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Sustained and Damped pH Oscillation in the Periodate–Thiosulfate Reaction in a Continuous-Flow Stirred Tank Reactor[1]

Gyula Râbai,[2a,b] Mihâly T. Beck,[2a] Kenneth Kustin,[2b] and Irving R. Epstein*,[2b]

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254, and Institute of Physical Chemistry, Kossuth Lajos University, Debrecen, Hungary

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The reaction between IO_4^- and $S_2O_3^{2-}$ exhibits a variable stoichiometry in acetate buffer. With a large excess of IO_4^-, the products are IO_3^- and SO_4^{2-}. In excess thiosulfate, IO_4^- is reduced to I^-, and $S_4O_6^{2-}$ is formed in addition to SO_4^{2-}. The ratio of $S_4O_6^{2-}$ to SO_4^{2-} increases with decreasing pH. In a flow reactor at high input concentrations, when the flow rate or temperature is changed or small amounts of a reactant are injected, an unbuffered reaction mixture initially in a steady state shows a strongly damped oscillatory response in pH and redox potential. At lower input concentrations, sustained pH oscillation is found. A simple model, consisting of an autocatalytic hydrogen ion production and a linear H^+ consumption, allows accurate simulation of all of these kinetic behaviors.

Introduction

Systematic measurement of the hydrogen ion concentration has played an integral role in the discovery and analysis of a number of oligooscillatory and oscillatory reactions.[3,4] In addition to the large-amplitude pH oscillations found in several reactions[5-10] in a continuous-flow stirred tank reactor (CSTR), Râbai and Beck[11] have observed a strongly damped oscillatory pH change in a closed system of iodate, thiosulfate, and sulfite ions. They were able to simulate this behavior using the known overall empirical rate laws of the iodate–sulfite and iodate–thiosulfate reactions, taking into account the catalytic effect of thiosulfate on the oxidation of sulfite and the inhibitory effect of sulfite on the oxidation of thiosulfate.

The partial regeneration of sulfite by the oxidation of thiosulfate is an essential feature of the IO_3^-–$S_2O_3^{2-}$–SO_3^{2-} reaction, which makes possible the oscillation in a closed system. The empirical rate law model shows an alternation between autocatalytic formation and quadratic consumption of hydrogen ion. The name "Alternator" has been suggested for a simplified model of this general class of chemical oscillators.[11] The Alternator resembles Lotka's first model[12] but is more realistic chemically. Oscillatory reactions of this type can be designed on the basis of Alternator. Such an oscillator requires three chemical reactions, one which produces hydrogen ion autocatalytically, a second to consume $[H^+]$, and a third that regenerates the reactant from which the hydrogen ion forms. In a CSTR, the third component process can be replaced by the input flow.

Thiosulfate is a promising reducing agent for designing pH oscillators of this type, because it can be oxidized both to sulfate, which produces hydrogen ion, usually autocatalytically, and to tetrathionate, which consumes hydrogen ion. The oxidations of thiosulfate by hydrogen peroxide[7] and by iodate[8] show pH oscillation in a CSTR.

We report here on a study of the oxidation of thiosulfate by periodate under both batch and flow conditions. We do indeed find sustained oscillations under some conditions in the CSTR. In addition, under a wide range of conditions when the system in the CSTR is in a steady state a temporary perturbation results in a large-amplitude damped pH oscillation. If a permanent change is made in one of the constraints, for example, flow rate or temperature, the system reaches a new steady state only after a fairly lengthy transient period of damped oscillation.

Such damped oscillatory behavior in a CSTR is rare. Only two experimental examples of damped chemical oscillation in a CSTR have been reported.[13,14] No model has yet been proposed to describe this behavior. We suggest here both an empirical rate law model and a simplified model that give rise to the behavior found in our experiments.

The kinetics and stoichiometry of the periodate oxidation of thiosulfate have not been investigated previously, though an analytical method for the determination of thiosulfate with periodate has been suggested.[15] We report on our findings of the rather complex stoichiometry of the reaction as well as on the kinetic behavior.

Experimental Section

Materials. The following analytical grade chemicals were used without further purification: potassium metaperiodate (Baker), iodine (Merck), potassium iodate, potassium iodide, sodium thiosulfate, acetic acid, sodium acetate, and sodium hydroxide (all Fisher). Iodide- and iodine-free potassium tetrathionate were prepared by the method of Schmidt and Sand.[16] Stock solutions were made with doubly distilled water, and their concentrations were checked by standard iodo- and iodimetric methods. The periodate solution was protected from light during storage.

Analytical Procedures. The reaction of periodate with manganous ion was used to detect periodate in acidic solution[17]

$$2Mn^{2+} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5IO_3^- + 6H^+$$

A brown-pink color is observed in the presence of periodate. Iodate does not interfere with the test. Detection of sulfate ion by precipitation with barium chloride in a solution containing periodate ion is complicated by the precipitation of barium periodate. Therefore, this method was used only when the periodate test was negative. In the case of a positive test, the periodate was first reduced with iodide. The formation of iodine was indicated by its characteristic yellow color.

