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Large Amplitude pH Oscillations in the Hydrogen Peroxide–Dithionite Reaction in a Flow Reactor

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The kinetics of the reaction between $\text{S}_2\text{O}_4^{2-}$ and H_2O_2 is found to be very complex both in a closed reactor and in a continuous-flow stirred tank reactor (CSTR) in an unbuffered aqueous solution. The main products of the oxidation are SO_4^{2-} and $\text{S}_2\text{O}_6^{2-}$ in excess H_2O_2 . The reaction is accompanied by acidification of the initially alkaline mixture. The measured pH–time traces show multiple inflection points in a closed reactor, suggesting that the reaction takes place in several distinct steps. Transient formation of $\text{SO}_3^{2-}/\text{HSO}_3^-$ buffer system is observed in the early stage of the reaction. Next, the sulfite ions are oxidized further to sulfate ions in an autocatalytic reaction. Simultaneously a small amount of dithionate ions is also formed. The pH exhibits very large amplitude relaxation oscillations in a CSTR in a narrow range of input concentrations, flow rate, and temperature. A simple empirical rate law model consisting of three redox reactions and three protonation equilibria is proposed. Numerical simulations based on this model agree well with the experimental results. The key to the pH-regulated oscillation is the H^+ -autocatalysis that results from the more rapid oxidation of the protonated than of the unprotonated sulfite intermediate.

Introduction

Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) is a powerful reducing agent. The average oxidation number of its sulfur atoms is +3, which is very easily oxidized. Understanding the stoichiometry, kinetics, and mechanism of its redox reactions is of importance because this compound is widely used in dyeing and bleaching processes. But its redox reactions are very difficult to study for at least two reasons: (i) $\text{S}_2\text{O}_4^{2-}$ is very sensitive to air oxygen, (ii) it undergoes rather rapid disproportionation in aqueous solution to form more stable sulfur compounds in different oxidation states ranging from HS^- to SO_4^{2-} . The main products of the decomposition are hydrogen sulfite ions and thiosulfate ions, which are formed according to the generally accepted eq 1:



Colloidal sulfur has also been identified as a product or intermediate that forms in small amounts. The rate of reaction 1 is greatly affected by the pH, being slow in alkaline medium and very rapid at low pH values. Furthermore, the hypothesis of an autocatalytic kinetics was put forward by Meyer¹ who found an S-shaped curve: An early induction period is followed by a rapid autocatalytic stage to completion. This observation was confirmed by others.^{2–7} Moreover, with an excess of sulfite ion, so as to minimize the effect of decomposition products, neither the induction period nor the fast reaction are detectable.

It has been reported that during the decomposition, at elevated temperatures, the concentration of dithionite ions and the pH show several small peaks in time, even in a system closed with respect to mass.⁸ Based on this report, the decomposition of

dithionite ion is thought to be an old example of the oscillatory chemical reactions. This view found its way into many review articles and books devoted to the oscillatory reactions. However, we point out that other laboratories have never confirmed these oscillations.^{6,7} Our own efforts repeatedly failed to reproduce pH oscillations of any kind in a closed reactor when we studied the disproportionation of $\text{S}_2\text{O}_4^{2-}$ in a concentration range 0.001–0.05 M and in a temperature interval 25–70 °C excluding the air oxygen. Only a minimum, followed by a single maximum, appeared on the experimental pH–time curves. We believe that the thermal decomposition of aqueous dithionite is not an oscillatory reaction, at least in a closed reactor.

