Inorg. Chem. **1992,** *31,* 3239–3242

Equilibria and Kinetics of the Fast Interaction between Copper(II) and Thiosulfate Ions in Aqueous Solution[1]

Gyula Rábai[2] and Irving R. Epstein*

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254-9110

Received March 5, 1992

The fast reduction of copper(II) by the thiosulfate ion in aqueous solution is preceded by the extremely rapid formation of a $Cu(S_2O_3)_2^{2-}$ complex with stability constant $\beta = (3.6 \pm 0.5) \times 10^4$ M^{-2} at 25.0 °C and ionic strength 0.2 M ($NaClO_4$). The tetrathionate ion and a (thiosulfato)copper(I) complex are formed in the redox reaction, the rate of which is second order in [Cu(II)] and independent of $[S_2O_3^{2-}]$ in high excess of thiosulfate. The limiting value of the observed second-order rate constant is $k_4 = (1.05 \pm 0.08) \times 10^5$ M^{-1} s^{-1}. The mechanism involves an intermolecular rate-determining step between two molecules of the bis(thiosulfato)copper(II) complex.

Introduction

Oscillatory kinetics have recently been reported for the oxidations of the thiosulfate ion by hydrogen peroxide[3] and by the peroxodisulfate ion[4] in a continuous-flow stirred tank reactor (CSTR). A catalytic amount of copper(II) was found to be essential for oscillation to occur in these systems.[5] It has long been known that copper(II) can greatly accelerate the oxidation of thiosulfate by a variety of oxidizing agents in aqueous solution.[6–8] It would therefore appear that an understanding of the Cu(II)–$S_2O_3^{2-}$ interaction should be a key element in deciphering the mechanism of copper-catalyzed chemical oscillators. The catalytic activity of copper(II) is usually explained by assuming that the copper(II) ion undergoes a facile, rapid reduction by the thiosulfate ion to copper(I), followed by a fast oxidation of Cu^+:

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

$$2Cu^+ + ox \rightarrow 2Cu^{2+} + ox^{2-} \qquad (2)$$

Reaction 1 is thermodynamically favored. From the redox potentials of 0.08 and 0.153 V for $S_2O_3^{2-}/S_4O_6^{2-}$ and Cu^{2+}/Cu^+, respectively,[9] its equilibrium constant is evaluated to be 300 M^{-1}. A detailed kinetics study of reaction 1 in the presence of excess ammonia in alkaline solution has been reported,[10] but the results obtained under these conditions are not directly applicable in the absence of ammonia. With excess ammonia, nearly all the copper(II) is present as a complex; the ammine complex reacts much more slowly than the aquacopper(II) complex, and it also reacts quite differently. The kinetics of reaction 1 in the absence of any additional complexing agent have not yet been investigated experimentally.

In order to obtain relevant kinetic data for modeling oscillatory systems containing thiosulfate and the copper(II) ions, and for better understanding of the catalytic effect of Cu^{2+} on nonoscillatory oxidations of $S_2O_3^{2-}$, it is important to collect as much experimental kinetics information as possible about reactions 1 and 2. Direct kinetics studies of the oxidations of copper(I) are scarce, owing to the high reactivity of the Cu^+ ion with molecular oxygen and to the ease of the disproportionation reaction $2Cu^+ \rightarrow Cu^{2+} + Cu$. A kinetics study of the reduction of Cu^{2+} appears to suffer from no such complication. We report here the results of our investigation of reaction 1. The principal objective in this study is to explore the interaction between copper(II) and thiosulfate in order to establish a firm basis for modeling the reported oscillatory reactions of the thiosulfate ion.

Visible evidence that this reaction is not immeasurably fast, and proceeds in steps, is easily obtained. When solutions of copper(II) perchlorate and sodium thiosulfate are rapidly mixed, a yellow intermediate forms instantaneously and then is quickly decolorized. This preliminary experiment suggests that the mechanism of the reaction involves incorporation of one or more thiosulfato ligands into the inner coordination sphere of the copper(II) ion prior to an electron-transfer step. The very fast complex-forming process can be completely separated from the rapid, but relatively slower, redox reaction by means of the stopped-flow technique. A similar technique was first applied by Országh et al.[11] to separate the fast reversible interaction between I_2 and SCN^- from the subsequent redox reaction.

