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Kinetic Role of CO_2 Escape in the Oscillatory $H_2O_2-HSO_3^--HCO_3^-$ Flow System

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Experiments have been performed in a CSTR closed to the air to clarify the kinetic role of CO_2 in the complex behavior observed during the autocatalytic oxidation of an aqueous solution of sulfur(IV) by hydrogen peroxide in the presence of hydrogen carbonate ions in a continuous-flow stirred tank reactor. Neither complex periodic nor chaotic oscillations, but simple periodic relaxation pH oscillations have been found if neither spontaneous escape nor controlled removal of CO_2 from the reactor to the air were allowed. State diagrams delineating the behavior of the system at 4.0 °C under various input concentrations and flow rates have been obtained. A simple empirical rate law model could be used to simulate the behavior of the reaction system in a wide range of conditions. The critical role of CO_2 escape is discussed.

Introduction

Systematic design of chemical oscillators using simple composite reactions as building blocks is of profound interest because the success of such a synthesis appears to be an important experimental test for the theoretical predictions of the necessary mechanistic and parametric conditions of the oscillations. On the other hand, design of new oscillators with specified properties may promote some practical applications of such systems. In this regard, the family of pH-regulated oscillators is considered to be the most promising candidate.

We have recently designed an oscillatory system based on the autocatalytic oxidation of diluted aqueous solution of sulfur(IV) by hydrogen peroxide in the presence of solid marble chips in a continuous-flow stirred tank reactor (CSTR).[1] We have found this reaction system to exhibit either periodic or chaotic pH oscillations depending on conditions. Here, marble provides the necessary negative feedback for oscillations as it removes H^+ when the reaction mixture becomes acidic as a result of the H^+-producing oxidation of the hydrogen sulfite ion. Later, we found that marble could be replaced by an input solution of $NaHCO_3$ to obtain a homogeneous chaotic flow system,[2] where HCO_3^- takes up proton and forms CO_2 in a relatively slow reaction for the negative feedback. Very recently, Frerichs and Thompson[3] reported that the presence of a very small amount of carbonate impurities in sulfite source, or even the air-carbon dioxide entering the reservoir or the reaction mixture, may also cause the sulfur(IV)−hydrogen peroxide reaction to oscillate in a CSTR. This important observation drives the attention to the possible kinetic role of carbonate impurities in other pH oscillators of this type. Namely, many known pH systems oscillate in a pH range where protonation of HCO_3^- takes place, so the presence of carbonate impurities may modify the dynamical behavior. In some cases, carbonate may be the true source of oscillations attributed to other species in previous communications.

TABLE 1: Composite Reactions and Rate Laws in the $H_2O_2-S(IV)-HCO_3^-$ System

no.	reaction	rate law
1	$H_2O_2 + HSO_3^- \rightarrow H^+ + SO_4^{2-} + H_2O$	$R_1 = (k_1 + k_1'[H^+])[HSO_3^-][H_2O_2]$
2	$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	$R_2 = k_2[HSO_3^-]$ $R_{-2} = k_{-2}[H^+][SO_3^{2-}]$
3	$CO_2\,(aq) + H_2O \rightleftharpoons H^+ + HCO_3^-$	$R_3 = k_3[CO_2\,(aq)]$ $R_{-3} = k_{-3}[H^+][HCO_3^-]$
4	$CO_2\,(aq) \rightarrow CO_2(gas)$	not used in calculations

Our earlier experiments showed that either spontaneous escape or controlled removal of CO_2 from the reaction mixture to the air always took place when chaotic or simple oscillatory behavior was observed in systems of this type. A simple scheme of the composite reactions and their empirical rate laws (Table 1) could be used to simulate the complex dynamical behavior. The model consists of an autocatalytic H^+-producing reaction (1), two protonation equilibria (2, 3), and a process of the escape of CO_2 (4). Later, detailed simulation calculations in a wider concentration range with a more general model[4] have revealed that not only stationary states but also simple periodic oscillations could be sustained under favorable conditions even if no CO_2 escape was allowed. However, according to our results, neither chaos nor any complex periodic oscillations could be expected without process 4 in such a pH oscillator. On the basis of these earlier experimental findings and recent simulations, we concluded that the escape of CO_2 (process 4) was not indispensable for simple periodic oscillations, but it was a necessary key step for period doubling and chaos to occur in such systems.[4]

However, Frerichs and Thompson[3] have reported not only simple periodic but also complex periodic and chaotic oscillations in the same reaction system even when the reactor was closed to the air preventing CO_2 from leaving the solution. Furthermore, according to their simulation calculations, a

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detailed mechanism could supposedly describe chaotic behavior without process 4.

