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# A Three-Variable Model for the Explanation of the “Supercatalytic” Effect of Hydrogen Ion in the Chlorite–Tetrathionate Reaction

Attila K. Horváth

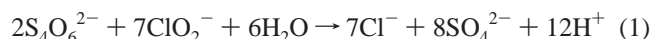
University of Szeged, Department of Physical Chemistry, Szeged, P. O. Box 105, H-6701, Hungary

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It has been shown that not only the slow direct but also the indirect (HOCl-catalyzed) reaction between chlorite and tetrathionate ions is second order with respect to hydrogen ion. Since the direct reaction was found to be orders of magnitude slower than the parallel HOCl-catalyzed pathway, a three-variable model is derived from the previously published five-step model taking into account the experimentally determined  $H^+$  concentration dependence of its rate coefficients by neglecting the direct reaction. The new three-variable model indicates that the “supercatalytic” effect of the hydrogen ion in the HOCl-catalyzed pathway arises from the pH dependence of the individual reactions of the five-step model. The new three-variable model also accounts for the continuous change of the stoichiometric ratio of the reactants and provides a simple kinetic law for involving it in the partial differential equation systems widely used in the study of spatiotemporal behavior of the chlorite–tetrathionate reaction.

## Introduction

It is well-known<sup>1</sup> that the initial rate of the chlorite–tetrathionate reaction is second-order with respect to  $[H^+]$ , that is, the reaction is “supercatalytic”. Diffusion-driven instabilities,<sup>2</sup> cellular acidity fronts,<sup>3</sup> spatial bistability,<sup>4,5</sup> and lateral instability<sup>6,7</sup> studies have brought the chlorite–tetrathionate reaction into the focus of interest by this supercatalytic effect of  $H^+$ . Although a complete mechanism of this reaction is still missing, preliminary investigation<sup>1</sup> suggested the following stoichiometry

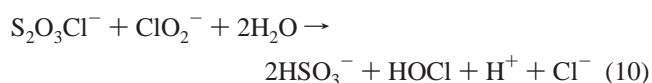
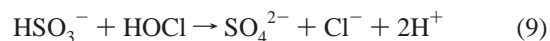
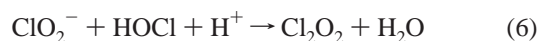
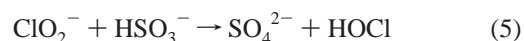
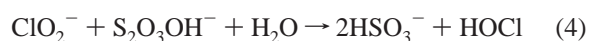
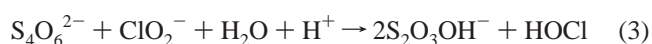


with the appropriate rate law

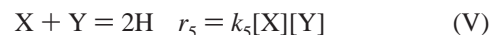
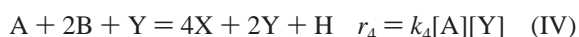
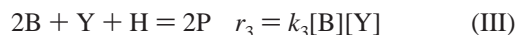
$$v = 10^9[S_4O_6^{2-}][ClO_2^-][H^+]^2 \quad (2)$$

that is extensively used in recent spatiotemporal behavior studies.<sup>2,4,5,7</sup> These investigations have revealed that eq 1 with its simple rate equation provides good qualitative agreement with the experiments as long as the stoichiometric ratio of the reactants is kept constant at 1:4. This evidently complex stoichiometry along with its rate equation was also used to investigate the velocity of the propagation in reaction–diffusion fronts.<sup>8</sup> This study, however, has provided experimental evidence that the model does not work properly at higher relative chlorite excess, and the rate coefficient of eq 1 appeared to be much lower than it was predicted to be earlier. Moreover, the velocity of the propagation fronts was found to show a maximum as a function of chlorite concentration, and this feature could not be interpreted by eq 1 along with its simple rate equation (eq 2).

