ions ($S_4O_6^{2-}$).[12] Experiments were carried out to estimate the consumption of thiosulphate ions ($S_2O_3^{2-}$) corresponding to different initial concentrations of Cu^{II}. The number of moles of $S_2O_3^{2-}$ consumed was estimated by determining, at the end of the reaction, the amount of unconsumed $S_2O_3^{2-}$ by means of an iodimetric titration. Since the analysis was performed when the optical density had reached zero, *i.e.* all the Cu^{II} was reduced to Cu^{I}, the number of moles of Cu^{II} consumed was equal to the initial moles of Cu^{II}. Representative stoicheiometric results are shown in Table 1.

TABLE 1

Stoicheiometry of the direct oxidation of thiosulphate by copper(II) ions at 30 °C and 0·20M-NH_3

$[Cu^{II}]_0$ M	$[S_2O_3^{2-}]_0$ M	$[S_2O_3^{2-}]_\infty$ M	$[S_3O_6^{2-}]_\infty$ M
0·005	0·025	0·020	trace
0·010	0·050	0·040	trace
0·030	0·100	0·076	0·0024
0·010	0·100	0·094 *	
0·030	0·100	0·085 *	0·0078 *
0·030	0·150	0·140 *	0·0079 *

* Final reaction solution set aside for 18 h under an atmosphere of argon gas before analysis.

If $S_4O_6^{2-}$ is the main sulphur-containing product of the reaction, the stoicheiometry of the reaction can be written as (1) (ligands bound to copper are omitted).

$$2Cu^{2+} + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2Cu^{+} \qquad (1)$$

This equation indicates that 1 mole of $S_2O_3^{2-}$ is consumed per mole of Cu^{II}, as do quantitative analyses performed immediately following completion of the reaction for those experiments in which low initial $[Cu^{II}]$ and $[S_2O_3^{2-}]$ were used (Table 1). It was found, however, that if the final reaction solution was analysed sometime after completion of the reaction, or immediately

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[14] J. N. Butler, 'Ionic Equilibrium,' Addison-Wesley, Reading, Mass., 1964, pp. 321—335.

[15] 'Stability Constants,' Chem. Soc. Special Publ. No. 17, London, 1964.

[16] J. Bjerrum, C. J. Ballhausen, and C. K. Jorgensen, *Acta Chem. Scand.*, 1954, **8**, 1275.

[17] R. E. Reeves and P. Bragg, *J. Amer. Chem. Soc.*, 1962, **84**, 2491.

after reaction for experiments with higher initial [Cu^{II}] and [$S_2O_3^{2-}$], trithionate ($S_3O_6^{2-}$) was formed along with a build-up of $S_2O_3^{2-}$ ions (Table 1). A separate test on a sample of $S_4O_6^{2-}$ in ammoniacal solution showed the formation of both $S_3O_6^{2-}$ and $S_2O_3^{2-}$ ions when the solution was set aside overnight under an atmosphere of argon gas. Thus, the initial products of the direct reaction between $S_2O_3^{2-}$ and Cu^{II} ions appear to be $S_4O_6^{2-}$ and Cu^I [equation (1)], the $S_4O_6^{2-}$ ions undergoing subsequent disproportionation to $S_3O_6^{2-}$ and $S_2O_3^{2-}$.

The decomposition of $S_4O_6^{2-}$ to higher and lower polythionate ions has been reported previously.[18,19] The reaction is highly catalyzed by the presence of thiosulphate ions and can be represented by the following scheme.

$$S_4O_6^{2-} + S_2O_3^{2-} \longrightarrow S_5O_6^{2-} + SO_3^{2-} \qquad (2)$$

$$SO_3^{2-} + S_4O_6^{2-} \longrightarrow S_3O_6^{2-} + S_2O_3^{2-} \qquad (3)$$

$$S_5O_6^{2-} + 3OH^- \longrightarrow 5/2S_2O_3^{2-} + 3/2H_2O \qquad (4)$$

$$2S_4O_6^{2-} + 3OH^- \longrightarrow 5/2S_2O_3^{2-} + S_3O_6^{2-} + 3/2H_2O \qquad (5)$$

This suggests that about 60% of the $S_2O_3^{2-}$ ions initially reacted with Cu^{II} will be reformed. The results of Table 1 for solutions analysed 18 h after completion of the reaction with Cu^{II} are in good agreement with this conclusion.