This contradiction between our results and those reported by Frerichs and Thompson[3] prompted us to perform new experiments and calculations on this system in a wide range of conditions to solve the discrepancy. Here we report on our new detailed experimental study in a CSTR, which was closed to the air avoiding any escape of CO_2 during experiments. Results of modeling of the oscillations and that of related dynamical behavior are also presented. We show that an earlier proposed simple set of differential equations based on the empirical rate laws of the composite reactions can describe the dynamical behavior not only in a CSTR open to air, but also in a CSTR closed to the air in a wide range of conditions. We show that this simple model and a detailed mechanism proposed by Frerichs and Thompson give almost the same results when no CO_2 escape occurs. These new results confirm that no chaos arises if no CO_2 escape is allowed, but simple periodic oscillations may take place under favorable conditions. We also try to give an explanation of what Frerichs and Thompson interpreted as chemical chaos in their recent work.[3]

TABLE 2: Rate Constants Used in the Calculations[a]

	25.0 °C	4.0 °C
k_1 M^{-1} s^{-1}	7.0	1.5
k_1' M^{-2} s^{-1}	1.48×10^7	6.5×10^6
k_2 s^{-1}	3.0×10^3	1.0×10^3
k_{-2} M^{-1} s^{-1}	5.0×10^{10}	1.0×10^{10}
k_3 s^{-1}	4.3×10^{-2}	1.1×10^{-2}
k_{-3} M^{-1} s^{-1}	9.6×10^4	2.5×10^4

[a] Apparent activation energies for the rate constants were used with values available at 25.0 °C to calculate values for 4.0 °C.

TABLE 3: Differential Equations in the H_2O_2−S(IV)−HCO_3^- Flow System[a]

$$\begin{aligned}
d[SO_3^{2-}]/dt &= R_2 - R_{-2} + k_0\,([SO_3^{2-}]_0 - [SO_3^{2-}]) \\
d[H_2O_2]/dt &= -R_1 + k_0\,([H_2O_2]_0 - [H_2O_2]) \\
d[HSO_3^-]/dt &= -R_1 - R_2 + R_{-2} - k_0\,[HSO_3^-] \\
d[H^+]/dt &= R_1 + R_2 - R_{-2} + R_3 - R_{-3} + k_0\,([H^+]_0 - [H^+]) \\
d[HCO_3^-]/dt &= R_3 - R_{-3} + k_0\,([HCO_3^-]_0 - [HCO_3^-]) \\
d[CO_2\,(aq)]/dt &= -R_3 + R_{-3} - k_0\,[CO_2\,(aq)]
\end{aligned}$$

[a] k_0 is in s^{-1}. The input concentrations in the feed (indicated with 0 in the subscript) and the actual concentrations in the reactor (no subscript) are given in M.

TABLE 4: Detailed Reaction Mechanism Proposed by Frerichs and Thompson[3]

no.	reaction	rate constant at 25.0 °C
F1	$H_2O_2 + SO_3^{2-} \rightarrow SO_4^{2-} + H_2O$	0.2 M^{-1} s^{-1}
F2	$H_2O_2 + HSO_3^- \rightarrow H^+ + SO_4^{2-} + H_2O$	3.5 M^{-1} s^{-1}
F3	$H_2O_2 + HSO_3^- + H^+ \rightarrow 2H^+ + SO_4^{2-} + H_2O$	1.5×10^7 M^{-2} s^{-1}
F4	$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	3.0×10^3 s^{-1}; 5.0×10^{10} M^{-1} s^{-1}
F5	$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	4.8 s^{-1}; 1.0×10^{11} M^{-1} s^{-1}
F6	$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$	8.6×10^6 s^{-1}; 5.0×10^{10} M^{-1} s^{-1}
F7	$H_2CO_3 \rightleftharpoons CO_{2(aq)} + H_2O$	16.5 s^{-1}; 4.3×10^{-2} s^{-1}