The stoichiometric experiments were made at reagent concentrations and pH's similar to the initial conditions of the kinetics runs. In contrast to the kinetics runs, the stoichiometric inves-

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TABLE I: Stoichiometric Ratio ($\Delta[S_2O_3^{2-}]/[IO_4^-]_0$) in the Periodate–Thiosulfate Reaction in Excess Thiosulfate[a]

	pH				
$[S_2O_3^{2-}]_0$, M	4.27	4.73	5.17	5.65	5.92
0.0619	7.45	7.425	6.65	4.95	2.90
0.0413	7.50	7.425	6.67	5.01	3.15
0.0206	7.41	7.405	6.675	5.00	3.05
0.0165	6.99	6.985	6.65	5.00	3.10
0.0123	*b*	*b*	*b*	4.98	3.10
0.0083	*b*	*b*	*b*	3.99	3.05

[a] $[IO_4^-]_0$ = 0.0020 M, T = 25 °C, pH maintained with acetate buffer. [b] All $S_2O_3^{2-}$ consumed.

tigations were carried out at a constant pH maintained by a sodium acetate–acetic acid buffer. The unreacted thiosulfate in the case of excess $S_2O_3^{2-}$, and the remaining oxidizing capacity in the case of excess periodate, were determined iodimetrically with starch as indicator.

Kinetics Experiments. In a closed system the reactions were initiated by injecting sodium thiosulfate stock solution into a thermostated reaction mixture containing potassium periodate. The reaction was followed by continuous monitoring of pH and sometimes the redox potential as well. The pH was measured with a combined glass–standard calomel electrode (SCE). The redox potential was determined with a bright Pt electrode and a SCE reference.

The flow experiments were carried out in a thermostated glass CSTR of volume 24.2 cm^3. The reactor was fed by a Sage Model 375A peristaltic pump through two inlet tubes (i.d. 2.5 mm). The flow rate [k_0 = (inflow volume per second)/(reactor volume)] could be varied continuously. The reactor was equipped with a magnetic stirrer. No stirring rate effect on the reaction rate was observed up to 700 rpm. All kinetics runs were done at 25 °C in a thermostated reaction vessel. To avoid the effects of oxygen and carbon dioxide, all pH measurements were performed under argon.

Results and Discussion

Experiments in a Closed System. It is important to determine which parts of this complex reaction play major roles in the peculiar kinetic phenomena found in our flow experiments. To investigate this question, we carried out a series of experiments in a closed system.

1. Stoichiometric Investigations. The stoichiometry of the reaction of thiosulfate with oxidizing agents usually depends on the ratio of initial concentrations of reactants and on the pH of the reaction mixture. In excess thiosulfate, the main product of the oxidations is tetrathionate ion, but some sulfate can also be detected.[18,19] We find that in the periodate oxidation of thiosulfate more sulfate forms than has been observed with other oxidants.

a. Stoichiometry in Excess Thiosulfate. As the data in Table I show, in a thiosulfate excess of about (5–30):1, the ratio of thiosulfate consumed to initial periodate ($\Delta[S_2O_3^{2-}]/[IO_4^-]_0$) does not change significantly with the initial concentration of thiosulfate, but it does decrease markedly with increasing pH.

The only iodine-containing species found at the conclusion of the reaction was I^-. Sulfate ions were detected even at the highest initial thiosulfate concentrations and the lowest pH values used in our experiments.

The above findings imply that there must be two limiting stoichiometries in excess thiosulfate:

$$IO_4^- + S_2O_3^{2-} + H_2O \rightarrow 2SO_4^{2-} + I^- + 2H^+ \qquad (1)$$

$$IO_4^- + 8S_2O_3^{2-} + 8H^+ \rightarrow 4S_4O_6^{2-} + I^- + 4H_2O \qquad (2)$$

At lower pH the reaction proceeds mainly according to eq 2, but we cannot decrease the pH to reach the limit of $\Delta[S_2O_3^{2-}]/[IO_4^-]_0$ = 8, where there is no contribution from (1), because of the acid-catalyzed decomposition of thiosulfate. If the pH is increased, the role of process 1 increases, and the $\Delta[S_2O_3^{2-}]/[IO_4^-]_0$ values decrease.

TABLE II: Stoichiometry of the Periodate–Thiosulfate Reaction in Excess Periodate[a]

$[IO_4^-]_0 \times 10^3$, M	oxidizing capacity × 100			Δ(*oxidizing capacity*) × 100	
		final			
	initial	pH = 4.27	pH = 5.92	pH = 4.27	pH = 5.92
8.00	64	60.10	59.95	3.90	4.05
6.00	48	44.05	44.15	3.95	3.85
4.00	32	28.15	28.15	3.85	3.85
2.00	16	12.25	12.20	3.75	3.80
1.00	8	5.65	5.40	2.35	2.60
0.50	4	2.45	2.10	1.55	1.90

[a] $[S_2O_3^{2-}]_0 = 5.0 \times 10^{-4}$ M; T = 25 °C; pH was adjusted with 0.1 M acetate buffer. The initial oxidation capacity was calculated and checked experimentally; the final one was determined by iodimetric titration. After the reaction was completed (10–15 h), excess KI was added to 10.0 mL of reaction mixture, acidified with acetic acid, and then titrated with 0.0100 M sodium thiosulfate solution. The volume (milliliters) of $Na_2S_2O_3$ solution consumed gives the (oxidizing capacity) × 100. The same values were also found at pH = 4.73, 5.17, and 5.65.

b. Stoichiometry in Excess Periodate. If the periodate is in at least 4-fold excess, all the thiosulfate is oxidized to sulfate, and only iodate can be identified as the reduction product of periodate. After the reaction was completed, some periodate was detected by the periodate–manganese(II) reaction. In this case the stoichiometry is clear:

$$4IO_4^- + S_2O_3^{2-} + H_2O \rightarrow 2SO_4^{2-} + 4IO_3^- + 2H^+ \qquad (3)$$

This stoichiometry was determined by measuring the change in the oxidizing capacity of the reaction mixture by adding potassium iodide and acetic acid to the mixture after the reaction was completed. The iodine formed was then titrated with thiosulfate (Table II). The first four lines of Table II show that the change in oxidizing capacity found corresponds to the oxidation of all of the thiosulfate to sulfate.