On the other hand, oxidation of a compound-containing sulfur atom in a low oxidation state usually shows oscillations if it is run in a continuous-flow stirred tank reactor (CSTR).⁹ For example, hydrogen peroxide oxidation of a mixture of hydrogen sulfite and thiosulfate exhibits chaotic and periodic pH oscillations if a continuous inflow of the reactants and an outflow of the reaction mixture are maintained in a CSTR.¹⁰ Since the decomposition of dithionite ions is supposed to lead to the formation of both sulfite and thiosulfate ions,⁷ a logical expectation is that an oscillatory reaction may take place in a mixture of hydrogen peroxide and sodium dithionite. Namely, one may expect that the decomposition of $\text{S}_2\text{O}_4^{2-}$ in aqueous solution continuously supplies $\text{S}_2\text{O}_3^{2-}$ and SO_3^{2-} at a more-or-less constant rate according to eq 1. These intermediates are expected to be used up by H_2O_2 periodically in an autocatalytic oxidation process. In such a way, periodic concentration changes would be expected to develop in the reaction system. To test this hypothesis we carried out experiments both in a closed reactor and in a CSTR. These experiments have revealed that the oxidation of dithionite ions by hydrogen peroxide in aqueous solution is, indeed, oscillatory in a CSTR under a certain range of experimental conditions.

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We think that discovery of a new pH oscillatory system is still of importance, because of the possible application of the pH oscillations in periodic control of pH-sensitive processes. For example, pH oscillators might be of importance in the temporally controlled periodic drug-delivery systems.^{11–13} Furthermore, understanding the mechanism of the oscillations in this particular reaction would provide valuable information for the mechanism of the oxidation of dithionite ions in general.

Here we report on the experimental study and simulation calculations of the large amplitude pH oscillations exhibited by the oxidation of dithionite ion with hydrogen peroxide in a CSTR.

Experimental Section

Materials. Reagent grade NaOH, H₂O₂ solution, and crystalline Na₂S₂O₄ of 85% purity (Fluka) were used without further purification. The contamination of sodium dithionite is mostly Na₂SO₄, which did not disturb our experiments. Some Na₂SO₃ is also found in the commercial sodium dithionite. Since SO₃^{2–} (or HSO₃[–]) appears to be an intermediate in the oxidation process, the sulfite-content might affect the kinetics. We studied the effect of a small amount of added Na₂SO₃ on the system's behavior. Apart from some small increases in the period length of oscillations, there was no noticeable effect of the added Na₂SO₃ on the observed kinetics. Doubly-distilled water used in preparing solutions was first purged with N₂ for elimination of O₂ and CO₂ impurities. Two input solutions were prepared daily: one contained H₂O₂, which was standardized with permanganate, and the other contained Na₂S₂O₄ and NaOH. NaOH prevented S₂O₄^{2–} from fast autocatalytic decomposition in the aqueous stock solution. Throughout the experiments in CSTR, the solution of S₂O₄^{2–} in its reservoir was bubbled with nitrogen gas to avoid autoxidation. In such a way we were able to stabilize the stock solution of sodium dithionite for at least 12 h. During storage for a longer time, the pH of the stock solution decreased, and colloidal sulfur precipitated in an autocatalytic decomposition process.

Reactor. The continuous flow experiments were carried out in a water-jacketed cylindrical-shaped glass reactor with a liquid volume of 19.5 mL. The reactor was closed with a silicon cap. A combination glass electrode, a thermometer, two input tubes, and three output tubes were led through the cap. The batch experiments were performed in a similar thermostated glass vessel but with a liquid volume of 50 mL.

Procedures. Reactant solutions were pumped into the reactor through the inlet tubes by means of a peristaltic pump (DESAGA). The excess reaction mixture was removed with the same pump through three outlet tubes. A magnetic stirrer was used to ensure uniform mixing. The maximum pumping rate was used to fill the reactor, and then the rate was gradually lowered to the desired value. The reactions in the batch system were initiated by the addition of the H₂O₂ solution. Constant temperature during the experiments was established. The pH and the temperature inside the reactor were continuously measured and the pH–time data were collected by a computer.

