pH Oscillations in the $BrO_3^-{-}SO_3^{2-}/HSO_3^-$ Reaction in a CSTR

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Large-amplitude pH oscillations have been measured during the oxidation of sulfur (IV) species by the bromate ion in aqueous solution in a continuous-flow stirred tank reactor in the absence of any additional oxidizing or reducing reagent. The source of the oscillation in this simple chemical reaction is a two-way oxidation of sulfur (IV) by the bromate ion: (1) the hydrogen-ion-producing self-accelerating oxidation to sulfur (VI) (SO_4^{2-}), and (2) a hydrogen-ion-consuming oxidation to sulfur (V) ($S_2O_6^{2-}$). In such a way, both the H^+-producing and H^+-consuming composite processes required for a pH oscillator take place in parallel in a reaction between two reagents in this system. A simple reaction scheme, consisting of the protonation equilibria of SO_3^{2-} and HSO_3^-, the oxidation of HSO_3^- and H_2SO_3 by BrO_3^- to SO_4^{2-}, and the oxidation of H_2SO_3 to $S_2O_6^{2-}$ has successfully been used to simulate the observed dynamical behavior. Simulation with this simple scheme shows that oscillations can be calculated even if only about 1% of sulfur (IV) is oxidized to $S_2O_6^{2-}$ along with the main product SO_4^{2-}. Agreement between calculated and measured dynamical behavior is found to be quite good. Increasing temperature decreases both the period length of oscillations in a CSTR and the Landolt time measured in a closed reactor. No temperature compensation of the oscillatory frequency is found in this reaction.

Introduction

pH oscillators[1,2] constitute the largest family of oscillatory chemical reaction systems discovered in a continuous-flow stirred tank reactor (CSTR) in the last two decades. In addition to the accidental discoveries,[3,4] many of the pH oscillators have been designed systematically using simple composite reactions as building blocks. One of the composite reactions required involves autocatalytic production of H^+ (for the positive feedback loop), while the other should consume H^+ with an appropriate time delay (negative feedback loop). Among many others, oxidation of a mixture of the sulfite and hydrogen sulfite ions by the bromate ion has been used as a positive feedback process for some pH-oscillator systems.[5−7] This reaction is known to exhibit clock-reaction behavior in a batch reactor: If no excess acid−base buffer is present, the pH suddenly drops after a lag period, which may be visualized by acid−base indicators. H^+ plays a great kinetic role in this oxidation through the fast protonation of SO_3^{2-} and HSO_3^-

$$SO_3^{2-} + H^+ \leftrightarrow HSO_3^- \qquad (1)$$

$$HSO_3^- + H^+ \leftrightarrow H_2SO_3 \qquad (2)$$

The oxidation of HSO_3^- and H_2SO_3 to SO_4^{2-} by BrO_3^- recovers the initially supplied proton (reactions 3 and 4) because of the low value of the protonation constant of the products SO_4^{2-} and Br^-.

$$3HSO_3^- + BrO_3^- \rightarrow 3SO_4^{2-} + Br^- + 3H^+ \qquad (3)$$

$$3H_2SO_3 + BrO_3^- \rightarrow 3SO_4^{2-} + Br^- + 6H^+ \qquad (4)$$

Obviously, the scheme (reactions 1−4) represents a self-accelerating H^+ production in a closed reactor, because the rate constant of reaction 4 is much larger[8] than that of reaction 3. The relative concentration of the more reactive H_2SO_3 increases as the reaction proceeds because of the increasing concentration of H^+. As a result, the overall reaction rate increases with increasing H^+ concentration. The oxidation of the nonprotonated SO_3^{2-} by BrO_3^- is negligibly slow under the circumstances, so its direct oxidation does not need to be taken into account in the acidic or neutral media covered by the oscillations. Both experimental results[5] and theoretical considerations[9] known so far suggest that the bromate−sulfite reaction alone exhibits bistability between two steady states under flow conditions, but not oscillations because of the lack of the negative feedback. One of the stable states is characterized by low pH (pH $\approx$ 3), which corresponds to high conversion of the overall reaction (thermodynamic branch). The other state is characterized by high pH (pH $\approx$ 7−8) that corresponds to low conversion (kinetic branch). According to experimental findings and theoretical considerations, an oscillatory system may be obtained in a CSTR if this reaction is coupled with another reaction in which linear or more complex decay of H^+ takes place. Several types of hydrogen-ion-consuming reactions have been used for this purpose in earlier works. The oxidation of $Fe(CN)_6^{4-}$ by BrO_3^- (reaction 5) is the oldest known example of the H^+-consuming composite reactions applied successfully in many experiments.[5,10−15] Reaction 5 is a light-sensitive, multistep process[16] that makes the oscillatory system of $BrO_3^-{-}HSO_3^-{-}Fe(CN)_6^{4-}$ rather complex mechanistically. It is also important to note that $Fe(CN)_6^{3-}$, a product of reaction 5, oxidizes HSO_3^- in a slow reaction causing further complications in the mechanism.

