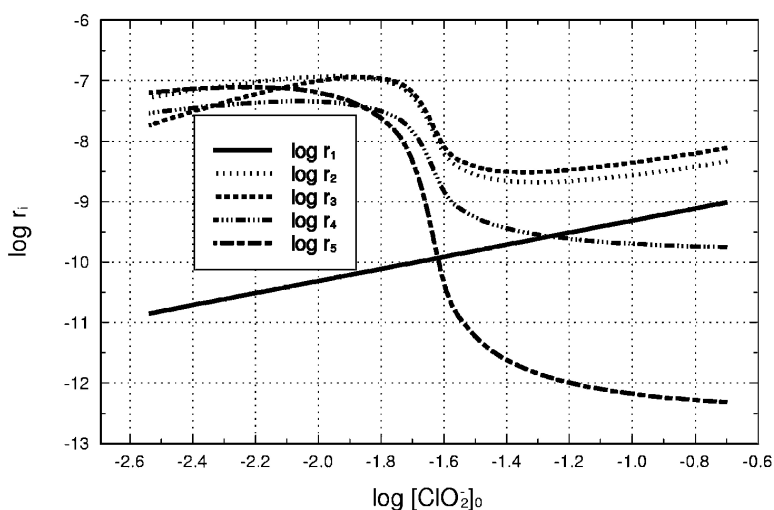


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Autocatalysis and Self-Inhibition: Coupled Kinetic Phenomena in the Chlorite–Tetrathionate Reaction

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The chlorite–thiosulfate reaction displays a remarkable range of “exotic” phenomena, including complex periodic and aperiodic oscillation in a flow reactor,¹ autocatalysis² and stochastic reaction time distributions under batch conditions,³ and propagation of reaction fronts in unstirred mixtures.⁴ Ultimately, one would hope to understand and describe quantitatively these and related phenomena, a task that requires insight into the mechanism of the reaction. As a part of the effort to elucidate the mechanism of the chlorite–thiosulfate reaction, several subsystems of the parent reaction have been investigated. The kinetics and mechanism of the chlorite–hypochlorous acid,⁵ thiosulfate–chlorine dioxide,⁶ tetrathionate–hypochlorous acid,⁷ chlorine dioxide–hypochlorite,⁸ and chlorine dioxide–tetrathionate⁹ reactions have been established. We now report here the results of our investigation of the chlorite–tetrathionate reaction. It is already known⁴ that the initial rate of the reaction increases slightly with $[\text{Cl}^-]$ and is second order with respect to $[\text{H}^+]$, i.e., the reaction is “supercatalytic”. This feature plays a key role in the diffusion-driven instabilities,¹⁰ cellular acidity fronts,¹¹ and lateral front instabilities¹² observed in the ClO_2^- – $\text{S}_4\text{O}_6^{2-}$ system. The experiments presented here were conducted in acetic acid–acetate buffer ($I = 0.5$ M adjusted with sodium acetate, $\text{p}K = 4.55$); thus, the “supercatalytic” effect of H^+ was completely suppressed.

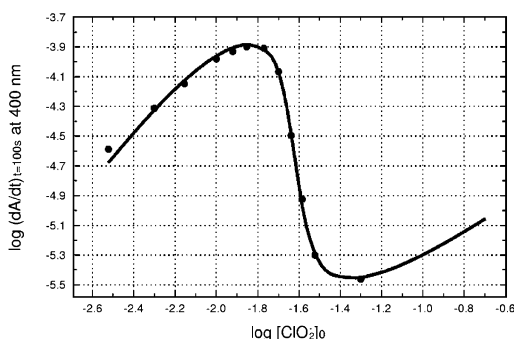
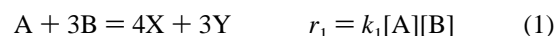


Figure 1. Dependence of stabilized rate (symbols: measured, solid line: calculated) on $[\text{ClO}_2^-]_0$. $[\text{S}_4\text{O}_6^{2-}]_0 = 0.0005$ M, $\text{pH} = 4.95$. All other initial concentrations are zero in the simulation.

