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Bisulfite-Driven Autocatalysis in the Bromate–Thiosulfate Reaction in a Slightly Acidic Medium

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Supporting Information

ABSTRACT: The thiosulfate–bromate reaction has been studied by high-performance liquid chromatography, monitoring the concentrations of thiosulfate and tetrathionate simultaneously. It is found that concentration–time curves of both species display a sigmoidal shape in a slightly acidic, well-buffered medium. Unlike the previously reported complex reaction systems involving bromate, this nonlinear dynamical behavior originates from neither proton nor bromine(III) autocatalysis under our experimental conditions. We demonstrated that sulfur(IV) species significantly accelerates the reaction; therefore, it acts as an autocatalyst. To the best of our knowledge, no reaction system has yet been reported among the pH-driven oxysulfur–oxyhalogen systems, where sulfur(IV) has such a remarkable role. On the basis of the simultaneous evaluation of [$S_2O_3^{2-}$] and [$S_4O_6^{2-}$] time series, an eight-step kinetic model is proposed to account for the experimental observations. The model employed here may serve as a solid starting point to extend it for other oxysulfur–oxyhalogen systems where such a seemingly general phenomenon may become observable.

Oxyhalogen and oxysulfur compounds have been extensively used to study oscillations and pattern formations in recent years.[1] In the case of the catalyzed[2,3] and uncatalyzed[4] bromate-driven system, positive feedback arises from bromine(III) autocatalysis, but this phenomenon generally occurs at strongly acidic conditions, where the pH is often less than 1.0. In the case of the pH-driven [BrO_x ($x = 2, 3$) oxysulfur substrate[5]] systems, the nonlinearity, however, is usually explained by H^+ autocatalysis. Among these systems, the possibility of the autocatalytic feature being maintained by substances other than protons has so far avoided any significant attention.

In this Communication, we prove that the batch thiosulfate–bromate reaction in a slightly acidic, buffered medium (pH = 4.25–5.0) is autocatalytic with respect to sulfur(IV) species. The fact that this species is not a final product of the reaction, meaning that the autocatalysis is driven by a long-lived intermediate, gives a further unique feature of this system. This phenomenon was discovered meanwhile by investigating the detailed kinetics of the thiosulfate–bromate reaction, but we believe it is worth reporting because the autocatalytic role of sulfur(IV) species may be more general in oxyhalogen–oxysulfur chemistry.

The thiosulfate–bromate reaction was followed by high-performance liquid chromatography (HPLC); the details are given in the Supporting Information (SI). Figure 1 shows that the formation of tetrathionate as well as the consumption of thiosulfate follows a sigmoidal-shaped curve, meaning that some sort of autocatalysis is involved. It should be emphasized that the appearance of a sigmoidal-shaped concentration–time curve of a product alone does not necessarily mean autocatalysis. A striking counterexample (often seen in common textbooks but not emphasized clearly) is a simple first-order consecutive process via a long-lived intermediate. In that case, the formation of a product proceeds through an apparent induction period because its formation is delayed, but no autocatalysis is involved. If, however, the sigmoidal-shaped concentration–time curves of the reactant and product are simultaneously observed, the presence of autocatalysis is clearly suggested. The phenomenon of autocatalysis can easily be proven experimentally by the addition of an autocatalyst to the reacting solution, which results in a shortening of the induction period. Because the thiosulfate–bromate reaction may have two limiting stoichiometries

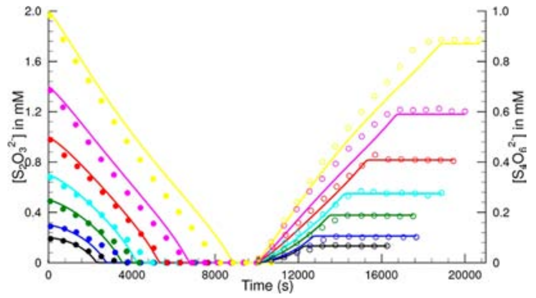

Figure 1. Measured (dots) and calculated (lines) concentration–time curves at $[BrO_3^-]_0 = 10.0$ mM and pH = 4.75. $[S_2O_3^{2-}]_0$/mM = 0.2 (black), 0.3 (blue), 0.5 (green), 0.7 (cyan), 1.0 (red), 1.4 (magenta), and 2.0 (yellow). Filled and empty symbols denote the concentrations of $S_2O_3^{2-}$ and $S_4O_6^{2-}$, respectively. Note that the time for the [$S_4O_6^{2-}$] is shifted by 10000 s along the *x* axis for better visibility.