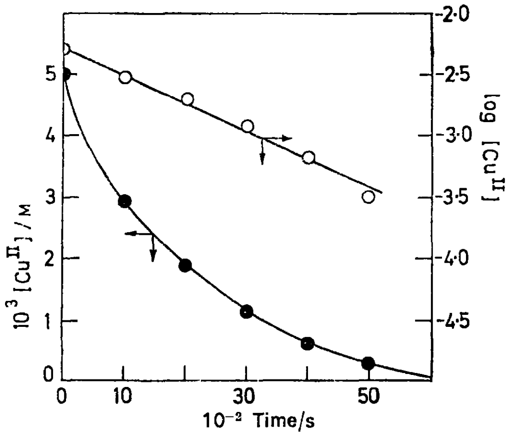

FIGURE 1 Representative rate plot for the reaction of copper(II) ions with thiosulphate (0·10M) in aqueous ammonia solution (0·2M) at 30 °C

Kinetics.—The kinetics of the reaction were investigated by following, continuously as a function of time, the decrease in absorption of the copper(II)-ammonia solution at 612 nm. Figure 1 shows a representative plot of [Cu^{II}] against time which analyses well for a first-order dependence on [Cu^{II}]. Experiments for various initial copper(II)-ion concentrations in the range 0·005—0·010M were carried out at 0·05M-thiosulphate and 0·2M-ammonia at 30 °C. Plots of log [Cu^{II}] against time were linear and had essentially the same slope (Table 2), thus confirming the first-order dependence on [Cu^{II}]. These results suggest a rate law of the form (6), where $k' = k[S_2O_3^{2-}]^m[NH_3]^n$. Since the con-

$$-d[Cu^{II}]/dt = k'[Cu^{II}] \qquad (6)$$

centrations of $S_2O_3^{2-}$ and NH_3 remain essentially constant during the reaction, the kinetics are pseudo-first order.

In order to investigate the effect of the thiosulphate-ion concentration on the reaction, a number of experiments using initial [$S_2O_3^{2-}$] in the range 0·025—0·20M were carried out at [Cu^{II}] = 0·005M and [NH_3] = 0·20M at 30 °C (Table 2). A plot of k' against [$S_2O_3^{2-}$] was linear, suggesting a first-order dependence on [$S_2O_3^{2-}$] up to 0·10M. When the ionic strength of the reaction solution was kept constant by the addition of sodium sulphate, slightly lower reaction rates were observed (Table 2); however, a first-order dependence on [$S_2O_3^{2-}$] was still obtained. Experiments at higher [$S_2O_3^{2-}$] indicated that the dependence on [$S_2O_3^{2-}$] tended toward a higher order above 0·15M.

TABLE 2

Summary of kinetic data at 30 °C

$10^2[Cu^{II}]$ / M	$10[S_2O_3^{2-}]$ / M	$[NH_3]$ / M	$10^4k'$ / s^{-1}
0·50	0·50	0·20	2·17
0·60	0·50	0·20	2·31
0·80	0·50	0·20	2·26
1·00	0·50	0·20	2·18
0·50	0·12	0·20	0·33
0·50	0·25	0·20	1·05
0·50	0·75	0·20	3·13
0·50	1·00	0·20	4·64
0·50	1·50	0·20	7·35
0·50	2·00	0·20	11·7
0·50	4·00	0·20	25·0
0·50	0·25	0·20	0·99 [a]
0·50	0·50	0·20	1·77 [a]
0·50	1·00	0·20	4·05 [a]
0·50	1·50	0·20	6·90 [a]
0·50	0·50	0·10	3·95
0·50	0·50	0·13	3·07
0·50	0·50	0·40	0·99
0·50	0·50	0·60	0·67
0·50	0·50	0·80	0·40
0·50	0·50	1·00	0·31
0·50	0·50	0·20 [b]	0·15

[a] Constant ionic strength 0·20M using Na_2SO_4. [b] Ethylenediamine in place of NH_3.

The reduction of Cu^{II} by $S_2O_3^{2-}$ ions is extremely rapid in a purely aqueous solution. In the presence of NH_3 the reaction is much slower and the rate is dependent on [NH_3]. The latter was investigated in the range 0·1—1·0M-NH_3 at [Cu^{II}] = 0·005M and [$S_2O_3^{2-}$] = 0·05M at 30 °C. The results shown in Table 2 suggest an inverse dependence of the reaction rate on [NH_3] [equation (7)]

$$-d[Cu^{II}]/dt = k[Cu^{II}][S_2O_3^{2-}]/[NH_3] \qquad (7)$$

and a plot of k' against $[NH_3]^{-1}$ is linear. The value of k at 30 °C, determined from the slope of a plot of k' against [$S_2O_3^{2-}$], was found to be $8·5 \times 10^{-4}$ s^{-1}; a value of $8·0 \times 10^{-4}$ s^{-1} for k was determined from the slope of a plot of k' against $[NH_3]^{-1}$. Kinetic measurements over the temperature range 27—39 °C, for two concentrations

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[18] A. Fava, *J. Amer. Chem. Soc.*, 1955, **77**, 5792.

