Activation of Copper(II) Ammine Complexes by Molecular Oxygen for the Oxidation of Thiosulphate Ions

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The stoicheiometry and kinetics of reaction of aqueous-ammonia (0·1–1·0M) solutions of copper(II) ions with thiosulphate ion in the presence of oxygen have been examined. The amount of oxygen consumption and the relative amounts of the final sulphur products, namely trithionate and sulphate ions, are dependent on the initial $[S_2O_3]^{2-}$ concentration and pH. The detailed kinetics of the reaction at pH 11·2 suggest mechanisms in which O_2 becomes axially associated with amminethiosulphatocopper(II) species. In this role O_2 assists in electron transfer between $[S_2O_3]^{2-}$ and Cu^{II}. The most active species for $[S_3O_6]^{2-}$ formation is a tetra-amminecopper(II) complex having one axial $[S_2O_3]^{2-}$ and one axial O_2 ligand. A triamminecopper(II) complex, having both axial and equatorial $[S_2O_3]^{2-}$ ligands as well as an axial O_2, is suggested as the reactive intermediate for $[SO_4]^{2-}$ formation. The role of the intermediate Cu^{II} species is one of complexing both oxidant and reductant, in that it provides a mechanism for electron transfer and allows O_2 to interact *via* an ionic mechanism.

THE oxidation of thiosulphate, $[S_2O_3]^{2-}$, in aqueous solution by molecular oxygen, under ambient conditions of temperature and pressure, is known to be extremely slow.[1] Since copper(II) undergoes facile reduction to copper(I) by $[S_2O_3]^{2-}$ in aqueous solution, and reactions catalysed by copper complexes in aqueous solution often involve oxidation-reduction systems composed of a Cu^I–Cu^{II} redox cycle,[2] catalysis by Cu^{II} of the oxidation of $[S_2O_3]^{2-}$ by O_2 would seem feasible. Catalysis by Cu^{II} of the peroxodisulphate, $[S_2O_8]^{2-}$, oxidation of $[S_2O_3]^{2-}$ has been reported.[3,4] However, at temperatures up to 50 °C and atmospheric pressure, copper(I)-thiosulphate species resulting from reduction of Cu^{II} ions in water by excess of $[S_2O_3]^{2-}$ are stable with respect to reoxidation to Cu^{II} by O_2.[5] When ammonia is initially present in solution, such a reoxidation is found to occur.[6,7] Recently, we reported a detailed kinetic study on the reduction of Cu^{II} ammine complexes by $[S_2O_3]^{2-}$ in the absence of O_2[6] and also a preliminary report on the reaction with oxygen present.[7] In the present paper the results of a detailed kinetic study of the reaction in aqueous ammonia solution in the presence of oxygen are given and discussed in terms of mechanisms which involve copper(II)-oxygen complexes as intermediates.

EXPERIMENTAL

Materials.—Stock solutions of copper(II) ions in aqueous ammonia were prepared from $Cu[SO_4]\cdot5OH_2$ (B.D.H., AnalaR) and concentrated volumetric solutions of ammonium hydroxide (B.D.H.). All dilutions were made up with distilled water. Oxygen was Linde high-purity grade. The salt $Na_2[S_2O_3]\cdot5OH_2$ was B.D.H. AnalaR and $K_2[S_3O_6]$ was prepared according to the method of Stamm and Goehring.[8] All other chemicals used were of reagent-grade quality.

Determination of Reaction Products.—Determination of $[S_2O_3]^{2-}$ was carried out using a standard iodimetric-titration method.[9] Qualitative analysis for sulphur anions was made according to the methods given by Karchmer.[10] The method of Kelly *et. al.*[11] was used in determining $[S_3O_6]^{2-}$ ions quantitatively. U.v.–visible spectra were recorded on a Beckman DK–2A ratio recording spectrophotometer.

Determination of Reaction Rates.—Kinetic measurements were made by following the consumption of oxygen at constant pressure using the apparatus and procedure described earlier.[12] The partial pressure of oxygen was varied

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[3] C. H. Sorum and J. O. Edwards, *J. Amer. Chem. Soc.*, 1952, **74**, 1204.

[4] L. B. Morgan, *Trans. Faraday Soc.*, 1946, **42**, 169.

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[6] J. J. Byerley, S. A. Fouda, and G. L. Rempel, *J.C.S. Dalton*, 1973, 889.

[7] J. J. Byerley, S. A. Fouda, and G. L. Rempel, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 879.

[8] H. Stamm and M. Geohring, *Z. anorg. Chem.*, 1942, **250**, 226.

[9] A. I. Vogel, ' Quantitative Inorganic Analysis,' Longmans, Green, and Co. Ltd., London, 1961, pp. 351—353.

[10] J. H. Karchmer, ' The Analytical Chemistry of Sulfur and its Compounds,' Chemical Analysis Series, vol. 29, part 1, pp. 237—247, Wiley–Interscience, New York, 1970.

[11] D. P. Kelly, L. A. Chambers, and P. A. Trudinger, *Analyt. Chem.*, 1969, **41**, 898.

[12] B. R. James and G. L. Rempel, *Canad. J. Chem.*, 1966, **44**, 233.

from *ca.* 130 to 735 mmHg and the corresponding concentration in solution estimated from the solubility data of Seidell[13] assuming the solubility to be the same as in pure water.*

RESULTS

Colourless solutions of Cu^{I} in 0·2M-ammonia, which result from reduction of Cu^{II} by $[S_2O_3]^{2-}$ in the absence of oxygen,[6] underwent rapid reoxidation to Cu^{II} on exposure to oxygen or air. On displacement of oxygen from these solutions, reduction of Cu^{II} by $[S_2O_3]^{2-}$ still present in solution occurred. The visible absorption spectra of the initial copper(II)–ammonia solutions [$\lambda_{max.}$ 612 nm (ε 45 l mol^{-1} cm^{-1}) for 1mM-Cu^{II} in 0·2M-NH_3] prior to reduction by thiosulphate ion (0·05M-$[S_2O_3]^{2-}$) were essentially the same as that for the Cu^{II} solution obtained on treatment of the colourless Cu^{I} solutions with O_2.

These results suggested the possibility of a continuous process in the presence of O_2, providing $[S_2O_3]^{2-}$ ions were present, as shown in reactions (1) and (2) and the overall equation (3). If a simple redox cycle, as suggested in reactions (1) and (2), is involved, a kinetic analysis, on the basis

$$2[Cu(NH_3)_n]^{2+} + 2[S_2O_3]^{2-} \longrightarrow 2[Cu(NH_3)_{n-m}]^{+} + [S_4O_6]^{2-} + 2m\,NH_3 \quad (1)$$

$$2[Cu(NH_3)_{n-m}]^{+} + 2m\,NH_3 + \tfrac{1}{2}\,O_2 + H_2O \longrightarrow 2[Cu(NH_3)_n]^{2+} + 2\,OH^- \quad (2)$$

$$2[S_2O_3]^{2-} + \tfrac{1}{2}\,O_2 + H_2O \longrightarrow [S_4O_6]^{2-} + 2\,OH^- \quad (3)$$

of oxygen-consumption rate measurements, should be consistent with the kinetics obtained by following the rate of decrease of Cu^{II} concentration in the absence of O_2.[6] Stoicheiometric and kinetic results indicated, however, that such a simple sequence was definitely not the major path for $[S_2O_3]^{2-}$ oxidation in the presence of O_2. Apart from the fact that oxidation of $[S_2O_3]^{2-}$ was much more rapid in the presence of O_2, the oxidized products were also found to be different.

Stoicheiometry.—The stoicheiometry of the reaction was established from oxygen-consumption measurements and quantitative analyses of the sulphur-containing products in solution when oxygen consumption had ceased. The major sulphur-containing species, on completion of oxygen uptake, were sulphate, $[SO_4]^{2-}$, and trithionate ions, $[S_3O_6]^{2-}$. These species were stable toward further oxidation under the reaction conditions employed. Thus, $[S_3O_6]^{2-}$ was not an intermediate for $[SO_4]^{2-}$ formation under the experimental conditions used in this study. Thiosulphate and/or tetrathionate ions, $[S_4O_6]^{2-}$, were not present in the final reaction solutions. Quantitative analyses for $[SO_4]^{2-}$ using standard gravimetric methods were not carried out due to the interference of $[S_3O_6]^{2-}$ present in the final reaction solutions. However, reliable quantitative analyses for $[S_3O_6]^{2-}$ could be carried out.[11] These analyses indicated that the percentage of total sulphur present as $[S_3O_6]^{2-}$ was dependent on the initial $[S_2O_3]^{2-}$, as was the number of moles of oxygen consumed per mol of $[S_2O_3]^{2-}$ reacted. The effect of pH on the stoicheiometry of the reaction was also examined by using ammonium nitrate while maintaining a constant ammonia concentration (0·2M) and a constant ionic strength of 0·2M ($NaNO_3$). As the pH of the system was lowered the percentage conversion of $[S_2O_3]^{2-}$ to $[S_3O_6]^{2-}$ increased.

