Appendix

Analysis of eq 6 reveals an extremely sensitive dependence of K_0 on d. For instance, the ionic radius of Cs_+ ($r \cong 1.7 \times 10^{-8}$ cm) is larger than that of K^+ ($r \cong 1.3 \times 10^{-8}$ cm) by about 0.4 Å. If d is increased from 2×10^{-8} to 2.4×10^{-8} cm, the value of K_0 decreases from 3×10^4 to 681 M^{-1} by keeping $\epsilon = \epsilon_{00} = 4.1$. This substantial change in K_0 would only partially account for the reported[2] K values ranging from $10^{11.14}$ M^{-1} for K^+ cryptate down to $10^{4.1}$ M^{-1} for Cs^+ cryptate.

Mei et al.[10] studied the variation of the ^{133}Cs chemical shift of the Cs^+ cryptate as a function of temperature in propylene carbonate solvent. Comparison with similar data obtained in dimethylformamide and acetone indicates that the chemical shift is no longer solvent dependent at low temperatures, where an inclusive complex predominates. At high temperatures the cation is only partially accommodated inside the cryptand cavity and is thus only partially insulated from solvent effects. For the scheme

$$Cs^+ + C222 \rightleftarrows Cs^+{\cdot}222C \text{ (exclusive)}$$

the values $\Delta H°_{12} = -8.6 \pm 0.4$ kcal mol^{-1} and $\Delta S°_{12} = -13.7 \pm 1.5$ cal mol^{-1} K^{-1} were reported. From these data it follows that at $T = 298$ K, $\Delta G°_{12} = -4.52 \pm 0.8$ kcal mol^{-1} and $K_{12} = (2.06 \pm 0.30) \times 10^3$ M^{-1}. For the scheme

$$Cs^+{\cdot}222C \text{ (exclusive)} \rightleftarrows Cs^+{\cdot}222C \text{ (inclusive)}$$

the values $\Delta H°_2 = -2.9 \pm 0.4$ kcal mol^{-1} and $\Delta S°_2 = -7.0 \pm 1.5$ mol^{-1} K^{-1} were reported,[10] yielding $\Delta G°_2 = -0.81 \pm 0.85$ kcal mol^{-1} and $K_2 = 3.9 \pm 8$ at $T = 298.2$ K.

Recalling that $K_{12} = K_0K_1$ in process 3 of the present text, it follows that if $K_0 = 681$ M^{-1}, $K_1 = 3.0$, and $K_2 \cong 4$, we have $K = K_0(1 + K_1 + K_1K_2) = 1.1 \times 10^4$, which is close to the experimental value[2] of $K = 1.3 \times 10^4$ M^{-1}. This would suggest that $K_1 = 3 > 1$ and $K_2 \cong 4 > 1$ rather than $K_1 \gg 1$ and $K_2 \gg 1$. Furthermore, the uncertainty in K_2 is quite large. The NMR work[10] shows that the contact versus exclusive and the exclusive versus inclusive species are of comparable concentrations for Cs^+ cryptate. Because of these considerations we have decided against analyzing the Cs^+ cryptate data with eq 7, 8, 10, and 11, which we felt were appropriate for K^+ cryptate and Rb^+ cryptate.

Registry No. $NaClO_4$, 7601-89-0; $KClO_4$, 7778-74-7; $RbClO_4$, 13510-42-4; $CsClO_4$, 13454-84-7; propylene carbonate, 108-32-7; kryptofix 222, 23978-09-8.

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Exotic Kinetic Phenomena and Their Chemical Explanation in the Iodate–Sulfite–Thiosulfate System

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An extremely sharp minimum has been found on the pH versus time curves in the iodate–sulfite–thiosulfate system in a limited range of initial concentrations of the reactants in a static system, while sustained oscillation in pH occurs in a CSTR. This system seems to be the simplest chemical oscillator that can be described by two empirical rate laws, one acid–base equilibrium, and the flow terms. For the extremely sharp change of pH the catalytic effect of thiosulfate on the iodate oxidation of sulfite and the inhibiting effect of sulfite on the oxidation of thiosulfate by iodate are responsible. No explanation could be offered for the extreme temperature sensitivity of the oscillatory behavior in the flow system.

Introduction

The peculiar kinetic behavior of the iodate–sulfite system, that is, that elementary iodine appears abruptly in the solution after a rather long time lag, was observed by Landolt.[1] The autocatalytic character of the reaction and the role of iodate–iodide reaction in it has been elucidated by Eggert and Scharnow's systematic studies.[2] The clock reactions then become popular lecture demonstrations. There is a revived interest for the iodate–sulfite reaction since a number of exotic kinetic phenomena are connected with this reaction.

