# Fluctuations and Stirring Rate Effects in the Chlorite–Thiosulfate Reaction<sup>1</sup>

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The stoichiometry, kinetics, and mechanism of the reaction between chlorite and thiosulfate have been studied at 25 °C and pH 6–9. In excess thiosulfate, the stoichiometry is  $4S_2O_3^{2-} + ClO_2^- + 2H_2O = 2S_4O_6^{2-} + 4OH^- + Cl^-$ . In excess chlorite, sulfate is produced as well, the stoichiometry being a mixture of the above reaction and  $S_2O_3^{2-} + 2ClO_2^- + H_2O = 2SO_4^{2-} + 2Cl^- + 2H^+$ . The rate of production of OH<sup>-</sup> is  $d(\delta[OH^-])/dt = k_{expt}[S_2O_3^{2-}][ClO_2^-][H^+]$ , but the rate constant  $k_{expt}$  varies with the  $[ClO_2^-]/[S_2O_3^{2-}]$  ratio, being about twice as large in excess  $S_2O_3^{2-}$  as in excess  $ClO_2^-$ . A mechanism is proposed involving the complex intermediates  $S_2O_3ClO^-$  and  $S_2O_3Cl^-$ , a key reaction between the simpler intermediates  $SO_3^{2-}$  and  $ClO^-$ , and the "supercatalytic" chlorite-tetrathionate reaction. At pH  $\approx 11$  in unbuffered solution, the reaction behaves as a "clock" reaction, with an initial rise in pH followed by an abrupt drop. The reaction time, however, varies irreproducibly, even in identically prepared samples. Careful analysis of the reaction time distribution and its variation with temperature, volume, reactant concentrations, and stirring rate leads to the conclusion that the switch from net OH<sup>-</sup> production to net H<sup>+</sup> generation is induced by random fluctuations within the solution. The implications of this interpretation are discussed.

#### Introduction

The chlorite-thiosulfate reaction exhibits the most exotic dynamical behavior found among the recently discovered chloritedriven chemical oscillators. The reaction is autocatalytic under batch conditions,<sup>3</sup> it exhibits oscillation,<sup>3</sup> complex periodic, and aperiodic (chaotic) behavior<sup>4,5</sup> in a continuous stirred tank reactor (CSTR), and chemical waves may be generated in the unstirred system.<sup>6</sup> The ultimate goal of interpreting these phenomena demands a knowledge of the detailed mechanism of the reaction. Because of the highly overlapping spectra of the reactants, intermediates, and products, spectrophotometric methods appear to be inadequate for kinetic studies of this system. Previous investigations based on classical titrimetric analytical methods showed<sup>7</sup> that the reaction is very slow in alkaline solution even at 90 °C, but it is autocatalytic in H<sup>+</sup>. This feature of the reaction opens up two further possibilities for studying its kinetics at room temperature. The reaction may conveniently be followed in slightly buffered solution by monitoring the pH change. It can also, in principle, be studied as a clock reaction in an unbuffered, slightly alkaline solution. The results of such studies are presented in this paper. In addition, we report the discovery and interpretation of several remarkable phenomena in this system including extreme sensitivity to stirring rate and the apparent role of internal fluctuations in determining the course of the reaction.

## **Experimental Section**

*pH-Metric Studies.* All chemicals were of the highest purity available and were used, except as noted below, without further purification. After a systematic search for buffer components that do not react with the reactants, intermediates, or products, the following two buffers were selected: (I) 0.05 M NH<sub>4</sub>Ac + 0.05 M NaAc + 0.07 M NaH<sub>2</sub>PO<sub>4</sub> + 0.07 M tris(hydroxymethyl)-aminomethane; (II) 0.1 M NaAc + 0.1 M NaH<sub>2</sub>PO<sub>4</sub> + 0.02 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.

Buffer I was used in most of our runs. About 30% of the experiments, however, were repeated in buffer II to ensure that neither the ammonia nor the tris base affects the reaction. The results of the two sets of trials agreed within experimental error;

thus they are treated together in the following discussion. The ionic strength of all solutions was adjusted to 1.00 M with NaClO<sub>4</sub>. The temperature of the stock solutions and the reaction mixtures was kept constant at  $25.00 \pm 0.05$  °C.

Four solutions were prepared for the kinetic runs: (1) 0.100 M  $Na_2S_2O_3$  + buffer in (4-20)-fold dilution +  $NaClO_4$ ; (2) 0.100 M  $NaClO_2$  + buffer in (4-20)-fold dilution +  $NaClO_4$ ; (3) buffer in (4-20)-fold dilution +  $NaClO_4$ ; (4) 1.00 M  $NaClO_4$ .

The dilution of the buffer was varied for different sets of measurements and pH ranges, but it was always the same for solutions 1-3 within a single set of runs. The pH of solutions 1-3 was adjusted to the same initial value (between pH 6.5 and 8.5) by dropwise addition of 1 M HClO<sub>4</sub> or NaOH just before filling the volumetric flasks.

By appropriate selection of the initial pH and the concentrations, the rate of change in pH could be restricted to the range 0.01-0.10units/min; thus the reaction could be conveniently followed with a glass electrode. The electrode system was calibrated for -log [H<sup>+</sup>] according to Irving et al.<sup>8</sup> Two different types of measurements were performed. In one series, at lower initial pH in strongly buffered solution, the reaction was followed up to 70–95% conversion (0.5–3 h) in order to determine the stoichiometry. In the other set of experiments, initial rate studies were carried out in weakly buffered solutions at initial pH 8–9. A pH change of 0.15-0.4 unit was detected in this range, corresponding to initial 2–4% conversion. In addition, classical iodometric titrations, IR measurements, and other standard analytical methods were used to check the stoichiometry and to examine the proposed mechanism of the reaction.