$$6Fe(CN)_6^{4-} + BrO_3^- + 6H^+ \rightarrow 6Fe(CN)_6^{3-} + Br^- + 3H_2O \qquad (5)$$

A simpler example of the H^+-removing composite process is reaction 6, which takes place when solid marble chips are

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placed in the reactor.[6] $CaCO_3$ contained in marble removes H^+ selectively according to reaction 6 without adding any further redox reactions to the system. Reaction 6 seems to be simple

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (6)$$

mechanistically, but the dynamical behavior of the system is complicated by the ever-changing solid−liquid interface on the marble that influences the rate of reaction 6. Furthermore, the product HCO_3^- is involved in protonation−deprotonation equilibria, which affects the system dynamics, resulting in chaotic behavior under certain conditions.[6]

Recently, a third possibility[7] of H^+ consumption has been recognized. It is known that sulfurous acid and its related anions (sulfur (IV) species) may be oxidized not only to sulfate but also to dithionate ions in an aqueous solution depending on the nature of the oxidizing agent. The ratio of the two products depends principally upon whether the oxidizing agent favors a 1 or 2 equiv reaction.[18] The main product of the oxidation by 2 equiv oxidizing reagents is SO_4^{2-}, while 1 equiv reagents oxidize sulfur (IV) in two different ways producing both SO_4^{2-} and $S_2O_6^{2-}$. In an oscillatory system discovered recently,[7] MnO_4^- was used to oxidize some part of HSO_3^- to $S_2O_6^{2-}$

$$2MnO_4^- + 10HSO_3^- + 6H^+ \rightarrow 2Mn^{2+} + 5S_2O_6^{2-} + 8H_2O \qquad (7)$$

BrO_3^- belongs to the category of 2 equiv reagents. Accordingly, the product of its reaction with sulfur (IV) is mostly SO_4^{2-} (reactions 3, 4), but some small amount of $S_2O_6^{2-}$ is also formed simultaneously in acidic solution as reported by Higginson and Marshall.[17] It is remarkable that reaction 8, in contrast with

$$BrO_3^- + 6HSO_3^- \rightarrow 3S_2O_6^{2-} + 3H_2O + Br^- \qquad (8)$$

reactions 3 and 4, does not recover the initially supplied protons bonded to the sulfite. Thus, in principle, the bromate−sulfur (IV) reaction itself contains both the hydrogen-ion-producing and -consuming composite reactions required for a pH-oscillatory system. With this feature taken into account, the question arises whether the reaction between bromate and sulfur (IV) alone can produce pH oscillations in a CSTR without any additional reagent. Surprisingly, this important question has not yet been investigated in the literature. We addressed this question in the present paper. Our model calculations predict and our recent experiments showed that large-amplitude periodic pH oscillations can be measured in the bromate−sulfite reaction in the absence of any additional reagent if the input concentration of protons was chosen to be low enough. It should be much lower than that applied in earlier studies when oscillations were observed only in the presence of a third reagent. We think that this is an important new feature of the sulfur (IV)-based pH oscillators, which has not been recognized before. In this study, we summarize our recent experimental findings and propose a simple scheme that accounts for the oscillations observed in this reaction. We also report on the effect of temperature on the dynamical behavior of this system.