It was observed that by perturbing the iodate–sulfite reaction, and a number of other clock reactions based on reduction of halogenates, with an appropriate reactant oligooscillatory systems can be obtained in which either the halide concentration[3-5] or hydrogen ion concentration[6] or both exhibit several extrema in time. The kinetics of these reactions could be quantitatively described based on the overall rate equations of the corresponding subsystems.

Recently, Edblom, Orbán, and Epstein[7] found that the iodate–sulfite system exhibits bistability in CSTR, and by perturbing the system with hexacyanoferrate(II) they discovered oscillatory behavior in pH. Gáspár and Showalter[8] could semiquantitatively describe the oscillatory reaction by taking into account the empirical rate laws of the corresponding subsystems and the flow terms.

Similar behavior was most recently observed by us[9] in the iodate–sulfite–thiourea system, in closed system oligooscillation, while in CSTR sustained oscillation in pH, iodide concentration, and the redox potential occurs. It could be quantitatively described by the way followed by Gáspár and Showalter. In this model the well-known reaction between iodate and iodide (Dushman reaction[10]) plays a key role. However, the rate of the Dushman

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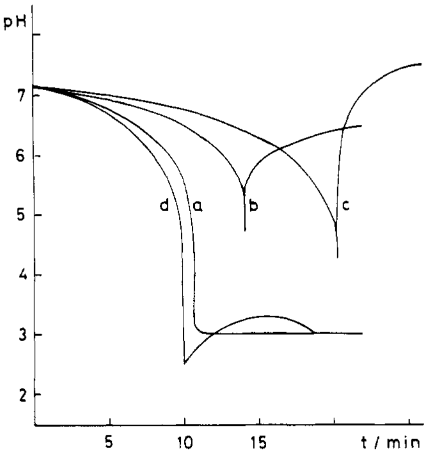

Figure 1. pH vs time curves in the iodate–sulfite–thiosulfite system. $[IO_3^-]_0 = 0.010$, $[SO_3^{2-}]_0 = 0.025$, $[S_2O_3^{2-}]_0 = 0.010$; $[H^+]_0 = 0.0105$ (a), 0.0095, (b), 0.008 (c). In case of curve d $[IO_3^-]_0 = 0.0125$, $[SO_3^{2-}]_0 = 0.025$, $[S_2O_3^{2-}]_0 = 0.010$, $[H^+]_0 = 0.0105$ M.

reaction is high enough only below pH 4, in comparison with the rate of the direct oxidation of hydrogen sulfite by iodate. We conjectured that if in a nonbuffered system, having an initial pH about 7, another reductant is present the oxidation of which results in an increase of pH, oscillatory behavior can be observed in pH without the formation and consumption of iodine, that is, without the significant contribution of Dushman reaction to the chemical events. Thiosulfate appeared as a proper perturbing agent since it is directly oxidized by iodate and simultaneously hydrogen ions are consumed. The experiments revealed that in CSTR oscillatory reaction occurs in the iodate–sulfite–thiosulfate system and that a unique sharp minimum of pH in time was found in a closed system. The chemical events could be described surprisingly simply.

Experimental Section

Reagent grade chemicals were used without further purification. Stock solutions of KIO_3, $Na_2S_2O_3$, H_2SO_4, and Na_2SO_3 were prepared with deoxygenated distilled water. The concentrations of the Na_2SO_3 and the $Na_2S_2O_3$ solutions were checked daily by using iodometric titration. The pH of the 0.10 M Na_2SO_3 stock solution was measured and maintained at 9.5.

The flow experiments were carried out in a thermostated flow reactor[9] at 20 °C. The four solutions (sodium sulfite, sodium thiosulfate, potassium iodate, and sulfuric acid) were pumped into the reactor by a Desaga PLG-132100 peristaltic pump. Initially 5 mL of water was poured in the reactor to avoid local acidification and iodine formation in the initial reaction mixture. The reactor was filled at the highest pump speed ($k_0 = 0.01$ s^{-1}, k_0 being flow rate/tank volume). The pump speed was then reduced.

The pH was followed with a combined glass electrode. A bright platinum electrode and a SCE were used to measure the redox potential. The iodide ion concentration was determined with an iodide ion specific electrode.