A five-step model taking the coupled autocatalytic and self-inhibitory effects into account in the chlorite–tetrathionate reaction<sup>9</sup> at constant pH was published recently. It was derived from the following mechanism



by making the simplifying assumption that reactions 4 and 10 and the well-known<sup>10</sup> fast reaction 7 occur essentially instantaneously, allowing us to eliminate the intermediates  $S_2O_3OH^-$ ,  $Cl_2O_2$ , and  $S_2O_3Cl^-$ . The five-step model therefore consists of the following reactions



where A, B, H, X, Y, and P denote  $S_4O_6^{2-}$ ,  $ClO_2^-$ ,  $H^+$ ,  $HSO_3^-$ , HOCl, and  $\cdot ClO_2$ , respectively. Only one product ( $\cdot ClO_2$ ) is indicated in the five-step model, since its concentration was followed experimentally. Note, moreover, that H was not

involved in the previous five-step model, as the experiments were carried out at constant pH, but it has to be taken into account for the interpretation of the supercatalytic effect in unbuffered solution. The reported model properly takes into account the apparently independent kinetic characteristics of the reaction, that is, the high formal kinetic order of the tetrathionate ion and the self-inhibitory effect of the chlorite ion for the formation of chlorine dioxide at a given pH. It was also pointed out<sup>9</sup> that in buffered solutions the key species of the model is the autocatalyst HOCl.

The aim of this work was to investigate whether the five-step model is able to provide an explanation for the supercatalytic effect of the hydrogen ion and to derive a simplified three-variable model involving the effect of hydrogen ion for the kinetics of the chlorite–tetrathionate reaction based on the five-step model reported previously. A more precise description for the kinetics adopted into the partial differential equation system describing the spatiotemporal behavior of the chlorite–tetrathionate reaction may pave the way not only for the explanation of the systematic deviation between the prediction of the old model and the experiments in propagating reaction front studies but also for a better understanding of the inherent feature of the reaction and even to the discovery of the possibility of new spatiotemporal structures.

### Model Reduction

As a first step for reducing the five-step model further to contain only three variables (*A*, *B*, and *H*), it is assumed that *X* and *Y* are steady-state intermediates, that is

$$\frac{dX}{dt} = 4k_1AB - k_2BX + 4k_4AY - k_5XY \cong 0 \quad (11)$$

$$\frac{dY}{dt} = 3k_1AB + k_2BX - k_3BY + k_4AY - k_5XY \cong 0 \quad (12)$$

It was found and illustrated in our previous work that, if  $A_0/B_0 \gtrsim 0.02$  is fulfilled, then the first term of the algebraic equation is negligible ( $k_1AB \ll k_4AY$ ).

Solving eqs 11 and 12 for *X* and *Y* without the  $k_1AB$  term, we obtain

$$Y = B \cdot \frac{k_2}{k_5} \cdot \frac{5RG - 1}{3RG + 1} \quad (13)$$

and

$$X = A \cdot \frac{k_4}{k_5} \cdot \frac{5RG - 1}{2RG} \quad (14)$$

where  $R = A/B$  and  $G = k_4/k_3$ . Since the steady-state concentrations of *X* and *Y* can only be positive numbers, therefore the inequality  $RG > 0.2$  must also be fulfilled.

By the help of the steady-state concentrations of *X* and *Y*, one can easily obtain the three-variable ordinary differential equation system as follows

$$\frac{dA}{dt} = -k_4AY = -\frac{k_2k_4}{k_5} \cdot \frac{5RG - 1}{3RG + 1} AB \quad (15)$$

$$\begin{aligned} \frac{dB}{dt} = & -k_2BX - 2k_3BY - 2k_4AY = \\ & -\frac{k_2k_4}{k_5} \left( \frac{5RG - 1}{2RG} + 2 \cdot \frac{5RG - 1}{3RG + 1} \right) AB - 2 \cdot \frac{k_2k_3}{k_5} \cdot \frac{5RG - 1}{3RG + 1} B^2 \end{aligned} \quad (16)$$

$$\begin{aligned} \frac{dH}{dt} = & k_4AY + 2k_5XY - k_3BY = \\ & \frac{k_2k_4}{k_5} \left( \frac{5RG - 1}{3RG + 1} + 2 \cdot \frac{(5RG - 1)^2}{2RG(3RG + 1)} \right) AB - \frac{k_2k_3}{k_5} \cdot \frac{5RG - 1}{3RG + 1} B^2 \end{aligned} \quad (17)$$

Since  $RG > 0.2$ , the following inequalities must hold

$$0 < \frac{5RG - 1}{3RG + 1} < \frac{5}{3} \quad 0 < \frac{5RG - 1}{2RG} < \frac{5}{2} \quad (18)$$