$$6S_2O_3^{2-} + BrO_3^- + 6H^+ \rightarrow 3S_4O_6^{2-} + Br^- + 3H_2O \qquad (1)$$

$$3S_2O_3^{2-} + 4BrO_3^- + 3H_2O \rightarrow 6SO_4^{2-} + 4Br^- + 6H^+ \qquad (2)$$

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tetrathionate and especially bromide ions might be good candidates as autocatalysts. Figure 2, however, clearly demonstrates that neither of them is responsible for autocatalysis under our experimental conditions. Hypobromite and bromite ions have also been probed to act as possible autocatalysts, but in both cases, we found that a trace amount of these species results in a sudden drop of the $[S_2O_3^{2-}]$ and a simultaneously rapid rise of $[S_4O_6^{2-}]$ (see the SI). This fact can be easily explained by rapid reactions between thiosulfate and bromite as well as between thiosulfate and hypobromite. Because bromine also reacts very rapidly with thiosulfate and tetrathionate,[6] this indicates that none of the conceivable bromine-containing species is responsible for the autocatalytic effect.

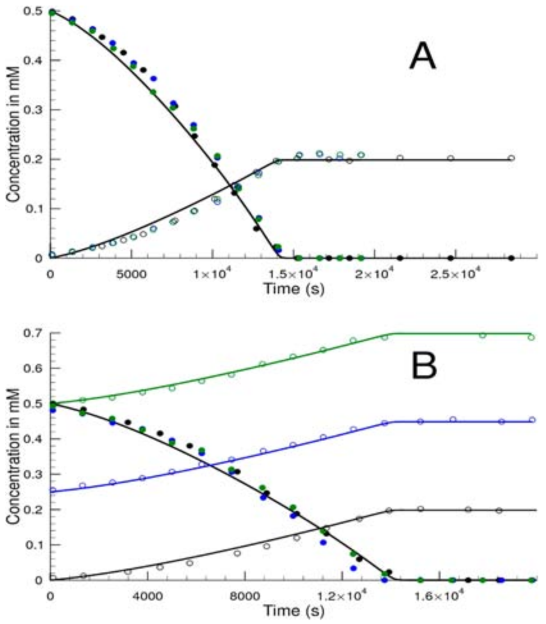

Figure 2. Effect of Br^- (A) and $S_4O_6^{2-}$ (B) on the measured (symbols) and calculated (lines) concentration−time curves at $[S_2O_3^{2-}]_0$ = 0.5 mM, $[BrO_3^-]_0$ = 10.0 mM, and pH = 5.0. (A) $[Br^-]_0$/mM = 0.0 (black), 1.0 (blue), and 2.0 (green). (B) $[S_4O_6^{2-}]_0$/mM = 0.0 (black), 0.25 (blue), and 0.5 (green). Filled and empty symbols stand for $[S_2O_3^{2-}]$ and $[S_4O_6^{2-}]$, respectively.

A further systematic search among the possible intermediates showed that the addition of a trace amount of sulfite significantly shortened the induction period, as shown in Figure 3. These experiments clearly prove that (bi)sulfite is the autocatalyst under our experimental conditions. We also noticed that, in the absence of initially added sulfite, the induction period is more pronounced at lower thiosulfate (see Figure 1) and bromate concentrations (see the SI) but a decrease of the pH significantly shortens the induction period. To account for all of the experimental observations, we employed the following kinetic model by program package *ZiTa*.[7] Rate coefficients determined by nonlinear simultaneous parameter estimation are illustrated in Table 1. The average deviation was found to be 2.8% by a relative fitting procedure. Altogether only five fitted parameters were used, and the rest of the parameters were directly taken from previous reports. The SI contains all of the fitted kinetic data besides Figures 1−3.