Experimental Section

H_2SO_4 solution and crystalline $KBrO_3$ and Na_2SO_3 are reagent-grade chemicals used without further purification in this study. Deionized water used in preparing solutions was first purged with N_2 to eliminate O_2 and CO_2 impurities. Two input solutions were prepared daily: one contained $KBrO_3$ and the other contained Na_2SO_3 and the necessary amount of H_2SO_4. A CSTR configuration was employed, in which a water-jacketed cylindrical-shaped glass reactor with a liquid volume of 19.5 mL was maintained at constant temperature with circulating water from a thermostat. The reactor was sealed with a silicon cap in all the experiments. A pH electrode and the input (i.d. 1.0 mm) and output (i.d. 2.0 mm) flexible silicon tubes were led through the cap for peristaltic feeding. An MP4 Gilson peristaltic pump was used for feeding the reactor. The excess liquid was removed with the same pump. A Teflon-covered magnetic stirrer (1.0 cm long) was used to ensure uniform mixing at around 900 rpm. pH−time data were collected by a computer and were recorded on a disk.

Results and Discussion

Modeling. First, we carried out simulations in order to predict the dynamical behavior of this reaction under different conditions. In the scheme proposed earlier for the BrO_3^-−HSO_3^- reaction, composite reactions 1−4 combine to generate the "clock" behavior in the closed system, with steady states and bistability, but not oscillations, in the CSTR.[9] We have found that the addition of reaction 8 to the scheme makes the model capable of simulating not only the steady states and bistability between them, but also oscillations, at appropriate flow rate values. The composite reactions of the model used in the calculations and the corresponding rate laws with rate constant values at 25 °C are summarized in Table 1.

Using this model and rate laws, we simulated the expected dynamical behavior in a CSTR at different flow rates. The values of the rate constants, except k_8, were taken from ref 9. The value of k_8 is not available in the literature. Since reaction 8 cannot be studied separately, we estimated a value for k_8 with which the best fit was achieved between the measured and calculated dynamical behavior. Note that the contribution of reaction 8 to the overall stoichiometry is small: Less than 2% of sulfite is oxidized to dithionate under the conditions used in this work. The general algorithm used for the numerical integration of the differential equations was based on a semi-implicit Runge−Kutta method using Kaps and Rentrop's scheme.[17] Figure 1 shows typical calculated pH oscillations (dashed line) along with their measured counterparts (solid line).

An important feature of this calculated oscillation is that the system stays in both the high and low pH states for a long time, and the transitions between low and high pH states are very sharp. According to the results of our simulations, reaction 8 is an essential part of the model. pH oscillations are predicted by calculations only if reaction 8 is considered. The rate constant of reaction 8 can be varied on a large scale, but no oscillations are calculated when $k_8 = 0$. The minimum value of k_8 necessary for the oscillation is 0.5 M^{-1} s^{-1}. This is seen in Figure 2 where the reaction behavior is shown in the k_0 versus k_8 phase plane. The region of calculated oscillations is marked out by a triangular-shaped curve in Figure 2.

We have also simulated how the system reacts to the change in the flow rate. Figure 3 shows the calculated dynamical behavior at different flow rates. A steady state with low pH exists when the flow rate is chosen to be low. A steady state of high pH can be calculated when high flow rate values are taken into account.

Experimental Results. In light of the simulations, we carried out systematic experiments with the bromate−sulfite−sulfuric acid reaction system to see whether predicted pH oscillations

TABLE 1: Composite Reactions, Empirical Rate Laws, and Rate Constant Values for the Oscillatory $BrO_3^-{-}SO_3^{2-}/HSO_3^-$ Reaction

