# Mechanistic studies of oscillatory copper(II) catalyzed oxidation reactions of sulfur compounds

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## Abstract

Trace amounts of copper ion catalyst induce exotic phenomena in the oxidation of several inorganic sulfur compounds by peroxides in aqueous solution. Simple and complex oscillations and several kinds of bistability are observed when the copper(II)-catalyzed oxidation of $S_2O_3^{2-}$ by either $H_2O_2$ or $S_2O_8^{2-}$ is carried out in a CSTR and when $SCN^-$ ions are oxidized with $H_2O_2$ in the presence of copper ions under either batch or flow conditions. For the $S_2O_3^{2-}$–$H_2O_2$–Cu(II) reaction, a four-step model is proposed, in which formation of the intermediate $HOS_2O_3^-$ and attack on that species by $S_2O_3^{2-}$ and $H_2O_2$ play key roles. When this core of reactions is extended with additional steps, computer simulations yield good agreement between the experimentally observed and calculated pH oscillations, bistability and batch behavior. In the oscillatory $S_2O_3^{2-}$–$S_2O_8^{2-}$–Cu(II) flow reaction, Cu(I), Cu(II) and Cu(III) species as well as $SO_4^{\bullet-}$ and $S_2O_3^{\bullet-}$ are postulated to participate in a free radical mechanism, which successfully simulates the oscillations. To model the experimentally observed oscillations and bistability in the $H_2O_2$–$SCN^-$–Cu(II) system, we have proposed a complex mechanism involving 30 reactions and 26 independent species. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Nonlinear dynamics; Kinetics; Simulation; CSTR; Sulfur oscillators; Copper(II)-catalysis

## 1. Introduction

Among the several families of chemical oscillators (Epstein & Pojman, 1998), the reactions derived from the chemistry of oxysulfur species are perhaps the most complex, owing to the multiple oxidation states available to sulfur and the possibility of forming a wide range of polynuclear and heteronuclear species. A major subfamily of sulfur-based chemical oscillators consists of reactions in which the oxidation of a sulfur compound is catalyzed by copper(II). The experimental behavior of several copper-catalyzed oscillating reactions has been summarized (Orbán, 1990). Here we present additional experimental data and simulations based on both detailed mechanisms and simplified models for three important copper-catalyzed, sulfur-based oscillators: the hydrogen peroxide–thiosulfate reaction (A), the peroxodisulfate–thiosulfate reaction (B) and the hydrogen peroxide–thiocyanate reaction (C). Each of these systems exhibits both oscillations and bistability in a continuously fed stirred tank reactor (CSTR). In addition, system (A) shows oscillations under semibatch conditions (Rábai & Epstein, 1992), while system (C) oscillates in batch. In each case, the simulations yield satisfactory agreement with experiment, and the proposed mechanism sheds light on the role of copper(II) in the catalytic cycle.

## 2. Experimental and results

### 2.1. System (A): Hydrogen peroxide–thiosulfate–copper (II)

Oscillations in the pH and in the potential of both Pt and Cu(II)-selective electrodes and bistability between low and high pH stationary states and between the oscillatory and one of the stationary states have been observed in System (A) in a CSTR (Orbán & Epstein, 1987). Experimental oscillatory responses in pH and in potential of Pt electrode are shown in Fig. 1.

The stoichiometry of the reaction depends on the initial pH. At pH < 5 the reaction quantitatively yields

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**Nomenclature**

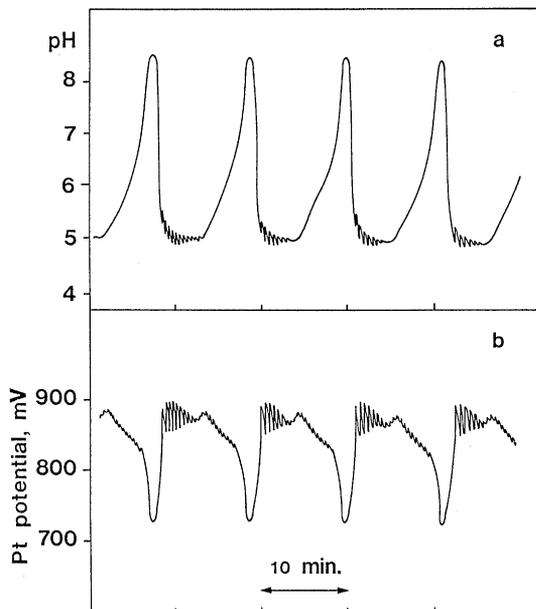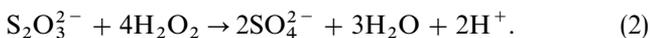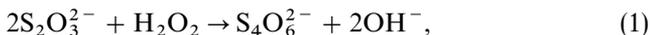| | |
|---|---|
| $k_i$ | forward rate constant for reaction $i$ |
| $k_{-i}$ | reverse rate constant for reaction $i$ |
| $k_i'$ | rate constant in additional rate term |
| $v_i$ | forward reaction rate for step $i$ |
| $v_{-i}$ | reverse reaction rate for step $i$ |



Fig. 1. Experimentally observed oscillations in pH (a) and in potential of Pt electrode for the hydrogen peroxide–thiosulfate–copper(II) system. $[H_2O_2] = 0.1$ M, $[S_2O_3^{2-}] = 0.01$ M, $[H_2SO_4] = 0.001$ M, $[Cu(II)] = 2.5 \times 10^{-5}$ M, flow rate $k_0 = 4.5 \times 10^{-3}$ s$^{-1}$.