Experimental Section

Materials. Analytical grade reagents were used without further purification. In order to avoid complex-forming anions, we used $Cu(ClO_4)_2{\cdot}5H_2O$ instead of the more commonly used copper(II) sulfate. The ionic strength was adjusted with $NaClO_4$. A few experiments were performed in acetate buffer, which was found to form an acetato complex with Cu^{2+}, thereby modifying the equilibria and the kinetics of the reaction. Other known buffers are expected to form complexes with copper(II) as well. Since the pH does not change during the reaction, we chose to omit the buffer, and most of the kinetics runs were performed in unbuffered solution with $HClO_4$ used to adjust the hydrogen ion concentration. The stock solutions were made up by weight and diluted for use in the experiments. Two working solutions were prepared for each run, one containing $Cu(ClO_4)_2$, the necessary amount of $HClO_4$, and half the necessary amount of $NaClO_4$ and the other containing $Na_2S_2O_3$ and the remainder of the $NaClO_4$. In order to avoid the acid-accelerated decomposition of thiosulfate, no $HClO_4$ was added to its working solutions. All solutions were deoxygenated with argon before the kinetics runs. Sodium thiosulfate solutions were discarded after 1 week.

Methods. Unless noted otherwise, all stopped-flow measurements were conducted at 25.0 ± 0.1 °C. The stopped-flow apparatus is based on a HI-TECH SF-3L mixing unit in which the prethermostated reactant solutions are mixed in a ratio of 1:1 by volume. The formation of the yellow intermediate was complete within the mixing time (5 ms) of the

---

(1) Series Systematic Design of Chemical Oscillators. 83. Part 82: Lengyel, I.; Li, J.; Epstein, I. R. *J. Phys. Chem.*, in press.

(2) Permanent address: Institute of Physical Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary.

(3) Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 101.

(4) Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1989**, *111*, 2891.

(5) Orbán, M. *React. Kinet. Catal. Lett.* **1990**, *42*, 343.

(6) Abel, E. *Monatsh. Chem.* **1913**, *34*, 1361.

(7) Abel, E. *Ber. Dtsch. Chem. Ges.* **1923**, *56*, 1076.

(8) Sarala, R.; Rabin, S. B.; Stanbury, D. M. *Inorg. Chem.* **1991**, *30*, 3999.

(9) Kimura, M.; Ishibashi, M. *Inorg. Chim. Acta* **1987**, *129*, 69.

(10) Byerley, J. J.; Fouda, S. A.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1973**, 889.

(11) Országh, I.; Bazsa, Gy.; Beck, M. T. *Inorg. Chim. Acta* **1972**, *6*, 271.

0020-1669/92/1331-3239$03.00/0

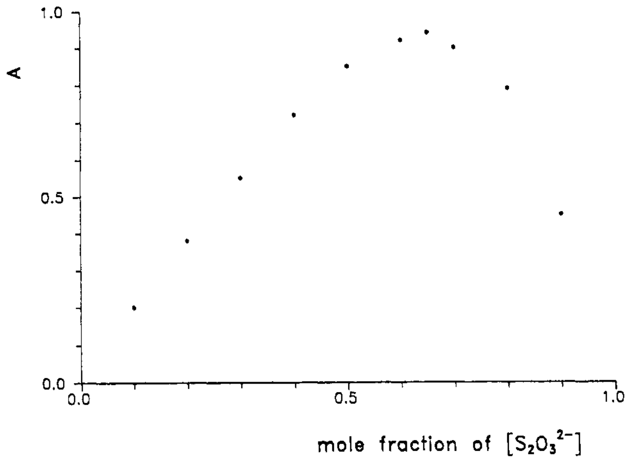

Figure 1. Absorbance at 400 nm immediately after mixing a copper(II) solution with thiosulfate in the stopped-flow cell as a function of mole fraction of $S_2O_3^{2-}$. The position of the maximum indicates the formation of a 1:2 copper(II):thiosulfate complex. $[Cu^{2+}] + [S_2O_3^{2-}] = 0.0050$ M; $I = 0.20$ M; $T = 25.0$ °C.