no.	reactions	rate laws	rate constant values at 25 °C
1	$SO_3^{2-} + H^+ \leftrightarrow HSO_3^-$	$r_1 = k_1[SO_3^{2-}][H^+]$; $r_{-1} = k_{-1}[HSO_3^-]$	k_1: 1.0×10^{10} $M^{-1}\,s^{-1}$; k_{-1}: 1.0×10^3 s^{-1}
2	$HSO_3^- + H^+ \leftrightarrow H_2SO_3$	$r_2 = k_2[HSO_3^-][H^+]$; $r_{-2} = k_{-2}[H_2SO_3^-]$	k_2: 6.0×10^9 $M^{-1}\,s^{-1}$; k_{-2}: 1.0×10^8 s^{-1}
3	$3HSO_3^- + BrO_3^- \rightarrow 3SO_4^{2-} + Br^- + 3H^+$	$r_3 = k_3[HSO_3^-][BrO_3^-]$	k_3: 0.0653 $M^{-1}\,s^{-1}$
4	$3H_2SO_3 + BrO_3^- \rightarrow 3SO_4^{2-} + Br^- + 6H^+$	$r_4 = k_4[H_2SO_3][BrO_3^-]$	k_4: 18 $M^{-1}\,s^{-1}$
8	$6H_2SO_3 + BrO_3^- \rightarrow 3S_2O_6^{2-} + Br^- + 3H_2O + 6H^+$	$r_8 = k_8[H_2SO_3][BrO_3^-]$	k_8: 0.70 $M^{-1}\,s^{-1}$

can be observed in a CSTR experimentally. First, we confirmed the earlier reports[9] on the existence of two stable states and a large-scale bistability between them. Important parameters for the occurrence of oscillations in the system are bromate, sulfite, and sulfuric acid concentrations and the flow rate at constant temperature. When the input concentrations of 0.050 M $KBrO_3$, 0.050 M Na_2SO_3, and 0.00125 M H_2SO_4 were used for feeding the CSTR, large-amplitude oscillations could be measured at 35 °C in a narrow range of flow rates. Figure 1 shows typical measured oscillations along with their calculated counterparts.

Dynamical Behavior of the System. Measured and calculated dynamical behavior of the reaction mixture at different flow rates are presented in Figure 3. Similarly to the calculated behavior, the system stays in the steady state of low pH when a lower k_0 was adjusted, oscillatory behavior is observed for a medium k_0, and a steady state of high pH characterizes the system behavior in the case of high k_0 values. The oscillatory behavior is robust and readily reproducible. As it appears from the oscillatory curve shown in Figure 1, the amplitudes are as high as 4 pH units ranging from pH 3.5 to pH 7.5. The oscillatory waveforms are distinct from most of the other pH oscillations reported so far in that the high-pH stage and the low-pH stage are well-separated and that the transition between them are sharp in both directions. The lengths of the periods are very long, exceeding 3 h in some cases and can be varied on a large scale by varying the experimental constraints such as flow rate, temperature, and input reagent concentrations. Furthermore, durations of both high-pH and low-pH stages can easily be controlled over a wide range by choosing the input concentrations appropriately. These features of the bromate−sulfite pH oscillator might be of importance in the cases of possible practical applications. For example, periodic control of self-oscillations of swelling and deswelling of pH-sensitive hydrogels can easily be realized by such a pH oscillator.[15,19]

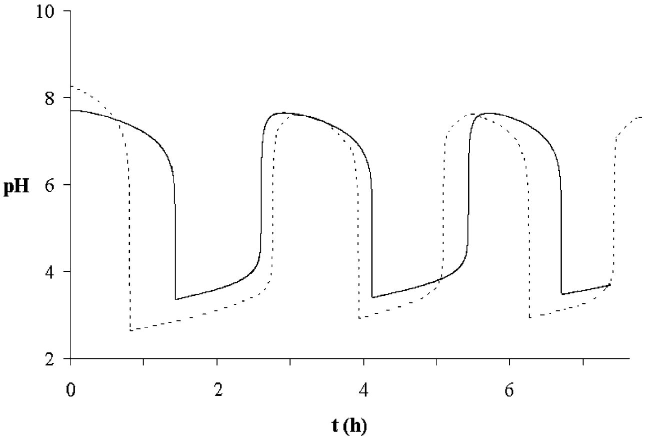

Figure 1. Typical calculated (dashed line) and measured (solid line) pH oscillations in the flow system of bromate−sulfite−hydrogen ion in a CSTR. Calculations were carried out on the base of the model shown in Table 1 using rate constants as follows: $k_1 = 1.0 \times 10^{10}$ $M^{-1}\,s^{-1}$; $k_{-1} = 1.0 \times 10^3$ s^{-1}; $k_2 = 6.0 \times 10^9$ $M^{-1}\,s^{-1}$; $k_{-2} = 1.0 \times 10^8$ s^{-1}; $k_3 = 0.0653$ $M^{-1}\,s^{-1}$; $k_4 = 18.0$ $M^{-1}\,s^{-1}$; $k_8 = 0.70$ $M^{-1}\,s^{-1}$. Input concentrations both in the measurements and in the calculations: $[SO_3^{2-}]_0 = 0.050$ M; $[BrO_3^-]_0 = 0.050$ M; $[H^+]_0 = 0.0025$ M. k_0 (reciprocal residence time) = 1.38×10^{-4} s^{-1}. Measurement was carried out at 35.0 °C. Period length exceeds 2 h. Observe the excellent agreement between the calculated and measured curves.