Clock Reaction Studies. The clock reaction studies were conducted in 96-mm-high sample dishes of outer diameter 24 mm and inner diameter 21 mm. The solutions were stirred with an 18-mm-long magnetic stirrer bar of diameter 9 mm. The stirrer was calibrated with a stroboscopic light source. Reproducibility of the stirring rate was about 25 rpm. All the clock reaction studies were undertaken at  $[ClO_2^{-}]_0/[S_2O_3^{2-}]_0$  ratios greater than 2. Under these conditions there is no need for an auxiliary acid-base indicator to detect the reaction, since the excess  $ClO_2^{-}$  decomposes in the resulting acidic solution within 1 s. The yellow color of the  $ClO_2$  thus produced appears suddenly at the end of the reaction.

A large number of preliminary experiments revealed no systematic change in the reaction time with the composition of the solution. Moreover, the reproducibility of the reaction time was extremely poor; in some cases it varied from 10 s to several hours under "exactly the same" initial conditions! In almost all cases,

Part 37 in the series Systematic Design of Chemical Oscillators. Part
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the reaction went to completion within 2 s once the stirring of the solution was stopped. Considerable effort was devoted to "stabilizing" the reaction time: all of the stock solutions were filtered and purged with nitrogen prior to reaction, an inert  $N_2$ atmosphere was introduced above the reacting solution, and the NaClO<sub>2</sub> was recrystallized twice from 80% ethanol-water mixture in the temperature range 25 to -20 °C. No Cl<sup>-</sup> and no alkaline impurities could be detected in the purified NaClO<sub>2</sub>, and iodometric titration showed that its purity was better than 99.5%. The reaction vessels were cleaned, even sterilized, with extreme care; the reaction was followed in glass- as well as in plasticware. In spite of all of these efforts, no reproducibility could be achieved. The reaction time continued to change in an apparently random manner.

Finally, we filled a long tygon tube with the reaction mixture and placed plastic clamps at 5-cm intervals along the tube. Separate experiments showed that when the clamps were closed the compartments formed in this way are completely independent of one another. No chemical wave<sup>6</sup> was able to pass the clamps for weeks. The time for the initiation of the reaction in the initially homogenous solution, divided into 100 independent cells in this manner, varied from 10 min to 3 days! These preliminary experiments convinced us that the irreproducibility is an inherent feature of the reaction. The only way to unravel it appeared to be to measure a substantial number of reaction times under identical experimental conditions and to study their probability distribution. Because of the peculiar nature of these experiments, where every, usually insignificant, experimental detail may be of importance, further particulars of the experiments are given below together with the results and discussion.

### Calculations

For analysis of our pH-metric studies, the measured pH vs. time curves were transformed to plots of  $\delta[OH^-]$  vs. t, where  $\delta[OH^-]$ is the concentration of OH<sup>-</sup> liberated by the reaction. To facilitate the transformation, the titration curves of solutions 1-3 were measured individually. The curves for solutions 1 and 3 were found to be identical, as expected. The curves for solution 2 were slightly different, because of the base content of the unpurified NaClO<sub>2</sub>. Therefore a weighted average of the pH-metric curves was used in the transformation, the weighting factors being the volume ratios of solutions 1-3 for the given experiment. The transformation was carried out by quadratic interpolation.

In the initial rate studies, where the pH change did not exceed 0.4 unit, appropriate portions of the titration curves were approximated by the linear equation,  $\delta pH = x\delta[OH^{-}]$ . The x values were also calculated from the weighted average of the titration curves. The concentrations of the buffer components were chosen to give as nearly linear a titration curve as possible. Preliminary calculations showed that the rate of OH<sup>-</sup> production was directly proportional to the hydrogen ion concentration; i.e.

$$d(\delta[OH^{-}])/dt = k'[H^{+}]$$
(1)

Because of the linear relation between  $\delta pH$  and  $\delta [OH^-]$ ,

$$d(\delta pH)/dt = xk'[H^+]$$
(2)

The integrated form of eq 2 yields

$$1/[H^+] = 1/[H^+]_0 + 2.303xk't$$
 (3)

In accordance with eq 3, plots of  $[H^+]^{-1}$  vs. t were found to be straight lines from whose slopes the values of k' could be calculated.

### **Results and Discussion**

Stoichiometric Studies. The results of some of our stoichiometric studies are illustrated in Figures 1 and 2. Figure 1 shows that the amount of OH<sup>-</sup> liberated in large thiosulfate excess approaches 4 times the initial chlorite concentration. On the other hand, the amount of OH<sup>-</sup> liberated in large chlorite excess is only about half the initial thiosulfate concentration (Figure 2). These findings cannot be incorporated in a single stoichiometric equation; the stoichiometry must be different in the two limiting cases.



Figure 1. Representative plots of  $\delta[OH^-]/[ClO_2^-]$  vs. time in large excess of thiosulfate: (symbol;  $[S_2O_3^{2-}]_0$ , M;  $[ClO_2^{-}]_0$ , M;  $pH_{t=0}$ ;  $pH_{t=40s}$ ) =  $\Box$ ; 0.095; 0.005; 7.00; 8.40. **○**; 0.059; 0.001; 7.00; 7.69. **△**; 0.0975; 0.0025; 6.65: 7.77.