$S_4O_6^{2-}$ (Eq. (1)). In neutral and alkaline solutions a mixture of $S_4O_6^{2-}$ and $SO_4^{2-}$ is formed (Eqs. (1) and (2)). The presence of Cu(II) ions accelerates the reaction but does not change the stoichiometry.

$$2S_2O_3^{2-} + H_2O_2 \rightarrow S_4O_6^{2-} + 2OH^-, \quad (1)$$

$$S_2O_3^{2-} + 4H_2O_2 \rightarrow 2SO_4^{2-} + 3H_2O + 2H^+. \quad (2)$$

Schiller proposed a simple mechanism in which the intermediate $HOS_2O_3^-$ plays a key role (Schiller, 1987). Attack on that species by $H_2O_2$ and $S_2O_3^{2-}$ accounts for the formation of both tetrathionate and sulfate. A four-step mechanism, reactions (A1)–(A4) (with corresponding rates $v_1 - v_4$), based on Schiller's suggestion and including the dissociation equilibrium of water describes the chemistry.

$$H_2O_2 + S_2O_3^{2-} \rightarrow HOS_2O_3^- + OH^-, \quad (A1)$$
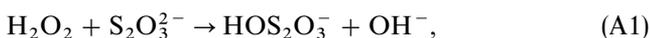
$$v_1 = k_1[H_2O_2][S_2O_3^{2-}]$$
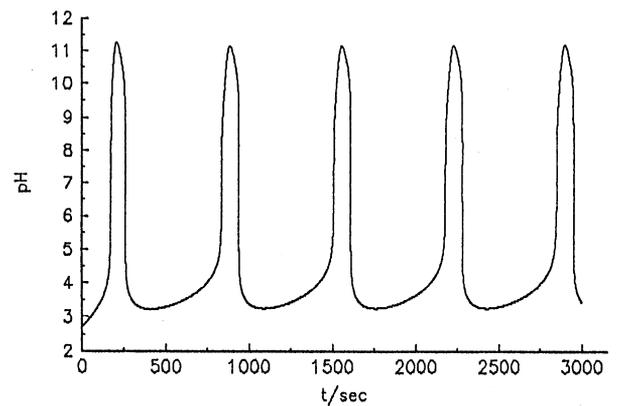$$\quad + k_1'[Cu^{2+}][OH^-][H_2O_2][S_2O_3^{2-}],$$



Fig. 2. Simulated pH oscillations with model (A1)–(A4) and $k_{1'} = 3 \times 10^7$ M$^{-3}$s$^{-1}$. $[H_2O_2] = 0.1$ M, $[S_2O_3^{2-}] = 0.01$ M, $[H_2SO_4] = 0.001$ M, $[Cu(II)] = 1 \times 10^{-5}$ M, $k_0 = 4.5 \times 10^{-3}$ s$^{-1}$.

$$3H_2O_2 + HOS_2O_3^- \rightarrow 2SO_4^{2-} + 3H^+ + 2H_2O, \quad (A2)$$

$$v_2 = k_2[H_2O_2][HOS_2O_3^-],$$

$$HOS_2O_3^- + S_2O_3^{2-} \rightarrow S_4O_6^{2-} + OH^-, \quad (A3)$$

$$v_3 = k_3[HOS_2O_3^-][S_2O_3^{2-}],$$

$$H_2O \leftrightarrow H^+ + OH^-, \quad (A4)$$
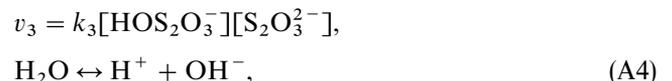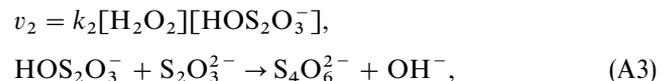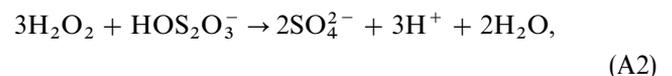
$$v_4 = k_4[H_2O],$$

$$v_{-4} = k_{-4}[H^+][OH^-].$$

The set of reactions (A1)–(A4) does not contain any feedback loop. It is therefore insufficient in itself to explain the oscillations and bistability. In the presence of Cu(II) ions — by analogy with other Cu(II)-catalyzed $H_2O_2$ oxidation reactions (Erlenmayer, Flierl & Sigel, 1969) — the second term in the rate equation for $v_1$ provides autocatalysis by $OH^-$ ions, thereby generating the positive feedback necessary for the exotic behavior. Fig. 2 demonstrates that this simple model does yield oscillations, but the amplitude and period differ from those observed experimentally (Fig. 1), and no bistability can be calculated.