apparatus. Kinetics runs over a range of wavelengths indicated that the intermediate has an absorbance maximum at 400 nm. The consumption of the intermediate was followed spectrophotometrically at 400 nm, where neither the reactants nor the products absorb light. In order to approach the conditions under which oscillatory behavior is found in the thiosulfate–hydrogen peroxide/peroxodisulfate–copper(II) systems, most of the runs were performed with a high excess of thiosulfate over copper(II). Each run was repeated at least five times. Kinetics data were digitalized and collected on a personal computer. The absorbance values extrapolated to zero time were used to determine the composition and the molar absorbance of the intermediate, as well as the equilibrium constant for its formation. The stopped-flow absorbance vs time curves enabled us to establish the rate law for the disappearance of the intermediate.

Results

Composition of the Intermediate. The composition of the (thiosulfato)copper(II) complex formed in the first stage of the reaction was determined by Job's method.[12] Initial absorbance values (A_0) obtained by extrapolation were determined for different $[Cu^{2+}]:[S_2O_3^{2-}]$ ratios at ionic strength 0.2 M. The sum $[Cu^{2+}] + [S_2O_3^{2-}]$ was kept constant. In excess Cu^{2+}, a much slower side reaction follows reaction 1, resulting in some precipitation. This side reaction did not interfere with our experiments, and it does not take place at all in excess thiosulfate. Representative absorbance data are shown in Figure 1. The curve shows a maximum in absorbance at 0.67 mole fraction thiosulfate. The position of the maximum is independent of the sum of the concentrations within the range $[Cu^{2+}] + [S_2O_3^{2-}] = 0.002$–$0.008$ M. Furthermore, it is independent of wavelength between 400 and 450 nm. The position of the maximum indicates that the intermediate contains 1 mol of Cu^{2+} to 2 mol of $S_2O_3^{2-}$. We conclude from these results that a bis(thiosulfato)copper(II) complex is rapidly formed in the mixture of aqueous Cu^{2+} and $S_2O_3^{2-}$ prior to the reduction of copper(II):

$$Cu^{2+} + 2S_2O_3^{2-} \rightleftarrows Cu(S_2O_3)_2^{2-} \tag{3}$$

It is surprising that no spectrophotometric sign of the formation of the neutral mono(thiosulfato)copper(II) complex (CuS_2O_3) could be detected by this technique. It appears either that this species is unstable in aqueous solution or that its absorbance is very small.

Stability Constant of the $Cu(S_2O_3)_2^{2-}$ Complex. In mixtures with $[Cu^{2+}] = 2 \times 10^{-4}$ M and $[S_2O_3^{2-}] \geq 0.01$ M, increasing $[S_2O_3^{2-}]$ gave no further increase in the zero-time absorbance. This observation implies that the complex formed is neither extremely stable nor very weakly bound. Therefore, it should be possible to determine its stability constants spectrophotometrically.

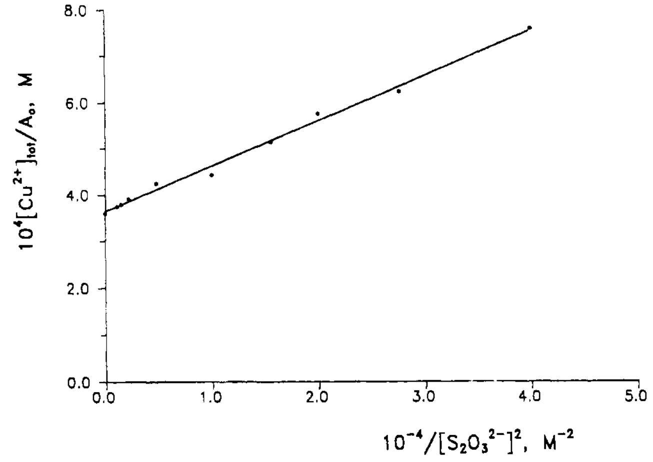

Figure 2. $[Cu^{2+}]/A_0$ vs $1/[S_2O_3^{2-}]^2$ plot for determination of the stability constant of the bis(thiosulfato)copper(II) complex. $[Cu^{2+}] = 2.0 \times 10^{-4}$ M; $I = 0.20$ M; $T = 25.0$ °C.