Results

Batch Experiments. Formation of colloidal sulfur was not observed in the reaction mixture when H₂O₂ was applied in high excess. This observation is significant because elementary sulfur usually appears as one of the products of the decomposition and oxidation of dithionite ions in aqueous solution. Based on the measured pH-change and the mole consumption ratio $[\Delta\text{H}_2\text{O}_2]/[\Delta\text{S}_2\text{O}_4^{2-}]$, a mixture of the sulfate ions and dithionate

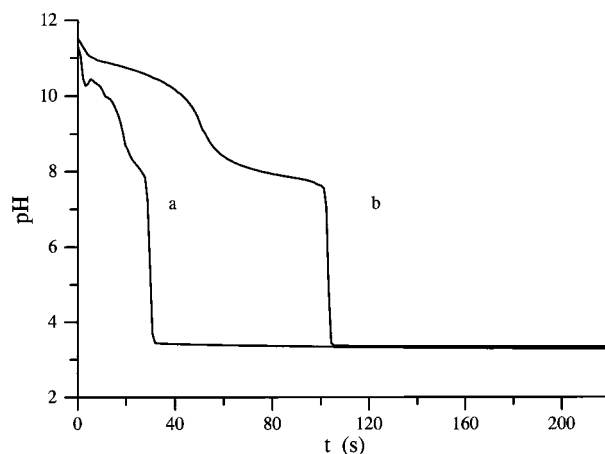
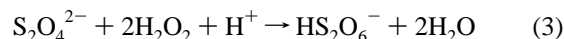
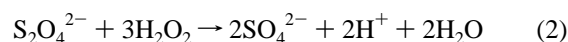


Figure 1. Measured pH–time traces in a closed reactor. $[\text{Na}_2\text{S}_2\text{O}_4]_0 = 0.00375$; $[\text{H}_2\text{O}_2]_0 = 0.020$ (a), 0.0105 (b) M; The initial pH = 11.5 was adjusted by adding NaOH to the dithionite solution before the addition of H₂O₂. $T = 21.0^\circ\text{C}$.

ions are assumed to form in the oxidation according to eqs 2 and 3, respectively. Contribution of reaction 2 to the overall stoichiometry is always high, but reaction 3 cannot be neglected under the conditions of our experiments.



Equation 2 predicts that the reaction is accompanied by a significant decrease in the pH in an unbuffered reaction mixture. On the contrary, reaction 3 consumes H⁺ as the protonation of dithionate ions takes place in acidic medium. In our experiments, the initial pH of the S₂O₄^{2–} solution was adjusted at pH 11–12 with NaOH. Most of the kinetic runs were carried out without a buffer. After starting the reaction by adding excess amount of neutral H₂O₂ solution to the alkaline S₂O₄^{2–} solution, we measured a significant decrease in the pH of the reaction mixture as a function of time, as expected. Shown in Figure 1 are typical pH–time curves. The pH traces exhibit multiple inflection points, strongly suggesting that the reaction takes place in several distinct steps. An induction period and an increasing slope can be observed during the early phase of the reaction. Then a plateau appears between pH 7 and 8 indicating a transient buildup of SO₃^{2–}/HSO₃[–] buffer system in the first stage of the reaction. This buffer keeps the pH at approximately 7, temporarily ($pK = 7$). Then, a final very rapid pH drop occurs, which is due to the autocatalytic H⁺ producing oxidation of HSO₃[–] to SO₄^{2–}. All portions of the pH traces slow with decreasing initial $[\text{H}_2\text{O}_2]_0$.

If the ratio $[\text{H}_2\text{O}_2]_0/[\text{S}_2\text{O}_4^{2-}]_0$ is chosen to be below 2.5, the final pH drop does not occur at all on the pH–time curve, and some white sulfur precipitate appears in the reaction mixture. H₂S evolution is also observed when the excess of H₂O₂ is not high enough. Formation of S and H₂S clearly indicates that the disproportionation of S₂O₄^{2–} takes place in the reaction mixture when the excess of H₂O₂ is not high enough to oxidize all the intermediates. The reproducibility of the kinetics experiments is about 10% because the side reactions such as disproportionation and oxidation by air oxygen are difficult to avoid. We found no pH oscillations in a closed reactor.