If the excess of periodate is less than 4-fold, the change in oxidizing capacity of the reaction system does not reach the value of 4 expected from eq 3 (last two lines of Table II). This observation indicates that a portion of the thiosulfate is oxidized to tetrathionate. Iodate ion, iodide ion, and a very small amount of elementary iodine can then be detected as the reduction products of periodate. No periodate remains at the end of the reaction. The mixed stoichiometry can be generated by considering reactions 3–6.

$$IO_3^- + 6S_2O_3^{2-} + 6H^+ \rightarrow 3S_4O_6^{2-} + 3H_2O + I^- \qquad (4)$$

$$IO_4^- + 2I^- + 2H^+ \rightarrow IO_3^- + I_2 + H_2O \qquad (5)$$

$$4IO_3^- + 3S_2O_3^{2-} + 3H_2O \rightarrow 6SO_4^{2-} + 4I^- + 6H^+ \qquad (6)$$

The stoichiometric significance of (6) is small, but it has a major kinetic role in the chemical oscillation of the thiosulfate–sulfite–iodate reaction in a closed system.[11] The iodate–iodide (Dushman) reaction (7) is negligible if the pH of the reaction mixture is high (pH > 4) and the iodide ion concentration is low ($[I^-] < 1 \times 10^{-4}$ M).

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (7)$$

2. Kinetic pH Measurements. The reaction shows oligooscillatory behavior in a closed system. The shape of the pH–time curves depends on the initial concentrations and on their ratios. With a large excess of periodate (Figure 1, curve a), the pH exhibits two large extrema as a function of time. If periodate is in somewhat smaller excess, $[IO_4^-]/[S_2O_3^{2-}] < 5$ (Figure 1, curve b), the last decrease in pH appears to be autocatalytic. The reaction mixture turns yellow at the pH maximum, indicating formation of elementary iodine. When thiosulfate is in excess (Figure 1, curve c), the last pH decrease is much smaller, and no yellow color is seen during the reaction.

These observations can be explained in the following way. At the beginning of the reaction only thiosulfate and periodate are

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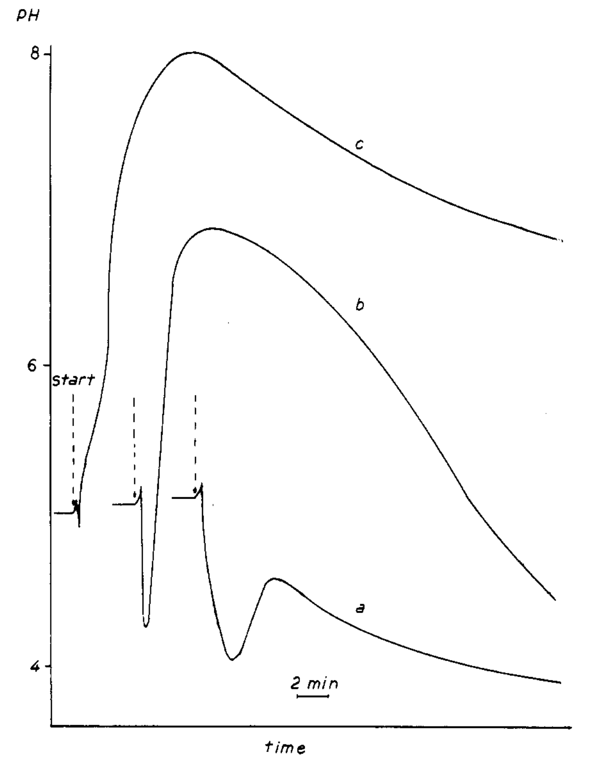

Figure 1. Measured pH–time curves in a closed periodate–thiosulfate system. $[IO_4^-]_0 = 5 \times 10^{-3}$ M. $[S_2O_3^{2-}]_0 = 5 \times 10^{-4}$ M (a), 1×10^{-3} M (b), and 1×10^{-2} M (c). $T = 25$ °C.

present, and the pH of the reaction mixture is about 5. Under these conditions reaction 3 dominates, resulting in an increase in $[H^+]$. As H^+ and IO_3^- are produced, the rate of reaction 4 rapidly increases. This latter reaction consumes H^+, so that at the minimum of pH the rate of reaction 4 just compensates the rate of reaction 3.

In the second stage of the reaction, process 4 becomes dominant, and the consumption of hydrogen ion exceeds its production, causing $[H^+]$ to decrease. In this stage of the reaction, all the thiosulfate is consumed, as can be seen from the appearance of a small amount of elementary iodine, produced by reaction 5, at the maximum in pH. Iodine cannot appear in the presence of thiosulfate, because of their well-known fast reaction.