[19] O. Foss, *Acta Chem. Scand.*, 1961, **15**, 1608.

of Cu^{II} (Table 3), yielded good Arrhenius plots and the activation parameters $\Delta H^{\ddagger} = 24{\cdot}5 \pm 0{\cdot}1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 3{\cdot}6 \pm 1$ cal K^{-1} mol^{-1}.

TABLE 3

Effect of temperature on the oxidation of thiosulphate by copper(II) ions in aqueous ammonia solution. $[S_2O_3^{2-}] = 0{\cdot}05$M, $[NH_3] = 0{\cdot}20$M

$10^2[Cu^{II}]$ M	Temp. °C	10^4k s^{-1}
0·50	27·0	7·13
0·50	30·0	8·74
0·50	34·5	15·80
0·50	39·0	27·90
1·00	27·0	7·60
1·00	30·0	8·67
1·00	34·5	14·40
1·00	39·0	31·50

Mechanism.—The kinetic results suggest that the mechanism of Cu^{II} reduction involves substitution of $S_2O_3^{2-}$ ion into the co-ordination sphere of a copper(II) ammine complex prior to an electron-transfer step. Since the reaction between $S_2O_3^{2-}$ and Cu^{II} in a purely aqueous solution is extremely rapid compared to the rates observed in the present investigation, the tri-ammine complex might be expected to be more reactive than that of the tetra-ammine. Consequently, the mechanism of the reaction can be explained on the basis of equations (8)—(10) (axial ligands are omitted), which would give a rate law of the form (11).

$$[Cu(NH_3)_4]^{2+} \underset{H_2O}{\overset{K}{\rightleftharpoons}} [Cu(NH_3)_3(H_2O)]^{2+} + NH_3 \quad (8)$$

$$[Cu(NH_3)_3(H_2O)]^{2+} + S_2O_3^{2-} \xrightarrow{k_1} [Cu(NH_3)_3(S_2O_3)] + H_2O \quad (9)$$

$$[Cu(NH_3)_3(S_2O_3)] \longrightarrow [Cu(NH_3)_3]^{+} + 1/2\, S_4O_6^{2-} \quad (10)$$

$$\begin{aligned} d[Cu^{I}]/dt &= -d[Cu^{II}]/dt \\ &= k_1K[Cu(NH_3)_4^{2+}][S_2O_3^{2-}]/[NH_3] \quad (11) \end{aligned}$$

Since approximately 97% Cu^{II} is in the form of the tetra-ammine species, equation (11) can be expressed as (12). This rate law is consistent with the kinetics observed, where k_1K is equal to the experimental rate constant k of equation (7). The value of k_1 at 30 °C, evaluated by using the literature [15] value of K and the value of k, is 0·095 1 mol^{-1} s^{-1}. The above mechanism, as written, involves an S_N2 substitution reaction in the rate-determining step followed by rapid electron transfer from $S_2O_3^{2-}$ to Cu^{II}. Since Cu^{II} only requires one electron to be reduced to Cu^{I}, a one-equivalent electron transfer takes place giving rise to a singly charged anion ($S_2O_3^-$). Thus, the final steps of the reaction may be expressed as in (13) and (14). The rapid dimerization of $S_2O_3^-$ to yield $S_4O_6^{2-}$ has previously been postulated in $S_2O_3^{2-}$ oxidation reactions.[20,21] The addition of a free radical inhibitor, namely mannitol, had no effect on the observed rate of the reaction, suggesting that the involvement of free radicals in the rate-determining step of the reaction is unlikely.

$$-d[Cu^{II}]/dt = k_1K[Cu^{II}][S_2O_3^{2-}]/[NH_3] \quad (12)$$

$$[Cu(NH_3)_3(S_2O_3)] \xrightarrow{\text{fast}} [Cu(NH_3)_3]^{+} + S_2O_3^{-} \quad (13)$$

$$2S_2O_3^{-} \xrightarrow{\text{fast}} S_4O_6^{2-} \quad (14)$$

It can be argued that the dependence on $[S_2O_3^{2-}]$ does not imply an associative mechanism if the substitution takes places as shown in equations (15) and (16). A steady-state condition for $Cu(NH_3)_3^{2+}$ yields the rate law (17), which at constant $[S_2O_3^{2-}]$ and $[NH_3]$ becomes equivalent to equation (6) where k' is given by (18).