CSTR Experiments. We performed a series of experiments in a CSTR, in which both the H₂O₂ and S₂O₄^{2–} concentrations and other experimental constraint parameters were varied. In

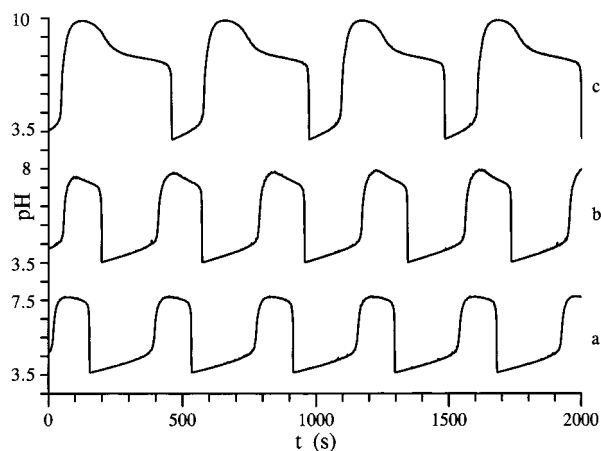


Figure 2. Measured pH oscillations in a CSTR at different flow rates (k_0). $[\text{Na}_2\text{S}_2\text{O}_4]_0 = 0.00375$; $[\text{H}_2\text{O}_2]_0 = 0.0115$ M; $T = 19.1$ °C; $k_0 = 2.0 \times 10^{-3}$ (a), 2.7×10^{-3} (b), 3.1×10^{-3} s $^{-1}$ (c). The pH of the input $\text{Na}_2\text{S}_2\text{O}_4$ solution was 11.5.

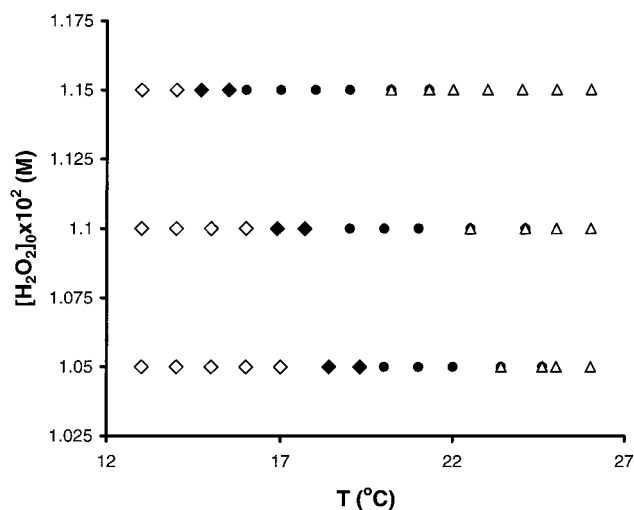


Figure 3. State diagram in the temperature– $[\text{H}_2\text{O}_2]_0$ plane. Fixed parameters: $[\text{S}_2\text{O}_4^{2-}]_0 = 0.00375$ M; pH of $\text{Na}_2\text{S}_2\text{O}_4$ was 11.5; $k_0 = 2.7 \times 10^{-3}$ s $^{-1}$; ◇ low pH steady state, △ high pH steady state, ● oscillatory state. Two symbols one on the other indicate bistability.

this way, the conditions for stable pH oscillations were systematically searched for with success. We found that hydrogen peroxide concentration should be applied in excess over dithionite concentration for the oscillations to be sustained. NaOH should be added to the input solution of $\text{S}_2\text{O}_4^{2-}$ in order to avoid spontaneous decomposition in the reservoir. On the other hand, NaOH is also needed to adjust the initial pH. The ratio $[\text{NaOH}]_0/[\text{S}_2\text{O}_4^{2-}]_0$ should be kept between 1.6 and 1.9 for the oscillations to occur in the CSTR.