Representative stoicheiometric results for $[S_2O_3]^{2-}$ consumed with respect to O_2 are shown in Table 1. The conversion of $[S_2O_3]^{2-}$ to $[S_3O_6]^{2-}$ and $[S_2O_3]^{2-}$ to $[SO_4]^{2-}$ can be represented by equations (4) and (5) respectively. On

$$3[S_2O_3]^{2-} + 2\,O_2 + H_2O \longrightarrow 2[S_3O_6]^{2-} + 2\,OH^- \quad (4)$$

$$[S_2O_3]^{2-} + 2\,O_2 + 2\,OH^- \longrightarrow 2[SO_4]^{2-} + H_2O \quad (5)$$

the basis of the analytical results obtained for $[S_3O_6]^{2-}$ produced and equations (4) and (5), the expected consumption of O_2 was calculated and found to agree fairly well with that measured as shown in Table 1. These calculations were based on the assumption that, apart from $[S_3O_6]^{2-}$, the only other oxidized product present in the final solution was $[SO_4]^{2-}$. This appeared to be a good assumption in that $[S_2O_3]^{2-}$ and $S_4O_6]^{2-}$ were definitely not present and dithionite, $[S_2O_4]^{2-}$, disulphite, $[S_2O_5]^{2-}$, and sulphite, $[SO_3]^{2-}$, underwent rapid quantitative oxidation to $[SO_4]^{2-}$ under the reaction conditions employed. The possibility of traces of dithionate, $[S_2O_6]$,$^{2-}$ in the final solution could not be discounted since no specific qualitative tests exist to confirm its presence when other polythionates are present. Furthermore, $[S_2O_6]^{2-}$ is not oxidized under the reaction conditions used. Qualitative tests for the presence of other polythionates were negative.

TABLE 1

Stoicheiometry of thiosulphate oxidation at $[Cu^{II}]$ = 1mM, $[NH_3]$ = 0·2M, p_{O_2} = 72·5 cmHg, and 30 °C using 5 cm³ solution

$[S_2O_3{}^{2-}]_0$/ mM	pH	% S converted to $[S_3O_6]^{2-}$	$\frac{\text{Moles } O_2 \text{ consumed}}{\text{Moles } [S_2O_3]^{2-} \text{ consumed}}$ obs.	calc.[a]
5·0	11·2	30·6	1·63	1·61
10·0	11·2	*b*	1·58	
15·0	11·2	42·2	1·48	1·44
25·0	11·2	50·4	1·35	1·33
25·0	11·2	*b*	1·23 [c]	
50·0	11·2	64·1	1·19	1·15
50·0	11·2	*b*	1·18	
50·0	11·2	*b*	1·13 [c]	
75·0	11·2	66·6	1·13	1·11
100·0	11·2	75·6	1·01	0·99
25·0	11·2	54·0	1·21 [d]	1·28
25·0	10·0	64·6	0·99 [d]	1·14
25·0	9·6	81·0	0·89 [d]	0·92
25·0	9·3	100·0	0·72 [d]	0·67

[a] On the basis that %S converted to $[SO_4]^{2-}$ = 100 − % converted to $[S_3O_6]^{2-}$. [b] No analysis made. [c] 0·5 mM-Cu^{II}. [d] 0·4 mM-Cu^{II}, pH adjusted by addition of $[H_4N][NO_3]$, ionic strength = 0·2M using $Na[NO_3]$.

Spectral Observations.—Over the concentration ranges of Cu^{II} (0·3—2·0mM) and ammonia (0·10—1·00M) used, the predominant species initially present in solution were $[Cu(NH_3)_4(OH_2)_2]^{2+}$, $[Cu(NH_3)_3(OH_2)_3]^{2+}$, and $[Cu(NH_3)_5(OH_2)]^{2+}$. This conclusion was arrived at by constructing a distribution diagram 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. 14. At pH > 10, the copper(II) amine species are reported as existing in equilibrium with significant concentrations of hydroxo-species. Approximate constants (K_i = 250, K_{ii} = 49 l mol^{-1}) for stepwise addition of two hydroxide

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* 1 mmHg ≈ 13·6 × 9·8 Pa, 1M = 1 mol dm^{-3}, 1 atm = 101 325 Pa.

[13] A. Seidell, 'Solubilities of Inorganic and Metal Organic Compounds,' 4th edn., van Nostrand, New York, 1958, vol. 1.

[14] 'Stability Constants of Metal–Ion Complexes,' *Chem. Soc. Special Publ.*, No. 17, London, 1964.

ions to the copper(II) ammine species have been reported [15] and similar values were also obtained in the present investigation. Consequently, ammine species in which one or two of the aqua-ligands are replaced by OH^- will be present at $pH > 10$. The spectrum of a solution of Cu^{II} ions in $0{\cdot}2M$-NH_3 (pH 11·2) showed a maximum absorption at 612 nm (ε 45 l mol^{-1} cm^{-1}) and a shoulder at 310 nm (ε 500 l mol^{-1} cm^{-1}). Addition of oxygen to a degassed solution of the copper(II) ammines gave no measurable O_2 consumption or noticeable u.v.–visible spectral change. However, addition of $[S_2O_3]^{2-}$ to such a solution did result in immediate appearance of a new absorbance peak at 330 nm as well as an increase in the absorbance of the 612 nm peak. The absorbances of the 330 and 612 peaks increased with increasing $[S_2O_3]^{2-}$. Addition of $[SO_4]^{2-}$ to ammoniacal solutions of Cu^{II} ions also resulted in formation of a peak at 320 nm in place of the 310 nm shoulder. With $[SO_4]^{2-}$ addition the absorbance of the peaks increased only slightly compared to $[S_2O_3]^{2-}$ addition of corresponding concentrations. This effect has previously been ascribed to association of anions at the axial positions of the copper(II) ammine complexes.[6] Out-of-plane bonding of anions in axial complexes of Cu^{II} ions has recently been reviewed.[16]

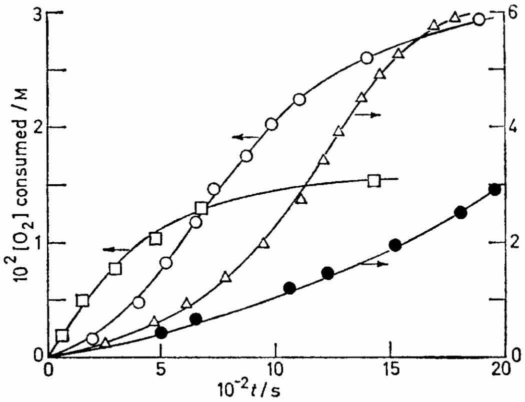

FIGURE 1 Representative oxygen-consumption plots for the reaction of Cu^{II} ions with $[S_2O_3]^{2-}$ in $0{\cdot}2M$-NH_3 solution at 1 atm total pressure and 30 °C: (□), $[Cu^{II}] = 4{\cdot}0 \times 10^{-4}$, $[S_2O_3{}^{2-}]_0 = 1{\cdot}0 \times 10^{-2}$; (○), $[Cu^{II}] = 4{\cdot}0 \times 10^{-4}$, $[S_2O_3{}^{2-}]_0 = 2 \times 10^{-2}$; (△), $[Cu^{II}] = 8{\cdot}0 \times 10^{-4}$, $[S_2O_3{}^{2-}]_0 = 5{\cdot}0 \times 10^{-2}$; (●), $[Cu^{II}] = 8{\cdot}0 \times 10^{-4}$, $[S_2O_3{}^{2-}]_0 = 7{\cdot}5 \times 10^{-2}M$

Spectral observations of a copper(II) ammine–$[S_2O_3]^{2-}$ solution saturated with oxygen indicated that oxidation of $[S_2O_3]^{2-}$ by Cu^{II} occurred at a much higher rate than in the absence of O_2. The extent of the oxidation was limited by the amount of oxygen dissolved in solution. If saturation of the solution with O_2 was maintained no decrease in Cu^{II} concentration occurred as $[S_2O_3]^{2-}$ was oxidized. These results are further exemplified on consideration of the kinetic data obtained from oxygen-consumption experiments. For such experiments, spectral examination of the reaction solution at a point where $[S_2O_3]^{2-}$ was less than 0·02M showed a maximum at 595 nm (ε 65 l mol^{-1} cm^{-1}) and a shoulder ($\lambda_{max.}$ *ca.* 320 nm).