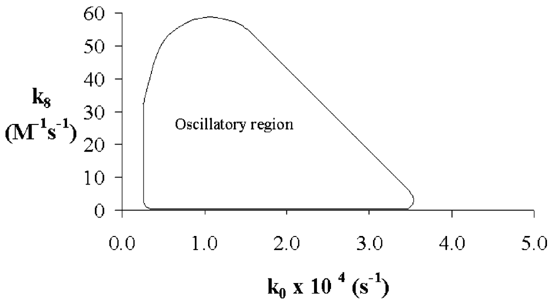

Figure 2. Calculated state diagram in the $k_0{-}k_8$ plane. Region of oscillations is bordered by the line. Calculations are based on the model shown in Table 1. Fixed input concentrations are $[BrO_3^-]_0 = 0.05$ M; $[SO_3^{2-}]_0 = 0.05$ M; $[H^+]_0 = 0.0025$ M.

Shown in Figure 4 is a typical cross-shaped state diagram obtained in the $[H^+]_0$ versus flow rate plane. Here, we have fixed the temperature at 35.0 °C, and the values of $[BrO_3^-]_0 = 0.05$ M and $[SO_3^{2-}]_0 = 0.050$ M. It is seen that oscillations are found in a narrow range of the input hydrogen ion concentration. On the opposite side of the oscillatory region, bistability is measured. Good agreement can be seen between the calculated and measured behavior.

Effect of Temperature on the Period Length. An important question is whether the period length of this oscillatory reaction can be independent of temperature; in other words, whether it can show temperature compensation. Temperature compensation is well-known in some biological rhythms, but it is an exceptional phenomenon in chemical oscillators. Our systematic search revealed that the bromate−sulfite reaction does not show temperature compensation under the conditions where oscillations could be observed. The reaction shows clock-reaction behavior in a batch reactor: The pH drops suddenly after a lag period. The length of this lag period decreases with increasing temperature, as shown in Figure 5. Similarly, the period length

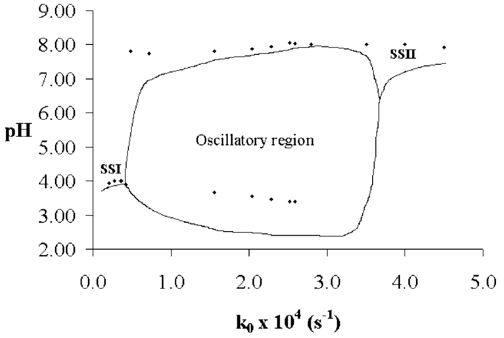

Figure 3. Calculated (solid line) and measured (points) low-pH steady states (SSI) at low flow rates, high-pH steady states at high flow rates, and oscillations between in a CSTR at 35.0 °C in the bromate−sulfite reaction. Lower and upper borders of the oscillatory region represent the minimum and maximum values of the pH in an oscillatory period, respectively. Rate laws and rate constant values used in the calculations are shown in Table 1; input concentrations are listed in Figure 1.