Finally, applying the  $R \approx A_0/B_0 = R_0$  approximation in eq 18, where  $A_0$  and  $B_0$  are the initial concentrations of the reactants and making some rearrangements, we arrive at the following differential equation system

$$\frac{dA}{dt} = -\frac{k_2k_4}{k_5} \cdot \frac{5R_0G - 1}{3R_0G + 1} AB$$

$$\begin{aligned} \frac{dB}{dt} = & -\frac{k_2k_4}{k_5} \cdot \frac{(5R_0G - 1)(7R_0G + 1)}{(3R_0G + 1)(2R_0G)} AB - \\ & 2 \cdot \frac{k_2k_3}{k_5} \cdot \frac{5R_0G - 1}{3R_0G + 1} B^2 \end{aligned} \quad (19)$$

$$\frac{dH}{dt} = \frac{k_2k_4}{k_5} \cdot \frac{(5R_0G - 1)(6R_0G - 1)}{(3R_0G + 1)(R_0G)} AB - \frac{k_2k_3}{k_5} \cdot \frac{5R_0G - 1}{3R_0G + 1} B^2$$

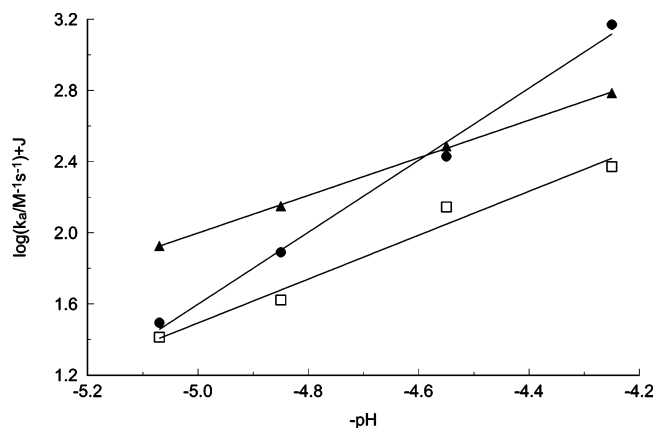
It is easily seen that two constant combinations are important in the reduced model, namely,  $k_2k_3/k_5$  and  $k_2k_4/k_5$ . The supercatalytic effect of the hydrogen ion is evidently hidden in the pH dependence of these rate-constant combinations. Therefore, we carried out our experiments at four different pH values of 4.25, 4.55, 4.85, and 5.07.

### Experimental Section

**Materials.** Commercially available Aldrich NaClO<sub>2</sub> was purified as described previously.<sup>10</sup> The purity of NaClO<sub>2</sub> was checked by standard iodometric titration and found to be better than 99.5%. No chloride impurities could be detected in the purified NaClO<sub>2</sub>. All other chemicals (K<sub>2</sub>S<sub>4</sub>O<sub>6</sub>, acetic acid, and sodium acetate) were of the highest purity available (Aldrich and Fluka) and were used without further purification.

Acetic acid–acetate buffer was used to maintain the pH. The ionic strength was adjusted to 0.5 M with sodium acetate as a buffer component, and the desired amount of acetic acid was added to adjust the pH, taking the pK<sub>a</sub> of the acetic acid of 4.55. At each pH, 14 kinetic runs were carried out at constant 0.005 M chlorite concentrations by changing the tetrathionate concentration between 0.0001 and 0.005 M, and 13 kinetic curves were taken at constant 0.0005 M tetrathionate concentration by changing the chlorite concentrations between 0.0001 and 0.03 M.

**Methods.** The kinetic measurements were carried out in a standard 1 cm quartz cuvette equipped with a Teflon cap and a magnetic stirrer. The cuvette was carefully sealed (beside the



**Figure 1.** Dependence of the logarithm of rate coefficients  $k_1$  (●),  $k_2$  (□), and  $k_4$  (▲) on pH. The  $\log k_a$  values were shifted along the y-axis by  $J = 6, -3.5$ , and  $0$  units in the case of  $\log(k_1)$ ,  $\log(k_2)$ , and  $\log(k_4)$ , respectively, in order to see the trends better. Fitted slopes were found to be  $2.02 \pm 0.12$ ,  $1.19 \pm 0.05$ , and  $1.06 \pm 0.03$  for  $\log(k_1)$ ,  $\log(k_2)$ , and  $\log(k_4)$ , respectively.