Kinetics.—The kinetics of oxidation of $[S_2O_3]^{2-}$ by copper(II) ammines in the presence of O_2 were studied by following the consumption of oxygen as a function of time. In the absence of Cu^{II}, no oxygen consumption was apparent up to 50 °C and 1·0 atm total pressure, the initial $[S_2O_3]^{2-}$ being unchanged over a period of many hours. When Cu^{II} ions were present in the absence of ammonia again no oxygen consumption was observed, although a rapid reaction between Cu^{II} and $[S_2O_3]^{2-}$ to yield a colourless solution did occur. Thus, for the continuous oxidation of $[S_2O_3]^{2-}$ in the presence of O_2, both Cu^{II} and ammonia were required.

Representative gas-consumption plots for the oxidation of $[S_2O_3]^{2-}$ are shown in Figure 1. The plots show an initial curved region followed by a maximum-rate region which falls off gradually as gas uptake ceases, the latter part of the uptake plot having the form of a first-order reaction. The attainment of the maximum-rate region was markedly influenced by $[S_2O_3{}^{2-}]_0$; it commenced sooner at lower initial $[S_2O_3{}^{2-}]$. Also solutions containing lower $[S_2O_3{}^{2-}]_0$ resulted in lower $[S_3O_6]^{2-}$ yields. When a Cu^{I}–$[S_2O_3]^{2-}$–NH_3 solution, prepared in the absence of O_2, was used as the starting solution for an oxygen-consumption experiment the nature, and rate of oxygen was the same as that obtained for a Cu^{II}–$[S_2O_3]^{2-}$–NH_3 solution of equal reactant concentrations. Copper(I) was oxidized very rapidly back to Cu^{II} and the reaction proceeded with the usual initial curved region followed by the maximum-rate region. Attainment of a maximum-rate region was also influenced by the pH of the reaction solution; the maximum-rate region commenced earlier at lower pH. However, the experiments at lower pH resulted in much lower maximum rates than those at higher pH. Furthermore $[S_3O_6]^{2-}$ yields were greatly increased at lower pH (see Table 1).

For experiments at pH 11·2, no simple kinetic analysis of the overall gas-consumption plots was possible. It was apparent, however, that experiments which resulted in high percentage conversions of $[S_2O_3]^{2-}$ to $[S_3O_6]^{2-}$ (Table 1) had lengthy curved regions prior to commencement of the maximum-rate region. Those experiments which gave low $[S_3O_6]^{2-}$ yields had short initial curved regions compared to the length of the maximum-rate region. Consequently, the uptake plots were analysed on the basis of the initial region, which was associated primarily with the production of $[S_3O_6]^{2-}$, and the maximum-rate region in which the production of $[SO_4]^{2-}$ became increasingly more important.

(i) *Initial-rate region:* $[S_3O_6]^{2-}$ *formation.* The kinetics of reaction for the initial region were examined by measuring the rate of oxygen consumption at a point corresponding to 10% of the total oxygen consumption. For experiments in which $[S_2O_3{}^{2-}]_0$ was greater than 0·03M the oxidized sulphur product at 10% reaction was essentially all in the form $[S_3O_6]^{2-}$. Consequently the rate of oxygen consumption could be associated solely with $[S_3O_6]^{2-}$ formation.

The results obtained (Table 2) indicate a good first-order dependence on $[Cu^{II}]$ at least up to 0·002M and a good first-order dependence on oxygen concentration over an oxygen partial-pressure range of 137—734 mmHg. These results suggest an experimental rate law of the form (6) where $k' = k[S_2O_3{}^{2-}]^m[NH_3]^n$.

$$-\,d[O_2]/dt = k'\,[Cu^{II}][O_2] \qquad (6)$$

In order to investigate the effect of $[S_2O_3{}^{2-}]$ on the rate of $[S_3O_6]^{2-}$ formation a number of experiments using $[S_2O_3{}^{2-}]_0$ in the range 0·025—0·075M were carried out at given $[Cu^{II}]$, $[O_2]$, and $[NH_3]$. The results obtained are shown in Table 2 and a plot of k' against $[S_2O_3{}^{2-}]_0$ (Figure 2) suggested an inverse dependence of reaction rate on $[S_2O_3{}^{2-}]$ over the range 0·025—0·075M. When the ionic strength of the media was kept constant at

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

[16] B. J. Hathaway, *Structure and Bonding*, 1973, 49—67; B. J. Hathaway and A. A. Tomlinson, *Co-ordination Chem. Rev.*, 1970, **5**, 1.

0·20M by the addition of $Na_2[SO_4]$ the rates obtained for the region of inverse dependence were essentially the same as those obtained under conditions of variable ionic strength. Experiments at $[S_2O_3^{2-}]_0$ less than or equal to 0·020M were not considered in the kinetic analysis of the $[S_3O_6]^{2-}$ producing reaction as the reaction which gave $[SO_4]^{2-}$ started to take place in the early stages of oxygen consumption.

TABLE 2

Summary of kinetic data for $[S_3O_6]^{2-}$ production at 30 °C

$10^4[Cu^{II}]$/M	$10^2[S_2O_3^{2-}]_0$/M	$10[NH_3]$/M	p_{O_2}/mmHg	$10^4[O_2]$/M	10^5 Initial rate of O_2 consumption/ mol l^{-1} s^{-1}	k' [a]/l mol^{-1} s^{-1}
3·0	5·0	2·0	37·1	5·71	0·34	19·8
4·0	5·0	2·0	37·1	5·71	0·48	21·0
6·0	5·0	2·0	37·1	5·71	0·76	22·2
8·0	5·0	2·0	37·1	5·71	1·17	25·6
10·0	5·0	2·0	37·1	5·71	1·47	25·8
10·0	5·0	2·0	37·1	5·71	1·44	25·2
20·0	5·0	2·0	37·1	5·71	2·50	21·9
6·0	5·0	2·0	13·7	2·11	0·23	18·1
6·0	5·0	2·0	17·1	2·63	0·30	19·1
6·0	5·0	2·0	26·7	4·12	0·58	23·4
6·0	5·0	2·0	36·5	5·62	0·70	20·7
6·0	5·0	2·0	42·9	6·61	0·84	21·3
6·0	5·0	2·0	55·3	8·50	1·06	20·8
6·0	5·0	2·0	58·6	9·00	1·15	21·3
6·0	5·0	2·0	73·4	11·30	1·45	21·4
8·0	2·5	2·0	72·5	11·15	3·40	38·1
8·0	2·5	2·0	72·5	11·15	3·64	40·8
8·0	5·0	2·0	72·5	11·15	2·10	23·6
8·0	5·0	2·0	72·5	11·15	1·88	21·0
8·0	7·5	2·0	72·5	11·15	1·29	14·5
10·0	4·0	2·0	72·5	11·15	3·20	28·7 [b]
10·0	5·0	2·0	72·5	11·15	2·30	21·1
10·0	5·0	2·0	72·5	11·15	2·52	22·8 [b]
10·0	6·0	2·0	72·5	11·15	2·15	19·3 [b]
10·0	7·5	2·0	72·5	11·15	1·50	13·5 [b]
5·0	5·0	1·0	72·6	11·18	0·47	8·4
5·0	5·0	1·5	72·6	11·18	0·78	13·9
5·0	5·0	1·5	72·6	11·18	0·84	15·4
5·0	5·0	2·0	72·5	11·15	1·34	24·2
5·0	5·0	2·0	72·5	11·15	1·27	22·8
5·0	5·0	3·0	72·4	11·05	1·52	27·5
5·0	5·0	4·0	72·4	11·05	1·48	26·9
5·0	5·0	6·0	72·0	10·90	1·51	27·7
5·0	5·0	8·0	71·6	10·78	1·25	23·2
5·0	5·0	10·0	72·3	11·04	0·94	17·6
8·0	2·5	2·0	72·5	11·15	3·50	39·3 [c]
8·0	2·5	2·0	72·5	11·15	3·00	33·8 [d]
10·0	5·0	2·0	72·5	11·15	2·50	22·5 [c]
4·0	2·5	2·0	72·5	11·15	1·20	26·9 [e,f]
8·0	2·5	2·0	72·5	11·15	2·60	29·2 [e,f]
4·0	2·5	2·0	72·5	11·15	1·46	32·7 [f,g]
4·0	2·5	2·0	72·5	11·15	1·48	33·2 [f,h]
4·0	2·5	2·0	72·5	11·15	1·48	33·2 [f,i]

[a] (Initial rate)/$[Cu^{II}][O_2]$. [b] I = 0·20M ($Na_2[SO_4]$). [c] [Mannitol] = 5mM. [d] [Mannitol] = 10mM. [e] pH 9·3 using $[H_4N][NO_3]$. [f] I = 0·20M using $Na[NO_3]$. [g] pH 9·6 using $[H_4N][NO_3]$. [h] pH 10·0 using $[H_4N][NO_3]$. [i] pH 11·2 using $[H_4N][NO_3]$.