Experimental Section

Materials. Reagent grade H_2O_2, H_2SO_4, Na_2SO_3, $NaHCO_3$ (all REANAL) were used without further purification. Doubly distilled water used in preparing solutions was first purged with N_2 for elimination of O_2 and CO_2 impurities. Two input solutions were prepared daily: one contained H_2O_2, the other contained the necessary amount of Na_2SO_3, $NaHCO_3$, and H_2SO_4. In this way a neutral hydrogen peroxide solution and a slightly alkaline (pH 8) sulfite solution were obtained. To avoid loss of carbon dioxide and sulfur dioxide in input solutions, Frerichs and Thompson prepared basic and acidic input solutions by premixing the acid with H_2O_2. We did not prefer the latter combination because introducing an acidic solution and a basic one may cause random local acidification in the CSTR during mixing. Since the hydrogen ion is the autocatalyst, such an acidification can initiate the autocatalytic reaction randomly. Because it was essential to avoid autoxidation of S(IV) in the reservoir, its solution was kept under N_2 but not bubbled to avoid the loss of the volatile components. Had this solution in the reservoir been bubbled, some loss of CO_2 and SO_2 would have been unavoidable despite the slightly alkaline pH. Both input solutions had been stored at 4.0 °C for 12 h before use and they were discarded after 24-hour storage. This care was necessary to obtain reproducible results. For example, the period of the oscillations was longer when freshly prepared sulfite solution was used than in the case of an old sulfite solution. The concentration of H_2O_2 was determined with permanganate solution, the sulfite was titrated with a standardized iodine solution.

Reactor. The continuous flow experiments were performed in a water-jacketed cylindrical-shaped glass vessel with a liquid volume of 12.5 mL. The reactor was perfectly sealed with a silicon cap in all the experiments. A pH electrode, the input (i.d. 1.0 mm) and output tubes (i.d. 2.0 mm) were led through the cap. A Teflon-covered magnetic stirrer (1 cm long) was used to ensure uniform mixing at around 500 rpm.

Procedure. pH change is very fast in the acidic region of the oscillation. It was difficult to follow it with a pH electrode at room temperature because of the slower than desired response of the electrode and the recording system. Our preliminary experiments showed that especially the pH minima could be measured only dubiously at room temperature. Thus, most of our present experiments were carried out at 4.0 °C where more reliable data in the pH minima could be collected. In some cases we reproduced Frerichs and Thompson's experiments at 25.0 °C. The reactor was fed with prethermostated input solutions by means of a peristaltic pump (Desaga). The excess liquid was removed with a second pump. The liquid level could be controlled by the vertical position of the outlet tubes. The pH and the temperature inside the reactor were continuously measured. The experiments were started by filling the reactor with the input solutions at the highest pump speed available (5.0 mL/min). After the reactor had been filled, the pump speed was reduced to the desired value.

Computation. A semiimplicit Runge−Kutta method[5] with an error parameter of 10^{-5} was used for numerical integrations. This low value of the error parameter proved to be necessary and sufficient for obtaining correct results. Calculated time points for making the figures were collected in every tenth of a second.

Results and Discussion

A Comparison of the Simple Empirical Rate Law Model and the Detailed Mechanism. The empirical rate law (erl) model[2] is shown in Table 1. A detailed reaction mechanism proposed by Frerichs and Thompson[3] is summarized in Table 4. Obviously the two schemes are very similar to each other. There are two differences worth mentioning. First, reaction F1 is taken into account in the mechanism but not in the erl. Second, the value of $k_1 = 7.0$ M^{-1} s^{-1} in the erl is 2-fold higher than in the mechanism (see constant for reaction F2). To obtain as simple a model as possible, we neglect F1 because it seems to

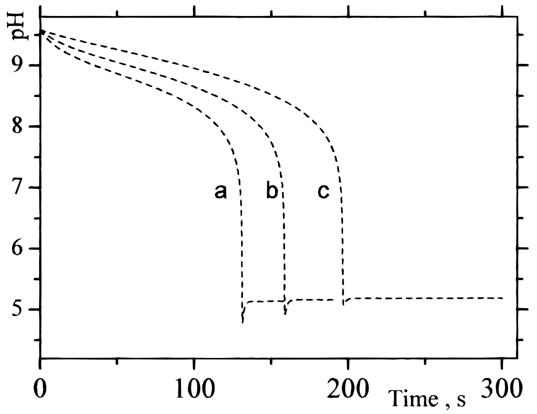

Figure 1. Calculated pH−time curves in the hydrogen peroxide−sulfite batch reaction at different assumed concentrations of CO_2. Calculations have been carried out with the mechanism shown in Table 4 using $k_2 = 7.0\ M^{-1}\ s^{-1}$. $[H_2O_2] = 0.050$, $[SO_3^{2-}] = 2.20 \times 10^{-3}$, $[H^+] = 1.20 \times 10^{-5}$, $[CO_3^{2-}] = 2.9 \times 10^{-6}$, $[CO_2] = 1.6 \times 10^{-5}$ (a), 8.0×10^{-6} (b), 1.6×10^{-6} (c) M.