Figure 2. Representative plots of  $\delta[OH^-]/[S_2O_3^{2-}]$  vs. time in excess chlorite: (symbol;  $[S_2O_3^{2^-}]_0$ , M;  $[ClO_2^{-}]_0$ , M;  $pH_{t=0}$ ;  $pH_{t=40s}$ ) = 0; 0.030; 

Iodometric titrations showed that 1 mol of  $ClO_2^{-}$  is consumed for 4 mol of thiosulfate in excess thiosulfate. The stoichiometry in this case is therefore

$$4S_2O_3^{2-} + ClO_2^{-} + 2H_2O = 2S_4O_6^{2-} + 4OH^{-} + Cl^{-}$$
 (4)

similar to the oxidation of the thiosulfate by several other oxidants.<sup>9-11</sup> In large chlorite excess, iodometric titrations give 1 mol of chlorite reacting with only about 2 mol of thiosulfate. The products were analyzed and were found to contain a mixture of sulfate and tetrathionate. No other sulfur-containing oxyanion could be detected. This observation implies that the reaction

$$S_2O_3^{2-} + 2ClO_2^{-} + H_2O = 2SO_4^{2-} + 2Cl^{-} + 2H^+$$
 (5)

takes place in excess chlorite, but reaction 4 overcompensates its pH-decreasing effect even in a relatively large excess of chlorite. An appropriate combination of the two reactions may explain the experimentally determined stoichiometric ratios; for example 5  $\times$  (4) + 4 × (5):

$$24S_2O_3^{2-} + 13ClO_2^{-} + 6H_2O = 8SO_4^{2-} + 10S_4O_6^{2-} + 12OH^{-}$$
(6)

The tetrathionate formed does not react further with the excess chlorite in the pH range studied. Separate experiments showed

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Figure 3. Rate constant  $k_{expt}$  as a function of log  $([S_2O_3^{2-}]_0/[ClO_2^{-}]_0)$ . Full line calculated by least-squares fit of eq 9.

that the reaction of tetrathionate and chlorite is extremely slow unless the pH is less than 6. This result also suggests that tetrathionate and sulfate are formed in two different reaction pathways; i.e., tetrathionate is not an intermediate in the production of sulfate.

Initial Rate Studies. Preliminary experiments showed that in a pH range of about 5-9 the first phase of the reaction (up to 10 h) is marked by the liberation of OH<sup>-</sup>, i.e., by an increase in pH, independent of the concentrations or the concentration ratio of the components. This finding is in sharp contradiction to our earlier result<sup>7</sup> at 90 °C, where autocatalysis by H<sup>+</sup> was established. The initial rate studies indicated that in large chlorite excess the rate of OH<sup>-</sup> production is proportional to the thiosulfate concentration. The rate is also linearly related to the chlorite concentration in large thiosulfate excess; i.e.

$$d(\delta[OH^{-}])/dt = k_{expt}[S_2O_3^{2-}][ClO_2^{-}][H^{+}]$$
(7)

The rate constants  $k_{expt}$  calculated at the extreme concentration ratios, however, are not the same; they differ from each other by a factor of about 2! Moreover, at comparable concentrations the value of the experimentally determined rate constant depends on the ratio of the concentration of the reactants, but is practically independent of their absolute values in the concentration range studied. These findings are illustrated in Figure 3, where all the  $k_{\text{expt}}$  values determined are plotted against the logarithm of  $[S_2O_3^{2-}]_0/[ClO_2^{-}]_0$ .

Proposed Mechanism. For a mechanistic interpretation of the results, we start with the rate-determining step (M1) proposed in our earlier study:7

$$H_2O + ClO_2^{-} \stackrel{1/K_a}{\leftrightarrow} HClO_2 + OH^-$$
 (M0)

$$HClO_2 + S_2O_3^{2-} \xrightarrow{k_1} S_2O_3ClO^- + OH^- \qquad (M1)$$

At 90 °C in alkaline solution, further reaction of S<sub>2</sub>O<sub>3</sub>ClO<sup>-</sup> leads almost exclusively to sulfate formation even in thiosulfate excess. At room temperature, however, the intermediate may react either with  $S_2O_3^{2-}$  or with  $ClO_2^{-}$  according to

$$S_2O_3ClO^- + S_2O_3^{2-} \xrightarrow{k_2} S_4O_6^{2-} + ClO^-$$
 (M2)

$$2H_2O + S_2O_3ClO^- + ClO_2^- \xrightarrow{k_3} 2SO_3^{2-} + 4H^+ + 2ClO^-$$
(M3)

The SO<sub>3</sub><sup>2-</sup> produced reacts further with ClO<sub>2</sub><sup>-</sup> and ClO<sup>-</sup> to produce sulfate:

$$SO_3^{2-} + ClO_2^{-} \xrightarrow{k_4} SO_4^{2-} + ClO^{-}$$
 (M4)

$$SO_3^{2-} + ClO^- \xrightarrow{\kappa_5} SO_4^{2-} + Cl^-$$
 (M5)

Steps M3-M5 by themselves would yield only sulfate and hydrogen ion in very large chlorite excess. This is not the case experimentally, however, even in a 100-fold excess of chlorite. In order to explain the observed behavior, we introduce a reaction between thiosulfate and hypochlorite to produce tetrathionate, presumably in two steps:

$$H_2O + S_2O_3^{2-} + ClO^- \xrightarrow{k_6} S_2O_3Cl^- + 2OH^- \quad (M6)$$

$$S_2O_3Cl^- + S_2O_3^{2-} \xrightarrow{k_7} S_4O_6^{2-} + Cl^-$$
 (M7)

The above mechanism is supported by the following additional evidence:

The reaction of a small amount of ClO- with excess thiosulfate at pH  $\sim$  7 increases the pH and leads to the formation of tetrathionate. Sulfate formation can be detected only at concentration ratios near unity.