The effect of $[NH_3]$ on the initial rate of oxygen consumption, for $[S_2O_3^{2-}]_0$ = 0·05M, was complex (Table 2). Figure 3 shows a plot of k' against $[NH_3]$ for a given set of experiments in which $[Cu^{II}]$, $[O_2]$, and $[S_2O_3^{2-}]$ were maintained constant. Over an $[NH_3]$ range of 0·2—0·7M the initial rates varied only slightly. However, at relatively low or high $[NH_3]$ the rates were definitely much lower. It is of interest that the maximum concentration of $[Cu(NH_3)_4]^{2+}$ with respect to the Cu^{II} concentrations used in this study would also occur over a range of *ca.* 0·2—0·7M-NH_3.[14,15] Thus, the active Cu^{II} species for $[S_3O_6]^{2-}$ formation probably contains a planar tetra-ammine species.

(ii) *Maximum-rate region:* $[S_3O_6]^{2-}$ *and* $[SO_4]^{2-}$ *formation reactions.* The kinetics of reactions occurring in the maximum-rate region were examined by measuring the total rate of oxygen consumption in this region. For experiments in which $[S_2O_3^{2-}]_0$ was less than 0·020M little if any initial curved region in the gas-consumption plot was apparent. The maximum rate in these experiments was essentially the initial rate and the overall oxygen-consumption plot had the form of a first-order reaction (Figure 1). Quantitative analyses for the final oxidized-sulphur products indicated that both $[S_3O_6]^{2-}$ and $[SO_4]^{2-}$ were produced when $[S_2O_3^{2-}]_0$ less than 0·020M was used. Since the number of moles of O_2 consumed per mol of $[S_2O_3]^{2-}$ was also a function of $[S_2O_3^{2-}]$, no simple analysis of the overall first-order plot to extract the kinetics of the two concurrent oxidation reactions was possible. However, the total rate of oxygen consumption (r_T) could be represented as the sum of the rate of oxygen consumption for $[S_3O_6]^{2-}$ production (r_I) and that for $[SO_4]^{2-}$ production (r_{II}). Under conditions of constant $[Cu^{II}]$, $[O_2]$, and $[NH_3]$, a rate equation of the form (7),

$$r_T = k_I^* [S_2O_3^{2-}]^a + k_{II}^* [S_2O_3^{2-}]^b \qquad (7)$$

where k_I^* is associated with $[S_3O_6]^{2-}$ formation and k_{II}^* is

TABLE 3

Summary of kinetic data for the maximum-rate region at 30 °C

$10^4[Cu^{II}]$ M	$10^2[S_2O_3^{2-}]_0$ M	$10[NH_3]$ M	$10^4[O_2]$ M	10^5r_T [a] / mol l^{-1} s^{-1}	10^5r_I [b] / mol l^{-1} s^{-1}	10^5r_{II} [c] / mol l^{-1} s^{-1}
3·0	5·0	2·0	5·71	1·55	0·58	0·97
4·0	5·0	2·0	5·71	2·07	0·77	1·30
6·0	5·0	2·0	5·71	3·12	1·15	1·97
8·0	5·0	2·0	5·71	4·11	1·53	2·58
0·6	2·5	2·0	11·15	0·44	0·23	0·21
2·0	2·5	2·0	11·15	1·60	0·75	0·85
3·0	2·5	2·0	11·15	2·34	1·13	1·21
4·0	2·5	2·0	11·15	3·04	1·50	1·54
5·0	2·5	2·0	11·15	3·73	1·87	1·86
6·0	2·5	2·0	11·15	4·55	2·25	2·30
6·0	5·0	2·0	2·11	1·15	0·43	0·72
6·0	5·0	2·0	2·63	1·45	0·53	0·92
6·0	5·0	2·0	3·52	1·74	0·71	1·03
6·0	5·0	2·0	4·12	2·19	0·83	1·36
6·0	5·0	2·0	4·85	2·55	0·98	1·57
6·0	5·0	2·0	5·62	3·04	1·14	1·90
6·0	5·0	2·0	6·61	3·10	1·34	1·76
6·0	5·0	2·0	9·00	3·64	1·82	1·82
6·0	5·0	2·0	11·30	4·20	2·28	1·92
3·0	5·0	2·0	2·85	0·87	0·29	0·58
3·0	5·0	2·0	5·71	1·55	0·58	0·97
3·0	5·0	2·0	7·62	1·79	0·77	1·02
3·0	5·0	2·0	8·70	2·00	0·88	1·12
3·0	5·0	2·0	9·62	2·10	0·97	1·13
3·0	5·0	2·0	11·15	2·31	1·13	1·18
4·0	1·0	2·0	11·15	1·76	1·50	0·26
4·0	1·25	2·0	11·15	2·15	1·50	0·65
4·0	1·5	2·0	11·15	2·48	1·50	0·98
4·0	1·75	2·0	11·15	2·61	1·50	1·11
4·0	2·0	2·0	11·15	2·92	1·50	1·42
4·0	2·5	2·0	11·15	3·12	1·50	1·62
5·0	5·0	1·5	11·15	3·92	1·87	2·05
5·0	5·0	2·0	11·15	3·73	1·87	1·86
5·0	5·0	2·5	11·15	3·63	1·87	1·76
5·0	5·0	3·0	11·15	3·50	1·87	1·63
4·0	2·5	2·0	11·15	1·75	1·50	0·25 [d]
4·0	2·5	2·0	11·15	1·20	1·20	0·00 [e]

[a] Total oxygen-consumption rate in maximum-rate region. [b] Oxygen-consumption rate for $[S_3O_6]^{2-}$ production in maximum-rate region. [c] Oxygen-consumption rate for $[SO_4]^{2-}$ production in maximum-rate region. [d] pH 10 using $[H_4N][NO_3]$. [e] pH 9·2 using $[H_4N][NO_3]$.

associated with $[SO_4]^{2-}$ formation, can be written. Since the overall uptake plot is first order in nature, the possible values of a and b, respectively, are 1 and 1, 1 and 0, or 0 and 1.

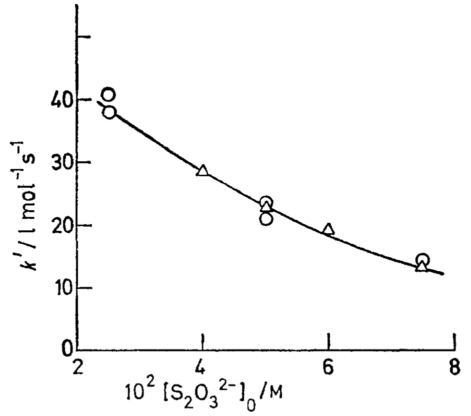

FIGURE 2 Dependence of k' on $[S_2O_3^{2-}]_0$ in 0·2M-NH_3 solution at 1 atm total pressure and 30 °C: (○), $[Cu^{II}] = 8{\cdot}0 \times 10^{-4}$; (△), $[Cu^{II}] = 10{\cdot}0 \times 10^{-4}$, $I = 0{\cdot}20$M

All these cases suggest that a plot of the maximum rate r_T, which is the initial rate of the first-order region, against $[S_2O_3^{2-}]_0$ should be linear. When $a = b = 1$ an intercept of zero should result for such a plot, whereas if either a or $b = 0$ a positive intercept should be obtained.