be slow enough to have no significant contribution to the route of oxidation of sulfite in the pH range of oscillations. The rate constant for F1 is $0.2\ M^{-1}\ s^{-1}$ at 25.0 °C[8], which should be compared with $k_1 = 7.0\ M^{-1}\ s^{-1}$ in Table 2. A comparison indicates that reaction F1 would only be competitive with F2 above pH 8 where $[SO_3^{2-}]$ would exceed $[HSO_3^-]$ by more than 1 order of magnitude (consider the $pK = 7$ for equilibrium 2). The values of the rate constants show that the oxidation of sulfur(IV) goes mainly through reactions F2 and F3 in the pH range of oscillations (pH below 8). Indeed, calculations proved that no significant differences were observable in the length of the oscillatory periods obtained with or without reaction F1. The difference is far less than the reproducibility of the period length in the experiments. In some cases, the mechanism produces bistability between a high pH steady state and an oscillatory state in CSTR mode in the absence of reaction F1. Such a bistability cannot be seen in the experiments indicating that reaction F1 represents an important channel for oxidation of sulfur(IV) at high pH. The experimental system is transferred from the high pH state to the oscillatory one through this channel. Frerichs and Thompson[3] suggest a smaller rate constant ($k_1 = k_{F2} = 3.5\ M^{-1}\ s^{-1}$) for reaction F2. If this smaller value is used in the calculations for F2, reaction F1 becomes more competitive with F2 even at lower pH values and its effect on the length of the period becomes more significant. It is not easy to decide which value is correct or, at least, which one is closer to the truth. Both values were obtained by fitting the same experimental clock type pH-time curves published earlier.[9] The difference is caused by the assumption of carbonate and carbon dioxide impurities by Frerisch and Thompson, which nicely explains the pH overshoot.[3] However, the estimated ratio $[CO_2]/[CO_3^{2-}]$ and the estimated amount of acid impurities strongly affect the reaction rate. Shown in Figure 1 are calculated clock type pH-time curves at different estimated $[CO_2]$. It is seen that the higher the $[CO_2]$ the faster the reaction, because CO_2 decreases the initial pH as a result of its hydration. Since the stock solutions for the considered experiments were freed from CO_2 with argon,[9] the CO_2 concentration should be close to 0, or much smaller than an equilibrium concentration in distilled water (1.6×10^{-5} M) as estimated in the fitting procedure by Frerichs and Thompson.[3] Obviously, the fitting results in a smaller rate constant than its true value if the CO_2 content is overestimated. Another difficulty is that the reproducibility of the clock-type curves is poor.[1] All in all, at this point we tend to accept the higher value $k_1 = 7.0$ for further considerations. Reaction 1 with a two-term rate law is considered in the erl model that represents mechanistic steps F2 and F3. Equilibrium F5 ($pK_{F5} \sim 10$) is not important in the oscillatory pH range (4.5−7.5) and it is neglected in the erl. Of course, one should consider equilibrium F5 if CO_3^{2-} and not HCO_3^- is used as input species. Since we used HCO_3^- as starting material in our experiments, we could neglect equilibrium F5 in the calculations. Hydration of CO_2 (F7) is slow compared to the ionization of H_2CO_3 (F6). Concentration of H_2CO_3 is always much lower than that of CO_2. At equilibrium $[H_2CO_3]$ is only about 10^{-3} as large as $[CO_2]$, and so H_2CO_3 has no significance in the erl model. Consequently, equilibria F6 and F7 can be drawn together in reaction 3. We have concluded and verified with calculations that these two schemes should give the same description of the dynamical behavior, provided that the same rate constants were used.