In order to explain the detailed behavior of the system, we extend model (A1)–(A4) by replacing reaction (A2) with reaction (A2′), adding a proton-dependent term in the rate law of step (A3), and adding steps (A5)–(A9). With the rate constants given in Table 1, this more complete description does an excellent job of simulating the experimental behavior in both batch and flow, as seen in Figs. 3–5. The only adjustable parameters are $k_1'$, $k_2$, $k_3$, $k_6$ and $k_6'$; all others are taken from the literature:

$$H_2O_2 + HOS_2O_3^- \rightarrow 2HSO_3^- + H^+, \quad (A2')$$

$$v_2 = k_2[H_2O_2][HOS_2O_3^-],$$

$$v_3 = k_3[HOS_2O_3^-][S_2O_3^{2-}]$$
$$\quad + k_{3'}[HOS_2O_3^-][S_2O_3^{2-}][H^+],$$

Table 1
Rate constants for the extended mechanism of the $H_2O_2$–$S_2O_3^{2-}$–Cu(II) reaction

| Rate constant | Value[a] |
| --- | --- |
| $k_1$ | $0.019\ M^{-1}\,s^{-1}$ |
| $k_{1'}$ | $3 \times 10^7$–$3 \times 10^8\ M^{-3}\,s^{-1}$ |
| $k_2$ | $1\ M^{-1}\,s^{-1}$ |
| $k_3$ | $50\ M^{-1}\,s^{-1}$ |
| $k_{3'}$ | $0$–$3 \times 10^5\ M^{-2}\,s^{-1}$ |
| $k_4[H_2O]$ | $1 \times 10^{-3}\ M\,s^{-1}$ |
| $k_{-4}$ | $1 \times 10^{11}\ M^{-1}\,s^{-1}$ |
| $k_5$ | $2.2 \times 10^{-2}\ s^{-1}$ |
| $k_{-5}$ | $1 \times 10^{10}\ M^{-1}\,s^{-1}$ |
| $k_6$ | $1 \times 10^{-5}$–$7 \times 10^{-1}\ M^{-1}\,s^{-1}$ |
| $k_{6'}$ | $0$–$2 \times 10^7\ M^{-2}\,s^{-1}$ |
| $k_7$ | $7\ M^{-1}\,s^{-1}$ |
| $k_{7'}$ | $1.48 \times 10^7\ M^{-2}\,s^{-1}$ |
| $k_8$ | $0.2\ M^{-1}\,s^{-1}$ |
| $k_9$ | $3 \times 10^3\ s^{-1}$ |
| $k_{-9}$ | $5 \times 10^{10}\ M^{-1}\,s^{-1}$ |

[a]For adjustable parameters, range of rate constant values explored in the simulations is shown.



Fig. 4. Bistability (hysteresis between high pH and low pH stationary states) calculated with extended model (A1)–(A9). $[H_2O_2] = 0.1$ M, $[S_2O_3^{2-}] = 0.01$ M, $[H_2SO_4] = 0.001$ M, $[Cu(II)] = 1 \times 10^{-5}$ M.