The surprising results of our investigations are illustrated in Figures 1 and 2. The absorbance of the chlorite–tetrathionate reaction mixtures at 400 nm, where chlorine dioxide is the only absorbing species ($\epsilon = 571.5$ $\text{M}^{-1} \text{cm}^{-1}$), was followed with a Zeiss S10 diode array spectrophotometer, excluding UV light to avoid complications from UV irradiation of tetrathionate ion.¹³ After a brief (<40 s) induction period, the rate of $^*\text{ClO}_2$ formation becomes nearly constant for 5–30 min, depending on the initial concentrations. This stabilized rate, calculated from the absorbances, goes

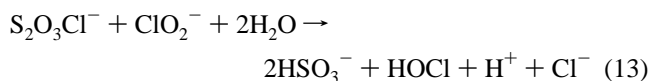
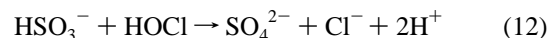
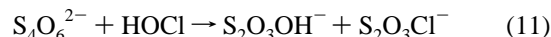
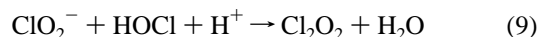
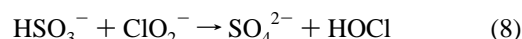
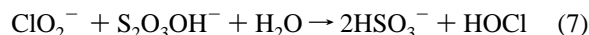
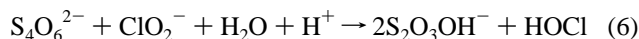
through two extrema as a function of initial chlorite concentration (Figure 1). Chlorite ion thus behaves not just as a simple reactant but also as a self-inhibitor, with a formal kinetic order, calculated as $d(\log(\text{rate}))/d(\log([\text{X}]_0))$, between +1.5 and –9.4! A similar analysis to determine the order of tetrathionate ion shows that the stabilized rate varies sigmoidally (Figure 2) as a function of initial tetrathionate concentration, giving a formal kinetic order of tetrathionate as high as 9!

Our aim here is to provide an explanation for this unusual kinetic behavior. After examining many candidate mechanisms, we propose the following scheme for the stabilized phase of the chlorite–tetrathionate reaction:



where A, B, X, Y, P denote $\text{S}_4\text{O}_6^{2-}$, ClO_2^- , HSO_3^- , HOCl , $^*\text{ClO}_2$, respectively.

Equations 1–5 are derived from the following mechanism:



by making the simplifying assumption that reactions 7 and 13 and the well-known fast reaction⁵ 10 occur essentially instantaneously, allowing us to eliminate the intermediates $\text{S}_2\text{O}_3\text{OH}^-$, Cl_2O_2 , and $\text{S}_2\text{O}_3\text{Cl}^-$. The only product shown in the scheme is the absorbing species, $^*\text{ClO}_2$.

Of the five rate constants in the scheme, two, $k_3 = 11.5$ $\text{M}^{-1} \text{s}^{-1}$ and $k_5 = 7.6 \times 10^8$ $\text{M}^{-1} \text{s}^{-1}$,^{5,14,15} were taken from the literature and fixed during the fitting procedure. The others, $k_1 = (8.4 \pm$

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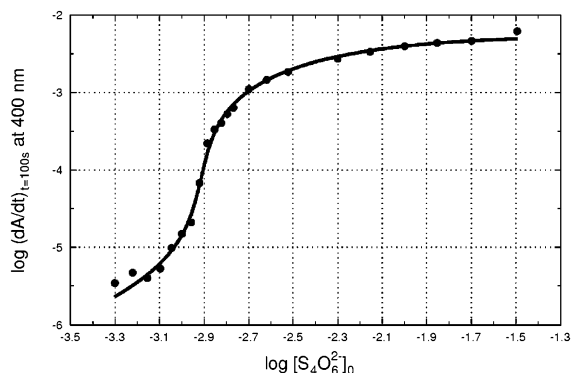


Figure 2. Dependence of the stabilized rate (symbols: measured, solid line: calculated) on $[S_4O_6^{2-}]_0$. $[ClO_2^-]_0 = 0.04822$ M, pH = 4.95. All other initial concentrations are zero in the simulation.

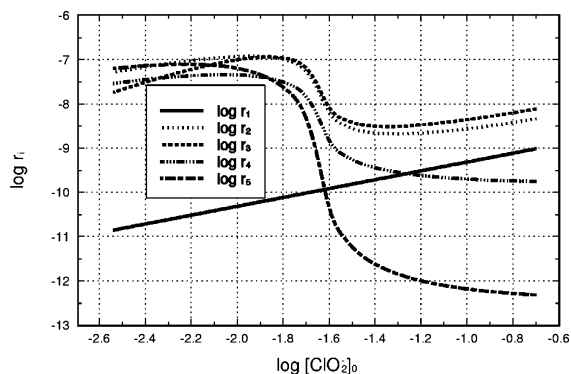


Figure 3. Calculated rates of eqs 1–5 at $t = 100$ s plotted against initial chlorite concentration. $[S_4O_6^{2-}]_0 = 0.0005$ M, pH = 4.95.