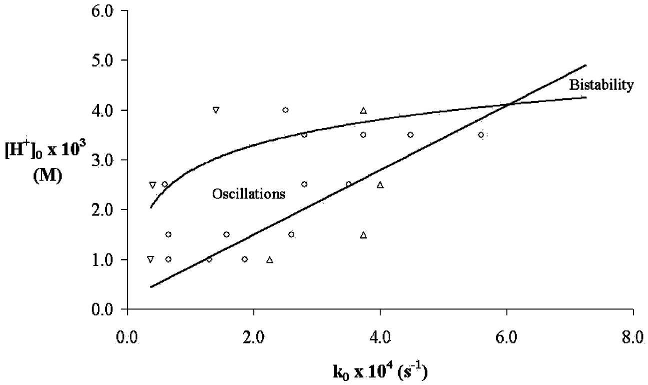

Figure 4. Cross-shaped state diagram in the k_0−[H$^+$]$_0$ plane. Oscillations can be calculated in the region bordered by the solid line. On the opposite side of the oscillatory region, bistability can be calculated between the two solid lines. Open circles indicate measured oscillations; open triangles indicate measured stable states. Fixed parameters: $[SO_3^{2-}]_0 = 0.050$ M; $[BrO_3^-]_0 = 0.050$ M; $T = 35.0$ °C. Calculations were carried out by the model shown in Table 1.

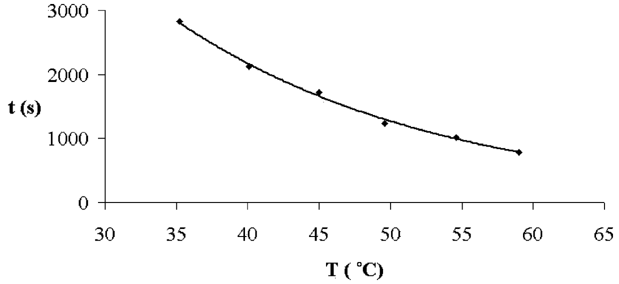

Figure 5. Measured Landolt time (t) as a function of temperature (T) in a batch reactor. $[SO_3^{2-}]_0 = 0.050$; $[BrO_3^-]_0 = 0.050$; $[H^+]_0 = 0.025$ M.

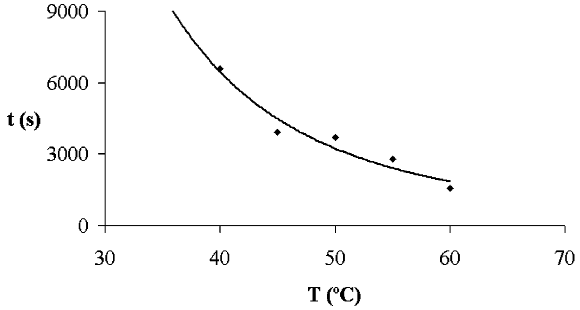

Figure 6. Measured period length (t) as a function of temperature (T). Input concentrations as in Figure 1. $k_0 = 1.38 \times 10^{-4}$ s^{-1}. Points indicate the measured values; the line is a fitted curve.

of oscillations also decreases with increasing temperature, as shown in Figure 6. On the basis of these temperature dependences, an apparent activation energy, characteristic of the reaction rate in the closed system, $E_a = 44.5$ kJ mol^{-1} could be determined by plotting the logarithm of the reciprocal Landolt time against $^1/_T$. With the reciprocal period length of the oscillations, the value of $E_a = 55.4$ kJ mol^{-1} was obtained for the apparent activation energy of the oscillations. Such values of E_a suggest an usual temperature dependence for both the composite reactions and the oscillatory system. The difference in the two activation energies indicates that the Landolt-type reaction leading to the formation of the sulfate ions is not the only important composite reaction of this system. Reaction 8 contributes to the temperature dependence as well. Both the low pH stage and the high pH stage of an oscillatory period become shorter with increasing temperature, indicating that temperature compensation is not expected in this reaction.

Conclusion

We observed large-amplitude regular pH oscillations in the bromate−sulfur (IV) reaction in a CSTR in the absence of any additional reagent. Oscillatory behavior in the absence of additional reagent is an important new feature of this reaction which has not been recognized before. We think that the mechanism of the oscillation in this system is simpler than that of the systems containing, for example, the ferrocyanide ions or marble, in addition to the bromate and sulfite. This reaction seems to be the simplest sulfur-based oscillator, because sulfur (IV) is oxidized here to sulfur (V) and sulfur (VI) simultaneously by the same oxidizing reagent. Oxidation to sulfur (V) is accompanied by consumption of hydrogen ions, while oxidation to sulfur (VI) produces hydrogen ions in an autocatalytic manner. In such a way, both composite reactions necessary for a pH oscillator are present in the system. The formation of sulfur (V) has previously been considered in an oscillatory system of bromate−sulfite−permanganate, but the permanganate ion was thought to be responsible for the formation of sulfur (V) in that work.