The equilibrium constant for reaction 3 is

$$\beta = \frac{[Cu(S_2O_3)_2^{2-}]}{[Cu^{2+}][S_2O_3^{2-}]^2} \tag{3'}$$

If we assume that $Cu(S_2O_3)_2^{2-}$ is the only light-absorbing species at 400 nm and that the total concentration of thiosulfate, $[S_2O_3^{2-}]_{tot}$, greatly exceeds the total concentration of copper(II), $[Cu^{2+}]_{tot}$, $[S_2O_3^{2-}]_{tot} \sim [S_2O_3^{2-}]$ and eq 3′ becomes

$$\frac{[Cu^{2+}]_{tot}}{A_0} = \frac{1}{\epsilon\beta[S_2O_3^{2-}]_{tot}^{\ 2}} + \frac{1}{\epsilon} \tag{3''}$$

where A_0 is the absorbance of the solution per unit path length and ϵ is the molar absorbance of the $Cu(S_2O_3)_2^{2-}$ complex. A typical plot of $[Cu^{2+}]_{tot}/A_0$ vs $1/[S_2O_3^{2-}]^2$ is shown in Figure 2. The intercept $1/\epsilon$ and the slope $1/\beta$ of the straight line were determined by least-squares methods and gave $\epsilon = 2770 \pm 140$ M^{-1} cm^{-1} and $\beta = (3.6 \pm 0.5) \times 10^4$ M^{-2} at 25.0 °C and $I = 0.20$ M ($NaClO_4$).

While the tendency of thiosulfate to form complexes with copper(II) is widely accepted, the only numerical value for the formation constant of such a complex was reported by Levin and Ukse[13] to be $\beta = 10^{12.29}$ M^{-2}. There is a huge difference between the β determined in this work and their value. Levin and Ukse used the cathode polarization method, a technique which requires a relatively long time for determining a stability constant. In view of the subsequent fast redox reaction between copper(II) and thiosulfate to form copper(I), we suggest that they measured, in fact, the stability constant of the bis(thiosulfato)copper(I) complex. This proposal is strongly supported by the reported values for the stability constant of bis(thiosulfato)copper(I)[14] ($10^{11.69}$–$10^{12.27}$), which are strikingly similar to the value reported by Levin and Ukse[13] for the copper(II) complex.

Stoichiometry and Kinetics of the Reduction of the $Cu(S_2O_3)_2^{2-}$ Complex. A variable stoichiometry is frequently observed when the thiosulfate ion is oxidized. In acidic solution and in excess thiosulfate, tetrathionate is expected to be the major product. If the oxidizing agent is in excess and the pH is in the alkaline range, the oxidation usually leads to formation of sulfate. The present investigation was carried out under the conditions favoring

---

[12] Job, P. *Ann. Chim. Phys.* **1928**, *9*, 113.

[13] Levin, A. I.; Ukse, E. A. *Sb. Statei Obshch. Khim* **1953**, *2*, 798 (*Chem. Abstr.* **1955**, *49*, 3695.2).

[14] Sillen, L. G.; Martell, A. E. *Stability Constants of Metal-Ion Complexes*; Special Publication No. 17; Chemical Society: London, 1964.