$1.3) \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = (1.0 \pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $k_4 = 98 \pm 7 \text{ M}^{-1} \text{ s}^{-1}$, were determined by nonlinear parameter estimation with the multipurpose kinetic program package ZiTa.¹⁶ The two data series (chlorite- and tetrathionate-dependence) were fitted separately. The value obtained for k_4 is within a factor of 3 of that found at very different pH and ionic strength in a study⁷ of the reaction of HOCl and $S_4O_6^{2-}$. Our k_2 differs by about a factor of 15 from that obtained in a study¹⁷ done in a large excess of sulfite rather than chlorite. The calculated and measured rates are in excellent agreement, as seen in Figures 1 and 2.

The unusual kinetic behavior of this system can be understood by referring to eqs 1–5. The key species is the autocatalyst Y (HOCl). To analyze the chlorite dependence, we focus on the competition between the nonautocatalytic and autocatalytic pathways 1 and 4. At low $[ClO_2^-]$, autocatalysis is the favored route, and its rate increases with $[ClO_2^-]$, because $r_2 > r_3$, resulting in net production of HOCl at a rate proportional to $[ClO_2^-]$. After these two rates cross (see Figure 3) at about $pClO_2^- = 1.85$ (maximum in Figure 1), autocatalysis becomes less important as ClO_2^- increases. Once the rate of step 4 falls below that of step 1, at $pClO_2^- \approx 1.3$ (minimum in Figure 1), autocatalysis is essentially shut down. Now the reaction is dominated by the nonautocatalytic production step 1, and the net rate begins to increase with $[ClO_2^-]$. The apparent selfinhibition in the range $1.85 < pClO_2^- < 1.3$ results from the switching between the relatively rapid autocatalytic route to the slower nonautocatalytic pathway. Note that ClO_2^- acts, in a sense, to buffer [HOCl], since, at low [HOCl], production of HOCl and removal of HSO_3^- in step 2 assume increased importance relative to step 3 and prevent step 5 from becoming a significant sink for HOCl.

When the initial tetrathionate concentration is varied as in Figures 2 and 4, we find that steps 1 and 4 have similar rates at low $[S_4O_6^{2-}]$

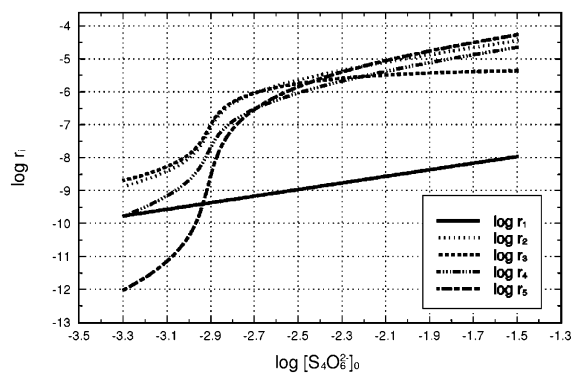


Figure 4. Calculated rates of eqs 1–5 at $t = 100$ s plotted against initial tetrathionate concentration. $[ClO_2^-]_0 = 0.04822$ M, pH = 4.95.

but that the autocatalytic pathway quickly comes to dominate as $[S_4O_6^{2-}]$ is increased, resulting in the rapid rise in the rate seen in Figure 2 for $pS_4O_6^{2-}$ around 3. As we continue to increase $S_4O_6^{2-}$, the HSO_3^- produced in steps 1 and 4 begins to capture a significant amount of the autocatalyst in step 5, which overtakes step 4 at about $pS_4O_6^{2-} = 2.7$ (Figure 4), causing the rate to show saturation behavior as $[S_4O_6^{2-}]$ is increased further. The high formal kinetic order with respect to $S_4O_6^{2-}$ arises from the turning on and turning off of the autocatalytic pathway as we sweep through a range of initial tetrathionate concentrations.

We emphasize that only the formation of chlorine dioxide, not the disappearance of tetrathionate and chlorite ion, becomes independent of $[S_4O_6^{2-}]_0$. It should also be noted that the net rate of chlorine dioxide formation may start to decrease at higher tetrathionate concentrations because of the increasing importance of the chlorine dioxide–tetrathionate reaction.⁹

Investigations are continuing in our laboratory to extend this mechanism so as to describe accurately the kinetics and mechanism of the chlorite–tetrathionate reaction over its entire time course.

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