A series of experiments were made at $[S_2O_3^{2-}]_0 \leqslant 0{\cdot}025$M for given $[Cu^{II}]$, $[O_2]$, and $[NH_3]$ and the results obtained are shown in Figure 4 and Table 3. A good linear relation did occur for a plot of r_T against $[S_2O_3^{2-}]_0$ for $[S_2O_3^{2-}]_0$ between 0·025 and 0·015M. Extrapolation to zero $[S_2O_3^{2-}]$ resulted in a positive intercept. This suggests that at the point of maximum rate, for experiments in which $[S_2O_3^{2-}]_0$ was greater than 0·015M, one of the oxygen-consumption reactions is first order in $[S_2O_3^{2-}]$ while the other one is zero order. Since at high $[S_2O_3^{2-}]$, *i.e.* $\geqslant 0{\cdot}035$M, the $[S_3O_6]^{2-}$-producing reaction definitely exhibited an inverse dependence on $[S_2O_3^{2-}]$, it seems reasonable to expect that this

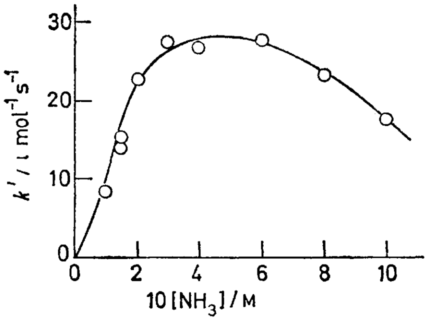

FIGURE 3 Dependence of k' on $[NH_3]$ at 1 atm total pressure, 30 °C, $[Cu^{II}] = 5{\cdot}0 \times 10^{-4}$, and $[S_2O_3^{2-}]_0 = 5{\cdot}0 \times 10^{-2}$M

reaction may tend to a zero-order dependence as $[S_2O_3^{2-}]$ decreases. It is highly unlikely that the $[S_3O_6]^{2-}$ production process changes from the definite inverse dependence observed to a first-order dependence as $[S_2O_3^{2-}]$ is gradually decreased. Therefore, it appears that at $[S_2O_3^{2-}]$ encountered in the maximum-rate regions the $[SO_4]^{2-}$ producing reaction is first order with respect to $[S_2O_3^{2-}]$ while a zero-order dependence on $[S_2O_3^{2-}]$ for the $[S_3O_6]^{2-}$ formation reaction occurs.

On the basis of a zero-order dependence on $[S_2O_3^{2-}]$ for $[S_3O_6]^{2-}$ formation occurring at $[S_2O_3^{2-}] < 0{\cdot}025\text{M}$ it is possible to calculate a value of the experimental rate constant defined by equation (8). The value of k' was calculated to

$$k' = k_I^*/[\mathrm{Cu^{II}}][\mathrm{O_2}] \qquad (8)$$

be 33·6 l mol^{-1} s^{-1} on the basis of the data provided in Figure 4. This value can be compared with the limiting value of k' obtained from initial-rate data for experiments having an initial curved region (Figure 2). The data shown in Figure 2 suggest a value of k' of *ca.* 38·0 l mol^{-1} s^{-1} at 0·025M. Thus, if a zero-order dependence on $[S_2O_3^{2-}]$ is in effect at 0·025M, this value should be equal to that obtained using equation (8). Considering that the transformation from an inverse to zero-order $[S_2O_3^{2-}]$ dependence is probably gradual and that the k' value at 0·025M-$[S_2O_3]^{2-}$ shown in Figure 2 will have some contribution from the $[SO_4]^{2-}$ producing process, the agreement between the values of k' is indeed very good.

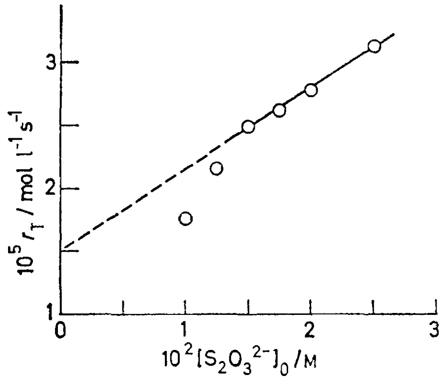

FIGURE 4 Dependence of r_T on $[S_2O_3^{2-}]_0$ in 0·2M-NH$_3$ solution at 1 atm total pressure, $[\mathrm{Cu^{II}}] = 4{\cdot}0 \times 10^{-4}$M, and 30 °C

In order to carry out a full kinetic analysis of the $[SO_4]^{2-}$ production reaction maximum-rate measurements were carried out for a series of experiments in which $[\mathrm{Cu^{II}}]$, $[O_2]$, and $[NH_3]$ were varied independently. Since the kinetics of the $[S_3O_6]^{2-}$ producing reaction were available [equation (8)], rates for $[SO_4]^{2-}$ production as a function of $[\mathrm{Cu^{II}}]$, $[O_2]$, $[S_2O_3^{2-}]_0$, and $[NH_3]$ could be readily calculated. The results obtained are summarized in Table 3. Plots of r_{II} against $[\mathrm{Cu^{II}}]$ were linear over the range 0×10^{-4}—$8{\cdot}0 \times 10^{-4}$M $[\mathrm{Cu^{II}}]$ indicating a first-order dependence on $[\mathrm{Cu^{II}}]$ for the $[SO_4]^{2-}$ production process. The effect of pressure (0—73 cmHg) on r_{II} was investigated at two different $[\mathrm{Cu^{II}}]$ and the results obtained are given in Table 3. The $[SO_4]^{2-}$ producing reaction showed a first-order dedependence on $[O_2]$ below *ca.* 5×10^{-4}M above which a tendency toward a zero-order dependence on $[O_2]$ was apparent. As seen in Figure 4 and Table 3, the reaction was first order in $[S_2O_3^{2-}]_0$. The effect of $[NH_3]$ on the r_{II} was studied over the range of 0·15—0·30M. The results (Table 3) indicate an inverse dependence on $[NH_3]$ over this range. Although the maximum-rate region was attained much sooner at lower pH, r_{II} was greatly decreased on lowering the pH of the solution. For example, decreasing the pH from 11·2 to 10·0 by addition of $[H_4N][NO_3]$ caused r_{II} to decrease by more than 80%. At a pH of 9·2, r_{II} was not observed, no $[SO_4]^{2-}$ being produced.

DISCUSSION

The stoicheiometric and kinetic results obtained for the oxidation of $[S_2O_3]^{2-}$ ion by copper(II) ammine complexes in the presence of O_2 indicate that the reaction is catalysed by the presence of O_2. A comparison of the initial rate of a given oxygen-consumption experiment with the rate of the oxidation reaction in the absence of O_2, under otherwise comparable reaction conditions, indicated that the initial rate of $[S_2O_3]^{2-}$ consumption in the presence of O_2 was at least 40 times as great as that in its absence. Consequently even the initial part of the oxygen-consumption reactions are concerned with more than a simple reoxidation of the $\mathrm{Cu^I}$ species known to form when $[S_2O_3]^{2-}$ reacts with copper(II) ammines in the absence of O_2.[6] In fact the direct reduction of $\mathrm{Cu^{II}}$ by $[S_2O_3]^{2-}$ which occurs in the absence of O_2 would appear to be of little importance, in view of the $[\mathrm{Cu^{II}}]$ and overall reaction times employed when the reaction is carried out under O_2.

In the presence of O_2 the reaction probably involves mechanistic paths [17] in which copper–oxygen complexes are involved. In such intermediate complexes the O_2 may activate copper for subsequent oxidation of $[S_2O_3]^{2-}$ or alternatively the copper could possibly activate the oxygen molecule for subsequent transfer to a co-ordinated $[S_2O_3]^{2-}$ ion. A consideration of stoicheiometric, spectral, and kinetic results obtained enables the formulation of plausible mechanisms for formation of both $[S_3O_6]^{2-}$ and $[SO_4]^{2-}$ resulting from the oxidation of $[S_2O_3]^{2-}$ by copper(II) ammines in the presence of O_2.

