Kinetics and Mechanism of the Oscillatory Bromate-Sulfite-Ferrocyanide Reaction

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The reaction of bromate, sulfite, and ferrocyanide ions in a continuous stirred tank reactor (CSTR) exhibits sustained oscillations at temperatures of 20, 30, and 40 °C. The oscillations, the behavior in a closed (batch) system, and the observed bistability in a CSTR are all in excellent agreement with simulations using a nine-step mechanism in which the reaction of BrO₃⁻ with Fe(CN)₆⁴⁻ plays a key role. The relationship between the present system and the "mixed Landolt" oscillator, in which bromate is replaced by iodate, is discussed.

Introduction

With the Belousov-Zhabotinskii (BZ) reaction serving as the prototype, bromate oscillators have played a dominant role in the study of chemical oscillation. They have provided a fruitful ground for mechanistic studies starting with the classic Field-Körös-Noyes (FKN) mechanism and have also served as prime examples of how, given a general mechanistic understanding of the parent system, one may generate new oscillators by well-chosen modifications of an existing oscillating reaction.

Here we investigate the reaction of bromate, sulfite, and ferrocyanide ions. The present system is derived from the iodate-sulfite-ferrocyanide oscillator recently discovered by Edblom, Orbán, and Epstein (EOE) by replacing the iodate ion of that "mixed Landolt" reaction by bromate. As anticipated, we do indeed obtain oscillatory behavior in a continuous stirred tank reactor (CSTR), though that behavior differs from that of the iodate system in several unforeseen ways. We have also studied the mechanism for this system and find that it must depart significantly from that proposed for the analogous iodate reaction in order to simulate our experimental results.

Experimental Section

A thermally regulated CSTR was used for all flow experiments. Both batch and flow experiments were carried out at 20, 30, and 40 °C. The reaction temperature was kept constant to ±0.1 °C. Reactant solutions were pumped into the reactor through four inlet tubes by means of a Sage 375A peristaltic pump. During all flow experiments reservoir concentrations were fixed while the inlet flow rate was changed. This pumping rate was varied in both directions in order to observe any hysteresis behavior. Sufficient time was allowed at each flow rate for the system to reach either an oscillatory or a stationary steady state.

Analytical grade KBrO₃ and K₄Fe(CN)₆·3H₂O produced by Fisher Co. and Reanal (Hungary) were used without further purification. All solutions were made with distilled water. The concentrations of sulfite and bromate solutions were determined by using iodometric titration methods while the ferrocyanide concentration was checked with a Ce(SO₄)₂ titration. The potentiometric progress of the reaction was monitored by a platinum redox electrode with a Hg/Hg₂SO₄/K₂SO₄ reference electrode. The pH was followed with a combined glass electrode. Some measurements were made using a bromide ion sensitive electrode (Orion).

Results

Batch. BrO₃⁻ + SO₃²⁻. In a closed system, the reaction between bromate and sulfite is less dramatic than its iodate counterpart. In both systems, large amounts of H⁺ are produced, resulting in a significant pH drop as the sulfite is depleted. In the iodate-sulfite reaction, the pH rises again later owing to reaction between iodide formed in the initial stages of the reaction and previously unreacted iodate. This rise is not observed in the bromate-sulfate system (see Figure 1a, solid line), presumably because the H⁺-consuming reaction between bromate and bromide is much slower than the iodide-iodate reaction. Because of this difference, we also fail to observe any bromine color, although in the Landolt system I₂ is easily visible at the transition point. In both systems, at the same time as the rapid pH drop, the Pt electrode potential undergoes a rapid autocatalytic transition. This potential change is of higher magnitude, but slower, in the bromate (Figure 2, solid line) as compared to the iodate system.

BrO₃⁻ + Fe(CN)₆⁴⁻. When bromate is mixed with potassium ferrocyanide in a solution at pH ≈ 3, the pH and the redox potential increase slowly and smoothly. The color change from pale to intense yellow, which results from the oxidation of ferrocyanide to ferricyanide, is as gradual as the change in potential. It is apparent that the reaction between bromate and ferrocyanide is much slower than that between bromate and sulfite. If the reagents are mixed in neutral solution, no reaction is observed after 1 h.

Temperature Effects. The effect of increasing temperature on the BrO₃⁻-Fe(CN)₆⁴⁻ reaction is so slight that it is barely noticeable. The bromate-sulfite reaction, in contrast, is strongly temperature dependent; a 20 °C increase results in almost a 4-fold increase in rate.