Results

Batchwise Experiments. The shape of the pH versus time curves in the iodate–sulfite–thiosulfate system are very different. Basically, the character of the curve is determined by the initial concentrations of the reactants. The main types of the pH versus time curves are shown on Figure 1. In case of the curves a, b, and c the following two inequalities are held

$$3[IO_3^-]_0 < [SO_3^{2-}]_0 + [S_2O_3^{2-}]_0 \qquad \text{(a)}$$

$$3[IO_3^-]_0 > [SO_3^{2-}]_0 \qquad \text{(b)}$$

Under these conditions the solutions remain always colorless; that is, no formation of iodine occurs in noticeable amount. In case of curve a the initial concentration of hydrogen ion exceeds that of the thiosulfate ion. It can be seen that after an autocatalytic decrease of pH a constant value is reached at pH 3. In case of curves b and c the ratio of the initial concentrations of hydrogen and thiosulfate ions is just the opposite. In these cases an extraordinary sharp minimum is exhibited on the pH versus time curve. In fact, the change of pH is so rapid and the pH change is so big that the potential of the glass electrode cannot follow it. That the pH of the reaction mixture in the minimum is much less than 4.5 monitored by the pH meter is clearly shown by adding certain indicators to the solution. The color of the solution in the presence of methyl orange turns just for a moment completely red, indicating that in the minimum the pH decreases at least to 3.

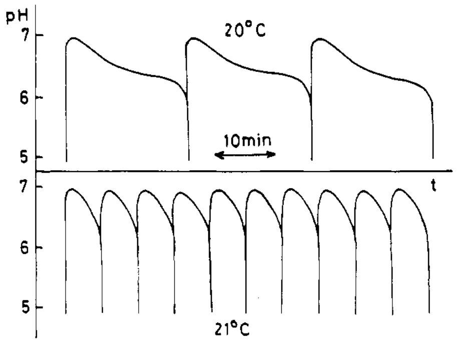

Figure 2. pH vs time curves in a flow system at 20.0 and 21.0 °C. Input concentrations in combined feed: $[IO_3^-]_0 = 0.0125$, $[SO_3^{2-}]_0 = 0.025$, $[S_2O_3^{2-}]_0 = 0.0104$, $[H^+]_0 = 0.0105$ M, $k_0 = 1.3 \times 10^{-3}$ s^{-1}.

In case of curve d the inequality (a) is not valid; that is, there is an excess of iodate and the initial concentrations of hydrogen ion is larger than that of the thiosulfate. There is a not so sharp minimum in the pH, and after reaching this minimum the solution turns yellow due to the formation of iodine. Then a very slow decrease of pH occurs.

The increase of the initial concentrations of hydrogen ions greatly accelerates the reaction: the time to reach the minimum in pH becomes shorter and shorter.

Experiments in CSTR. The iodate–sulfite–thiosulfate system exhibits bistability and, in a rather narrow range of initial concentrations, sustained oscillatory behavior. As it appears from the curves of Figure 2 there is a high-amplitude oscillation in pH and the character of the oscillation depends very much on the temperature. The amplitude is larger than indicated by the glass electrode. On addition of methyl orange to the reaction mixture the red color of the solution in each minimum indicates that the pH decreases at least to 3. The temperature dependence of the kinetic behavior of the system is remarkable indeed. Below 18 °C and above 22 °C there is no oscillatory behavior at the given initial concentrations and flow rate. In considering the rather exothermic nature of the reaction this extraordinary temperature sensitivity requires a very intensive heat exchange. Without particularly intensive and careful thermostating there is a small but continuous stepwise increase of temperature leading soon to the ceasing of the oscillatory character of the reaction. When the initial concentrations of the reactants were twice of the concentrations given in the text of Figure 2, the oscillations stopped after a few periods since the rate of the heat exchange is not high enough to keep the temperature of the reaction mixture in the very narrow range where oscillation occurs.

Discussion

Obviously, two subsystems should be considered in the description of the iodate–sulfite–thiosulfate system.