Mechanism for $[S_3O_6]^{2-}$ *Formation.*—For the experiments carried out at the higher $[S_2O_3^{2-}]$ it was apparent that the time necessary to attain the maximum rate of O_2 consumption was greatest for the highest $[S_2O_3^{2-}]$. Also the highest yields of $[S_3O_6]^{2-}$ were obtained for the highest $[S_2O_3^{2-}]$ or lowest pH used. Spectral observations (see Results section) for the oxidation system in the initial curved region of the oxygen-consumption plots together with the kinetics observed in this region are consistent with interaction of O_2 with a copper(II) ammine complex containing at least one axial $[S_2O_3]^{2-}$. Although replacements and isomerizations in the copper co-ordination sphere are known to be extremely fast (equilibrium often being reached in terms of less than a microsecond), the observed reaction-rate dependence on $[NH_3]$ in conjunction with the distribution of copper(II) ammines as a function of $[NH_3]$ would seem to suggest that the most active species for the $[S_3O_6]^{2-}$ formation reaction is a copper(II) tetra-ammine complex. At high $[NH_3]$ significant amounts of the penta-amminecopper(II) complex are likely. This would decrease the effective

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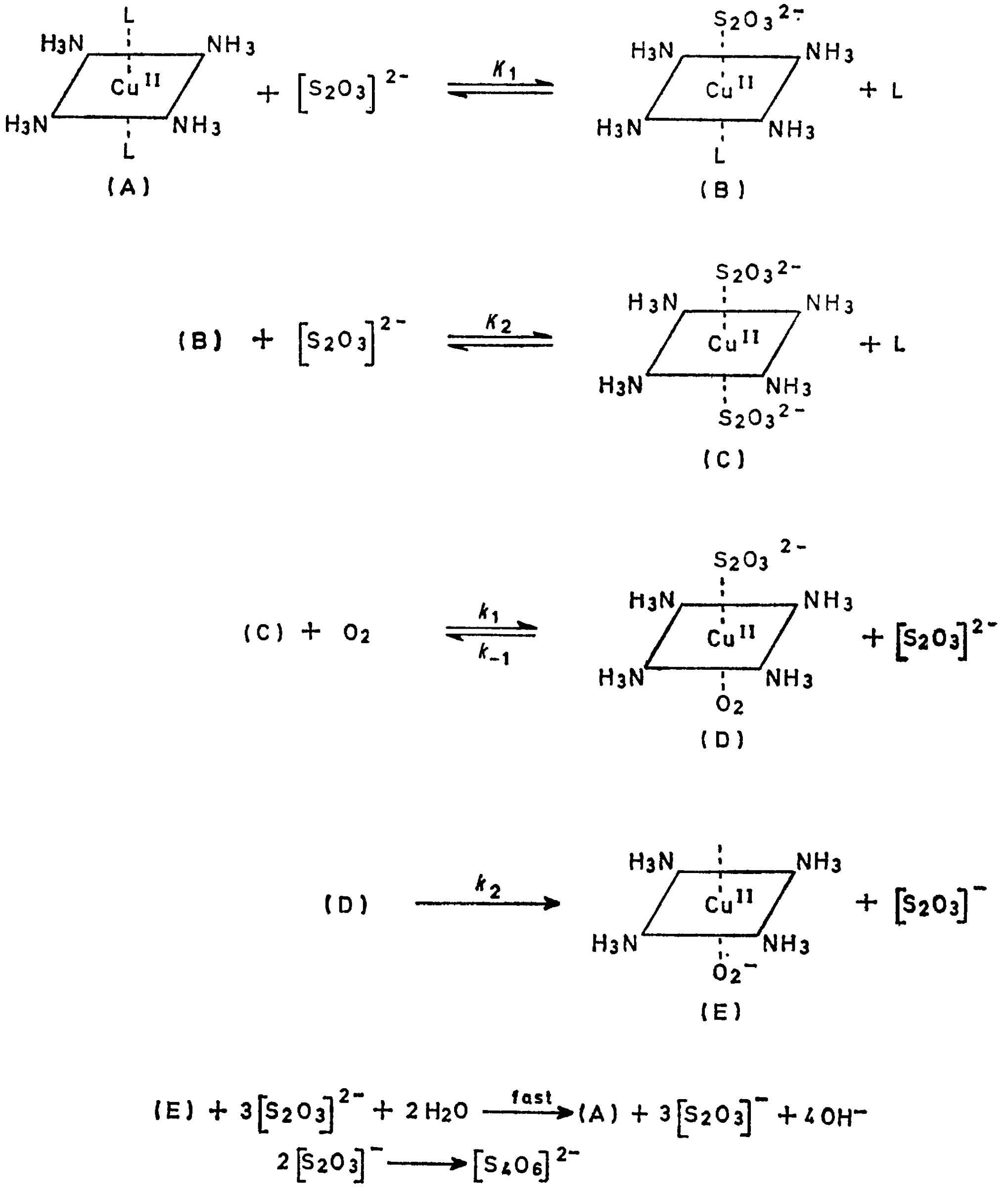
concentration of a tetra-ammine complex having one axial $[S_2O_3]^{2-}$ and an axial O_2 ligand. All these results and the observed dependences of reaction rate on $[Cu^{II}]$, $[O_2]$, and $[S_2O_3^{2-}]$ are accommodated by the mechanism shown in Scheme 1.



SCHEME 1 L = H_2O, NH_3, $[SO_4]^{2-}$, or OH^-.

Application of a steady-state approximation for species (D) in Scheme 1 results in the rate law (9). If it is

$$-\frac{d[O_2]}{dt} = \frac{k_1k_2[(C)][O_2]}{k_{-1}[S_2O_3^{2-}] + k_2} \qquad (9)$$

assumed at high $[S_2O_3^{2-}]$: $[Cu^{II}]$ ratios (*i.e.* greater than 50 : 1) that [(C)] is approximately equal to the total Cu^{II} concentration, equation (9) can be written in the form (10)

$$\frac{1}{k'} = \frac{k_{-1}}{k_1k_2}[S_2O_3^{2-}] + \frac{1}{k_1} \qquad (10)$$

where k' is the experimental rate constant for the reaction as defined in equation (6). A plot of $1/k'$ against $[S_2O_3^{2-}]$ (Figure 5) showed good linearity and yielded the values $k_1 \approx 300$ l mol^{-1} s^{-1} and $k_{-1}/k_2 = 265$ l mol^{-1}. Scheme 1 also accommodates the results obtained for intermediate $[S_2O_3^{2-}]$ (*i.e.* 0·025—0·015M) where a zero-order dependence on $[S_2O_3^{2-}]$ for $[S_3O_6]^{2-}$ formation is observed. At these $[S_2O_3^{2-}]$ the equilibrium shown in the second step of Scheme 1 is of minor importance. Species (B) may be involved in a rapid equilibrium with O_2 to generate (D) as shown in equation (11). Spectral changes observed at

$$(B) + O_2 \overset{K_2'}{\rightleftharpoons} (D) \qquad (11)$$

these concentrations of $[S_2O_3]^{2-}$ lend support to this postulated equilibrium. Under these conditions the rate law which results can be expressed as (12). This accounts

$$-\,d[O_2]/dt = k_2K_2'\,[(B)][O_2] \qquad (12)$$

for the zero-order dependence observed for $[S_2O_3{}^{2-}]$ over the range 0·015—0·025M. The tendency towards a zero-order dependence on $[S_2O_3{}^{2-}]$ probably begins once $[S_2O_3{}^{2-}]$ = *ca.* 0·035M.

Scheme 1 involves a tetra-amminecopper(II)–$[S_2O_3]^{2-}$–O_2 complex, (D), in which $[S_2O_3]^{2-}$ and O_2 are axially bound to Cu^{II}, as the reactive species for oxidation of $[S_2O_3]^{2-}$ to $[S_2O_3]^-$. Such an axial reduction process does not seem to be of any consequence in the absence of O_2.[6] Copper(II)–molecular-oxygen complexes have previously been postulated in the oxidation of co-ordinated *o*-phenylenediamine,[18] ascorbate,[19] and tetraglycine.[20]

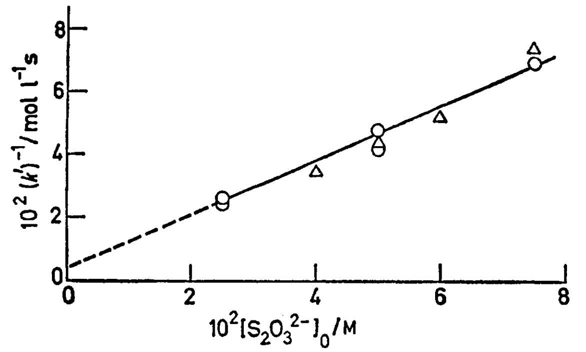


FIGURE 5 Dependence of initial rate of $[S_3O_6]^{2-}$ formation in 0·2M-NH_3 at 1 atm total pressure and 30 °C, plotted in accord with equation (10): (○), $[Cu^{II}] = 8{\cdot}0 \times 10^{-4}$; (△), $[Cu^{II}] = 10{\cdot}0 \times 10^{-4}$, I = 0·20M