Mixed System. When ferrocyanide is added to the bromate-sulfite system, the shape of the pH vs time trace remains nearly unchanged, but it terminates at slightly higher values than found in the bromate-sulfite system, and there is a small increase in pH at the end of the reaction (Figure 1a, dotted line). The redox potential vs time curve is markedly different, showing only one-tenth the increase observed in the ferrocyanide-free bromate-sulfite reaction (Figure 2, dotted line).

Flow. BrO₃⁻ + SO₃²⁻. In the CSTR, the bromate-sulfite system exhibits bistability. The solid lines in Figure 3a show the measured hysteresis loop. At high flow rates, the pH is high and the Pt potential is low. As the flow rate is decreased, the system retains these steady-state (SSI) characteristics until a critical pump setting is reached. At this point (kₑ = 4.0 × 10³ in Figure 3a on solid line SSI) [H⁺] jumps more than 4 orders of magnitude and the potential instantaneously increases 300 mV. The system remains

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Figure 1. Measured (a) and calculated (b) pH for batch bromate-sulfite (solid lines) and bromate-sulfite-ferrocyanide (dashed lines) reactions. Initial concentrations: \([\text{BrO}_3^-]_0 = 6.5 \times 10^{-2} \text{ M}, [\text{H}_2\text{SO}_4]_0 = 1.0 \times 10^{-2} \text{ M}, [\text{Na}_2\text{SO}_3]_0 = 7.5 \times 10^{-3} \text{ M}, [\text{K}_4\text{Fe(CN)}_6]_0 = 2.0 \times 10^{-3} \text{ M}. T = 30 \degree \text{C}.\) Reaction was initiated by adding the bromate to a mixture of the other components. For the simulations \([\text{Br}^-]_0 = 5.27 \times 10^{-2} \text{ M}\) was taken as the initial value.

Figure 2. Measured Pt potential for the batch bromate-sulfite (solid line) and bromate-sulfite-ferrocyanide (dashed line) reactions. Conditions as in Figure 1.

Figure 3. Experimental (a) and calculated (b) hysteresis loops in flow configuration for the bromate-sulfite (solid lines) and bromate-sulfite-ferrocyanide (dashed lines) systems. Conditions: \([\text{BrO}_3^-]_0 = 6.5 \times 10^{-2} \text{ M}, [\text{Br}^-]_0 = 5.27 \times 10^{-2} \text{ M}, [\text{H}_2\text{SO}_4]_0 = 1.0 \times 10^{-2} \text{ M}, [\text{Na}_2\text{SO}_3]_0 = 5.0 \times 10^{-3} \text{ M}, [\text{K}_4\text{Fe(CN)}_6]_0 = 2.0 \times 10^{-3} \text{ M}. T = 20 \degree \text{C}.\) Symbols: \(\Delta, \text{SSI} ; \text{A, SSII}.\)

Mixed System. Addition of \(2.0 \times 10^{-2} \text{ M} \text{ ferrocyanide to the bistable bromate-sulfite system under the conditions of Figure 3a markedly changes the behavior of the system. The effect on SSI is small, but SSII is altered dramatically as shown in the dashed lines of Figure 3a. At high flows an almost colorless SSI with high pH persists. However, at lower pumping rates \((k_0 = 2.9 \times 10^{-3} \text{ in Figure 3a}) the system jumps to the low-pH state, SSII, which is bright yellow because of the formation of ferri-cyanide. This transition occurs with an overshoot of about \(1/2\) pH unit, and it requires about 15 min for the pH to reach its final value. The behavior during the overshoot resembles that seen in the late stages of the mixed batch reaction. The change in Pt potential that accompanies the total pH change is only about 50 mV. Also, we now find it possible to return the system from SSII to SSI by increasing the flow rate. Thus, the addition of ferrocyanide to the bromate-sulfite reactions significantly reduces the range of bistability.

The most exciting new behavior observed upon the addition of ferrocyanide is the appearance of oscillations in color and pH and in the potentials of Pt and bromide-selective electrodes. Typical oscillatory traces of pH and Pt potential are shown in Figure 4. The measured phase diagrams showing the conditions under which we observe unique steady states, bistability, and oscillations are presented in Figure 5. While \(30 \degree \text{C}\) is the minimum temperature for oscillations in the iodate system, oscillations appear at lower temperatures as well in the bromate version (see Figure 5a). The broadening of the oscillatory region with increasing temperature is relatively slight here in comparison with the effect of tem-
The period and magnitude of the pH oscillations are comparable in the two systems, but both the shape and the absolute positions are quite different. Only very small (~50 mV, Figure 4b) changes in Pt response are observed here, while typical oscillations in the iodate system are some 200 mV in amplitude. These, however, are not the only striking disparities between the bromate and iodate systems. The EOE oscillator stays in the low-pH state for only a matter of seconds, while in the bromate analogue the low pH is maintained over a significant portion of the oscillation period (3–5 min). Near the cross points of the phase diagrams the oscillatory traces like that shown in Figure 4 begin to resemble square waves, with the system spending nearly equal time in the high- and low-pH states. Any satisfactory mechanism must account for these differences between the bromate and the iodate systems.