In the third stage of the reaction, the tetrathionate formed in reaction 4 reacts with excess periodate, yielding sulfate and hydrogen ion:

$$7IO_4^- + S_4O_6^{2-} + 3H_2O \rightarrow 4SO_4^{2-} + 7IO_3^- + 6H^+ \quad (8)$$

Separate experiments showed that reaction 8 between tetrathionate and periodate results in an autocatalytic pH–time curve similar to that found in the third phase of the periodate–thiosulfate reaction. While not extremely slow, the pH decrease observed in reaction 8 is much slower than that seen in the third phase of the IO_4^-–$S_2O_3^{2-}$ reaction. However, in this phase of the latter reaction a small amount of I_2 is present. As shown in Figure 2, elementary iodine has a strong catalytic effect on the tetrathionate–periodate reaction. Adding a small amount of I_2 to a tetrathionate–periodate mixture results in a reaction rate comparable to that measured in the third stage of the sulfate–periodate reaction. Previous studies have shown that there is no measurable reaction between iodate and tetrathionate,[11] and we find (Figure 2) that iodine has no noticeable catalytic effect on the iodate–tetrathionate reaction.

In a high excess of thiosulfate, the third phase of the reaction does not take place, because no periodate remains to react with the tetrathionate. Therefore, the pH does not decrease significantly.

In all our batch kinetic experiments we observed a small, very fast pH increase at the start of the reaction (Figure 1). At much lower initial concentrations (Figure 3), this initial pH increase was found to be larger, suggesting that it results from a chemical reaction rather than from mixing effects. A rapid H^+-mediated preequilibrium between iodate and thiosulfate has been proposed to occur in that reaction,[11] and we suggest that in the case of periodate a similar equilibrium takes place preceding the redox processes. Reaction M1 is responsible for the first, very fast increase in pH.

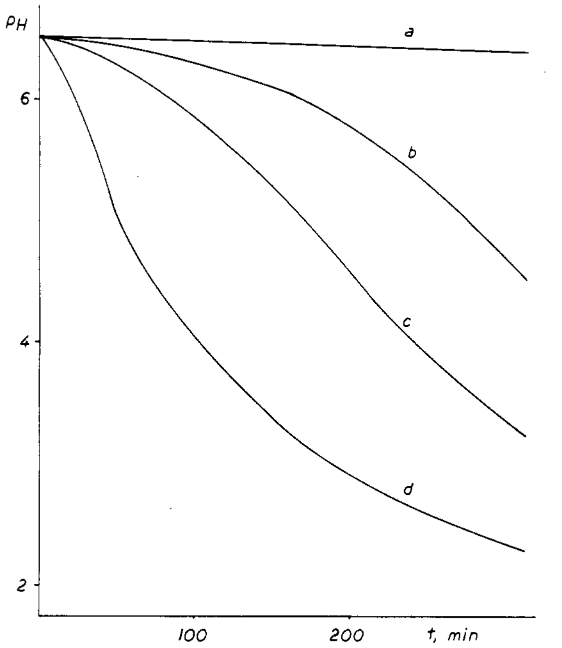

Figure 2. pH change during the oxidation of tetrathionate ($[S_4O_6^{2-}]_0 = 2 \times 10^{-3}$ M) by periodate and iodate. (a) $[IO_3^-]_0 = 5 \times 10^{-3}$ M, $[I_2]_0 = 5 \times 10^{-6}$ M; (b) $[IO_4^-]_0 = 5 \times 10^{-3}$ M; (c) $[IO_4^-]_0 = 5 \times 10^{-3}$ M, $[I_2] = 1 \times 10^{-6}$ M; (d) $[IO_4^-]_0 = 5 \times 10^{-3}$ M, $[I_2]_0 = 5 \times 10^{-6}$ M. $T = 25$ °C.

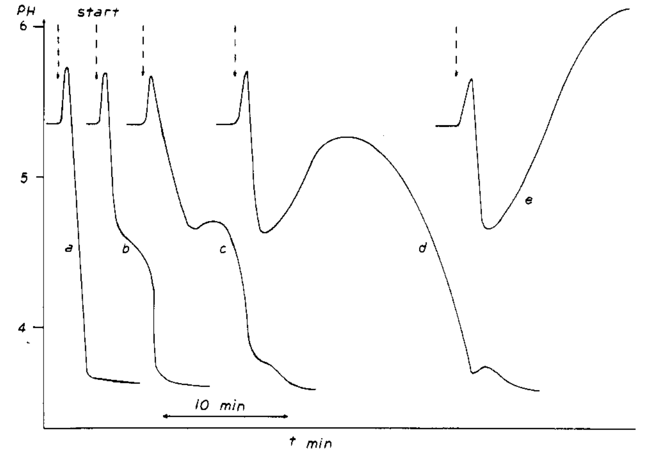

Figure 3. pH–time curves in a closed periodate–thiosulfate system at low initial concentrations. $[IO_4^-]_0 = 5 \times 10^{-4}$ M. $[S_2O_3^{2-}]_0 = 2.5 \times 10^{-4}$ M (a), 6.0×10^{-4} M (b), 7.0×10^{-4} M (c), 8.0×10^{-4} M (d), and 10×10^{-4} M (e). $T = 25$ °C.

$$IO_4^- + S_2O_3^{2-} + 2H^+ \rightleftharpoons H_2IO_4S_2O_3^- \quad (M1)$$

At low initial concentrations under some conditions a further maximum in pH appears at the end of the reaction (Figure 3, curve d). Although this last maximum appears to be small, the pH is about 3.6, so that the change in $[H^+]$ is actually as large as at the previous maximum. At this low pH value the Dushman reaction (7) is fast enough to consume hydrogen ion and to produce elementary iodine. The final pH decrease is probably due to the slow iodine–tetrathionate reaction (9).[20] Of course, there are

$$S_4O_6^{2-} + 7I_2 + 10H_2O \rightarrow 4SO_4^{2-} + 14I^- + 20H^+ \quad (9)$$

many other interactions between the intermediates of these com-

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[20] Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4548.