The reaction of  $SO_3^{2-}$  with either  $ClO_2^{-}$  or  $ClO^{-}$  is very fast compared to the chlorite-thiosulfate reaction.<sup>12-15</sup>

No reaction could be detected between chlorite and tetrathionate at pH  $\sim$  8 up to 24 h.

Introducing the notation  $A = [S_2O_3^{2-}], B = [ClO_2^{-}], H = [H^+],$  $X = [S_2O_3CIO^-], Y = [CIO^-], W = [SO_3^{2-}], Z = [S_2O_3CI^-], P$ =  $[S_4O_6^{2-}]$ , R =  $[SO_4^{2-}]$ , S =  $[Cl^-]$ , omitting H<sub>2</sub>O, and replacing OH<sup>-</sup> by H<sup>+</sup> on the opposite side of the equations,<sup>16</sup> the mechanism may be represented by Scheme I.

#### SCHEME I

$$2H + A + B \xrightarrow{k_1} X \qquad r_1 = k_1 ABH$$
$$X + A \xrightarrow{k_2} P + Y \qquad r_2 = k_2 AX$$
$$X + B \xrightarrow{k_3} 2W + 4H + 2Y \qquad r_3 = k_3 BX$$
$$W + B \xrightarrow{k_4} R + Y \qquad r_4 = k_4 BW$$
$$W + Y \xrightarrow{k_5} R + S \qquad r_5 = k_5 WY$$
$$2H + A + Y \xrightarrow{k_6} Z \qquad r_6 = k_6 AYH$$
$$Z + A \xrightarrow{k_7} P + S \qquad r_7 = k_7 ZA$$

The measured quantity in the present experiment is the rate of the liberation of  $OH^-$  (consumption of  $H^+$ ); thus

$$d(\delta[OH^-])/dt = 2k_1ABH - 4k_3BX + 2k_6AYH = k_{expt}ABH$$
(8)

Applying the steady-state treatment to the intermediates X, Y, W, and Z, a lengthy but straightforward computation yields the following expression for  $k_{expt}$ :

$$k_{expt} = k_1 \frac{(3k_r C - 2)}{(k_r C + 1)} + k^* + \left\{ \left( k^* - \frac{k_1 k_r C}{(k_r C + 1)} \right)^2 + 4k_1 k_r \frac{(k_r C + 4)}{(k_r C + 1)} \right\}^{1/2}$$
(9)

where  $k_r = k_2/k_3$ , C =  $[S_2O_3^{2-}]/[ClO_2^{-}]$ ,  $k^* = k_4k_6/k_5$ .

The surprising result is that the experimentally measured rate constant is determined by just three parameters,  $k_1$ ,  $k_r$ , and  $k^*$ .

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<sup>(16)</sup> Note that, because of our treatment of OH<sup>-</sup> and H<sup>+</sup> in this fashion,

some of the reactions in the scheme are no longer elementary in the sense that their kinetics can be derived from their stoichiometry. Reactions M1-M7 represent the true elementary reactions.

As found experimentally,  $k_{expt}$  depends only upon the *ratio* of the thiosulfate and chlorite concentrations. The solid line in Figure 3 was calculated by a least-squares fit of eq 9 to the experimental points. The agreement is satisfactory, though systematic deviations may be detected in some parts of the curve. It should be noted that the accuracy of the measured points is at best 5–10%. The calculated rate constants are  $k_1 = 4.7 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ ;  $k_r = 0.80$ ;  $k^* = 9.1 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ .

The mechanism proposed above explains only the first phase of the chlorite-thiosulfate reaction. It consists of six crucially important consecutive and parallel steps, even if the protonation of  $ClO^-$  and  $ClO_2^-$  and the presumably rapid step (M7) are disregarded. Elimination of any of these steps would result in some contradiction with the experimental results. The present mechanism, however, explains neither the autocatalytic role of H<sup>+</sup> nor the oscillatory behavior of the system in a CSTR. Explanation of these phenomena demands mechanistic knowledge of the further reaction between tetrathionate and chlorite.

Preliminary Results on the Kinetics of the Chlorite-Tetrathionate Reaction. The reaction of  $ClO_2^-$  with  $S_4O_6^{2-}$  was studied in the pH range 4.7-5.5 by using standard iodometric methods. The mechanism of the reaction appears to be extremely complex, partially because of the decomposition of  $ClO_2^-$  which also takes place in this pH range. Further experiments are needed to be able to propose a complete mechanism. Here we present only the most important results that play a significant role in the explanation of the clock reaction studies:

In chlorite excess the reaction always goes to completion and sulfate is the only S-containing product:

$$2S_4O_6^{2-} + 7ClO_2^{-} + 6H_2O = 8SO_4^{2-} + 7Cl^{-} + 12H^+$$
(10)

The initial rate of the reaction is first order with respect to both tetrathionate and chlorite, but it is second order with respect to  $H^+$ , i.e., the reaction is "supercatalytic".<sup>17</sup> The rate constant calculated from the initial rate,  $d[ClO_2^-]/dt = k_1$ - $[ClO_2^-][S_4O_6^{2-}][H^+]^2$ , is  $k_t = 1 \times 10^9 \text{ M}^{-3} \text{ s}^{-1}$ .

The reaction is catalyzed by the product chloride, probably through the chloride catalyzed decomposition of chlorite<sup>18</sup> (further supercatalysis).

The order of the reaction with respect to  $H^+$  increases during the course of the reaction, reaching almost three at 70–80% conversion.