**TABLE 1: Determination of Second-Order Rate Coefficients at Different pHs**

parameter/pH	5.07	4.85	4.55	4.25
$k_1 \times 10^5 \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	$3.12 \pm 0.15$	$7.76 \pm 0.46$	$26.8 \pm 3.40$	$148 \pm 13.8$
$k_2 \times 10^{-4} \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	$8.17 \pm 0.10$	$13.2 \pm 0.19$	$44.1 \pm 0.08$	$74.4 \pm 1.5$
$k_4 \times 10^{-1} \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	$8.42 \pm 0.07$	$14.1 \pm 0.2$	$30.6 \pm 0.4$	$61.0 \pm 0.9$

Teflon cap) with Parafilm to minimize the loss of chlorine dioxide. The reaction was followed at 400 nm by a Zeiss Specord S10 diode array spectrophotometer with exclusion of the UV light in order to avoid the photochemical decomposition of the tetrathionate ion.<sup>11</sup>

In the visible range, no other absorbing species was found beside the chlorine dioxide; therefore, the evaluation procedure was executed only at the single 400 nm wavelength. The experimental curves were analyzed with the program package *ZiTa*,<sup>12</sup> developed recently for fitting kinetic data.

## Results

We have analyzed the stabilized rate of chlorine dioxide formation in the initial phase of the reaction as before.<sup>9</sup> Step V of the model corresponds to the well-known fast reaction between  $\text{HSO}_3^-$  and  $\text{HOCl}$  studied thoroughly by Fogelman et al.<sup>13</sup> The rate coefficient was found to be  $7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , so this value was directly taken to our calculation as a fixed number. Step III corresponds to the rate-determining step of the chlorite–hypochlorous acid reaction. This reaction was studied by several authors.<sup>10,14–17</sup> The rate coefficient of the forward reaction ( $\nu_{\text{III}} = k_{\text{III}}[\text{HOCl}][\text{ClO}_2^-][\text{H}^+]$ ) was found to be between  $1.12 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$  and  $5.7 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ . The disagreement between these results apparently is due to the unrecognized general acid catalysis. Since the experimental circumstances here (ionic strength, buffer components, temperature) were the same as those used in Peintler et al.'s study,<sup>10</sup> the  $1.12 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$  value was taken to our calculation. The values of  $k_1$ ,  $k_2$ , and  $k_4$  were fitted as second-order rate coefficients at each pH. The results can be seen in Table 1. A plot of the logarithm of rate coefficients against the  $\log([\text{H}^+])$  revealed that  $k_2$  and  $k_4$  linearly depend on  $[\text{H}^+]$ , but  $k_1$  is proportional to  $[\text{H}^+]^2$  within the pH range used in our experiments! (see Figure 1). From these data, one can easily calculate that  $k_1 = (4.58 \pm 0.78) \times 10^5 [\text{H}^+]^2$ ,  $k_2 = (1.34 \pm 0.11) \times$

$10^{10} [\text{H}^+]$ , and  $k_4 = (1.08 \pm 0.05) \times 10^7 [\text{H}^+]$ . By comparing these values with the corresponding ones found in the literature, the following conclusion may be drawn.

For the rate coefficient of eq 1, a preliminary study<sup>1</sup> yielded a value of  $10^9 \text{ M}^{-3} \text{ s}^{-1}$ , but later from a front reaction study,  $7.28 \times 10^4 \text{ M}^{-3} \text{ s}^{-1}$  was estimated.<sup>8</sup> More recently in a spatial bistability study, the value of  $5 \times 10^6 \text{ M}^{-3} \text{ s}^{-1}$  was adjusted<sup>5</sup> to eq 1. Our  $4.58 \times 10^5 \text{ M}^{-3} \text{ s}^{-1}$  value for  $k_1$  lies just between these results. The comparison, however, should rather be made between the values of  $10^9 \text{ M}^{-3} \text{ s}^{-1}$  and  $(5/3)k'_2 = 3.17 \times 10^8 \text{ M}^{-3} \text{ s}^{-1}$  (the derivation of  $k'_2$  is discussed later in the text), since the direct reaction ( $k_1$ ) is only needed in the kinetic experiments to produce trace amount of  $\text{HSO}_3^-$  from which  $\text{HOCl}$  is formed to ignite the autocatalytic pathway. The factor of 3 deviation is therefore believed to be more than satisfactory compared to the value of  $10^9 \text{ M}^{-3} \text{ s}^{-1}$  found by Nagypál and Epstein.<sup>1</sup>