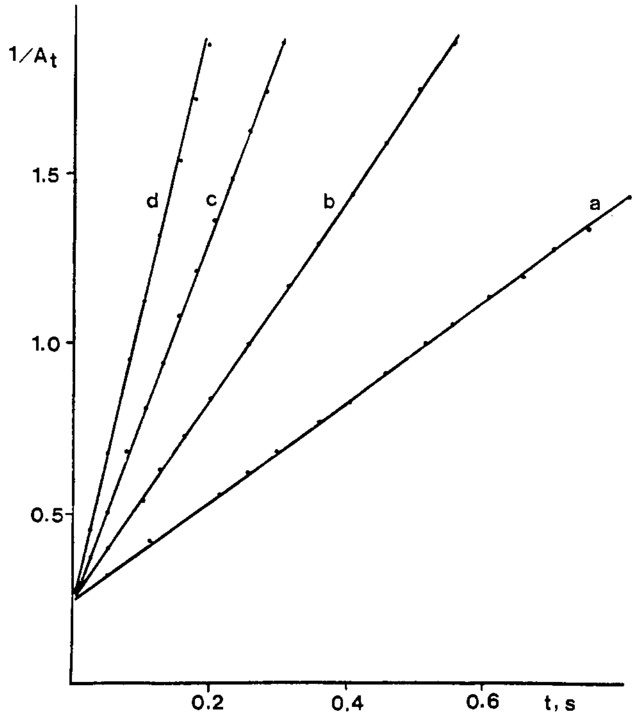

Figure 3. Typical $1/A_t$ vs t plots at several ionic strengths. $[Cu^{2+}] = 2.0 \times 10^{-4}$ M; $[S_2O_3^{2-}] = 0.010$ M; $T = 25.0$ °C; no H^+ added; I = (a) 0.030, (b) 0.130, (c) 0.43, (d) 0.83 M.

the formation of tetrathionate, and we could not detect any traces of sulfate by analysis with $Ba(NO_3)_2$ immediately after the reduction of the Cu(II) complex was completed. Thus, when thiosulfate is in large excess, the products of the fast redox reaction are expected to be tetrathionate and a stable (thiosulfato)copper(I) complex. In a smaller excess of thiosulfate or in excess copper(II), the fast redox reaction is followed by slower side reactions that result in the formation of elementary copper, copper sulfide, and sulfate:

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

$$2Cu^+ + S_2O_3^{2-} + H_2O \rightarrow Cu_2S + SO_4^{2-} + 2H^+$$

Under these conditions, no meaningful inference regarding the stoichiometry of the fast redox reaction can be drawn from analysis of the product solution.

Our kinetics experiments, which are discussed below, imply that only the coordinated and not the free thiosulfate is directly involved in the redox reaction:

$$2Cu(S_2O_3)_2^{2-} \rightarrow 2CuS_2O_3^- + S_4O_6^{2-} \qquad (4)$$

The absorbance vs time curves obtained by the stopped-flow technique show that the formation of the bis(thiosulfato)copper(II) complex is complete within the mixing time (5 ms) of the apparatus. Therefore, we are unable to obtain any information about the rate of formation of the complex (reaction 3). We can, however, measure the kinetics of its reduction (reaction 4). The shape of the absorbance–time curves suggests that reaction 4 is second order with respect to the light-absorbing bis(thiosulfato)copper(II) complex. As illustrated in Figure 3, in excess thiosulfate, plots of the reciprocal of the absorbance vs time give a straight line up to 90% completion. The slope of this straight line is k_4/ϵ, where ϵ is the molar absorbance of $Cu(S_2O_3)_2^{2-}$ and k_4 (M^{-1} s^{-1}) is the rate constant of reaction 4. We calculated this second-order rate constant by least-squares analysis of our experimental $1/A_t$–time data. The results are summarized in Table I. The values of k_4 are independent of the concentrations of Cu(II) and of H^+. As the thiosulfate concentration increases, the values of the rate constant increase until they reach a limiting value of $k_4 = (1.05 \pm 0.08) \times 10^5$ M^{-1} s^{-1}. Thus, in high excess of thiosulfate, the rate expression for reaction 4 is given by the simple second-order equation