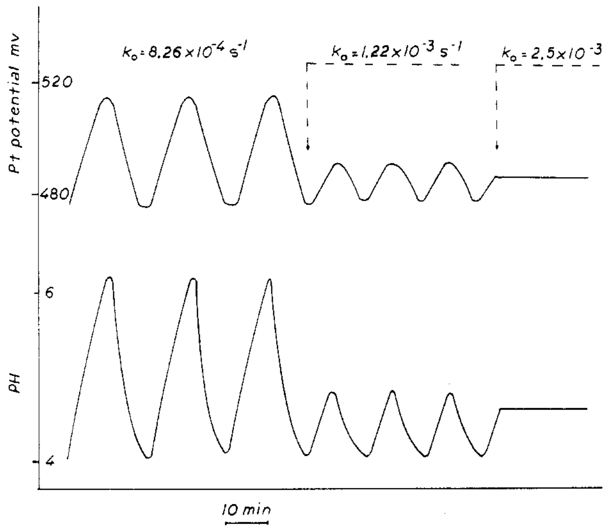

Figure 4. Sustained pH and redox potential oscillations in a CSTR. Input concentrations: $[IO_4^-]_0 = 5 \times 10^{-4}$ M, $[S_2O_3^{2-}]_0 = 6 \times 10^{-4}$ M. $T = 25$ °C.

TABLE III: Dynamical Behavior of the Periodate–Thiosulfate System in a CSTR

input concentrations, M		flow rate, s^{-1}	oscillation	
$[IO_4^-] \times 10^{-3}$	$[S_2O_3^{2-}] \times 10^{-3}$	$k_0 \times 10^{-3}$	damped	sustained
6.67	6.67	0.7–3.8	no	no
6.67	0.60–5.0	0.7–2.1	yes	no
3.33	2.90–10.0	0.7–3.8	no	no
3.33	0.33–2.80	0.7–2.1	yes	no
3.33	0.33–2.80	2.1–3.8	no	no
0.50	0.10–0.29	0.4–5.0	no	no
0.50	0.30–0.50	0.4–2.5	yes	no
0.50	0.60	0.4–1.4	no	yes
0.50	0.60	1.7–5.0	no	no
0.50	0.80	0.4–5.0	no	no

ponent reactions. The system is so complex that we are unable to simulate quantitatively its kinetic behavior at present.

Experiments under Flow Conditions. 1. Sustained Oscillations. Figure 4 shows sustained oscillations in both pH and redox potential when the reaction is run in the CSTR at relatively low input concentrations. Although we searched for bistability both between steady states and between the steady and the oscillatory states, none was found in the range of input concentrations and flow rates listed in Table III.

2. *Damped Oscillations.* At somewhat higher input concentrations in the CSTR the system reaches and remains in a well-characterized steady state after an initial transient period. This steady state can be disturbed by several kinds of perturbations:

a. *Variation of Flow Rate.* If the flow rate is increased or decreased, the reaction system reaches a new steady state corresponding to the new flow rate via a strongly damped pH oscillation. During this oscillation, the pH change can be as large as 1 unit (Figure 5).

b. *Injection of Reactants.* If the system in a steady state is perturbed by injection of a small amount of one of the reactants into the CSTR, a related phenomenon can be observed: the system shows a damped pH oscillation and then returns to the original steady state because the perturbation is temporary and the steady state is globally stable. Thiosulfate produces a much greater effect than does addition of the same amount of periodate (Figure 6).

c. *Variation of Temperature.* As shown in Figure 6, changing the temperature also produces a damped oscillation.

This surprising behavior, which is also seen in the redox potential, occurs over a range of about 1 order of magnitude in the input concentrations and nearly as much in the flow rates (Table III).

A Qualitative Explanation for the Behavior under Flow Conditions. As discussed above, the reaction in a closed system consists of three stages. Our experiments show that in the CSTR the third phase, which is the most complicated part of the reaction, takes place only after the flow is stopped. We can therefore conclude that only the first (component reaction 3) and second (component reaction 4) phases of the reaction are of significance under flow conditions. The chemistry of the system thus appears to be simpler under flow conditions than in batch; i.e., we can neglect the third phase in attempting to describe the behavior found in a CSTR.

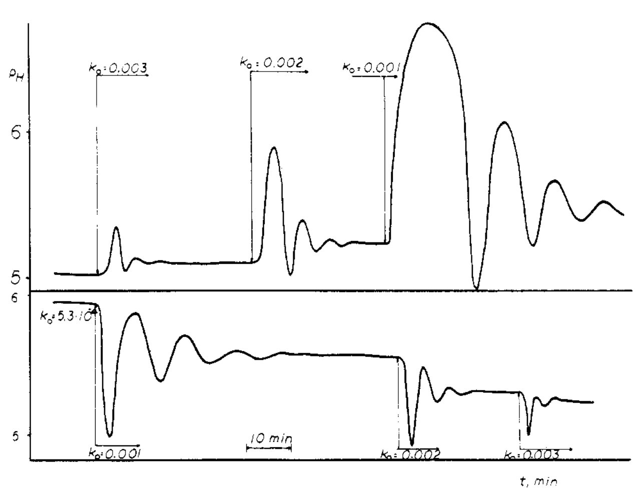

Figure 5. Oscillatory responses generated by change in flow rate. Input concentrations: $[IO_4^-]_0 = 6.67 \times 10^{-3}$ M, $[S_2O_3^{2-}]_0 = 2.0 \times 10^{-3}$ M. $T = 25$ °C.