Typical oscillatory time series obtained with different flow rates at fixed temperature are presented in Figure 2. We emphasize that the most striking feature of these oscillations is that the amplitude is extremely high, exceeding 6 pH units between pH 3.5 and 10 in certain cases. Such a high amplitude seems to be the largest one on record in the pH oscillator family reported so far. High amplitude pH oscillations are expected to be important for the possible control of pH-sensitive processes. The oscillatory waveform indicates that durations of both the high pH stage and the low pH stage within an oscillatory period are rather long, while transitions between the stages are rapid, which are characteristic for the relaxation oscillations. Fast transitions between the two stages are also advantageous for the periodic control of pH-sensitive processes.

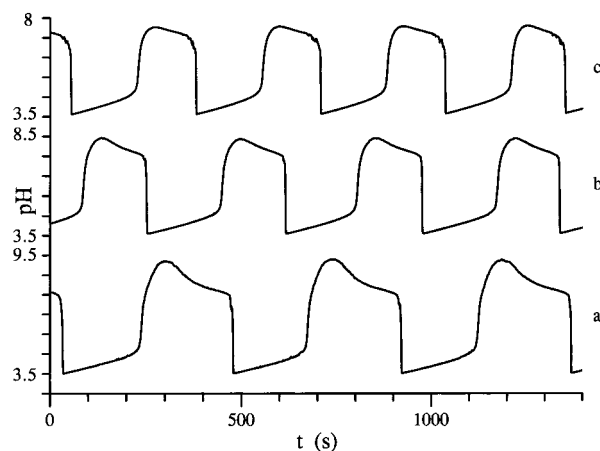


Figure 4. pH–time series measured in a CSTR at different temperatures. $[\text{Na}_2\text{S}_2\text{O}_4]_0 = 0.00375$; $[\text{H}_2\text{O}_2]_0 = 0.011$ M; $k_0 = 2.7 \times 10^{-3}$ s $^{-1}$; pH of the input solution of $\text{Na}_2\text{S}_2\text{O}_4$ was 11.5; $T = 20.4$ (a), 22.4 (b), 25.9 °C (c).

The effect of temperature on the parameters of chemical oscillations is of interest because of the theoretical possibility of a temperature-independent period length.¹⁵ A phase diagram is shown in Figure 3 in the temperature– $[\text{H}_2\text{O}_2]_0$ -plane observed in a CSTR. The flow system exhibits two stationary steady states, one with low pH (SSL) and the other with high pH (SSH). At low temperatures SSL is stable, while high pH steady state develops at high temperatures. Between the two stationary steady states an oscillatory state exists. Bistability between the oscillatory and steady states can be observed. Oscillations occur in a very narrow range of the temperature, hardly exceeding 5 degrees.

We examined the effect of temperature on the amplitude and on the period length of the oscillations. Shown in Figure 4 are pH–time series obtained at different temperatures when the flow rate was fixed. The amplitude increases with decreasing temperature. The length of the high pH stage of an oscillatory period increases, while the length of the low pH stage decreases with decreasing temperature. Although such an opposing effect of the temperature is a necessary precondition of the temperature-independent period length, such behavior could not be observed in the present reaction. On the contrary, we found that the overall period length increased with decreasing temperature.

Modeling. We attempted to use an empirical rate law approach to describe the dynamics of the H_2O_2 – $\text{S}_2\text{O}_4^{2-}$ reaction using overall stoichiometric processes rather than elementary steps. We propose a simple model derived from the stoichiometric eqs 2 and 3. The model contains three redox reactions (M1–M3) and three protonation equilibria (M4–M6). The composite reactions, their rate laws, and rate constant values are shown in Table 1. Formation of sulfate (eq 2) is assumed to take place in two stages (M1 and M2). Reaction M1 leads to the transient accumulation of sulfite/hydrogen sulfite ions in slightly alkaline medium. v_1 is a hypothetical rate law for M1 with an estimated rate constant value. Further oxidation of hydrogen sulfite ions in reaction M2 is known to be autocatalytic in H^+ . Reaction M2 is a composite reaction of several other known pH oscillators. v_2 is an empirical rate law, which was used in describing the kinetics of the H_2O_2 – HSO_3^- reaction¹⁴ and other pH oscillators.¹⁶ The other channel for the oxidation of dithionite is reaction M3 that leads to the formation of dithionate. Reaction M3 is a H^+ consuming composite reaction with an estimated rate law v_3 . Three known protonation equilibria are also taken into account (M4–M6). The ratios of