The pH-dependent rate coefficient of the oxidation of  $\text{HSO}_3^-$  by chlorite ion was determined by Huff Hartz<sup>18</sup> and Frerichs<sup>19</sup> and their co-workers. Huff Hartz et al. conducted their research in huge excess of  $\text{S(IV)}$  in order to maintain pseudo-first-order conditions. In this way, they established the value of  $5.01 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$ ; meanwhile, Frerichs et al. obtained  $2.19 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$  by simulating of the oscillatory behavior of the chlorite–sulfite reaction in the continuously stirred tank reactor (CSTR) system. The former value was calculated from taking  $\text{p}K_a(\text{SO}_2) = 1.90$ . However, by taking the uncertainty of  $\text{p}K_a(\text{SO}_2)$  and the different experimental circumstances into consideration, the 20-fold difference from our value of  $1.34 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$  may be regarded acceptable.

The rate coefficient of the tetrathionate–hypochlorous acid reaction was found to be  $32 \text{ M}^{-1} \text{ s}^{-1}$  at  $\text{pH} = 8.2\text{--}9.0$ .<sup>20</sup> At this pH range, the rate of reaction was shown to have a linear dependence on  $[\text{H}^+]$ . If this trend is valid throughout a long extrapolation to  $\text{pH} = 4.2$ , the validity of the  $1.08 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  value can also be accepted. To check the reality of the latter rate constant, further investigations are needed on the tetrathionate–hypochlorous acid reaction in slightly acidic medium.

## Discussion

Having the rate coefficients ( $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_4$ ,  $k_5$ ) in hand, we first focus on the simplifying assumptions that have been applied in the way of the derivation of the three-variable model. Condition, where the first assumption is valid, must fulfill the following inequality

$$Y \gg B \cdot \frac{k_1}{k_4} = B \cdot \frac{4.58 \times 10^5 [\text{H}^+]^2}{1.08 \times 10^7 [\text{H}^+]} = 4.24 \times 10^{-2} \cdot [\text{H}^+] \cdot B \quad (20)$$

Taking  $\text{pH} = 4.5$ , where the chlorite–tetrathionate reaction is already rapid enough to be completed within hundreds of seconds, and  $B = 0.01 \text{ M}$ , used in the study of investigating the propagation of reaction–diffusion fronts and our kinetic experiments, means that  $Y$  (concentration of  $\text{HOCl}$ ) must be higher than  $10^{-8} \text{ M}$ . This trace amount can easily be fulfilled, since a high initial concentration of chlorite may itself contain such a small amount of  $\text{HOCl}$ ; so, our calculation supports the validity of our first assumption. The chemical meaning of this inequality is that the starting reaction is only needed to produce a trace amount of  $X$  ( $\text{HSO}_3^-$ ); from that point, the reaction is governed by steps II–V, so step I is no longer needed. This feature of the model was already illustrated in our previous

paper,<sup>9</sup> where the rates of steps I–V were plotted against the initial concentrations of the reactants at a given point in time, indicating that the rate of step I is orders of magnitude slower than that of step IV. In other words, it means that the direct reaction between the tetrathionate ion and the chlorite ion is orders of magnitude slower than the net disappearance of the reactants caused by their individual reactions with HOCl produced in a trace amount in the direct reaction.

Analyzing our second condition essentially means that

$$R = \frac{A}{B} > \frac{1}{5G} = \frac{k_3}{5k_4} = \frac{1.12 \times 10^6 [\text{H}^+]}{5 \times 1.08 \times 10^7 [\text{H}^+]} \approx 0.02 \quad (21)$$

This inequality must easily be fulfilled by adjusting the initial concentrations of the reactants. It also indicates that application of a high excess of chlorite (more than 50-fold) prevents the usage of the simplified model. The chemical background of this feature is that a high excess of chlorite ion traps the autocatalyst HOCl throughout step III, resulting in cessation of the domination of the autocatalytic step IV. In this case, not only the second assumption but also the first one is violated, resulting in a collapse of the model. Maintaining the initial concentration ratio of the reactants in the proper range, however, allows everyone to use the simplified three-variable model providing a useful tool for studying the spatiotemporal behavior in this system.