The $[S_2O_3]^-$ species produced on oxidation of $[S_2O_3]^{2-}$ in Scheme 1 probably dimerizes rapidly to yield $[S_4O_6]^{2-}$. Such rapid dimerization reactions have previously been postulated in $[S_2O_3]^{2-}$ oxidation reactions.[21,22] Since no $[S_4O_6]^{2-}$ is found in the final reaction solutions, it seems very likely that $[S_4O_6]^{2-}$ ions undergo subsequent disproportion to $[S_3O_6]^{2-}$ and $[S_2O_3]^{2-}$. The decomposition of $[S_4O_6]^{2-}$ in aqueous solution to higher and lower polythionate ions is well substantiated.[1,23,24] This decomposition is highly catalysed by the presence of $[S_2O_3]^{2-}$ and is represented by reactions (13)—(15) which give rise to the overall reaction (16). Reaction (13) results in $[SO_3]^{2-}$ formation and, since it is well known that $[SO_3]^{2-}$ undergoes rapid oxidation in aqueous solution by O_2 to give $[SO_4]^{-2}$,[2,25,26] it may be expected that $[SO_4]^{2-}$ is also produced during the decomposition of $[S_4O_6]^{2-}$. However, experiments carried out with $[S_4O_6]^{2-}$ and $[S_2O_3]^{2-}$ in aqueous ammonia under O_2 but in the absence of Cu^{II} resulted only in $[S_3O_6]^{2-}$ production. No oxygen consumption or $[SO_4]^{2-}$ production occurred.

$$[S_4O_6]^{2-} + [S_2O_3]^{2-} \longrightarrow [S_5O_6]^{2-} + [SO_3]^{2-} \qquad (13)$$

$$[SO_3]^{2-} + [S_4O_6]^{2-} \longrightarrow [S_3O_6]^{2-} + [S_2O_3]^{2-} \qquad (14)$$

$$[S_5O_6]^{2-} + 3OH^- \longrightarrow \tfrac{5}{2}[S_2O_3]^{2-} + \tfrac{3}{2}H_2O \qquad (15)$$

$$2[S_4O_6]^{2-} + 3OH^- \longrightarrow \tfrac{5}{2}[S_2O_3]^{2-} + [S_3O_6]^{2-} + \tfrac{3}{2}H_2O \qquad (16)$$

The addition of a free-radical inhibitor, namely mannitol, had no effect on the observed rate in the initial region suggesting that the involvement of free radicals, at least in the rate-determining step, is unlikely. Furthermore, the total oxygen consumption was unaffected by the presence of mannitol.

The manner in which species (E) in Scheme 1 undergoes reaction with additional $[S_2O_3]^{2-}$ is not obvious. However, complexes have previously been described[27] which have co-ordinated $[O_2]^-$ and $[O_2]^{2-}$ ions. Thus (E) may undergo a subsequent rapid reaction with $[S_2O_3]^{2-}$ to provide additional $[S_2O_3]^-$ and a tetra-amminecopper(II) species having a co-ordinated peroxo-ligand, $[O_2]^{2-}$. In aqueous basic media the co-ordinated $[O_2]^{2-}$ probably undergoes rapid hydrolysis to form $[HO_2]^-$. In dilute aqueous solution H_2O_2 is more acidic than water and dissociates according to equation (17). This dissociation will be greatly favoured in basic solution and

$$H_2O_2 \longrightarrow H^+ + [HO_2]^- \ (K = 1{\cdot}5 \times 10^{-12}\ mol\ l^{-1}\ at\ 20\ °C) \qquad (17)$$

$[HO_2]^-$ would appear to be a likely species for oxidation of additional $[S_2O_3]^{2-}$ since hydrogen peroxide is known to oxidize $[S_2O_3]^{2-}$ to $[S_3O_6]^{2-}$.[28] Alternatively $[HO_2]^-$ could decompose according to equation (18). However,

$$2[HO_2]^- \longrightarrow 2\,OH^- + O_2 \qquad (18)$$

reaction (18) is known to be slow,[27] especially in a basic media saturated with O_2.

Results of experiments carried out to determine the effect of added H_2O_2 indicated that in the presence of an O_2 atmosphere the sulphur-product distribution was unchanged. Since some oxygen evolution from added H_2O_2 was found to occur, rate measurements *via* O_2 consumption were not possible. In the absence of an O_2 atmosphere (*i.e.* under argon) the reaction in the presence of a large excess of H_2O_2 resulted primarily in the production of $[S_3O_6]^{2-}$, with a small amount of $[SO_4]^{2-}$ being formed.

Mechanism for $[SO_4]^{2-}$ *Formation*.—When $[S_2O_3]^{2-}$ had decreased to less than 0·025M, for experiments in which $[S_2O_3{}^{2-}]_0$ was much higher, a maximum-rate region for oxygen consumption was observed. This

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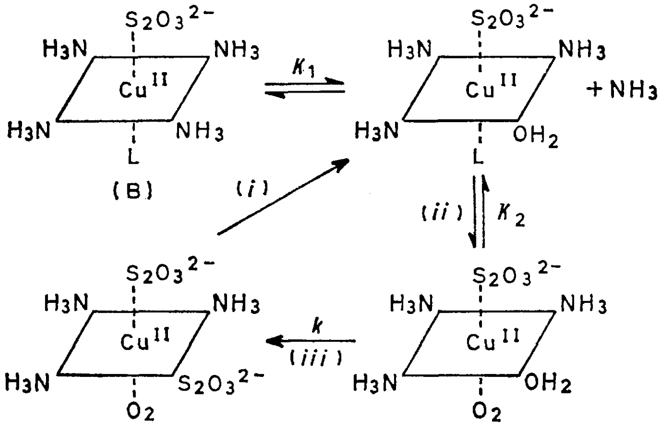
region commenced immediately for experiments carried out in which $[S_2O_3^{2-}]_0$ was less than 0·025M. Analysis of the oxygen stoicheiometry, suphur products formed, and observed reaction rate indicated that both $[S_3O_6]^{2-}$ and $[SO_4]^{2-}$ were being formed concurrently. The kinetics of the $[SO_4]^{2-}$ producing reaction were examined by subtracting the rate of oxygen consumption for $[S_3O_6]^{2-}$ formation from the total rate of oxygen consumption.



SCHEME 2 (*i*), $-[S_2O_5]^{2-}$; (*ii*), $+O_2 - L$; (*iii*), $+[S_2O_3]^{2-}$.

The observed reaction-rate dependences on $[Cu^{II}]$, $[O_2]$, $[S_2O_3^{2-}]$, and $[NH_3]$ for the $[SO_4]^{2-}$ formation reaction led to formulation of the mechanism shown in Scheme 2. Analysis of this mechanism for the rate of oxygen consumption provides the rate law (19), where $[Cu^{II}]_T =$

$$-\frac{d[O_2]}{dt} = \frac{kK_1K_2\,[Cu^{II}]_T\,[O_2]\,[S_2O_3^{2-}]}{[NH_3] + K_1 + K_1K_2[O_2]} \qquad (19)$$

total copper concentration and $-d[O_2]/dt = r_{II} =$ the rate of oxygen consumption for $[SO_4]^{2-}$ formation. Equation (19) can be expressed in the inverse form (20)

$$\frac{1}{k_{II}} = \frac{1}{k} + \frac{1}{kK_2[O_2]} + \frac{[NH_3]}{kK_1K_2[O_2]} \qquad (20)$$

where $k_{II} = r_{II}/[Cu^{II}]_T\,[S_2O_3^{2-}]$. Equation (20) suggests that plots of $1/k_{II}$ against $[NH_3]$ at a given $[O_2]$ or of $1/k_{II}$ against $1/[O_2]$ for a given $[NH_3]$ should be linear. A plot of $1/k_{II}$ against $[NH_3]$ (Figure 6) was linear and from the intercept and gradient values for k and K_2 were determined as 3·1 l mol^{-1} s^{-1} and $3·6 \times 10^4$ l mol^{-1} respectively, the value of K_1 being taken from the literature [15] as $8·92 \times 10^{-3}$ mol l^{-1}. Also plots of $1/k_{II}$ against $1/[O_2]$ (Figure 7) showed good linearity. Average values of k and K_2 determined from the plots in Figure 7 were 2·8 l mol^{-1} s^{-1} and $3·9 \times 10^4$ l mol^{-1}, respectively, in good agreement with those obtained from Figure 6.