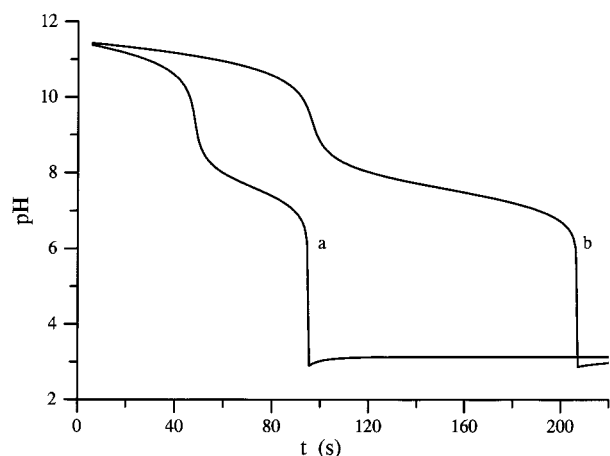


Figure 5. Simulated traces in a closed reactor. Conditions are the same as in Figure 1.

TABLE 1: Composite Reactions, Rate Laws, and Rate Constants of the H_2O_2 – $\text{S}_2\text{O}_4^{2-}$ Reaction

reactions		
$\text{H}_2\text{O}_2 + \text{S}_2\text{O}_4^{2-} \rightarrow 2\text{HSO}_3^-$		(M1)
$\text{H}_2\text{O}_2 + \text{HSO}_3^- \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{H}_2\text{O}$		(M2)
$2\text{H}_2\text{O}_2 + \text{S}_2\text{O}_4^{2-} + \text{H}^+ \rightarrow \text{HS}_2\text{O}_6^- + 2\text{H}_2\text{O}$		(M3)
$\text{H}^+ + \text{SO}_3^{2-} \rightleftharpoons \text{HSO}_3^-$		(M4)
$\text{H}^+ + \text{S}_2\text{O}_6^{2-} \rightleftharpoons \text{HS}_2\text{O}_6^-$		(M5)
$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$		(M6)
rate law		rate constants (at 25 °C)
$v_1 = k_1[\text{S}_2\text{O}_4^{2-}][\text{H}_2\text{O}_2]$		$k_1 = 0.60 \text{ M}^{-1} \text{ s}^{-1}$
$v_2 = (k_2 + k_2'[\text{H}^+])[\text{H}_2\text{O}_2][\text{HSO}_3^-]$		$k_2 = 4.0 \text{ M}^{-1} \text{ s}^{-1}$ $k_2' = 1.0 \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$
$v_3 = (k_3 + k_3'[\text{H}^+])[\text{H}_2\text{O}_2][\text{S}_2\text{O}_4^{2-}]$		$k_3 = 0.050 \text{ M}^{-1} \text{ s}^{-1}$ $k_3' = 1.24 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$
$v_4 = k_4[\text{SO}_3^{2-}][\text{H}^+]$		$k_4 = 5.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
$v_{-4} = k_{-4}[\text{HSO}_3^-]$		$k_{-4} = 3.0 \times 10^3 \text{ s}^{-1}$
$v_5 = k_5[\text{S}_2\text{O}_6^{2-}][\text{H}^+]$		$k_5 = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
$v_{-5} = k_{-5}[\text{HS}_2\text{O}_6^-]$		$k_{-5} = 3.98 \times 10^6 \text{ s}^{-1}$
$v_6 = k_6[\text{OH}^-][\text{H}^+]$		$k_6 = 1.0 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$
$v_{-6} = 1.0 \times 10^{-3} \text{ M s}^{-1}$		

rate constants for the forward and reverse reactions of the equilibria are chosen to be consistent with the known values of the equilibrium constants.