Clock Reaction Studies. In general 50 measurements were carried out under each set of experimental conditions. The reaction time distribution was studied first as a function of the volume of the reaction mixture. Solutions of 0.100 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and of 0.300 M NaClO<sub>2</sub>, each containing 0.001 M NaOH stock solution were freshly prepared each day and thermostated at  $20.00 \pm 0.05$  °C. Reaction vessels were heated to 130 °C prior to the measurements. They were then prethermostatted at 20 °C. The reactants were always mixed in a 1:1 volume ratio. The thiosulfate stock solution was transferred to the vessel first and stirred at 1500 rpm. Then the chlorite solution was added from a fast-delivery pipet. Care was taken to add the chlorite solution midway between the center of the stirring vortex and the wall of the dish. Delivery of the chlorite stock solution took at most 3 s. The stopwatch was started when about half the chlorite stock solution had been added. After 5-6 s, the stirring rate was decreased to 700 rpm. The entire procedure was carried out under a nitrogen atmosphere. The reaction was followed for 500 s, and the time of the sudden appearance of the yellow color  $(ClO_2)$  was noted, if the reaction occurred within this interval. We stress again that, in all samples in which the reaction did not take place within 500 s, it went to completion within 2 s after the stirring was stopped. The reaction time distribution is plotted as a function of the solution volume in Figure 4.



**Figure 4.** Cumulative probability distribution of reaction times at several solution volumes. Symbols:  $\bullet$ ,  $V = 2.00 \text{ cm}^3$ ;  $\triangle$ ,  $V = 6.00 \text{ cm}^3$ ;  $\bigcirc$ ,  $V = 10.00 \text{ cm}^3$ . Note that the points are equidistant vertically, being separated by 2%, since the distribution is based on 50 measurements. Dotted horizontal lines indicate probability that the reaction takes place within 500 s. Stirring rate 700 rpm, T = 20.0 °C.



Figure 5. Cumulative probability distribution of reaction times at several stirring rates in a 4.00-cm<sup>3</sup> reaction mixture at 20.0 °C. Symbols:  $\bullet$ , 500 rpm;  $\circ$ , 620 rpm;  $\diamond$ , 760 rpm.

The figure shows that the probability of the reaction taking place within a given time interval increases with the volume. It is tempting to assert that the distribution has some stepwise character at larger volumes. However, a change in the position of only 3–5 points would eliminate the "steps". Far more experimental data would be necessary to draw any firm conclusion regarding the fine structure of the distribution curves. Such studies

<sup>(17)</sup> We use the term "supercatalysis" to denote autocatalysis of order greater than one. Such kinetics can have important consequences, particularly in the case of competing reactions; see, e.g.; Eigen, M.; Schuster, P. Naturwissenschaften 1978, 65, 7.

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Figure 6. Cumulative probability distribution of reaction times at several stirring rates in a 4.00-cm<sup>3</sup> reaction mixture at 30.0 °C. Symbols: O, 620 rpm;  $\Delta$ , 760 rpm;  $\Box$ , 920 rpm.

will be undertaken at a later date when an appropriate automated apparatus has been developed.

Although the stirring rate of the magnetic bar was the same in the above experiments, it is likely that the efficiency of stirring decreases with increasing volume. Thus the next set of experiments was carried out using the same volume, but different stirring rates. The results are plotted in Figure 5. The stirring rate has a sizeable effect on the reaction time distribution. More than half the samples (27) reacted within 1 min at 620 rpm. When the stirring rate was increased by about 20%, only one sample reacted during the first minute. It is interesting to note, however, that the number of samples reacting between 100 and 300 s is virtually independent of the stirring rate, especially if one takes into account the difference in the number of samples surviving the first 100 s.

Figure 6 shows the reaction time distribution at several stirring rates at 30 °C. Two important effects of the increased temperature can be seen on comparing this figure with Figures 4 and 5. Only three samples (out of 300) reacted between 300 and 500 s in the 20 °C experiments; i.e., if a sample survived the first 300 s, it was likely to remain unreacted for 500 s or longer. At 30 °C, however, "stabilization" of a sample takes much more time; a steadily increasing distribution was found up to 1500 s. A second, less surprising effect is that the probability of reaction within a given time interval increases with the temperature.

The results presented so far pose an important question. Is the fate of a sample determined during the addition of the chlorite stock solution and during the first 5-6 s when it is stirred at high speed (1500 rpm), or are the processes responsible for the apparently random change of the induction period really governed by the fluctuations which occur later? To answer this question we performed parallel experiments in which the order of addition of the components was changed. Three solutions were used in these experiments: (1) distilled water; (2) 0.200 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 0.002 M NaOH; (3) 0.600 M NaClO<sub>2</sub>, 0.002 M NaOH. These solutions were mixed in three different orders. In the first group of runs, 2.00 cm<sup>3</sup> of water and 1.00 cm<sup>3</sup> of thiosulfate stock solution were introduced into the reaction vessel, followed by 1.00 cm<sup>3</sup> of the chlorite stock solution. In the second set of experiments, the thiosulfate was added last. Finally, 1.00 cm<sup>3</sup> each of thiosulfate and chlorite stock solutions were added simultaneously to 2.00 cm<sup>3</sup> of water. The results are plotted in Figure 7. Clearly, the order of mixing has some effect on the distribution of reaction times, but it is much less pronounced than the other effects discussed above. The difference, however, indicates that for a more detailed study of this phenomenon the elaboration of strictly defined mixing conditions is necessary, perhaps along the lines of a stopped flow kinetics experiment.