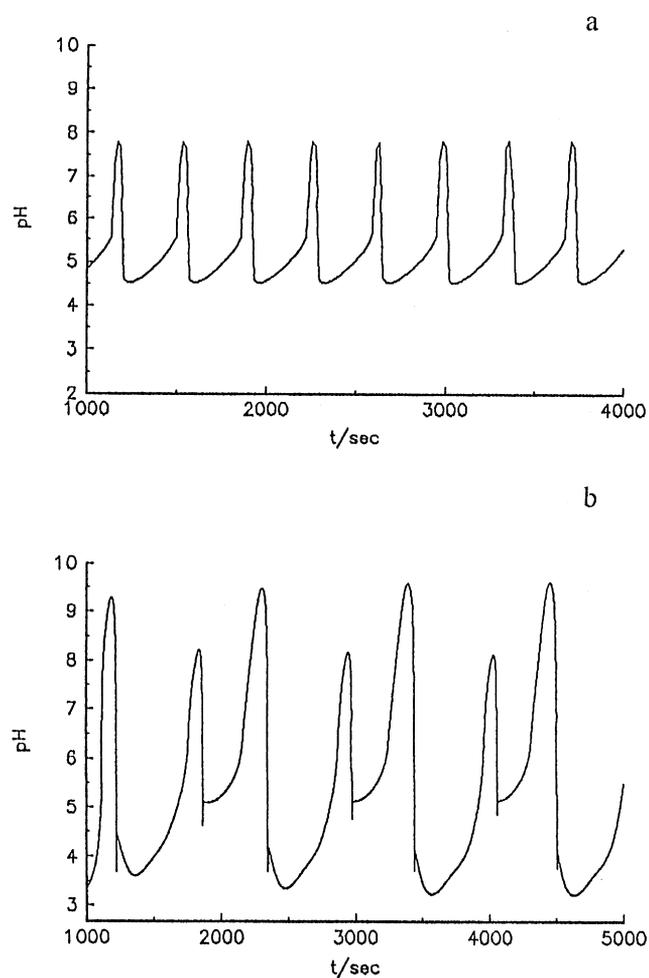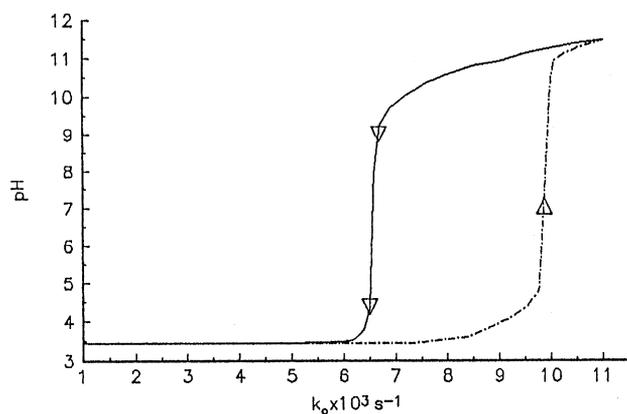Fig. 3. Simulated simple and complex pH oscillations with extended model (A1)–(A5). Input concentrations as in Fig. 2. $k_0 = 4.5 \times 10^{-3}\ s^{-1}$ (a), $k_0 = 1.5 \times 10^{-3}\ s^{-1}$(b).
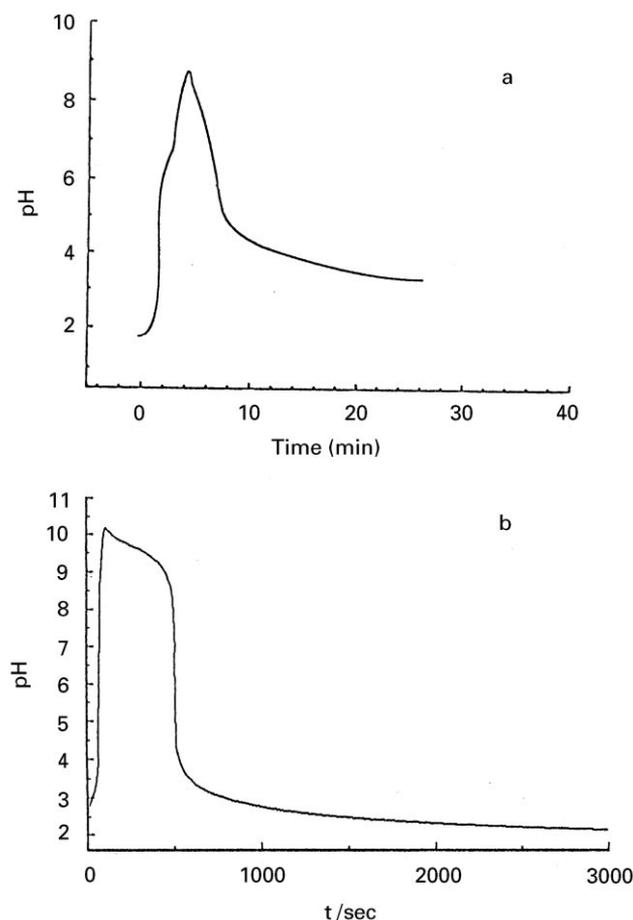


Fig. 5. Experimental (a) and simulated (b) batch behavior ($k_0 = 0$) using extended model (A1)–(A9). Input concentrations as in Fig. (1)a.

$$H_2O_2 \leftrightarrow H^+ + HO_2^-, \qquad (A5)$$

$$v_5 = k_5[H_2O_2],$$

$$v_{-5} = k_{-5}[H^+][HO_2^-],$$

$$H_2O_2 + S_4O_6^{2-} \rightarrow 2HOS_2O_3^-, \qquad (A6)$$
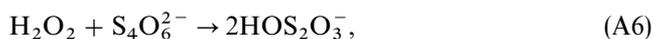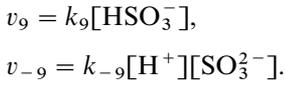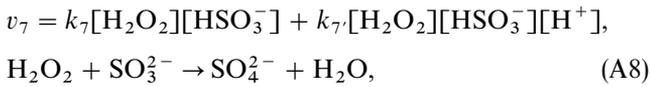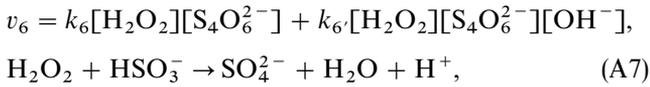
$$v_6 = k_6[H_2O_2][S_4O_6^{2-}] + k_{6'}[H_2O_2][S_4O_6^{2-}][OH^-],$$

$$H_2O_2 + HSO_3^- \rightarrow SO_4^{2-} + H_2O + H^+, \tag{A7}$$

$$v_7 = k_7[H_2O_2][HSO_3^-] + k_{7'}[H_2O_2][HSO_3^-][H^+],$$

$$H_2O_2 + SO_3^{2-} \rightarrow SO_4^{2-} + H_2O, \tag{A8}$$

$$v_8 = k_8[H_2O_2][SO_3^{2-}],$$

$$HSO_3^- \leftrightarrow SO_3^{2-} + H^+, \tag{A9}$$

$$v_9 = k_9[HSO_3^-],$$

$$v_{-9} = k_{-9}[H^+][SO_3^{2-}].$$

### 2.2. System (B): Peroxydisulfate–thiosulfate–copper (II)
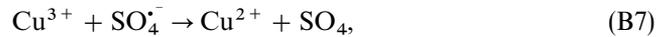
When $S_2O_8^{2-}$, $S_2O_3^{2-}$ and Cu(II) are mixed in a CSTR, oscillations can be observed in the redox potential, the pH and the concentration of dissolved oxygen (Orbán & Epstein, 1989). Examples of this behavior are shown in Fig. 6. The stoichiometry of the reaction, whether or not the copper catalyst is present, is