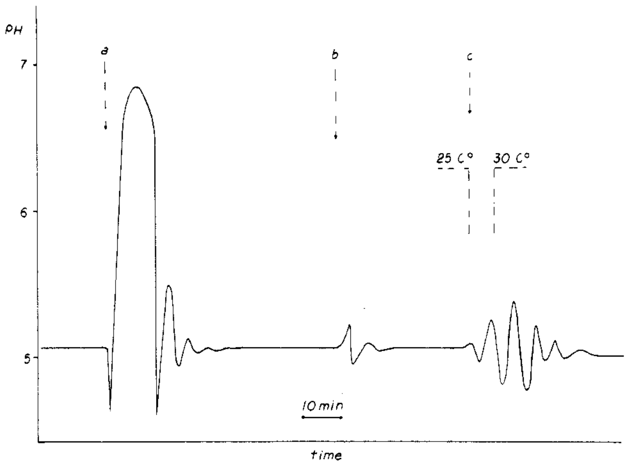

Figure 6. Oscillatory response generated in a CSTR initially in a steady state by injecting 0.1 mL of 0.1 M sodium thiosulfate (a) and 0.1 mL of 0.1 M sodium periodate (b) and by change in temperature (c). Input concentrations: $[IO_4^-]_0 = 6.67 \times 10^{-3}$ M, $[S_2O_3^{2-}]_0 = 2 \times 10^{-3}$ M.

Any steady state of this reaction in a CSTR must result from a balance between production (reaction 3) and consumption (reaction 4) of hydrogen ion. The hydrogen ion production in the periodate oxidation of thiosulfate to sulfate is expected to be autocatalytic in H^+. As $[H^+]$ increases, iodate ion forms in reaction 3, creating favorable conditions for the iodate oxidation of thiosulfate to tetrathionate, which consumes hydrogen ion in reaction 4. Eventually, a steady state develops in the flow system. If this steady state is perturbed in any way, the system can respond by either a monotonic or an oscillatory relaxation to the new steady state. A simple model suggests that, in the present system, processes 3 and 4 are sufficient to create an oscillatory response to perturbation. Our starting point is the Lotka model,[12] consisting of three elementary reactions.

$$A \rightarrow Y \qquad (L1)$$

$$X \rightarrow P \qquad (L2)$$

$$Y + X \rightarrow 2X \qquad (L3)$$

Reaction L1 can be replaced by an inflow of Y (thiosulfate or periodate) in a flow system. Species X is identified with the

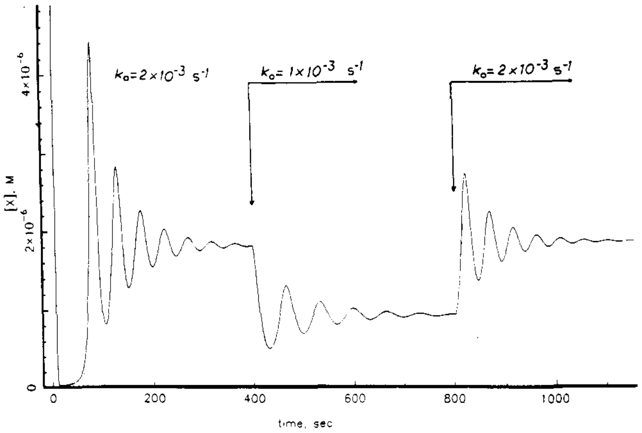

Figure 7. Oscillatory responses calculated from reactions L2 and L3 under flow conditions. $k_{L2} = 1$ s^{-1}, $k_{L3} = 1 \times 10^4$ M^{-1} s^{-1}; $Y_0 = 1 \times 10^{-3}$ M, $X_0 = 1 \times 10^{-5}$ M. The flow rate (k_0) was changed as indicated in the figure.

autocatalytically produced H$^+$, so step L2 corresponds to the consumption of hydrogen ion in process 4, while step L3 models its autocatalytic production in process 3. Calculations with this model show a damped oscillation in response to the types of perturbation used in the experiments on the periodate–thiosulfate reaction under flow conditions. As Figure 7 shows, the model flow system of Y and X reaches a stable steady state after a damped oscillatory transient stage. If this steady state is perturbed by changing the flow rate, the concentration of X undergoes damped oscillation before reaching its new steady-state value corresponding to the new flow rate. There is a qualitative similarity between the experimental observations in the real periodate–thiosulfate system (Figure 5) and this calculated behavior of the model.

The calculations also show damped oscillation when the concentration of X or Y is suddenly increased by a brief input to the system when it is at steady state. The perturbing effect of a change in temperature can be simulated by altering the rate constants, e.g., by increasing k_{L2} and k_{L3} to simulate a temperature increase. If we start in the steady state, this change creates a new steady state, which is approached by a damped oscillation.