In spite of these caveats, qualitative conclusions can be drawn from the present experiments. In another effort to answer the question raised above, we recorded the pH change during the reaction of 70 "identical" samples. Our initial attempts led to some surprising results. We started the reaction, then tried to put the combined electrode into the solution. We found that the probability of the reaction going to completion increased enor-



Figure 7. Cumulative probability distribution of reaction times in a 4.00-cm<sup>3</sup> reaction mixture at 20.0 °C stirred at 620 rpm with the order of adding the reactants varied. Symbols: •, water +  $Na_2S_2O_3$  +  $Na-ClO_2$ ;  $\Delta$ , water +  $NaClO_2$  +  $Na_2S_2O_3$ ; O, water + ( $Na_2S_2O_3$  +  $NaClO_2$ ) simultaneously.



Figure 8. Representative pH traces of the reaction at 20.0  $^{\circ}$ C (see text). Successive curves are shifted by 0.07 pH units for better viewing, since in the absence of a shift, the initial portions of the curves coincide.

mously when the electrode was inserted. The most likely explanation is that the presence of the electrode changes the convection pattern in the solution, perhaps producing some "dead" volume behind the electrode or between the electrode and the wall of the vessel. Initiation of the reaction is much more probable in this small, imperfectly mixed part of the solution. The reaction then spreads throughout the entire volume. To avoid these difficulties we increased the reaction mixture to 10 cm<sup>3</sup> in order to be able to place the electrode in the center of the stirring vortex. Reagent concentrations and other experimental details were the same as in Figure 4, but the combined electrode was placed in the solution before addition of the NaClO<sub>2</sub> and the stirring rate was kept at 1200 rpm.

The pH traces obtained show wide variation; some of them are illustrated in Figure 8. In 12 of the samples, the lifetime of the unreacted solution was less then 60 s. The pH steadily increased in all of these samples; then it suddenly dropped and the yellow color appeared within 2 s. The lifetime exceeded 1200 s in 26 samples, most of them manifesting a steady and very smooth increase in pH, illustrated in Figure 8a. In some, however, after a short smooth period the pH became "noisy", though with the same average value as in the smooth curves (Figure 8b). The lifetime varied between 100 and 1200 s in the remaining 32 samples. In some of these, the pH rise was quite smooth, followed by a sudden pH drop (Figure 8e). In most, noise developed after some time and this was followed by a sudden pH drop (Figure 8c,d). The important point to be stressed, however, is that in all



Figure 9. Cumulative probability distribution of reaction times at several values of  $[OH^-]_0$  in a 4.00-cm<sup>3</sup> reaction mixture at 20.0 °C stirred at 620 rpm.  $[ClO_2^-]_0 = 0.150 \text{ M}, [S_2O_3^{2-}]_0 = 0.050 \text{ M}. [OH^-]_0, \text{ M: O, 0.0015;} \bullet, 0.0010; \Delta, 0.0005.$ 



**Figure 10.** Cumulative probability distribution of reaction times at several values of  $[ClO_2^{-}]_0$  in a 4.00-cm<sup>3</sup> reaction mixture at 20.0 °C stirred at 620 rpm.  $[OH^{-}]_0 = 0.001 \text{ M}$ ,  $[S_2O_3^{2^{-}}]_0 = 0.050 \text{ M}$ .  $[ClO_2^{-}]_0$ , M: O, 0.120;  $\bullet$ , 0.150;  $\Delta$ , 0.180.

cases the pH change followed almost the identical pattern until the sudden end of the reaction. This observation implies that the scatter of reaction times is not the consequence of the small variations inherent in starting the reaction, but is a characteristic feature of the chemical process itself.

Figures 9–11 illustrate the reaction time distribution as a function of the initial concentrations of the reactants. Note that the ----- curves represent the same set of experiments in all three figures. Four stock solutions were prepared and prethermostated



Figure 11. Cumulative probability distribution of reaction times at several values of  $[S_2O_3^{2-}]_0$  in a 4.00-cm<sup>3</sup> reaction mixture at 20.0 °C stirred at 620 rpm.  $[ClO_2^{-}]_0 = 0.150 \text{ M}, [OH^{-}]_0 = 0.001 \text{ M}. [S_2O_3^{2-}]_0, \text{ M}: \text{ O}, 0.040; •, 0.050; •, 0.060.$ 

for this series of experiments: (1) water; (2) 0.005 M NaOH; (3) 0.200 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> + 0.001 M NaOH; (4) 0.600 M NaClO<sub>2</sub> + 0.001 M NaOH. The solutions were transferred to the reaction vessel in the above order; the last component was always the chlorite stock solution. The most important conclusion to be drawn from these Figures is that the concentration range where the system exhibits "peculiar" behavior is relatively wide. Intuitively one might have expected a much narrower concentration range. Further analysis of these curves will be given below in conjunction with out attempts to explain the experimental phenomena.

Interpretation of the Clock Reaction Studies. The results presented in Figures 4–11 offer strong support for our contention that concentration fluctuations are responsible for the unusual behavior observed. Fluctuation-induced transitions are well-known in other branches of nonlinear dynamics<sup>19</sup> and have been predicted to occur in chemical reactions as well.<sup>20,21</sup> Thus far, however, no experimental evidence has been presented on the role of fluctuations in chemical kinetics. The task is therefore to elucidate those specific features of the present system which make it so extremely sensitive to random fluctuations. No quantitative explanation is attempted here, because the problem is extremely complex and many details are still unknown. Thus only a qualitative interpretation is given, based mainly on "common sense" chemical considerations.