$$S_2O_8^{2-} + 2S_2O_3^{2-} \rightarrow 2SO_4^{2-} + S_4O_6^{2-} \tag{3}$$
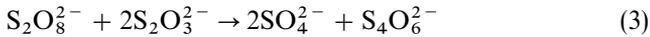
Sorum and Edwards proposed a free radical mechanism for reaction (3) involving $S_2O_3^{\bullet-}$, $SO_4^{\bullet-}$ and $OH^{\bullet}$ radicals (Sorum & Edwards, 1952). In the presence of Cu(II), the rate law for Eq. (3) is of the form (Patat & Prölls, 1967):
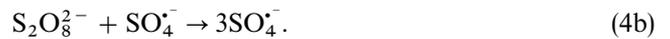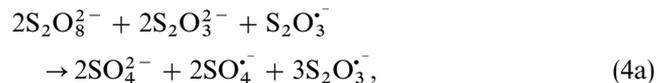
$$v = k[S_2O_8^{2-}][Cu(II)].$$

Based on an analysis of the literature on peroxydisulfate oxidations, we propose the following model for the catalyzed system:

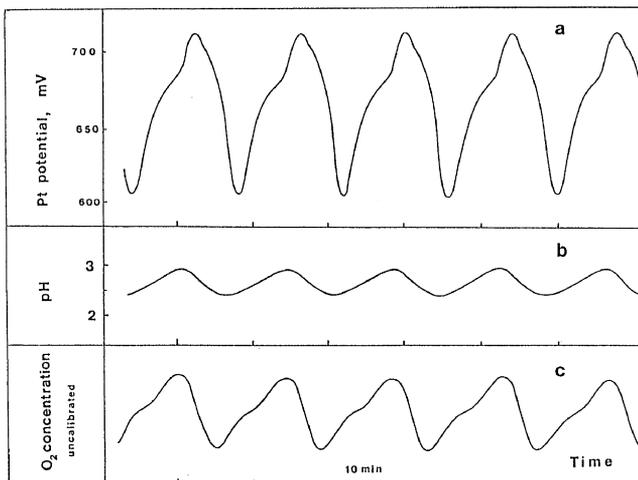$$Cu^{2+} + S_2O_3^{2-} \rightarrow Cu^+ + S_2O_3^{\bullet-}, \tag{B1}$$

Fig. 6. Experimental oscillations in redox potential (a), in pH (b) and in dissolved oxygen concentration (c) in the peroxydisulfate–thiosulfate–copper(II) system in a CSTR. $[S_2O_8^{2-}] = 0.025$ M, $[S_2O_3^{2-}] = 0.005$ M, $[Cu(II)] = 2.5 \times 10^{-5}$ M, $k_0 = 3.5 \times 10^{-3}$ s$^{-1}$.

$$S_2O_3^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet-} + S_2O_3, \tag{B2}$$

$$S_2O_3 + S_2O_3^{2-} \rightarrow 2S_2O_3^{\bullet-}, \tag{B3}$$

$$2S_2O_3^{\bullet-} \rightarrow S_4O_6^{2-}, \tag{B4}$$

$$Cu^+ + S_2O_8^{2-} \rightarrow Cu^{2+} + SO_4^{2-} + SO_4^{\bullet-}, \tag{B5}$$

$$Cu^{2+} + S_2O_8^{2-} \rightarrow Cu^{3+} + SO_4^{2-} + SO_4^{\bullet-}, \tag{B6}$$

$$Cu^{3+} + SO_4^{\bullet-} \rightarrow Cu^{2+} + SO_4, \tag{B7}$$

$$SO_4 + SO_4^{2-} \rightarrow 2SO_4^{\bullet-}, \tag{B8}$$

$$2SO_4^{\bullet-} \leftrightarrow S_2O_8^{2-}. \tag{B9}$$

The catalytic cycle in this mechanism may be represented schematically as
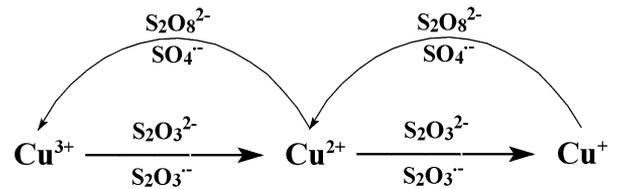
Reactions (B1)–(B9) constitute our simple model for this system. Two autocatalytic loops — composite reaction (4a), composed of steps (B1) + (B2) + (B3) + (B5), and composite reaction (4b), consisting of steps (B6) + (B7) + (B8) — can be written for the radicals $S_2O_3^{\bullet-}$ and $SO_4^{\bullet-}$:

$$2S_2O_8^{2-} + 2S_2O_3^{2-} + S_2O_3^{\bullet-}$$
$$\rightarrow 2SO_4^{2-} + 2SO_4^{\bullet-} + 3S_2O_3^{\bullet-}, \tag{4a}$$

$$S_2O_8^{2-} + SO_4^{\bullet-} \rightarrow 3SO_4^{\bullet-}. \tag{4b}$$

In reaction (4a) the $Cu^{2+}/Cu^+$ couple, in reaction (4b) the $Cu^{3+}/Cu^{2+}$ couple, promotes the positive feedback. The role of the negative feedback is played by the chain termination steps (B4) and (B9). This simple model is able to simulate the oscillations in redox potential (see Fig. 7), but owing to the many rate constants that we have had to estimate the agreement between the experiments and the calculations is far from satisfactory. The rate laws and rate constants used in our simulations are summarized in Table 2.