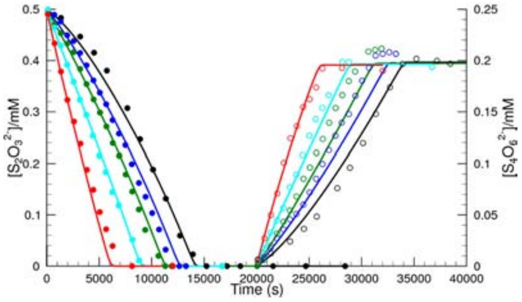

Figure 3. Effect of sulfite ion on the measured (symbols) and calculated (solid lines) concentration−time curves at $[S_2O_3^{2-}]_0$ = 0.5 mM, $[BrO_3^-]_0$ = 10.0 mM, and pH = 5.0. $[SO_3^{2-}]_0$/mM = 0.0 (black), 0.005 (blue), 0.01 (green), 0.02 (cyan), and 0.04 (red). Filled and empty symbols denote $[S_2O_3^{2-}]$ and $[S_4O6^{2-}]$, respectively. Note that the time for the $[S_4O_6^{2-}]$ is shifted by 20000 s along the *x* axis for better visibility.

The following facts have to be emphasized to support the kinetic model. (a) The rate equation of step R1 controls the induction period of the reaction, indicating that the autocatalytic nature is more pronounced at high pHs and low reactant concentrations. (b) The positive feedback cycle is maintained by steps R3 and R6 producing HSO_3^- autocatalytically, resulting in an increase of its concentration. Although at first sight this would suggest that bromite is also involved in the autocatalytic loop, one should bear in mind that bromite is consumed instantaneously (see the rate coefficients of R2 and R3) as long as thiosulfate is present; therefore, its concentration is controlled at such a low level (around 10^{-10} M) that it cannot act as an autocatalyst. The observation that the addition of bromite only decreases the initial concentration of thiosulfate (see Figure S4 in the SI) also supports this statement. The concentration of bisulfite, however, continuously increases in the induction period (it may even reach the 5×10^{-5} M level under our experimental conditions) because its removal via step R7 is slower than its production via step R3 and via the indirect route of step R2 followed by step R5. After thiosulfate is completely consumed, excess bromate diminishes bisulfite quickly via steps R6−R8. In addition to the clear qualitative picture, it should also be noted that k_{R6} is in very sound agreement with the value reported previously in an unbuffered medium,[8] which gives strong support of our kinetic model. (c) The formation of tetrathionate is usually explained by the rapid step R4 in different oxidation reactions of thiosulfate.[9] We found the rate coefficient of this reaction to be in total correlation with k_{R5}, meaning that we could calculate only the ratio of k_{R5}/k_{R4} from our experiments. The essence of step R5 is also well understood; this helps to provide an additional source of bisulfite besides step R3. Because the rate of step R5 is proportional to $[H^+]$, it also provides a straightforward explanation of the pH dependence of the kinetic curves in which the autocatalytic nature drives the reaction. (d) Lee and Lister[10] reported that thiosulfate reacts rapidly with bromite in two parallel pathways, leading to the formation of tetrathionate and sulfate. This observation is also fulfilled by our kinetic model because the bromite−thiosulfate reaction has to be fast enough to compete with the rapid removal of bromite via step R7. An opposite case would mean that (bi)sulfite cannot be accumulated to such an extent to be the autocatalyst. The only difference between our study and Lee and Lister's report is that the formal kinetic order of thiosulfate is greater than 1 under our experimental conditions. This fact was confirmed by nonlinear parameter estimation because if we ignore k_{R2}' from the model, the average deviation would increase to 4.5%, indicating systematic deviations at higher $[S_2O_3^{2-}]$. The difference may be explained by quite different experimental conditions. (e) The