It is known that traveling fronts and jumping fronts can be observed in the bromate−sulfite reaction[20] if the solution is not stirred. Presently, there is no satisfactory model for describing these phenomena. It remains to be seen whether traveling and jumping fronts can be simulated by the model presented here.

We suspect that formation of the relatively stable $S_2O_6^{2-}$ species along with the main product SO_4^{2-} plays a significant role in the rich, exotic dynamical behavior of the reaction in other instances of the oxidation of sulfur (IV). For example, the H_2O_2 oxidation of HSO_3^- is known to be an important composite reaction of several pH oscillators.[1,21−23] Frerichs and Thomson[24] reported that the presence of a very small amount of carbonate impurities in the sulfite source, or even the atmospheric carbon dioxide entering the solution, may cause the sulfur (IV)−hydrogen peroxide reaction to oscillate in a CSTR. In light of our findings presented here, we suggest that the formation of $S_2O_6^{2-}$ rather than the CO_2 impurities might be the source of the negative feedback necessary for the oscillations to occur in that system.

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References and Notes

(1) Rábai, Gy.; Orbán, M.; Epstein, I. R. *Acc. Chem. Res.* **1990**, *23*, 258.
(2) Rábai, Gy. *ACH − Models Chem.* **1998**, *135*, 381.
(3) Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1985**, *107*, 2302.
(4) Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 101.
(5) Edblom, E. C.; Luo, Y.; Orbán, M.; Kustin, K.; Epstein, I. R. *J. Phys. Chem.* **1989**, *93*, 2722.
(6) Rábai, Gy.; Hanazaki, I. *J. Phys. Chem.* **1996**, *100*, 10615.
(7) Okazaki, N.; Rábai, Gy.; Hanazaki, I. *J. Phys. Chem. A* **1999**, *103*, 10915.
(8) Williamson, F. S.; King, E. L. *J. Am. Chem. Soc.* **1957**, *79*, 5397.
(9) Hanazaki, I.; Rábai, Gy. *J. Chem. Phys.* **1996**, *105*, 9912.
(10) Rábai, Gy.; Kaminaga, A.; Hanazaki, I. *J. Phys. Chem.* **1996**, *100*, 16441.
(11) Zagora, J.; Voslaø, M.; Schreiberova, L.; Schreiber, I. *Faraday Discuss.* **2001**, *120*, 313.
(12) Zagora, J.; Voslaø, M.; Schreiberova, L.; Schreiber, I. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1284.
(13) Pešek, O.; Kašpar, P.; Schreiberova, L.; Schreiber, I. *J. Phys. Chem. A* **2004**, *108*, 2436.
(14) Kaminaga, A.; Rábai, Gy.; Mori, Y.; Hanazaki, I. *J. Phys. Chem.* **1996**, *100*, 9389.
(15) Crook, C. J.; Smith, A.; Jones, R. A. L.; Ryan, A. J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1367.

(16) Rábai, Gy.; Epstein, I. R. *Inorg. Chem.* **1989**, *28*, 732.

(17) Kaps, P.; Rentrop, P. *Numer. Math.* **1979**, *33*, 55.

(18) Higginson, W. C. E.; Marshall, J. W. *J. Chem. Soc.* **1957**, 447.

(19) Yoshida, R.; Ichijo, H.; Hakuta, T.; Yamaguchi, T. *Macromol. Rapid Commun.* **1995**, *16*, 305.

(20) Keresztessy, A.; Nagy, I. P.; Bazsa, Gy.; Pojman, J. A. *J. Phys. Chem.* **1995**, *99*, 5379.

(21) Rábai, Gy. *J. Phys. Chem. A* **1997**, *101*, 7085.

(22) Rábai, Gy.; Hanazaki, I. *J. Phys. Chem. A* **1999**, *103*, 7268.

(23) Straube, R.; Müller, S. C.; Hauser, M. J. B. *Z. Phys. Chem.* **2003**, *217*, 1427.

(24) Frerichs, G. A.; Thompson, R. C. *J. Phys. Chem. A* **1998**, *102*, 8142.