Table I. Stopped-Flow Kinetics Data

$10^4[Cu^{2+}]$, M	$10^3[S_2O_3^{2-}]$, M	$10^4[HClO_4]$, M	I ($NaClO_4$), M	$10^{-4}k_1$, M^{-1} s^{-1}
1.00	25.0	0.00	0.20	10.1
2.00	25.0	0.00	0.20	10.3
3.00	25.0	0.00	0.20	10.3
5.00	25.0	0.00	0.20	10.4
2.00	10.0	0.00	0.20	10.8
2.00	10.0	1.00	0.20	10.5
2.00	10.0	3.00	0.20	11.0
2.00	10.0	5.00	0.20	10.8
2.00	10.0	10.0	0.20	10.9
2.00	1.00	1.00	0.20	0.953
2.00	2.00	1.00	0.20	2.60
2.00	3.00	1.00	0.20	4.31
2.00	4.00	1.00	0.20	5.75
2.00	5.00	1.00	0.20	7.40
2.00	6.00	1.00	0.20	8.59
2.00	7.00	1.00	0.20	9.72
2.00	8.00	1.00	0.20	10.3
2.00	9.00	1.00	0.20	10.4
2.00	12.0	1.00	0.20	10.3
2.00	12.0	1.00	0.20	10.6
2.00	15.0	1.00	0.20	10.5
2.00	20.0	1.00	0.20	10.8
2.00	25.0	1.00	0.20	10.3
2.00	30.0	1.00	0.20	9.96
2.00	10.0	1.00	0.030	4.02
2.00	10.0	1.00	0.130	8.50
2.00	10.0	1.00	0.230	10.9
2.00	10.0	1.00	0.430	16.1
2.00	10.0	1.00	0.830	24.2

$$v_4 = \frac{d[Cu(S_2O_3)_2^{2-}]}{dt} = k_4[Cu(S_2O_3)_2^{2-}]^2 \qquad (4')$$

Under these conditions essentially all the copper(II) is complexed, so the concentration of the complex can be replaced by the total concentration of copper(II):

$$v_4 = k_4[Cu^{2+}]_{tot}^2 \qquad (4'')$$

Equation 4″ with $k_4 = 1 \times 10^5$ M^{-1} s^{-1} should provide a satisfactory rate law for reaction 1 in modeling systems containing a high excess of thiosulfate with copper(II) present at catalytic levels. In a smaller excess of thiosulfate, the rate expression should reflect that the velocity increases with increasing $[S_2O_3^{2-}]$. In this case a significant fraction of the copper(II) remains uncomplexed by thiosulfate in the early stages of the redox reaction. Taking into account equilibrium 3, the concentration of the complex is given by

$$[Cu(S_2O_3)_2^{2-}] = \frac{\beta[Cu^{2+}]_{tot}[S_2O_3^{2-}]^2}{1 + \beta[S_2O_3^{2-}]^2} \qquad (5)$$

Combining eqs 4′ and 5, we obtain the complex rate law

$$v_4 = k_4\left(\frac{\beta[Cu^{2+}]_{tot}[S_2O_3^{2-}]^2}{1 + \beta[S_2O_3^{2-}]^2}\right)^2 \qquad (4''')$$

At high thiosulfate concentrations, the first term in the denominator is negligible, and eq 4‴ reduces to the simpler form of eq 4′.

The value of k_4 increases with ionic strength of the solution (Table I). This observation indicates that the rate-determining step involves two positive or two negative ions. However, a plot of log k_4 vs $I^{1/2}$ or vs $I^{1/2}/(1 + I^{1/2})$ is not linear, so no meaningful inference regarding the charge of the reacting ions could be drawn from the observed effect of ionic strength.

We have studied the temperature dependence of k_4. Least-squares analysis of an Arrhenius plot of the data yields the enthalpy of activation as $\Delta H^{*} = 38.0 \pm 3$ kJ/mol and the entropy of activation as $\Delta S^{*} = -25 \pm 4$ J/(mol K).