Our suggested final simplification, where  $R_0 = A_0/B_0$  was used instead of  $R = A/B$  in eq 18, means a good average value for terms  $(5RG - 1)/(3RG + 1)$  and  $(5RG - 1)/2RG$  that vary within a narrow range as a function of the concentrations of the reactants, allowing us further simplification in the kinetic model. Taking  $G = k_4/k_3 \approx 10$ , the terms of eq 18 will be reduced to

$$\frac{5RG - 1}{3RG + 1} \approx \frac{50R_0 - 1}{30R_0 + 1} \text{ and } \frac{5RG - 1}{2RG} \approx \frac{50R_0 - 1}{20R_0} \quad (22)$$

We must also bring up the question regarding how the cubic autocatalysis can be interpreted by the new three-variable model, as a necessary condition of lateral instability. To do this, we have to focus on the terms  $k_2k_3/k_5$  and  $k_2k_4/k_5$  of the model. The value of the rate coefficient  $k_5$  hits almost the limit of diffusion control, so no essential pH dependence of it can be expected. Therefore, substituting the values determined above yields

$$\frac{k_2k_3}{k_5} = \frac{1.34 \times 10^{10} [\text{H}^+] \cdot 1.12 \times 10^6 [\text{H}^+]}{7.6 \times 10^8} = 1.97 \times 10^7 \cdot [\text{H}^+]^2 \quad (23)$$

$$\frac{k_2k_4}{k_5} = \frac{1.34 \times 10^{10} [\text{H}^+] \cdot 1.08 \times 10^7 [\text{H}^+]}{7.6 \times 10^8} = 1.90 \times 10^8 \cdot [\text{H}^+]^2 \quad (24)$$

where both terms depend on the power of 2 of the hydrogen ion concentration, meaning that all the terms of the ordinary differential equation system contain second-order dependence on  $[\text{H}^+]$ . By substituting eqs 22–24 into eq 19, denoted by  $k'_1 = 1.97 \times 10^7 \text{ M}^{-3} \text{ s}^{-1}$  and  $k'_1 = 1.90 \times 10^8 \text{ M}^{-3} \text{ s}^{-1}$ , we finally arrive at the model believed to help in a more quantitative investigation of spatiotemporal behavior of the chlorite–tetrathionate reaction

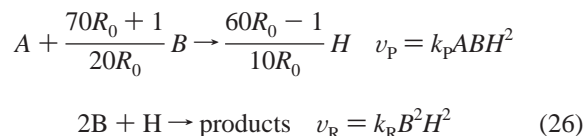
$$\frac{dA}{dt} = -\frac{50R_0 - 1}{30R_0 + 1} \cdot k'_2 \cdot ABH^2$$

$$\frac{dB}{dt} = -\frac{(50R_0 - 1)(70R_0 + 1)}{(30R_0 + 1)20R_0} \cdot k'_2 \cdot ABH^2 - 2 \cdot \frac{50R_0 - 1}{30R_0 + 1} \cdot k'_1 \cdot B^2H^2 \quad (25)$$

$$\frac{dH}{dt} = \frac{(50R_0 - 1)(60R_0 - 1)}{(30R_0 + 1)10R_0} \cdot k'_2 \cdot ABH^2 - \frac{50R_0 - 1}{30R_0 + 1} \cdot k'_1 \cdot B^2H^2$$

This set of differential equations clearly indicates the following:

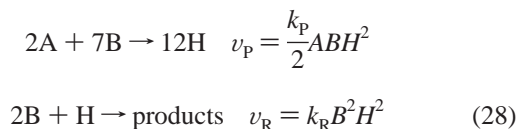
(i) Within the range  $0.02 < R_0 \lesssim 0.2$ , the following two-step chemical model is operating properly



where

$$k_p = \frac{k_2k_4}{k_5} \cdot \frac{50R_0 - 1}{30R_0 + 1} \text{ and } k_r = \frac{k_2k_3}{k_5} \cdot \frac{50R_0 - 1}{30R_0 + 1} \quad (27)$$

(ii) Using the ratio of the initial concentrations of the reactants within the range  $0.2 \lesssim R_0 \lesssim 2$ , however, allows anyone to use a more simple two-step kinetic model with fixed stoichiometric numbers



(iii) Further increase in  $R_0$  (i.e., the usage of high excess of tetrathionate) means that step III of the five-step model becomes insignificant, resulting in a case where  $\nu_p$  alone is capable of a good description of the kinetics of the chlorite–tetrathionate reaction in studies of spatiotemporal behavior, so eq 1 along with its rate equation, eq 2, is suitable for the proper kinetic part of the partial differential equation system.