The simple model (B1)–(B9) does not explain the experimentally found periodic $O_2$ evolution and the oscillatory variation of the pH. We propose extending this core mechanism with the additional steps (B10)–(B15), which should make it possible to simulate all the observed oscillations. This extended model should serve as a solid starting point for detailed simulations to be undertaken in the near future:

$$SO_4^{\bullet-} + H_2O \rightarrow HSO_4^- + OH^{\bullet}, \tag{B10}$$

$$S_2O_3^{2-} + OH^{\bullet} \rightarrow S_2O_3^{\bullet-} + OH^-, \tag{B11}$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}, \tag{B12}$$

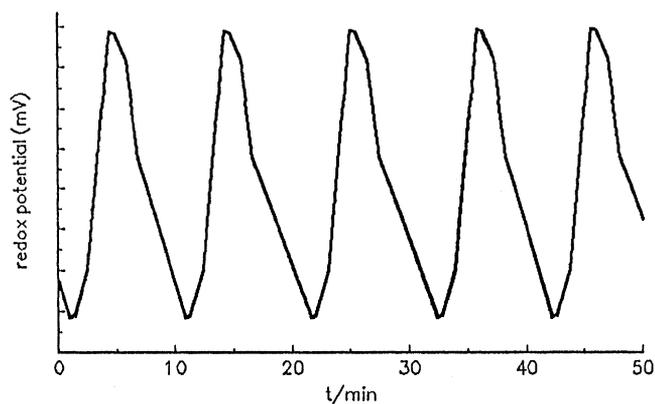$$S_2O_3^{\bullet-} + O_2 + H^+ \rightarrow S_2O_3 + HO_2^{\bullet}, \tag{B13}$$

Fig. 7. Simulated oscillations in redox potential in the peroxydisulfate–thiosulfate–copper(II) system using the mechanism (B1)–(B9). Input concentrations and flow rate as in Fig. 6.

Table 2
Rate laws and rate constants for the mechanism (B1)–(B9)

| Step | Rate law | Rate constant |
|------|----------|---------------|
| B1 | $k_1[S_2O_3^{2-}][Cu^{2+}]$ | $1 \times 10^5$ M$^{-1}$s$^{-1}$ |
| B2 | $k_2[S_2O_3^{-}][S_2O_8^{2-}]$ | $1 \times 10^3$ M$^{-1}$ s$^{-1}$ |
| B3 | $k_3[S_2O_3][S_2O_3^{2-}]$ | $1 \times 10^6$ M$^{-1}$ s$^{-1}$ |
| B4 | $k_4[S_2O_3^{-}]^2$ | $3.6 \times 10^9$ M$^{-1}$s$^{-1}$ |
| B5 | $k_5[S_2O_8^{2-}][Cu^+]$ | $6.4 \times 10^3$ M$^{-1}$ s$^{-1}$ |
| B6 | $k_6[S_2O_8^{2-}][Cu^{2+}]$ | $6.4 \times 10^3$ M$^{-1}$ s$^{-1}$ |
| B7 | $k_7[SO_4^{-}][Cu^{3+}]$ | $1 \times 10^8$ M$^{-1}$ s$^{-1}$ |
| B8 | $k_8[SO_4^{-}][SO_2^{-}]$ | $1 \times 10^8$ M$^{-1}$ s$^{-1}$ |
| B9 | $k_9[SO_4^{-}]^2 - k_{-9}[S_2O_8^{2-}]$ | $3.6 \times 10^9$ M$^{-1}$ s$^{-1}$, 40 s$^{-1}$ |

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2, \tag{B14}$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O. \tag{B15}$$

### 2.3. System (C): Hydrogen peroxide–thiocyanate–copper (II)

In an alkaline solution (pH > 10), the $H_2O_2$–SCN$^-$–Cu(II) reaction (Orbán, 1986) exhibits three different types of bistability in a CSTR, involving two stationary states and one oscillatory state. The color (yellow ⇔ colorless), the redox potential and the rate of $O_2$ evolution can oscillate in either flow or batch configuration. Travelling wave pattern can develop in a thin solution layer. Typical experimental oscillators behavior is shown in Fig. 8.

The following stoichiometry for the oxidation of SCN$^-$ by $H_2O_2$ at 4 < pH < 12 was established (Wilson & Harris, 1960):

$$4H_2O_2 + SCN^- \rightarrow HSO_4^- + NH_4^+ + HCO_3^- + H_2O. \tag{5}$$
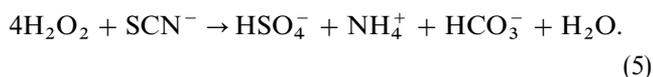
We find a moderate acceleration of the reaction but no evidence of strong autocatalysis in the presence of the Cu(II) catalyst.