Kinetics of the Iodate–Sulfite Reaction. The direct oxidation of sulfite by iodate occurs when the pH of the solution does not decrease below pH 4:

$$IO_3^- + 3HSO_3^- \rightarrow I^- + 3SO_4^{2-} + 3H^+ \qquad (1)$$

The kinetics of this reaction was most carefully studied by Skrabal and Zahorka[11] who evaluated the following rate law:

$$-d[IO_3^-]/dt = 5.3 \times 10^5[H^+][HSO_3^-][IO_3^-] + 6.7 \times 10^{16}[H^+]^2[SO_3^{2-}]^2[IO_3^-]$$

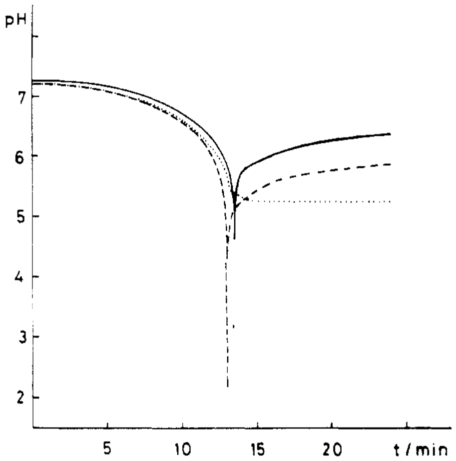

Figure 3. Measured (—) and calculated pH vs time curves in static system. The dotted line is calculated by using eq 1′ and 3′; the dashed curve is calculated by using eq 1″ and 3″ $[IO_3^-]_0 = 0.010$, $[SO_3^{2-}]_0 = 0.025$, $[S_2O_3^{2-}]_0 = 0.010$, $[H^+]_0 = 0.009$ M, $T = 20$ °C.

The two rate constants are given in minutes. The second term can be given differently:

$$-d[IO_3^-]/dt = k_1[IO_3^-][HSO_3^-][H^+] + k_1'[IO_3^-][HSO_3^-] \qquad (1')$$

In considering the reversible dissociation of hydrogen sulfite ion

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

The rate constants are as follows: $k_1 = 8.8 \times 10^3$ M^{-2} s^{-1}; $k_1' = 6.7 \times 10^{16} \times K_2^2/60$. Since the value of $K_2 = 1 \times 10^{-7}$ M, $k_1' = 11$ M^{-2} s^{-1}.

Kinetics of the Iodate–Thiosulfate Reaction. In contrast to the oxidation of sulfite the oxidation of thiosulfate consumes hydrogen ions:

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

The kinetics of the obviously rather complicated reaction has been studied by Rieder[12] and Indelli[13] and they have found the same simple rate law

$$-6d[IO_3^-]/dt = k_3[H^+]^2[IO_3^-][S_2O_3^{2-}]^2 \qquad (3')$$

but for the rate constant k_3 they gave extremely different numerical values: Rieder, 5×10^8 M^{-4} s^{-1} (at room temperature); Indelli, $(2.5\text{–}4.5) \times 10^{12}$ M^{-1} s^{-1} (at 25 °C). Rieder followed the reaction by titrating acetic acid with sodium hdyroxide in the reaction mixture containing initially a given amount of acetic acid and sodium acetate, while Indelli applied a more precise iodometric determination of the unreacted thiosulfate. The discrepancy between the two rate constants is apparent and is due to the fact the rate of the hydrogen ion concentration when a high concentration of sodium acetate is present can be correctly given on the following way

$$\frac{d[H^+]}{dt} = \frac{d[S_2O_3^{2-}]}{dt}\frac{K_d}{[Ac]} = 6\frac{d[IO_3^-]}{dt}\frac{K_d}{[Ac]}$$

where K_d is the acidic dissociation constant of acetic acid. Since the value of K_d is 1.85×10^{-5} M and the concentration of sodium acetate was 0.1 M, the corrected value evaluated from Rieder's experiments is 2.7×10^{12} M^{-4} s^{-1} in rather good agreement with the value determined by Indelli. We repeated the kinetic experiments at 20 °C using the iodometric determination of unreacted thiosulfate and found that $k_3 = (3.4 + 0.2) \times 10^{12}$ M^{-4} s^{-1} and used this value in the calculations.