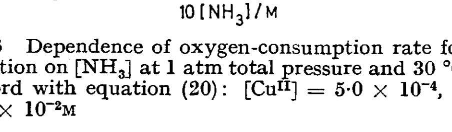


FIGURE 6 Dependence of oxygen-consumption rate for $[SO_4]^{2-}$ production on $[NH_3]$ at 1 atm total pressure and 30 °C, plotted in accord with equation (20): $[Cu^{II}] = 5·0 \times 10^{-4}$, $[S_2O_3^{2-}]_0 = 5·0 \times 10^{-2}$M

The large value obtained for K_2 according to the above rate-law analysis suggests that the intermediate complex $[Cu(NH_3)_3(OH_2)(S_2O_3)(O_2)]$ in Scheme 2 may be present in an appreciable concentration when the $[S_2O_3^{2-}]$ is such that primarily $[SO_4]^{2-}$ is the oxidation product. Some change in the visible-absorption spectra of the reaction solution might be expected due to some build-up of this triammine dioxygen complex. Spectral examination of the reaction solutions for which $[S_2O_3^{2-}] \leqslant 0·02$M did in fact show a downward shift in $\lambda_{max.}$ of *ca.* 15 nm (see Results section). The rate-determining step is similar to the one postulated for the reaction in the absence of oxygen.[6] Oxidation of the equatorially bound $[S_2O_3]^{2-}$ may be visualized as taking place *via* a path involving activation of $[S_2O_3]^{2-}$ and O_2 with subsequent transfer of oxygen to thiosulphate. However, in view of the ability of co-ordinated $[S_2O_3]^{2-}$ to reduce Cu^{II} to Cu^{I} and the facile conversion of Cu^{I} back to Cu^{II} by oxygen, a redox mechanism would appear more reasonable. Such transfers of electrons through metal ions have often been suggested.[17-19,29] The final step of the redox process at the copper site probably involves $[O_2]^-$ transfer to the co-ordinated $[S_2O_3]^-$ to form disulphite, $[S_2O_5]^{2-}$. Although the manner in which this transfer takes place is not clear, $[S_2O_5]^{2-}$ would appear to be the most reasonable sulphur product resulting from the proposed active copper species shown in Scheme 2. If the $[S_2O_3]^-$ species did not combine with $[O_2]^-$, it would probably undergo dimerization to $[S_4O_6]^{2-}$ followed by disproportionation to $[S_3O_6]^{2-}$ and $[S_2O_3]^{2-}$. This would not, however, account for the $[SO_4]^{2-}$ produced. The

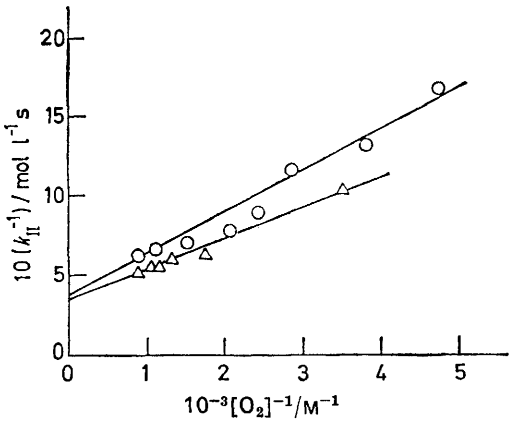


FIGURE 7 Dependence of oxygen-consumption rate for $[SO_4]^{2-}$ production on $[O_2]$ in 0·2M-NH_3 solution at 30 °C, plotted in accord with equation [20]: (○), $[Cu^{II}] = 6·0 \times 10^{-4}$, $[S_2O_3^{2-}]_0 = 5·0 \times 10^{-2}$; (△), $[Cu^{II}] = 3·0 \times 10^{-4}$, $[S_2O_3^{2-}]_0 = 5·0 \times 10^{-2}$M

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[29] P. K. Adolf and G. A. Hamilton, *J. Amer. Chem. Soc.*, 1971, **93**, 3420.

possibility of an outer-sphere reaction between $[S_2O_3]^{2-}$ and $[Cu(NH_3)_3(OH_2)(S_2O_3)(O_2)]$ in the rate-determining step followed by transfer of an $[O_2]^-$ to unbound $[S_2O_3]^-$ to generate $[S_2O_5]^{2-}$ cannot be ruled out on the basis of the kinetic data.

The existence of $[S_2O_5]^{2-}$ in aqueous solution is known[30] and, in view of its unsymmetrical structure which contains a S–S bond,[31] *i.e.* $[O_2S\text{–}SO_3]^{2-}$, its formation from $[O_2]^-$ and $[S\text{–}SO_3]^-$ at the copper site is reasonable. Subsequent oxidation of $[S_2O_5]^{2-}$ may occur *via* a mechanism involving $[S_2O_5]^{2-}$ still bound to the copper site and/or with uncomplexed $[S_2O_5]^{2-}$. In the absence of copper(II) ammines and $[S_2O_3]^{2-}$, an aqueous-ammonia solution of $[S_2O_5]^{2-}$ was stable to oxidation by O_2 under the normal reaction conditions employed (Table 3). When $[S_2O_3]^{2-}$ was added to such a solution oxidation of $[S_2O_5]^{2-}$ did occur but at a very slow rate compared to the observed rates for $[SO_4]^{2-}$ formation in the presence of Cu^{II} species (Table 3). This slow oxidation of $[S_2O_5]^{2-}$ in the presence of $[S_2O_3]^{2-}$ may be represented by equations (21) and (22) which involve dithonite, $[S_2O_4]^{2-}$, as an intermediate. Dithionite was found to

$$[S_2O_5]^{2-} + [S_2O_3]^{2-} \longrightarrow 2[S_2O_4]^{2-} \text{ (rate determining)} \tag{21}$$

$$[S_2O_4]^{2-} + 3\,O_2 + 2\,OH^- \longrightarrow 2[SO_4]^{2-} + H_2O \text{ (rapid)} \tag{22}$$

undergo very rapid oxidation by O_2 in aqueous-ammonia solution at 30 °C.

Experiments carried out on $[S_2O_5]^{2-}$ oxidation in the presence of copper(II) ammine complexes indicated, however, that the most important mechanism by which $[SO_4]^{2-}$ formation occurs from $[S_2O_5]^{2-}$ involves a copper-catalysed step. Quantitative oxidation of $[S_2O_5]^{2-}$ to $[SO_4]^{2-}$ in the presence of copper(II) ammines and O_2 was extremely rapid compared to the rate-determining step in Scheme 2. This mechanism may involve transfer of O_2 to $[S_2O_5]^{2-}$ (or alternatively $[O_2]^-$ to $[S_2O_5]^-$) at the copper site. The resulting sulphur product is probably disulphate, $[S_2O_7]^{2-}$. At 25 °C $[S_2O_7]^{2-}$ rapidly hydrolyses in water.[32] In basic solution quantitative conversion of $[S_2O_7]^{2-}$ to $[SO_4]^{2-}$ takes place according to equation (23).

$$[S_2O_7]^{2-} + 2OH^- \longrightarrow 2[SO_4]^{2-} + H_2O \tag{23}$$

The effect of a free-radical inhibitor, namely mannitol, on the rate of $[SO_4]^{2-}$ production was studied. The results obtained (Table 4) indicated that the amount and rate of oxygen consumption are rather insensitive to the presence of mannitol in the reaction system. Compared to the effects of mannitol on reactions actually involving free radicals, *e.g.* $[SO_3]^{2-}$ oxidation,[25] the slight effects shown in Table 4 are negligible with respect to the involvement of free radicals in the main oxidation process. The observed effects may be the result of some scavenging of an $[O_2]^-$ species, possibly resulting in $[S_3O_6]^{2-}$ formation.

TABLE 4

Effect of mannitol on the oxidation of thiosulphate at $[Cu^{II}] = 4{\cdot}0 \times 10^{-4}$, $[S_2O_3^{2-}]_0 = 2{\cdot}5 \times 10^{-2}$, $[NH_3] = 0{\cdot}2$, $[O_2] = 11{\cdot}15 \times 10^{-4}$M, and 30·0 °C

10^2 [Mannitol]/ M	$\dfrac{\text{Moles } O_2 \text{ consumed}}{\text{Moles } [S_2O_3]^{2-} \text{ consumed}}$	$10^5 r_T$ */ mol l^{-1} s^{-1}
0	1·25	3·12
0·5	1·25	3·00
1·0	1·23	2·85
1·5	1·22	2·54
2·5	1·23	2·70

* Total oxygen-consumption rate in maximum-rate region.

With respect to the $[SO_4]^{2-}$ formation process, the role of the Cu^{II} species is seen to be one of complexing both oxidant and reductant in that it provides a mechanism for electron transfer and allows O_2 to interact *via* an ionic mechanism. Transfer of O_2 to oxidizable substrates at a metal-ion site *via* an ionic mechanism has been suggested previously.[29,33]

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