As can be seen from the mechanism proposed above, sulfate and tetrathionate are formed in parallel reactions, one of which produces  $OH^-$  while the other produces  $H^+$ . If only the deterministic rate laws are relevant, then the  $OH^-$  production always surpasses the production of  $H^+$ , and the pH increases. Competition between the two processes, however, might lead to a situation in which the production of  $H^+$  temporarily becomes the dominant process in a small but finite portion of the reaction mixture as a result of random fluctuations. Such an occurrence has no observable consequence if the solution is buffered, because the

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#### The Chlorite-Thiosulfate Reaction

bulk hydrogen ion concentration cannot change significantly. If, however, no buffer is present, then the hydrogen ion concentration can reach a value within this small volume at which the further reaction of the chlorite and tetrathionate is initiated. This reaction is—as we have seen—supercatalytic (second order in hydrogen ion, and catalyzed by the product chloride as well) and produces several hydrogen ions. As a result of the stirring, the H<sup>+</sup> excess spreads throughout the entire volume, accelerating the reaction, i.e., the OH<sup>-</sup> production. In this case the only measurable effect is the pH fluctuation (noise) illustrated in Figure 8. Random fluctuation and the "fortunate" interplay between these processes, however, might initiate the chlorite-tetrathionate reaction to such an extent that it cannot be mixed away. It then propagates throughout the solution and the reaction takes place within seconds. If the system avoids this initiation for a sufficiently long time, then the OH<sup>-</sup> concentration will have increased to the point where the reaction is so slow that it is extremely unlikely to produce fluctuations large enough to overcome the OH<sup>-</sup> excess. The system becomes more and more stable and behaves according to the deterministic rate law.

This interpretation is further supported by the experiments conducted in the tygon tube divided into noninteracting cells and filled with an initially homogeneous unreacted mixture. In these experiments there was no stirring after the tube was filled. Thus, once the reaction was initiated in a small volume, a chemical wave transformed that cell. The wave started in 5 cells within 6 h, in an additional 3 cells within 24 h, and at 76-78 h in the remaining 92 cells.

The reaction time distribution curves offer further evidence in favor of our qualitative interpretation. On increasing the volume of the system, the number of small regions in which the reaction can be initiated increases, in agreement with Figure 4. The more effective the stirring, the greater the probability of mixing away the small reacted volumes (cf. Figures 5 and 6). Figures 7 and 8 show that experimental variations at the start of the reaction do not play a decisive role in determining the distribution. Figure 9 demonstrates that the probability of the reaction's being initiated within a given time interval decreases with the initial [OH<sup>-</sup>]. The effects of the chlorite and thiosulfate concentrations are not simple. The ratio of the concentrations appears to play a more important role in determining the reaction time distribution than the absolute values. The optimum stoichiometric ratio for promoting the reaction occurs at  $[ClO_2^-]/[S_2O_3^{2-}] = 3$ , at least in the concentration range studied here (see Figures 10 and 11).

More detailed analysis of our proposed mechanism reveals another feature of the system that may play a significant role in the "random" initiation of the reaction. The reaction of sulfite and hypochlorite (M5) exerts a decisive influence on the course of the reaction. If we were to omit this reaction from the scheme, then in large chlorite excess, where the rate of step M2 is negligible compared to that of (M3), each instance of the rate-determining step (M1) would produce 10 OH<sup>-</sup> and 4 H<sup>+</sup> through the further rapid steps; i.e., the net  $OH^-$  production via (M0) + (M1) + (M3)+ 2(M4) + 4(M6) + 4(M7) would be 6. In large thiosulfate excess, where (M2) is much more rapid than (M3), only four OH<sup>-</sup> ions would be produced for each rate-determining step via the sequence (M0) + (M1) + (M2) + (M6) + (M7). Without (M5), then, the experimentally measured k would be 6/4 or 1.5 times higher in excess chlorite than in excess thiosulfate. According to Figure 3, however, the rate of OH<sup>-</sup> production in excess chlorite is only about half that found in excess  $[S_2O_3^{2-}]$ . Hence a significant amount of hypochlorite must be consumed in process M5. If, on the other hand, we were to assume that this reaction is extremely rapid, the net result would be that sulfate and chloride would be formed in the single step (M3) + (M5), and step M4 could be neglected. In this case the reaction in excess chlorite would produce only sulfate, with two protons for each (M1) step; i.e., the pH would decrease. These stoichiometric considerations clearly demonstrate that process M5 regulates the delicate balance between the production of  $OH^-$  and  $H^+$  ions.

Both reactants in (M5), sulfite and hypochlorite, are intermediates in the reaction. Their concentrations may be quite low;

i.e., the reaction between them is likely to be extremely sensitive to fluctuations! Moreover, they are formed in the same step, and are therefore near to each other in space at the moment of their formation. Stated somewhat differently, their "relative" concentrations in each other's environment are considerably higher than their bulk concentrations; they are spatially correlated. The more effective the stirring of the solution, the more probable it becomes that this correlation will dissipate before the ions have time to react, so that they will be separated and will react further according to the bulk deterministic rate law. With less effective stirring their effectively increased local concentration makes their reaction more probable, which, as argued above, shifts the reaction into the H<sup>+</sup>-producing pathway. This line of reasoning may explain the striking result that the reaction always occurred within seconds of the stirring being stopped.

#### Conclusion

As we have seen, there are two specific chemical features of the system-competition between the acid- and base-forming reactions, and the SO<sub>3</sub><sup>2--</sup>ClO<sup>-</sup> elementary step---that may account for the fluctuation and stirring rate sensitivity of the reaction. In addition, the supercatalytic tetrathionate-chlorite reaction enormously amplifies any fluctuations, thus pushing the reaction toward completion. It is very important to differentiate between the two chemical effects. If the acid-base competition is the crucial ingredient, then it is a feature peculiar to the present reaction, and similar behavior should not be widespread. If, however, the further reaction of two low-concentration intermediates formed in the same step, i.e., near each other in space, is responsible for the fluctuation and stirring rate sensitivity, then it must be a general phenomenon.