In further calculations the simpler erl model was used without process 4, which is not relevant in the present case. This model clearly shows how the oscillations are generated in this system. The autocatalytic H^+-producing reaction 1 (positive feedback) is coupled with a slow H^+ consumption (negative feedback). Composite reaction 3 removes and preserves H^+ in the form of CO_2. Kinetics of the composite reactions have been studied separately, and the measured rate constant values are available[1] (Table 2). It is important that both the hydration of CO_2 (reaction 3) and the consumption of H^+ in the reverse reaction −3 are slow[6,7] (compared with other very fast protonation equilibria) in the pH range of interest. Consequently, the autocatalytic generation of H^+ can be completed before significant removal of H^+ takes place (time delay between the positive and the negative feedbacks). If reaction 3 were a fast equilibrium, it would rather act as an acid−base buffer and would, of course, prevent any pH oscillation in the system.

Experimental Results and Calculated Behavior. Typical calculated and measured relaxation pH oscillations are compared in Figure 2. As one can see, the shape of the calculated and measured oscillatory curves were found to be strikingly similar to each other when the same initial concentrations of reaction components and flow rates were used both in the simulations and in the measurements. A typical period is composed of a long *high* pH state (pH 7.0−7.3) and a very short *low* pH state (pH 5.5). Transition between the two states is always very sharp. The length of a period increases with increasing flow rate on both the calculated and the measured curves. However, there are some differences between calculated and measured values of period length. Note that the measured period length is the less reproducible peculiarity in this oscillation. It is very sensitive to the initial conditions. Even the age of the stock solution of the sulfite ion influences it: The period was found to be longer when the experiment was performed with freshly prepared sulfite solution and shorter if the sulfite solution had been stored under nitrogen for several hours before use. To look for systematic trends, the influence of species concentrations on the period length has been measured systematically. Calculated and measured period lengths obtained under different input feed concentrations are compared in Table 5. Taking into account the rather poor reproducibility of the period length in the experiments, the agreement between the measured and calculated values is acceptable. More importantly, both the calculated and measured values vary in the same direction with changing input concentrations. With increasing sulfite ion and hydrogen carbonate ion concentrations, or with decreasing hydrogen ion concentration, the period length increases sharply.

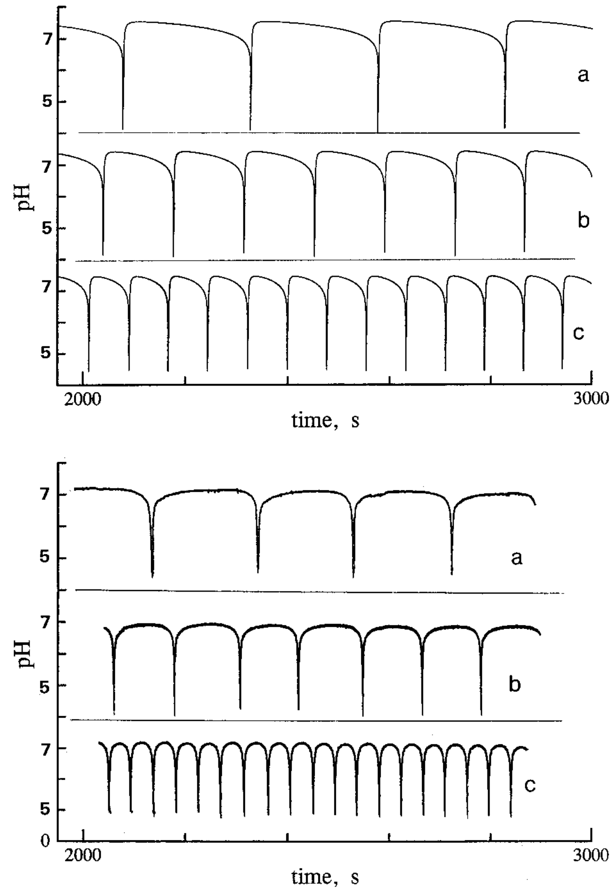

Figure 2. Calculated (top) and measured (bottom) pH oscillations in a CSTR at $T = 4.0$ °C, at different flow rates (k_0, reciprocal residence time 1.19×10^{-3} (a), 1.01×10^{-3} (b), and 0.80×10^{-3} s^{-1} (c)). Concentrations in the combined input feed: $[H_2O_2]_0 = 0.050$, $[SO_3^{2-}]_0 = 0.010$, $[H^+]_0 = 2.2 \times 10^{-4}$, and $[HCO_3^-]_0 = 3.0 \times 10^{-4}$ M. Rate constants given in Table 2 for 4.0 °C were used in the simulation.