Related Systems. In addition to studying the bromate analogue of the EOE system, we also investigated the corresponding chlorite and chlorate reactions. In batch, the chlorite system shows a change from colorless to yellow accompanied by a nearly instantaneous pH drop of about 4 units on addition of ClO$_2^-$ to a sulfite-ferrocyanide solution. The pH subsequently increases and then falls to its final value of about 4. Bistability between high- and low-pH steady states was observed at 30 °C, but no oscillations
TABLE I: Reaction Mechanism for the Bromate–Sulfite–Ferrocyanide Oscillator

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
<th>rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>BrO$_3^-$ + HSO$_3^-$ → HBO$_2^-$ + SO$_2^{2-}$</td>
<td>8.0 x 10$^{-2}$ M$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>B2</td>
<td>HBO$_2^-$ + Br$^- + H^+$ → 2HBr</td>
<td>9.5 x 10$^{-1}$ M$^{-2}$s$^{-1}$</td>
</tr>
<tr>
<td>B3</td>
<td>HBO$_2^-$ + Br$^- + H^+$ → Br$_2^-$ + H$_2$O</td>
<td>1.6 x 10$^{-6}$ M$^{-3}$s$^{-1}$</td>
</tr>
<tr>
<td>B4</td>
<td>Br$_2^-$ + H$_2$O → HBO$_2^-$ + Br$^- + H^+$</td>
<td>1.1 x 10$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>B5</td>
<td>2HBrO$_2^-$ → BrO$_3^-$ + HBO$_2^- + H^+$</td>
<td>3.0 x 10$^{-1}$ M$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>B6</td>
<td>Br$_2^-$ + HSO$_3^-$ + H$_2$O → 2Br$^- + SO_2^{2-} + 3H^+$</td>
<td>1.0 x 10$^{-4}$ M$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>B7</td>
<td>H$^+$ + SO$_2^{2-}$ → SO$_3^{2-}$</td>
<td>5.0 x 10$^{-1}$ M$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>B8</td>
<td>HBO$_2^-$ + H$_2$O → BrO$_3^-$ + H$^+$</td>
<td>3.0 x 10$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>B9$^*$</td>
<td>BrO$_3^-$ + 2Fe(CN)$_6^{3-}$ + 3H$^+$ → HBO$_2^-$ + 2Fe(CN)$_6^{2-}$ + H$_2$O</td>
<td>3.2 x 10$^{-2}$ M$^{-1}$s$^{-1}$</td>
</tr>
</tbody>
</table>

*Rate law as in eq. 3.

could be obtained. The chlorate system proved considerably less interesting, giving only a slow production of acid at pH's below 4 in batch; we found no evidence of either bistability or oscillation in flow.

**Mechanism**

The BrO$_3^-$SO$_2^{2-}$Fe(CN)$_6^{4-}$ oscillator can be viewed as derived from either of two other oscillatory systems: BrO$_3^-$SO$_2^{2-}$Mn$^{2+}$ with Mn$^{2+}$ replaced by Fe(CN)$_6^{4-}$ or IO$_3^-$SO$_2^{2-}$Fe(CN)$_6^{4-}$ (EOE) with BrO$_3^-$ substituted for IO$_3^-$. For each of the model systems, a mechanism has been proposed that successfully simulates the observed dynamical behavior.$^{7,10}$ The BrO$_3^-$SO$_2^{2-}$Mn$^{2+}$ system is a typical bromate-driven oscillator, for which Br$^-$ inhibits the oscillator behavior and suppresses it completely if Br$^-$ > 10$^{-4}$ M. The high concentration of bromide ion (≈10$^{-2}$ M), the relatively low acid input required, and the large-amplitude pH oscillations found in the present system all suggest that from a mechanistic point of view the analogy to the mixed Landolt oscillator is the preferable one.