Kinetics of the Iodate Oxidation of a Mixture of Sulfite and Thiosulfate. First we tried to describe the kinetics by using the rate laws and rate constants of the two subsystems. As it appears from Figure 3 the calculated curve does not reflect at all the characteristic shape of the experimentally found one. A simple consideration indicates that the observed extraordinary sharp minimum in pH can be described if hydrogen sulfite inhibits the oxidation of thiosulfate by iodate, but thiosulfate acts as a catalyst of the oxidation of sulfite by iodate. These effects are given by the modified rate laws:

$$v_1'' = -d[IO_3^-]/dt = k_1[IO_3^-][HSO_3^-][H^+] + K_1'[IO_3^-][HSO_3^-]^2 + k_c[IO_3^-][HSO_3^-][S_2O_3^{2-}][H^+]^2 \qquad (1'')$$

$$v_3'' = -6d[IO_3^-]/dt = k_3[H^+]^2[IO_3^-][S_2O_3^{2-}]^2/(1 + k_iHSO_3^-) \qquad (3'')$$

from these rate laws and besides the independently determined rate constants (k_1, k_1' and k_3) assuming $k_c = 1 \times 10^{11}$ M^{-4} s^{-1} and $k_i = 5 \times 10^4$ M^{-1} and considering the (2) dissociation equilibrium, the calculated curves reflect the main characteristics of the experimentally found ones (Figure 3). Note that on the calculated curves the pH minimum is much lower than those obtained by monitoring the pH using glass electrode. However, as was mentioned earlier, the real value of pH in the minimum is much lower according to the experiments using indicators. Since the pH of the solutions certainly decreases below pH 3 the contribution of the Dushman reaction and the iodine oxidation of sulfite and thiosulfate should be reconsidered.

The rate of the iodate oxidation of iodide

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (4)$$

is given by the following rate law

$$-d[IO_3^-]/dt = k_4[IO_3^-][I^-]^2[H^+]^2 \qquad (4')$$

As it appears from the curves of Figure 4 the rates of the iodate oxidation of sulfite and thiosulfate exceed that of the Dushman reaction in general by many orders of magnitude. Furthermore these curves illustrate that because of the catalytic and inhibition effects, a considerable part of the conversion takes place in less than tenths of a second in a reaction which is followed kinetically for 20 min!

Modeling the Oscillatory Reaction in CSTR. To the two rate equations describing the irreversible redox reactions and the protonation equilibrium the flow terms should be added to give an account on the chemical events in a CSTR. This approach requires the solution of the system of five differential equations:

$$d[IO_3^-]/dt = -v_1'' - v_3'' + k_3([IO_3^-]_0 - [IO_3^-]) \qquad (5)$$

$$d[HSO_3^-]/dt = -3v_1'' - v_2 + v_{-2} - k_0[HSO_3^-] \qquad (6)$$

$$d[SO_3^{2-}]/dt = v_2 - v_{-2} + k_0([SO_3^{2-}]_0 - [SO_3^{2-}]) \qquad (7)$$

$$d[S_2O_3^{2-}]/dt = -6v_3'' + k_0([S_2O_3^{2-}]_0 - [S_2O_3^{2-}]) \qquad (8)$$

$$d[H^+]/dt = 3v_1'' - 6v_3'' + v_2 - v_{-2} + k_0([H^+]_0 - [H^+]) \qquad (9)$$

As it appears from Figure 5, this simple model can semiquantitatively describe the oscillatory behavior of the system in CSTR: both the amplitude and the frequency are in good agreement with the observed ones. In connection with the amplitude, we stress that the minimum pH values are much less than measured by the glass electrode: the experiments by indicators show that the pH goes below 3.

Qualitatively, the oscillatory behavior in CSTR can be explained as follows: The oxidation of sulfite produces hydrogen ions in an autocatalytic manner, but the oxidation of thiosulfate is completely inhibited. However, when the oxidation of sulfite is practically complete, there is an explosion-like oxidation of thiosulfate leading to the fast increase of pH approaching the initial one. The pH remains then for a relatively long time at about this value until the input of the reactants increases the rate of oxidation of sulfite by iodate to begin the next cycle.

Unfortunately, this model cannot explain at all the extreme temperature sensitivity of the oscillatory reaction in CSTR. Our