TABLE 5: Measured and Calculated Period Length at 4.0 °C, $k_0 = 1.0 \times 10^{-3}$ s^{-1}, $[H_2O_2]_0 = 0.050$ M

$[H^+]_0 \times 10^4$ (M)	$[HCO_3^-]_0 \times 10^4$ (M)	$[SO_3^{2-}]_0$ (M)	period length (s) measured	period length (s) calcd
2.2	3.0	0.010	141	134
2.0	3.0	0.010	213	191
1.8	3.0	0.010	356	389
1.7	3.0	0.010	no osc.	636
2.0	3.0	0.0050	33	27
2.0	3.0	0.0070	70	62
2.0	3.0	0.0090	148	137
2.0	3.0	0.011	298	326
2.0	3.0	0.013	no osc.	no osc.
2.0	2.5	0.010	163	168
2.0	3.5	0.010	197	216
2.0	4.0	0.010	233	245

As a further test of the erl model we calculated the oscillatory region in the k_0-$[SO_3^{2-}]_0$ plane and compared it with the measured behavior (Figure 3). One can see that the measured oscillations (open circles) fall, almost exclusively, inside the calculated oscillatory region (marked by dashed line in Figure 3). Measured steady states (marked by ×) exist mostly outside the calculated oscillatory region, as expected. It might be surprising that neither experiments nor simulations indicated the existence of bistability in the k_0-$[SO_3^{2-}]_0$ plane. A state diagram was calculated in the same plane at 25.0 °C and was compared with Frerichs and Thompson's experimental diagram (Figure 4). The agreement is acceptable.

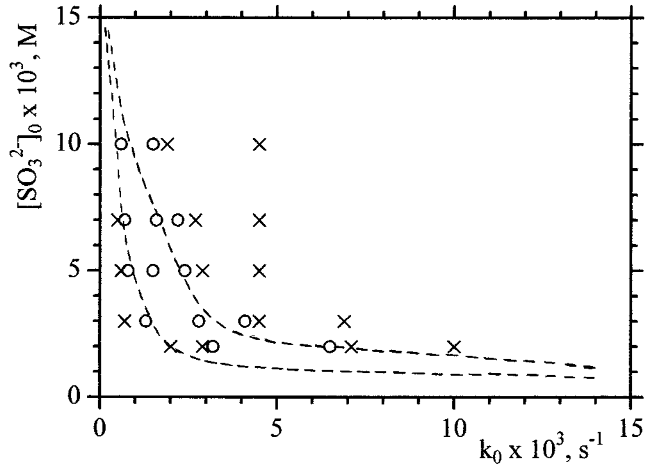

Figure 3. Calculated border of the oscillatory region is marked by dashed line, measured oscillations at 4.0 °C are indicated by open circles, steady states are indicated by × in the $[SO_3^{2-}]_0$−k_0 plane. Fixed parameters: $[H_2O_2]_0 = 0.030$, $[H^+]_0 = 2.2 \times 10^{-4}$, and $[HCO_3^-]_0 = 3.0 \times 10^{-4}$ M. Rate constants for calculations are given in Table 2 for 4.0 °C.

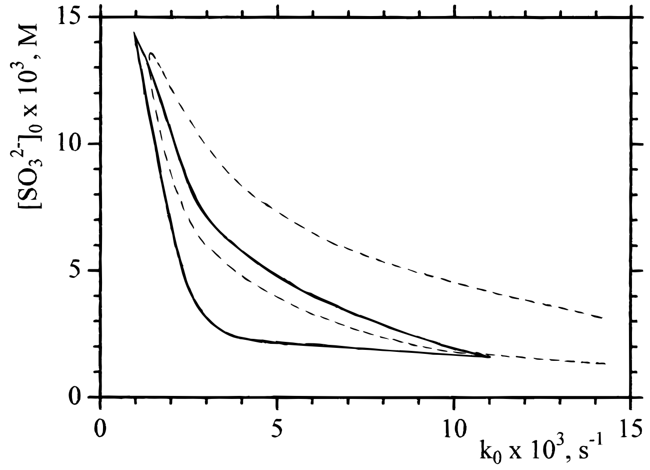

Figure 4. State diagram at 25.0 °C. Calculated border of the oscillatory region is marked by dashed line, oscillatory region measured by Frerichs and Thompson is marked by solid line. Fixed parameters: $[H_2O_2]_0 = 0.030$, $[H^+]_0 = 5.2 \times 10^{-4}$, and $[CO_3^{2-}]_0 = 3.0 \times 10^{-4}$ M. (In the calculations with erl model $[H^+]_0 = 2.2 \times 10^{-4}$ and $[HCO_3^-]_0 = 3.0 \times 10^{-4}$ M, and rate constants given in Table 2 for 25.0 °C were considered.)