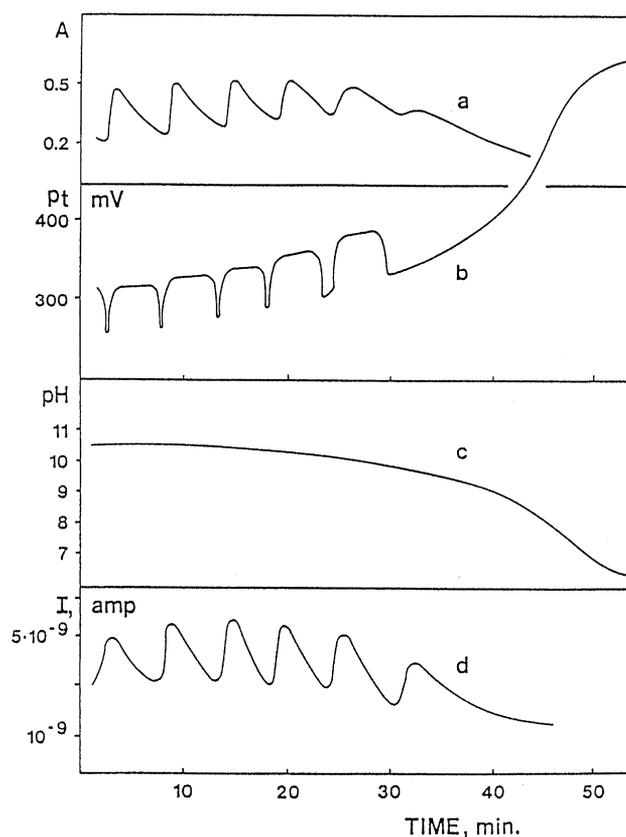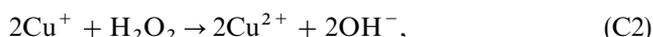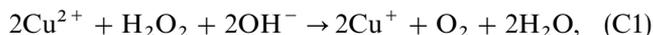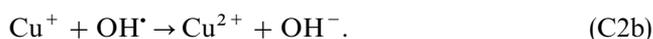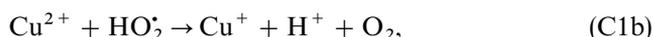Fig. 8. Experimental oscillations in the absorbance at 375 nm (a), in redox potential (b) and ionic current in a mass spectrometer tuned to mass number 32 (d) in the batch reaction of hydrogen peroxide, thiosulfate and copper(II). The change in pH (c) is not oscillatory. $[H_2O_2] = 0.25$ M, $[KSCN] = 0.0375$ M, $[Cu(II)] = 7.5 \times 10^{-5}$ M, $[NaOH] = 0.025$ M.
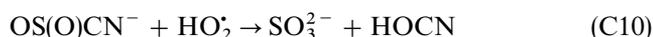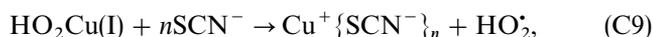
To a first approximation, the oscillations arise primarily from the chemistry responsible for the Cu(II)-catalyzed autocatalytic decomposition of hydrogen peroxide. The role of SCN$^-$ is to transiently stabilize Cu$^+$ as a complex, resulting in a time delay in its reoxidation to Cu$^{2+}$. In its simplest form, the oscillatory cycle can be written as reactions (C1) and (C2), which sum to reaction (C3):

$$2Cu^{2+} + H_2O_2 + 2OH^- \rightarrow 2Cu^+ + O_2 + 2H_2O, \tag{C1}$$

$$2Cu^+ + H_2O_2 \rightarrow 2Cu^{2+} + 2OH^-, \tag{C2}$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O. \tag{C3}$$

Each of the composite reactions (C1) and (C2) can be further broken down to elementary steps:

$$Cu^{2+} + HOO^- \rightarrow Cu^+ + HO_2^{\bullet}, \tag{C1a}$$

$$Cu^{2+} + HO_2^{\bullet} \rightarrow Cu^+ + H^+ + O_2, \tag{C1b}$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- + OH^{\bullet}, \tag{C2a}$$

$$Cu^+ + OH^{\bullet} \rightarrow Cu^{2+} + OH^-. \tag{C2b}$$

Luo, Orbán, Kustin and Epstein (1989) have proposed a more detailed mechanism consisting of 30 reactions and 26 variables, which simulates very well the experimentally observed behavior in both batch and flow configurations. We do not reproduce the full model here, but instead summarize its essential features by reference to the key steps (C4)–(C10):

$$2H_2O_2 + SCN^- \rightarrow OS(O)CN^- + 2H_2O, \tag{C4}$$

$$2OS(O)CN^- \rightarrow OOS(O)CN^- + OSCN^-, \tag{C5}$$

$$H_2O + OS(O)CN^- + OOS(O)CN^-$$
$$\rightarrow 2OS(O)CN^{\bullet} + 2OH^-, \tag{C6}$$

$$OS(O)CN^{\bullet} + Cu^+\{SCN^-\}_n$$
$$\rightarrow OS(O)CN^- + Cu^{2+} + nSCN^-, \tag{C7}$$