Discussion

The oxidation of thiosulfate by transition metal ion oxidants has been found to proceed either through metal–thiosulfato complexes formed prior to an irreversible electron transfer or without any change in the inner coordination sphere of the metal ion. The latter mechanism is characteristic of oxidation by substitution-inert metal complexes.[8] In the case of copper(II), our experiments provide clear spectrophotometric evidence for the formation of an inner-sphere complex in which an electron is then transferred from the ligand to the metal ion. This reversible charge transfer oxidizes one thiosulfate. Since two oxidized thiosulfate ions are needed for the formation of a tetrathionate ion, and the copper(II) ion cannot accept more than one electron, intramolecular formation of tetrathionate inside the coordination sphere is not likely. In agreement with this, the second-order dependence of the rate on the complex concentration found in our experiments indicates that the rate-determining step of the irreversible redox reaction is an intermolecular interaction between two molecules of the bis(thiosulfato)copper(II) complex:

$$\{S_2O_3\text{–}Cu\text{–}S_2O_3\}^{2-} + \{S_2O_3\text{–}Cu\text{–}S_2O_3\}^{2-} \rightarrow \{S_2O_3\text{–}Cu\}^{-} + S_4O_6^{\,2-} + \{Cu\text{–}S_2O_3\}^{-}$$

This mechanism avoids generating the $S_2O_3^-$ radical, which has been widely suggested as an intermediate in oxidations of thiosulfate to tetrathionate. The redox potential for the $S_2O_3^-/S_2O_3^{2-}$ couple was estimated to be 1.35 V in a recent critical summary.[15] This high redox potential implies that formation of the $S_2O_3^-$ radical is quite unfavorable thermodynamically in this system. A similar mechanism with a bimolecular rate-determining step that avoids cyanogen radicals and instead involves two molecules of a cyano complex has been proposed[16] for the redox reaction between the cyanide ion and copper(II). In our system, copper(I) is stabilized by the excess thiosulfate in the form of either mono- or bis(thiosulfato) complexes.

The results presented here suggest some observations on the mechanism of the catalytic activity of Cu(II) in the hydrogen peroxide oxidation of thiosulfate. As mentioned above, two component processes have been proposed to explain the copper catalysis: reduction of copper(II) by thiosulfate (reaction 1) and oxidation of copper(I) by hydrogen peroxide (reaction 2 with ox = H_2O_2 and ox^{2-} = 2OH$^-$). The key question is, which of the two component reactions determines the rate of the catalytic cycle? Abel[6] suggested that since reaction 1 is very fast, reaction 2 determines the rate, giving the following rate law for the catalytic term:

$$v_2 = k_2[H_2O_2][Cu^{2+}]$$

where $k_2 = 1100$ min^{-1} M^{-1} = 18.3 s^{-1} M^{-1}. Our results indicate that reaction 2 is the slow step only under certain conditions. Using Abel's data for reaction 2 and the results reported here for reaction 1, we find that the two rates become equal when

$$10^5[Cu^{2+}] = 18.3[H_2O_2]$$

We see that if $[H_2O_2]$ is low relative to $[Cu^{2+}]$ ($[Cu^{2+}] \gg 2 \times 10^{-4}[H_2O_2]$), the slow step is reaction 2, and the rate of the catalytic oxidation does indeed depend on the concentration of H_2O_2. This condition holds in most of Abel's experiments. However, a typical reaction mixture showing oscillatory kinetics in a CSTR[3] has $[H_2O_2] > 0.1$ M and $[Cu^{2+}] \approx 2 \times 10^{-5}$ M, indicating that the two rates are comparable, so that reaction 2 cannot be treated as the rate-determining step in the catalytic cycle. In a description of the oscillatory kinetics, one should take into account rate law 4″ suggested here for reaction 1.

While other aspects of the sulfur chemistry remain to be clarified, we believe that these results represent an important step toward the goal of understanding the mechanisms of copper-catalyzed sulfur-containing oscillators. Attempts to utilize the rate laws developed here in modeling some of these systems are now under way.

Acknowledgment. This work was supported by the National Science Foundation (Grant, CHE-9023294) and by a U.S.-Hungarian cooperative grant from the NSF and the Hungarian Academy of Sciences. We thank Kenneth Kustin for helpful discussions.

Registry No. Cu^{2+}, 15158-11-9; $S_2O_3^{2-}$, 14383-50-7.

---

(15) Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *33*, 69.
(16) Nord, G.; Mathes, H. *Acta Chem. Scand.* **1974**, *A28*, 13.