Stirring rate sensitivity has been studied experimentally in a number of systems in a CSTR,<sup>22-24</sup> but our survey of the literature revealed no investigations of this type of behavior in batch reactions and only a brief report<sup>25</sup> on the effects of stirring on oscillations in the Belousov-Zhabotinskii (BZ) reaction. Patonay and Noszticzius<sup>26</sup> suggest that the effects attributed to stirring by Farage and Janjic<sup>25</sup> are due rather to differences in the rate of O<sub>2</sub> transfer to the liquid phase. The results presented here and our analysis of ref 25 and 26 suggest that both oxygen dissolution and stirring affect the BZ reaction with the former exerting a greater influence on the number, and the latter on the amplitude, of oscillations. There appears to be no need to invoke the existence of dissipative structures<sup>25</sup> to explain the observations.

On the theoretical side, the CSTR stochastic model of Horsthemke and Hannon<sup>27</sup> appears to be easily adaptable to treating batch experiments of the type described here, though practical difficulties may arise in including such a complex mechanism. There are, of course, many studies of the effects of mixing and stirring in fast reactions and in heterogeneous reactions, but these are outside the scope of this work. All the mechanisms which have been proposed for chemical reactions that exhibit stirring rate sensitivity in a CSTR<sup>28-30</sup> include steps in which a pair of intermediates is formed which then subsequently react further with each other. The only exception appears to be the  $Fe^{2+}$ -HNO<sub>3</sub> system, for which the transition between steady states in a CSTR has been reported to be insensitive to stirring,<sup>31</sup> and whose proposed mechanism<sup>32</sup> contains no similar set of elementary steps. Given

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the existence of several plausible explanations, both chemical and physical, to account for the stirring rate sensitivity of reactions in a CSTR, it would seem reasonable to study these systems first in batch before attempting to tackle the more complex CSTR behavior. We have carried out a number of additional experiments to try to differentiate between the various possible effects. A detailed account of these will be given in subsequent papers. Some of the most important findings, however, are summarized below:

The redox electrode potential measured in the chlorite-thiosulfate system exhibits extremely rapid fluctuations in certain concentration ranges. The distribution of the fluctuations is Gaussian with a half-width of 3-5 mV.

At higher concentrations in a well-buffered solution, the pH traces are also sensitive to the stirring rate.

The chlorite-iodide reaction-which has been extensively studied in a CSTR<sup>22-24,33</sup>—also shows some "irregular" clock reaction behavior.

These preliminary results strongly suggest that the role of low-concentration intermediates is decisively important in the stirring rate sensitivity of the reactions; i.e., the phenomenon appears to be a general one which has avoided discovery so far.

One might argue that more effective stirring could eliminate the phenomena discussed and that therefore we are dealing with an artifact generated by the limitations of our apparatus rather than with a feature inherent in the chemistry of the system. We offer two rebuttals to this argument, one from a practical, the other from a more fundamental point of view. The stirring rates we have used, taking into account the small reaction volumes, are considerably higher than is common in general laboratory practice. The more telling response, however, is that the ratio of OH<sup>-</sup> and H<sup>+</sup> production depends on the temperature; the reaction is completely shifted to the H<sup>+</sup>-producing pathway at 90 °C. Therefore there must be an intermediate temperature at which the H<sup>+</sup> and OH<sup>-</sup> production are completely balanced. Fluctuations are then the only factor which drives the reaction in one of the two possible directions. At this temperature there will be no way to "mix away" the fluctuations, even if the reaction could be stirred with ideal effectiveness. In other words, the present experiments have not been conducted under the most fluctuation-sensitive conditions of concentration and temperature. They do appear, however, to have been quite near to the point where fluctuations cannot be dispersed by using typical stirring conditions. It will be of considerable interest to examine the behavior of the system as the critical temperature is approached, to see if the fluctuations grow in amplitude and, if so, what law governs their growth.

The role of local fluctuations in initiating transitions in chemically reacting systems has received attention in the context of thermal ignition in combustion systems.<sup>34,35</sup> A key parameter is the coherence length or the size of local fluctuations required to induce a transition. In the view presented above, increasing the stirring rate has the effect of increasing the mean time required to produce a critical fluctuation, since the size of a typical homogeneous packet will decrease with the stirring speed.

A theoretical study of direct relevance to the present model has recently appeared<sup>36</sup> in which a simplified model for the reaction between ferrous ion and nitric acid<sup>32</sup> is analyzed by stochastic techniques. The authors calculate the first two moments of the concentration distributions and estimate the volume at which fluctuations should become significant. While this volume is much smaller than that used in our experiments, the reaction studied possesses none of the properties (competition between pathways, supercatalysis, formation and consumption of intermediates in successive steps) suggested above to enhance the effects of fluctuations in the chlorite-thiosulfate reaction.

One should also bear in mind that our mechanistic studies were conducted at pH  $\leq$  9, while the clock reaction experiments were carried out at about pH 11. The CSTR investigations of oscillatory beahvior<sup>3-5</sup> and Beck and Rábai's work<sup>37</sup> on oligooscillation of the pH in this system were performed in acidic medium. It is therefore possible that reaction steps not considered here, which become important only in other pH ranges, play an important role in the peculiar kinetic behavior of this fascinating system.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE-8419949) and by a U. S.-Hungarian Cooperative Grant (INT-8217658) from the NSF and the Hungarian Academy of Sciences. We thank G. Bazsa, M. T. Beck, R. E. Connick, W. P. Huskey, and K. Kustin for many helpful discussions of various aspects of these studies.

**Registry No.** ClO<sub>2</sub><sup>-</sup>, 14998-27-7; S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, 14383-50-7.

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