Table 1. Fitted and Fixed Rate Coefficients of the Proposed Model[a]

reaction no.	chemical equation	rate equation	parameter
R1	$S_2O_3^{2-} + BrO_3^- + H^+ \rightarrow S_2O_3OH^- + HBrO_2$	$k_{R1}[S_2O_3^{2-}][BrO_3^-][H^+]$	$59.4 \pm 4.5\ M^{-2}\ s^{-1}$
R2	$2S_2O_3^{2-} + BrO_2^- \rightarrow 2S_2O_3OH^- + Br^-$	$k_{R2}[S_2O_3^{2-}][BrO_2^-] + k_{R2}'[S_2O_3^{2-}]^2[BrO_2^-]$	$k_{R2} = 10^8\ M^{-1}\ s^{-1}$, $k_{R2}'/k_{R2} = 1900 \pm 600\ M^{-1}$
R3	$S_2O_3^{2-} + BrO_2^- + H_2O \rightarrow 2HSO_3^- + Br^-$	$k_{R3}[S_2O_3^{2-}][BrO_2^-]$	$k_{R3}/k_{R2} = 1.42 \pm 0.22$
R4	$S_2O_3^{2-} + S_2O_3OH^- + H^+ \rightarrow S_4O_6^{2-} + H_2O$	$k_{R4}[S_2O_3^{2-}][S_2O_3OH^-]$	$>10^2\ M^{-1}\ s^{-1}$
R5	$BrO_3^- + S_2O_3OH^- + H_2O \rightarrow 2HSO_3^- + BrO_2^- + H^+$	$k_{R5}[S_2O_3OH^-][BrO_3^-][H^+]$	$k_{R5}/k_{R4} = 51.2 \pm 7.1\ M^{-1}$
R6	$HSO_3^- + BrO_3^- \rightarrow SO_4^{2-} + BrO_2^- + H^+$	$k_{R6}[HSO_3^-][BrO_3^-][H^+]$	$7460 \pm 980\ M^{-2}\ s^{-1}$
R7	$HSO_3^- + BrO_2^- \rightarrow SO_4^{2-} + HOBr$	$k_{R7}[HSO_3^-][BrO_2^-]$	$3 \times 10^7\ M^{-1}\ s^{-1}$
R8	$HSO_3^- + HOBr \rightarrow SO_4^{2-} + Br^- + 2H^+$	$k_{R8}[HSO_3^-][HOBr]$	$10^9\ M^{-1}\ s^{-1}$

[a] No error indicates that the given value was fixed during the fitting procedure.

rate coefficient k_{R7} was reported by Hartz et al.,[11] and it was fixed during the calculation process. It should also be noted that, although bromite is the major bromine(III) species under our experimental conditions,[12] bromous acid ($pK_a = 3.43$) might also be able to open up other pathways at different experimental conditions, especially at higher bromate excess and lower pHs throughout the well-known equilibrium

$$HBrO_2 + BrO_3^- + H^+ \leftrightarrow Br_2O_4 + H_2O \tag{3}$$

followed by subsequent reactions of Br_2O_4 such as in eq 4:

$$S_2O_3^{2-} + Br_2O_4 + H_2O \rightarrow S_2O_3OH^- + 2BrO_2^- + H^+ \tag{4}$$

Under our experimental conditions, however, the roles of eqs 3 and 4 in autocatalysis can be ruled out (see the SI, Figure S4), and this makes another significant difference between the present reaction and other bromate-driven systems[3] exhibiting nonlinear dynamics. The same can also be said about the role of HOBr. To be completely consistent with our experiments, we tentatively propose eq 5 to be included with a reasonably large rate coefficient to explain the perturbation effect of hypobromite initially added to the reacting solution.

$$S_2O_3^{2-} + HOBr \rightarrow S_2O_3OH^- + Br^- \tag{5}$$

However, eq 5 was found to be unnecessary for the description of the kinetic curves, except for the ones in which the effect of the initially added hypobromite was investigated. Therefore, we would rather not include it in the final model. The reason can also be understood easily because after initiation there is already enough bisulfite to prevent the accumulation of HOBr and, as was pointed out previously, the bisulfite concentration starts to decrease only after thiosulfate is completely removed. As a result, there is no need for eq 5 to remove hypobromous acid unless it is intentionally added to study its effect.

Of course, the proposed model may further be improved especially at higher thiosulfate concentrations, but it is per se capable of explaining all of the most inevitable experimental findings, providing a solid starting point for future studies to explore the more intimate details of this promising system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the kinetic experiments and additional measured and calculated kinetic curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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