We therefore attempted initially to model the BrO$_3^-$SO$_2^{2-}$ Fe(CN)$_6^{4-}$ reaction by replacing each iodine-containing species in the mechanism of the EOE oscillator by its bromine analogue. For most of these substituted reactions, rate constants are available from experiment or from simulations of other systems, notably the BZ reaction.$^{1,11}$ There is some controversy over the values of some of these rate constants.$^{12,13}$ but regardless of the (plausible) values employed, we were unable to simulate the bistability or the oscillations found experimentally in the bromate–sulfite–iodate reaction in a CSTR, though we were able to reproduce the sigmoidal behavior pH vs. time curve. The reason for this failure was found to be that the most reliable value,$^{14,15}$ for the rate constant of reaction 1, 2.1 M$^{-3}$s$^{-1}$, is 3–5 orders of magnitude less than that of its iodine counterpart.$^{15}$

BrO$_3^-$ + Br$^- + 2H^+ → HBO$_2^- +$ HBr (1)

This rate is far too low to allow reaction 1 to play the role of the negative feedback as its iodine analogue does in the EOE system. Major revision is called for in the negative feedback pathway, which, together with the flow, must bring the pH back to its initial value. The iodate mechanism, ferrocyanide reacts only with I$_2$ and I$_3^-$. Here its reactions with bromine species other than Br$_2$ and Br$_2^-$ will need to be taken into consideration.

**Choice of Reactions.** In Table I we list the reactions that comprise our mechanism for the bromate–sulfite–ferrocyanide reaction. Seven of the nine reactions have their counterparts in the mechanism$^4$ for the EOE system. Only steps B3 and B9 are different. Reactions B1–B4 and B6 are necessary for the autocatalytic generation of H$^+$ and Br$^-$ with overall stoichiometry

BrO$_3^- + 3$HSO$_3^- → Br^- + 3H^+ + 3SO$_4^{2-}$ (2)

The equilibrium between sulfite and bisulfite, steps B7 and B8, remains unchanged.

The disproportionation of HBrO$_2$, reaction B5, is included to maintain [HBO$_2^-$] at a reasonable level (<10$^{-3}$ M). The comparable HIO$_3$ reaction was irrelevant to the modeling of the EOE reaction because there the consumption of HIO$_3$ by I$^-$ and HOI is nearly 10$^{5}$ times faster than the corresponding bromine reactions. The reduction of BrO$_3^-$ to HBO$_2^-$ by two molecules of Fe(CN)$_6^{4-}$, reaction B9, is the key new element in the mechanism of the present system. Because of its high H$^+$ consumption, (B9) provides the essential negative feedback. It is not an elementary step, but rather a composite stoichiometric process with a possible pathway through the formation of BrO$_3^-$ radical as proposed by Birk and Kozub. Field et al.$^{15}$ showed that the single-electron reduction of BrO$_3^-$ by Fe(CN)$_6^{4-}$ is almost diffusion controlled. In order to reduce the number of independent variables, only the stoichiometry of the net process is listed in the mechanism, but the rate law of the rate-determining step, single-electron reduction of BrO$_3^-$ to BrO$_2^-$ radical by one molecule of Fe(CN)$_6^{4-}$, is used in the kinetic calculation as described below.

The above nine equations are found to be necessary and sufficient to produce all major dynamical features found experimentally in this new chemical oscillator. To understand the dynamics of the oscillation, one must first note that, despite the presence of a significant amount of H$_2$SO$_4$, the input flow is a threshold level. Without the other processes, the flow would remain high, much as it does in the closed system. However, once the induced reaction period, we observe a sharp drop in the pH as soon as [H$^+$] reaches a threshold level. Without the other processes, the flow would be insufficient to restore the system to its initial high pH, and [H$^+$] would remain high, much as it does in the closed system. However, process B9, which is negligible at the high pH of the induction period, now comes into play, consuming large amounts of H$^+$ at a rate proportional to [H$^+$]. As long as [H$_2$SO$_4$] is relatively low, H$^+$ is consumed faster than it is produced, and the pH rises. When the flow has replenished the sulfite ion and the original pH has been reached, the cycle starts again. The flow is then essential in helping to restore the initial basic state of the system and in resupplying the reagents, notably sulfite, consumed by the reaction.

**A summarized in Table II.** several reactions obtained by the substitution of bromine for iodine species in the elementary step mechanisms of the EOE system, (D1)–(D6), or the BZ mechanism, (D7)–(D9), were also included at earlier stages of the calculation with the rate constants listed in the table. They were.
however, found to have little influence on the calculated results and have therefore been dropped from the final mechanism. It is somewhat surprising that the reaction between Br₂ and Fe(CN)₆⁴⁻ does not play a role in the negative feedback as did its analogue in the EOE system. The lesser importance of the Br₂ reduction by Fe(CN)₆⁺⁺ may be attributed to the higher order dependence on [H⁺] in (B9) than in the iodine analogue of (D3).