The Empirical Rate Law Model. The empirical rate laws of the overall component reactions have been used successfully to describe the complex kinetic behavior of some oligooscillatory[21,22] and oscillatory[6] reactions. In the present case the two component reactions are periodate–thiosulfate and iodate–thiosulfate whose stoichiometries are given by eq 3 and 4. The rate law for 3 is not known. We postulate a simple expression autocatalytic in hydrogen ion:

$$v_3 = -\mathrm{d}[S_2O_3^{2-}]/\mathrm{d}t = k_3[IO_4^-][S_2O_3^{2-}][H^+]^2 \qquad (3')$$

The rate equation of reaction 4 has been determined, and the value of rate constant k_4 has been given.[8,23,24]

$$v_4 = -\mathrm{d}[IO_3^-]/\mathrm{d}t = k_4[IO_3^-][S_2O_3^{2-}]^2[H^+]^2 \qquad (4')$$

No other reactions or rate terms need be assumed in order to describe the main qualitative features of the damped oscillatory pH response generated by perturbation of the periodate–thiosulfate system. Figure 8 demonstrates how calculations based on these two empirical rate laws reflect the response of the system to changes in flow rate. If the flow rate is increased from $k_0 = 1 \times 10^{-3}$ s^{-1} to $k_0 = 2 \times 10^{-3}$ s^{-1} (Figure 8, point a), the damped oscillation starts with increasing [H$^+$], and the system reaches its new steady state corresponding to the new flow rate. If the flow rate is decreased back to the original value (Figure 8, point b), the damped oscillation in [H$^+$] shows a decreasing envelope, and the previous steady state will be reached. If the perturbation instead consists of a transient increase in the input concentration of one of the reactants (Figure 8, point c), the system again returns to its original state via a damped oscillatory response. The effect of changing the temperature was simulated by varying k_3 and k_4. The value of k_3 was increased by a factor of 2, while k_4 was increased by a factor of 1.5. These changes correspond to about a 5 °C increase in temperature. In this case, the system shows a new steady state that is approached by a strongly damped oscillation (Figure 8, point d).

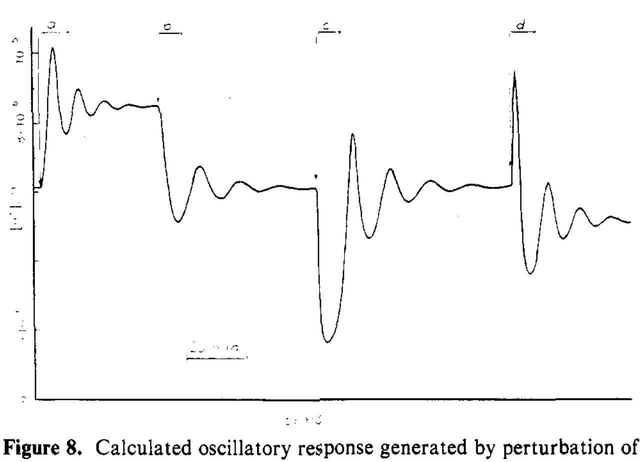

Figure 8. Calculated oscillatory response generated by perturbation of the periodate–thiosulfate reaction in a CSTR. Equations 3, 4, 3″, and 4′ were used with the following set of rate constants and input concentrations: $k_3 = 5 \times 10^7$ M^{-3} s^{-1}, $k_4 = 6 \times 10^{11}$ M^{-4} s^{-1}; $[IO_4^-]_0 = 6.67 \times 10^{-3}$ M, $[S_2O_3^{2-}]_0 = 2.0 \times 10^{-3}$ M, $[H^+]_0 = 4 \times 10^{-6}$ M. At point a the flow rate k_0 was increased from 1×10^{-3} to 2×10^{-3} s^{-1}. At b k_0 was decreased to 1×10^{-3} s^{-1}. At c the concentration of thiosulfate was increased with a short additional input to 4×10^{-3} M. At d the rate constants k_3 and k_4 were increased to 1×10^8 M^{-3} s^{-1} and 9×10^{11} M^{-4} s^{-1}, respectively.

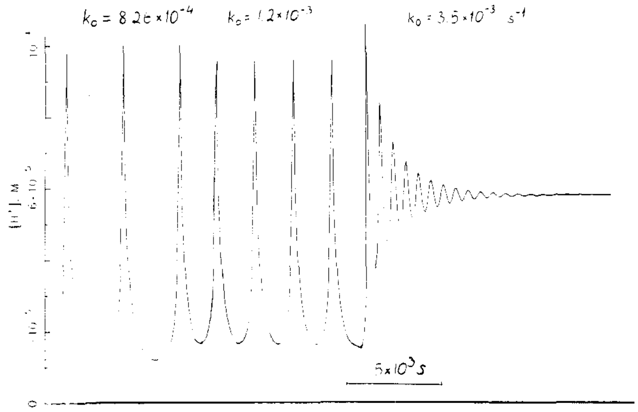

Figure 9. Calculated sustained oscillation at different flow rates. $k_3 = 5 \times 10^7$ M, $k_3' = 2 \times 10^{13}$ M^{-4} s^{-1}, $k_4 = 6 \times 10^{11}$ M^{-4} s^{-1}. $[IO_4^-]_0 = 5 \times 10^{-4}$ M, $[S_2O_3^{2-}]_0 = 5 \times 10^{-4}$ M, $[H^+]_0 = 1 \times 10^{-5}$ M.