Oscillations were obtained in a rather narrow range in the $[H^+]_0$−$[HCO_3^-]_0$ plane at fixed concentrations of H_2O_2 and SO_3^{2-} and flow rate. Typical calculated oscillatory region and measured oscillatory points (open circle) and steady states (marked by ×) are shown in Figure 5. It is seen that all of the measured oscillations are located in the calculated region. However, only steady states were found experimentally in some part of the calculated oscillatory region. Similar to Frerichs and Thompson's finding, an optimum ratio $[H^+]_0/[HCO_3^-]_0$ was found to be very important for oscillations to occur. It is seen in Figure 5 that $[HCO_3^-]_0$ should exceed $[H^+]_0$ for oscillations to occur, but a high excess of hydrogen carbonate is not favorable.

All in all, the agreement between simulation and measurement of the dynamical behavior is good in a rather wide range of species concentration and flow rate. The erl model can be used for prediction of the dynamical behavior of this reaction system under various conditions. Both our experiments and simulations show that this system can exhibit only steady states and regular

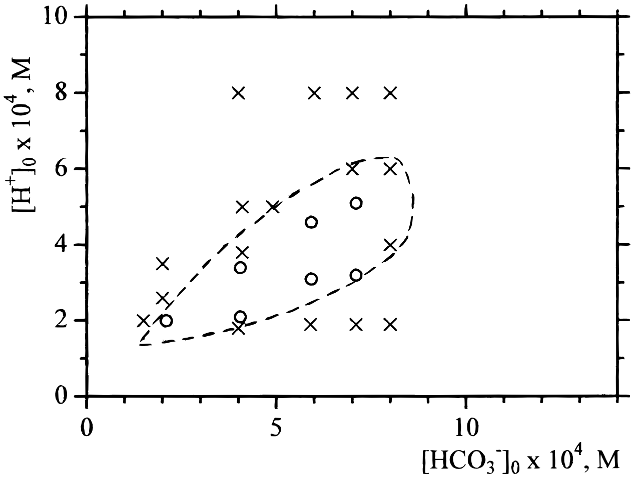

Figure 5. State diagram at 4.0 °C. Calculated border of the oscillatory region is marked by dashed line. Measured oscillatory compositions are indicated by open circles, × represents steady states. All of the measured oscillations are found in the calculated oscillatory region but not all of the measured steady states are located outside the calculated oscillatory region. Fixed parameters: $[H_2O_2]_0 = 0.050$ M, $[SO_3^{2-}]_0 = 0.010$ M, and $k_0 = 1.0 \times 10^{-3}$ s^{-1}.

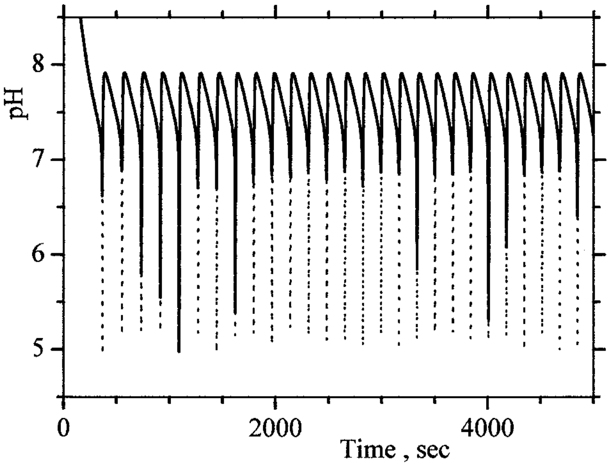

Figure 6. Irregularities in the pH minima caused by the insufficient number of time points in the calculations. Calculations were carried out by the erl model using rate constant values at 25.0 °C. Solid lines indicate irregular pH minima obtained using 600 time points, dashed lines show more regular pH minima obtained based on 5000 time points. Input concentrations: $[H_2O_2]_0 = 0.117$, $[SO_3^{2-}]_0 = 1.25 \times 10^{-2}$, $[H^+]_0 = 5.1 \times 10^{-6}$, $[HCO_3^-]_0 = 7.4 \times 10^{-6}$, $[CO_2]_0 = 1.6 \times 10^{-5}$ M. Here, $k_0 = 6.745 \times 10^{-4}$ s^{-1}.