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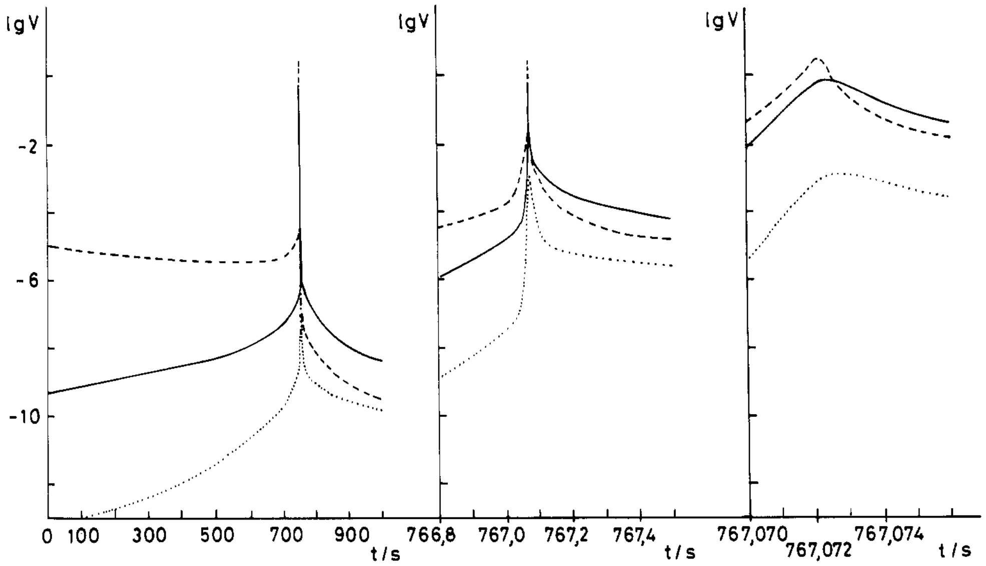

Figure 4. Calculated rates of the component reactions in the iodate–sulfite–thiosulfate system at different time scales: (- - -) log v_1'', (—) log v_3'', (···) log v_4.

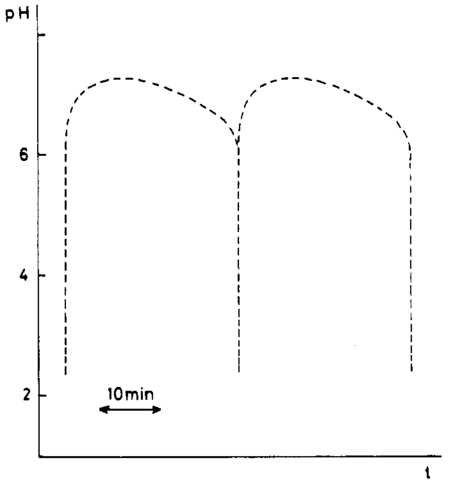

Figure 5. pH vs time curve in a flow system. Calculated on the basis of eq 18–22 $[IO_3^-]_0 = 0.0125$, $[SO_3^{2-}]_0 = 0.025$, $[S_2O_3^{2-}]_0 = 0.0104$, $[H^+]_0 = 0.0105$ M, $k_0 = 1.3 \times 10^{-3}$ s^{-1}, $k_1 = 8800$ M^{-2} s^{-1}, $k_1' = 11$ M^{-2} s^{-1}, $k_c = 1 \times 10^{11}$ M^{-4} s^{-1}, $k_3 = 3.4 \times 10^{12}$ M^{-1} s^{-1}, $k_i = 5 \times 10^4$ M^{-1}.

experimental and theoretical work is focused to solve this rather enigmatic, but well reproducible feature of the reaction.

It is worth mentioning that, although the catalytic and inhibition effects are essential features of this system, catalysis of sulfite oxidation by thiosulfate and inhibition of oxidation of thiosulfate by sulfite are not necessary conditions of oscillatory behavior in CSTR. When rate eq 1′ and 3′ instead of (1″) and (3″) are used in the model represented by eq 5–9 and the numerical value of k_5 is decreased by 2 orders of magnitude, an oscillatory change of pH occurs, although the shapes of the curves are still completely different from the experimentally found ones.

Conclusion

The oscillatory behavior of the iodate–sulfite–thiosulfate system in CSTR provides the simplest example of periodic reactions: there are two reactions which result in opposite changes in the hydrogen ion concentration. Because of the differences in rate laws of the two reactions, and particularly due to the buffer equilibrium in which only one of the two reductants are involved, there is a phase shift of the oxidation of sulfite and thiosulfate manifested in the pH minimum. The occurrence of the pH minimum in a static system, however, is not a sufficient condition of the oscillatory change of pH in CSTR. If the rate laws are given in the form of (1′) and (3′) there is a very shallow pH minimum in the static system but no oscillation can be calculated by adding the flow terms. When the rate constant k_3 is decreased by 1 order of magnitude, the pH minimum will be less shallow and the model exhibits oscillatory behavior in CSTR. However, the observed extremely sharp pH minima are due to the cross catalytic-inhibition effects expressed by rate laws (1″) and (3″).

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Registry No. IO_3^-, 15454-31-6; SO_3^{2-}, 14265-45-3; $S_2O_3^{2-}$, 14383-50-7.