The results of our simulations are only in qualitative agreement with the experiments shown in Figure 5. The calculated amplitudes are much smaller than those of the experiments, and the range of input concentrations under which the system shows the oscillatory response is broader in the calculations. These two simple empirical rate laws cannot reflect the sustained oscillation found at lower input concentrations. To describe the sustained oscillation, it is necessary to include an additional term in the rate law (3′).

$$v_3' = (k_3[H^+]^2 + k_3'[H^+]^3)[IO_4^-][S_2O_3^{2-}] \qquad (3'')$$

Using eq 3″ instead of eq 3′ with $k_3' = 1 \times 10^{13}$ M^{-4} s^{-1}, sustained oscillation is found at lower input concentrations as in the experiments (Figure 9).

Overall Dynamics. The above models are clearly oversimplifications of the full system. Nevertheless, they allow us to simulate, and afford some insight into, the key features of the dynamical

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behavior, i.e., the sustained oscillation and especially the damped oscillatory response to several types of perturbation of the steady state in a CSTR. While damped oscillation is relatively rare in the literature, there seems no reason why many more such systems should not exist. From a dynamical point of view, all that is required is that a steady state be a stable focus over a reasonably broad range of parameters and that the relaxation to that steady state be relatively slow compared with the period of oscillation about the focus. In mathematical terms we require that the absolute value of the real part of the least negative (complex pair of) eigenvalues of the Jacobian matrix evaluated at the steady state be small relative to the imaginary part. It seems likely that this condition will be fulfilled by many systems, particularly those, like the present one, in which a second-order autocatalytic production of a species like H^+ is balanced by a negative feedback in which the autocatalytic species is consumed by a product (here IO_3^-) of the autocatalytic process. A characterization of these processes in the periodate–thiosulfate reaction in terms of elementary steps must await further studies.

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Chaotic Forcing Generates Wrinkled Boundary[†]

Otto E. Rossler,[*,‡] John L. Hudson,[§] and Michael Klein[‡]

Institute for Physical and Theoretical Chemistry, University of Tubingen, 7400 Tubingen, West Germany, and Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22901

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A chaotic model reaction system is used to force a single-variable chemical switch. If one scans initial conditions in the x,y plane, where x is the initial forcing and y the initial state of the switch, a boundary of complex shape is obtained that looks a bit like a mountain range. Such a boundary has, apparently, not been seen before in a continuous system.

Introduction

New types of dynamical behavior sometimes arise out of familiar ingredients. For example, coupling a two-variable oscillator with a single-variable switch may result in chaos, as was demonstrated in a chemical context.[1,2] Therefore, it is a straightforward question to ask what happens when the hierarchy is continued, that is, when a three-variable chaos generator is coupled to a single-variable switch. Hereby the simplest case obviously is the one in which the switch is purely passively coupled (chaotic forcing).

In the following a preliminary study of a chemical system of this type will be presented that suggests that the generated boundary is of a Julia-boundary-like complexity.

Model System

The following system of—in part Michaelis–Menten type—chemical rate equations was used:

$$\begin{aligned} \dot{x} &= 22 + 2.2x - 4.4(y + z)x/(x + 0.01) \\ \dot{y} &= 1.2x - y \\ \dot{z} &= 14x - 140z/(z + 0.05) \\ \dot{w} &= 0.5w - (2 + a)w/(w + 0.05) - 0.1w^2 + ax \qquad (1) \end{aligned}$$

Here the first three variables refer to a chaos-generating reaction system that has been described in detail in ref 3. The regime generated at the rate constants chosen represents "spiral chaos" with "strong overlap".[3]

The fourth variable, w, is a "chemical switch". It is a bistable autocatalytic subsystem with a Michaelis–Menten type outflux. Note that the switch is purely passively forced (by x).

In the following, we choose exactly the same parameters and initial conditions (except for x_0, which is varied) as were used in ref 3. The initial condition for the added switch, w_0, will be varied along with x_0. (The numerical simulations involved a Runge–Kutta–Merson integration routine with variable step size (maximum step error 10^{-4}) as the only method. Every initial point in the x,w plane, with the resolution of pixels chosen, corresponds to a new trajectory calculated. Dependent on which attractor the trajectory turned out to go toward, at the criteria mentioned in the caption to Figure 1, the pixel in question was colored either white or black, and then the next pixel was chosen, and so forth.)

Zero-Coupling Case

The behavior of the system of eq 1 is easy to understand when the only coupling parameter, a, is equal to zero. In this case, the boundary between the "exploded" (upper stable steady state) and the "nonexploded" (lower stable steady state) attracting regime of w is a horizontal straight line in the x_0,w_0 plane. That is, all initial conditions of w *greater* than the unstable steady state explode irrespective of what initial value is chosen for the chaos generator, while all those that are *less* than the unstable steady state do not. This constant "threshold" which coincides with the unstable steady state of w can be considered as a "basin boundary".[8] Note that apart from x, the initial states of y and z could also have been included into consideration, so that the boundary in fact represents a three-dimensional manifold in four-space (a hyperplane). Consideration of the x,w plane will suffice in the present case, however. An excuse for one's being allowed to do so, even in the case of finite coupling, is provided by the strong dissipativity of the chaotic system used for the forcing.

While the boundary itself—at the numerical value of the unstable steady state of w—cannot be determined with infinite precision in general, even a very low resolution scanning of initial values in the x,w plane (with prospective exploding points rendered in white and the others black, say) gives one a fair indication of the boundary's appearance. Nevertheless it will be worth keeping

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[†] Paper dedicated to Dick Noyes on the occasion of his 70th birthday.

[*] To whom correspondence should be addressed.

[‡] Institute of Physical and Theoretical Chemistry, Auf der Morgenstelle 8, 7400 Tubingen, FRG.

[§] University of Virginia.

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