Finally, in an earlier study, it was found<sup>8</sup> that the velocity of propagation of reaction–diffusion fronts in the chlorite–tetrathionate reaction shows a maximum as a function of initial chlorite concentration. The simple kinetic model, based on eqs 9–10, however, predicts a continuous increase in the velocity versus chlorite concentration (see Figure 6 of the original paper). It also suggests a much higher value (Figure 5 of the original paper) for the velocity at lower tetrathionate concentration. This deviation stems from a shift in the chemical mechanism claimed by the authors. The ordinary differential equation system of our new model contains a negative term that depends on the square of the chlorite concentration that is responsible for explaining the inhibitory effect of the chlorite ion in the kinetic curves and may also be suitable for supporting the experimental results of the front velocity study.

The proposed two-step model may also be suitable for further investigations of the decay of the autocatalyst with irreversible binding<sup>21</sup> in the present system by simply varying the initial concentration ratio of the reactants.



Another important remark has to be emphasized as well. The extension of the pH studies to lower acidity may reveal that even at a higher than cubic (second order with respect to  $[H^+]$ ) autocatalysis might occur in the chlorite–tetrathionate reaction. There is indeed an allusion in the literature to this fact in an earlier work<sup>1</sup> at higher conversion in the chlorite–tetrathionate reaction. Our new model may support this fact, because the  $H^+$  dependence of the model arises from the  $H^+$  dependence of the combination of  $k_2k_3/k_5$  and  $k_2k_4/k_5$ . The dependence of  $k_2$  on the power of  $[H^+]$  greater than 1 is easily conceivable chemically, since not only is the  $pK_a$  of  $SO_2$  (or  $H_2SO_3$ ) around 1.90 but also that of  $HClO_2$  is 1.86.<sup>22</sup> The greater reactivity of unsymmetrical protonated oxychlorine and oxysulfur species toward each other is well-known. This realization has led to the systematic design of the propagation of reaction fronts.<sup>23</sup>

## Conclusions

It was convincingly demonstrated in our previous paper<sup>9</sup> that the chlorite–tetrathionate reaction proceeds via two parallel pathways: a direct reaction and an HOCl-catalyzed reaction. In this paper, the result of a preliminary investigation<sup>1</sup> was confirmed in which the direct reaction is “supercatalytic” with respect to the hydrogen ion, and it is clearly shown that the HOCl-catalyzed route also has second-order dependence of  $[H^+]$  that may even grow further with increasing  $[H^+]$ . It was pointed out in our previous paper<sup>9</sup> that apart from the very beginning stage of the reaction the HOCl-catalyzed route governs the reaction having a rate an order of magnitude greater than that of the direct reaction. Therefore, a new simplified three-variable model has been proposed for the kinetics of the chlorite–tetrathionate reaction, which neglects the slow direct reaction, to adapt it into investigations of the spatiotemporal behavior of the chlorite–tetrathionate reaction. The new model was derived from the five-step model that explains the most important characteristics of the kinetic curves in this reaction, taking the pH dependence of the reactions into consideration. It is, however, quite remarkable that along with the simplifications the unexpected maximum in chlorite dependence of the propagation of reaction–diffusion fronts is still an inherent feature of the three-variable model throughout its irreversible hydrogen ion-consuming second step. It also indicates indirectly that the HOCl-catalyzed pathway is probably responsible for the behavior of the system. It seems likely that the fortunate coincidence of the second-order  $[H^+]$  dependence of the direct and indirect pathways makes it possible to use eqs 1 and 2 for the proper kinetic parts of the reaction–diffusion models at the strict  $A_0/B_0 = 1:4$  initial concentration ratio of the reactants with the stoichiometry in eq 1. The new three-variable model also offers a convenient tool for more quantitative investigations of the lateral instabilities and other spatiotemporal behaviour in this system, because it relieves the restriction of the fixed ratio

of the initial concentration of the reactants (1:4) compared to the old model.

It should also be mentioned, however, that the chemistry of the chlorite–tetrathionate reaction still needs further refinements in order to take into account, for example, the chlorate formation and the chloride dependence on its rate. Further investigations are continuing in our lab to unravel the kinetics and mechanism of the chlorite–tetrathionate reaction. Despite the fact that the mechanism of this reaction is still not explored entirely, the model works remarkably well. It is also hoped that the present refinement of the kinetic model may contribute to a deeper understanding of the spatiotemporal behavior of the chlorite–tetrathionate reaction.

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