$$H_2O_2 + Cu^{2+} + OH^- \rightarrow HO_2Cu(I) + H_2O, \tag{C8}$$

$$HO_2Cu(I) + nSCN^- \rightarrow Cu^+\{SCN^-\}_n + HO_2^{\bullet}, \tag{C9}$$

$$OS(O)CN^- + HO_2^{\bullet} \rightarrow SO_3^{2-} + HOCN \tag{C10}$$
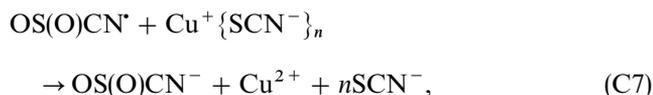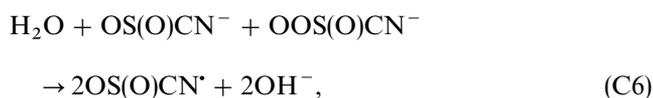
In this model the formation (C8) and consumption (C9) of the yellow intermediate $HO_2Cu(I)$ is responsible for the color oscillations. The positive feedback species is the intermediate $OS(O)CN^-$, which is generated autocatalytically through formation and reduction of the $OS(O)CN^{\bullet}$ radical in the sequence of steps (C4)–(C7). The negative feedback starts with the accumulation of $HO_2^{\bullet}$ via steps (C8) and (C9), which consumes the autocatalytic species in reaction (C10). The complex $Cu^+\{SCN^-\}_n$ reinitiates the positive feedback, and the intermediates $SO_3^{2-}$ and HOCN end up as products $SO_4^{2-}$, $HCO_3^-$ and $NH_4^+$. The calculated oscillations are shown in Fig. 9.

## 3. Discussion

In the oxidation of sulfur compounds by various peroxides, copper(II) ions can induce oscillations, probably because they are able to participate in both oxidation and reduction processes, thanks to the fact that the $Cu^{3+}/Cu^{2+}$ and $Cu^{2+}/Cu^+$ couples have redox potentials spanning the range from 0.1 to 1.8 V depending on the counter ions or ligands present. What seems to be common in the oscillatory mechanism of systems (A), (B) and (C) is that the actual oxidant species are Cu(II) and/or Cu(III) ions in each case. The Cu(I) ions formed strongly interact with the substrate sulfur compounds, therefore their reoxidation to higher oxidation states by peroxides occurs through more enhanced but time separated processes. Catalysis by copper ions on both oxidation and reduction steps together with time delay
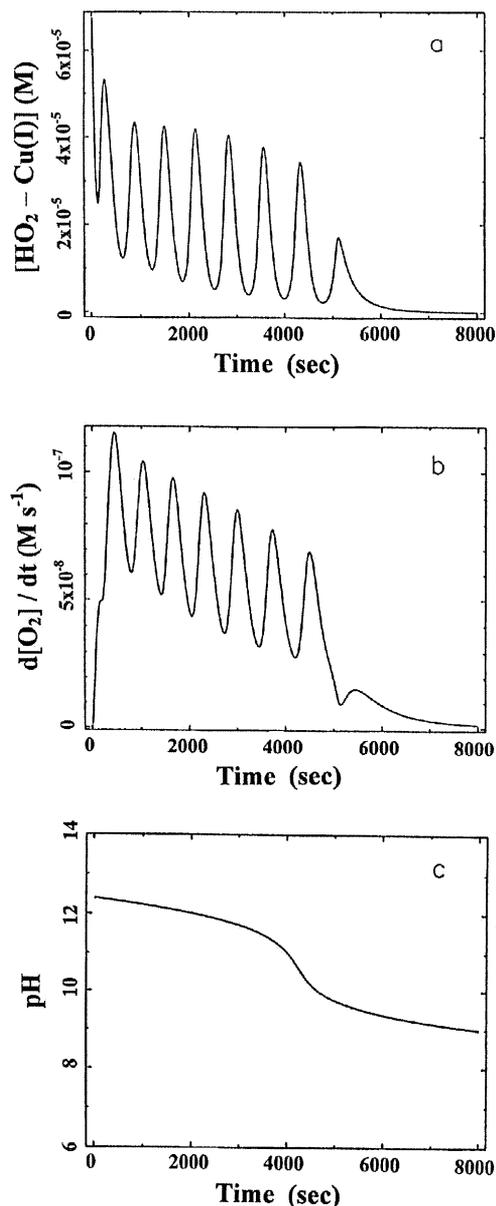


Fig. 9. The calculated batch oscillations in yellow $[HO_2$–Cu(I)] species (a), and in rate of oxygen evolution (b). The pH curve (c) is monotonic. Initial concentrations as in Fig. 7 but [KSCN] = 0.025 M.

constitute the major factor in bringing about exotic behavior in the copper(II)-catalyzed oxidation reactions of sulfur compounds.

The contribution of the oxidation mechanism of the sulfur species to the oscillatory behavior is significantly greater in the sulfur–peroxide systems than in the analogous sulfur–bromate/chlorite/permanganate oscillators, which do not require a copper(II) catalyst. Each system discussed here represents a completely different oscillatory mechanism; system (A) is a pH-driven oscillator, in system (B) a radical chain mechanism gives rise to oscillations, in system (C) the catalytic decomposistion of the oxidant with the assistance of thiocyanate results in

oscillatory behavior. Because of the key involvement of the detailed sulfur chemistry, development of a substrate-independent general model similar to those proposed for bromate, chlorite, manganese or pH oscillatory systems is not likely to be possible for the sulfur–peroxide oscillators.

## Acknowledgements

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