Simulations of the Closed System Kinetics. The model proposed here served as the basis for numerical simulations. The system of differential equations based on the rate laws of the component reactions in Table 1 was solved numerically by a semiimplicit Runge–Kutta method¹⁷ with an error parameter of 10^{-5} . Calculated time points for making the pH–time curves were collected in every tenth of a second. For the calculations the initial concentration of OH^- was derived from the measured initial pH.

As a comparison of calculated pH–time curves (Figure 5) with the measured ones (Figure 1) demonstrates that our simulations are able to reproduce well the shape of the experimental curves obtained in a closed vessel. But, the pH change appears to be more rapid in the experiments than in the calculations.

Simulations of the pH Oscillations in a CSTR. To simulate the kinetic behavior in a CSTR, we added appropriate flow terms to the model including input flows for H_2O_2 , $\text{S}_2\text{O}_4^{2-}$, and OH^- and output flows for all the variable species. Figure 6 shows calculated pH oscillations in a CSTR. The agreement between the experimental and simulated oscillations is quite good. The calculated and measured concentration range of oscillations are

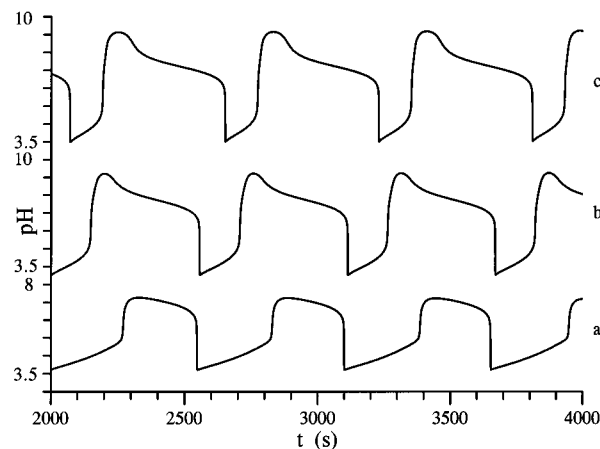


Figure 6. Calculated pH oscillations under flow conditions. Input concentrations: $[\text{NaOH}]_0 = 0.00313$; $[\text{Na}_2\text{S}_2\text{O}_4]_0 = 0.00375$; $[\text{H}_2\text{O}_2]_0 = 0.0115 \text{ M}$; $k_0 = 2.0 \times 10^{-3}$ (a) 2.7×10^{-3} (b), $3.1 \times 10^{-3} \text{ s}^{-1}$ (c). Measured oscillations are shown in Figure 2.

very similar. The shape, the period length, and the amplitude all agree well with their calculated counterparts.

Conclusion

A new sulfur-based oscillator is reported in this paper. The mechanism of the sulfur-based oscillators is very complex because of the large number of possible reactive intermediates. An experimentalist should face considerable difficulties in monitoring these species spectrophotometrically or potentiometrically. Here we applied a pH measurement for collecting information about the kinetics of such a reaction system.

Because of the complexity and the experimental difficulties, the sulfur-based oscillators have been among the last to yield to mechanistic analysis. Rushing et al.⁹ have just proposed a general model for the oscillatory oxidation of sulfur(–II) species. Their model is capable of simulating very large amplitude pH oscillations both in a CSTR and in a closed reactor, assuming both hydrogen-ion producing and consuming composite reactions. A significant portion of their model is the transient formation and further oxidation of hydrogen sulfite ions by the oxidant. Such a formation of hydrogen sulfite ion is an important part in the dithionite-hydrogen peroxide system. We think that the general model may be valid, with some modification, for the oscillatory systems containing not only sulfur(–II) species, but also sulfur species of higher oxidation state.

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