periodic oscillations in a flow reactor closed to the air. The most important result is that we have not seen any convincing sign of complex periodic or chaotic oscillations unless the escape or controlled removal of CO_2 from the liquid to the air takes place. Frerichs and Thompson[3] have reported just the opposite. In the following paragraph we will point out some difficulties in the experiments and in the calculations which may be the source of some misunderstanding in the interpretation.

Difficulties in Experiments and Calculations. Frerichs and Thompson[3] have claimed that they found period doubling leading to chaos at 25.0 °C in the present system when no CO_2 escape is allowed. However, they have presented only calculated but not measured curves to support their claim. When we performed some experiments at 25.0 °C, we found that the pH change in the low pH range was so fast that it could not be followed reliably by a glass electrode because response of the electrode was not fast enough. As a result, the actual minimum values of the pH could not be determined exactly. Some nonreproducible irregularities in the value of the pH minima could certainly be observed during oscillations. However, a next return map of the pH minima and other data transformations did not indicate any sign of deterministic origin. We have concluded that the observed irregularity was obviously a result of experimental limitations rather than of deterministic chemical origin.

In light of the very short time of the pH minima, we believe that the simulated period doubling and chaos are not originated from the chemical mechanism either. We suspect that the limitation of their computer program is responsible for the appearance of random pH minima on the calculated curves. They used SIMULATE for numerical integration. This program calculates dynamical behavior of chemical reaction systems following mass-action kinetics. It uses GEAR algorithm for solving the stiff system of differential equations. The problem is that, according to the program description, this program collects equidistant time points for making a figure. Supposedly, they collected too few points to represent the true pH minima and they had not enough time points to cover smoothly the pH−time curves in their figures. We performed control calculations to show how important the number of time points is in the present case. We used the detailed mechanism shown in Table 4 with rate constant given at 25.0 °C for calculating a chaotic time series given by Frerichs and Thompson in Figure 8 (d) of their paper.[3] The solid line in Figure 6 shows an oscillatory curve obtained with 600 time points; the dashed lines indicate the minima obtained by using 5000 time points. As the number of points increases, the pH minima tend to equalize, indicating that the irregularity observed in the pH minima is a result of an insufficient number of points.

Conclusion

We have performed experiments and simulation calculations in the oscillatory $H_2O_2-HSO_3^--HCO_3^-$ reaction system in a CSTR closed to the air. Our aim was to answer the question whether oscillations and chaos exist in this system without the escape of CO_2 to the air. In addition to high pH and low pH steady states, regular relaxation pH oscillations were observed in our experiments depending on conditions. That means that regular oscillations are sustained even when CO_2 cannot leave the reactor to the air. However, we have not found any sign of period doubling and chaos similar to that reported by Frerichs and Thompson under these conditions. Only random variation of nondeterministic origin could be observed in the pH minima in some experiments. Our simulations confirmed the experimental results. The simple erl model is capable of simulating regular pH oscillations if no CO_2 escape is taken into account. The reaction system is a true CSTR oscillator because all six variables of the erl model oscillate at the same time. We note that the number of variables can be reduced to four without loosing the oscillatory character of the model because $[H_2O_2]$ can be treated as constant and there is a stoichiometric connection between SO_3^{2-} and HSO_3^-. We demonstrated that a detailed mechanism proposed by Frerichs and Thompson gave the same results in the simulations as did the erl model.

Finally, we emphasize the critical contribution of the CO_2 to the dynamical behavior of the present system. Oscillatory formation and consumption of dissolved carbon dioxide is important in chemical systems and may have biochemical implications as well. We think that our present work provides enough evidence that complex periodic oscillations and chaos cannot exist in the systems of this type unless CO_2 can leave the reactor through not only the common liquid outflow but also through a separate channel (escape to the air). CO_2 can be regarded as a hidden supply of H^+. Therefore the removal of CO_2 appears to be an additional channel for the negative feedback in the oscillatory system.

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