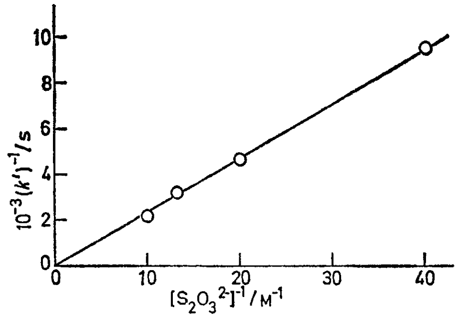

FIGURE 2 Plot of $1/k'$ against $[S_2O_3^{2-}]^{-1}$ for the reaction of copper(II) ions (5×10^{-4}M) with thiosulphate in 0·2M-ammonia at 30 °C

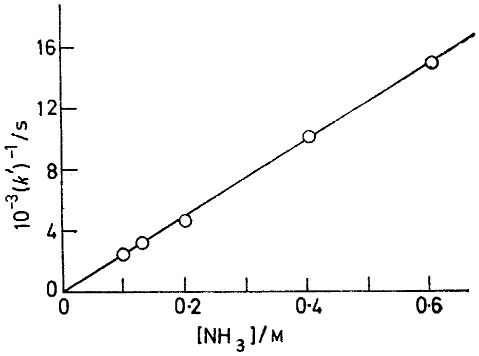

FIGURE 3 Plot of $1/k'$ against $[NH_3]$ for the reaction of copper(II) ions (5×10^{-4}M) with thiosulphate (5×10^{-2}M) at 30 °C

$$[Cu(NH_3)_3(H_2O)]^{2+} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} [Cu(NH_3)_3]^{2+} + H_2O \quad (15)$$

$$[Cu(NH_3)_3]^{2+} + S_2O_3^{2-} \xrightarrow{k_c} [Cu(NH_3)_3(S_2O_3)] \quad (16)$$

$$-\frac{d[Cu^{II}]}{dt} = \frac{k_ak_cK[Cu^{II}][S_2O_3^{2-}]}{k_b[NH_3][H_2O] + k_c[S_2O_3^{2-}][NH_3]} \quad (17)$$

$$k' = \frac{k_ak_cK[S_2O_3^{2-}]}{k_b[NH_3][H_2O] + k_c[S_2O_3^{2-}][NH_3]} \quad (18)$$

Values of k' calculated from the experimental results are shown in Table 2. A plot of $1/k'$ against $[S_2O_3^{2-}]^{-1}$ (Figure 2) is linear over the range of $[S_2O_3^{2-}]$ investigated and its gradient yields a value of 0·19 s for (k_b/k_ak_c). A plot of $1/k'$ against $[NH_3]$ (Figure 3) is also reasonably linear up to $[NH_3] = 0{\cdot}6$M and from the gradient of this

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[20] I. Baldea and G. Niac, *Inorg. Chem.*, 1970, **9**, 110.

[21] M. I. Edmonds and K. E. Howlett, *J. Chem. Soc.* (*A*), 1970, 2866.

plot and the value of (k_b/k_ck_a) obtained from Figure 2, a value of $k_a = 0{\cdot}14$ s^{-1} is obtained. Furthermore, if $k_a = 0{\cdot}14$ s^{-1}, the value of $k_b/k_c = 0{\cdot}027$. These results suggest that $k_b[NH_3][H_2O] \gg k_c[S_2O_3^{2-}][NH_3]$ in equation (17) for the range of $[S_2O_3^{2-}]$ investigated. Consequently, the rate law given by equation (17) is also consistent with the kinetics observed.

In order to differentiate between the mechanisms which lead to the rate laws given by equations (12) and (17) respectively, experiments at $[S_2O_3^{2-}] = 1$—2M appear to be necessary. Such an investigation was precluded, however, since the $[S_2O_3^{2-}]$ dependence above $[S_2O_3^{2-}] = 0{\cdot}2$M tended to be somewhat greater than first order suggesting that another reaction path becomes important at higher $[S_2O_3^{2-}]$.

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