**Rate Constants.** Listed in Table I are the rate constants used to simulate the experimental results. Most of the reactions involving bromine intermediates have been discussed in detail in mechanistic studies of the BZ and related systems. In general, we have started from the most recent experimental or theoretical estimates available; where controversy exists, we have performed simulations with both sets of rate constants. When no value was found in the literature, the rate constants were estimated by fitting the simulations to the experiments. Each reaction is discussed briefly below.

**Reaction B1.** Williamson and King¹⁸ studied the kinetics of bromate-sulfite reaction at temperatures and pH's similar to those in our oscillatory experiments. In batch, they observed different reaction rates in different pH ranges, similar to the autocatalysis in H⁺ that we find in our experiments. However, they attributed these differences in rate solely to differences in the concentration of differently protonated sulfite species. On this basis, the derived rate law has a second-order term (first order in bromate, first order in sulfite) at high pH plus other terms reflecting the autocatalysis in H⁺. The autocatalysis in Br⁻ was not taken into account in their work. For this reason, their rate constant for the term zero in H⁺. The autocatalysis in Br⁻ was not taken into account in our work. However, we attribute these differences in rate solely to differences in the concentration of differently protonated sulfite species. On this basis, the derived rate law has a second-order term (first order in bromate, first order in sulfite) at high pH plus other terms reflecting the autocatalysis in H⁺. The autocatalysis in Br⁻ was not taken into account in our work. However, we attribute these differences in rate solely to differences in the concentration of differently protonated sulfite species. On this basis, the derived rate law has a second-order term (first order in bromate, first order in sulfite) at high pH plus other terms reflecting the autocatalysis in H⁺. The autocatalysis in Br⁻ was not taken into account in our experiments, and in flow simulations, the oscillations damped out.

Sensitivity analysis (see below) showed that the behavior of the system is very sensitive to small changes in k₁, whereas most other rate constants can be changed by several orders of magnitude without significant variations in the simulated results. The best agreement between simulated and experimental results (oscillation period and induction period in batch) was obtained with k₁ = 8.0 × 10⁻² M⁻¹ s⁻¹.

**Reaction B2.** This reaction occurs in the original FKN mechanism for the BZ reaction. The value of the rate constant (at room temperature), however, has been significantly reduced in a recent critical study by Field and Försterling²⁰ to 3 × 10⁶ M⁻² s⁻¹ from the original FKN number of 2 × 10⁷ M⁻² s⁻¹. We find that the FKN value is too high that it causes the oscillation to damp out after two spikes. The value k₂ = 9.5 × 10⁶ M⁻² s⁻¹ best reproduces the experimental oscillation period. The reverse of this reaction has a very low rate constant, k₃ = 1.0 × 10⁻⁴ M⁻¹ s⁻¹. In addition, [HOBr] is much lower than [HBrO₂] and [Br⁻] throughout the reaction. The inclusion of the reverse reaction had no effect on the simulation, and it was deleted from the mechanism.

**Reactions B3 and B4.** The values are taken from Eigen and Kustin's temperature-jump study of the kinetics of halogen hydrolysis.

**Reaction B5.** Field and Försterling¹⁷ have reinvestigated this reaction as well as reaction B1. The new experimental evidence favors a higher pK₆ for HBrO₂₅ than in the disproportionation of HBrO₂, k₅ = 3.4 × 10⁴ M⁻¹ s⁻¹, which is employed here. The original FKN value, 4.0 × 10⁷ M⁻¹ s⁻¹, leads to oscillations with a period almost twice as long as that found in our experiments. The reverse reaction with a third-order rate constant of 1.0 × 10⁶ M⁻² s⁻¹ plays no significant role and is omitted from the mechanism for simplicity.

**Reaction B6.** A qualitative study by Halban and Eisner²⁰ showed the rate constant for Br₂ reduction by HSO₄⁻ to be greater than 10³ M⁻¹ s⁻¹. In our simulations, k₆ = 1.0 × 10⁶ M⁻¹ s⁻¹ gives good agreement with experiment.

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undergoes a transition from very sharp peaks to a maximum of \( 32.5 \text{ M}^{-2} \text{s}^{-1} \) as for the pH overshoot phenomenon noted above when the system is between 0.03 and 0.02 M, out of phase with the pH. \([\text{Br}_2]\) shows the pH drop. The minimum concentration for \([\text{Br}_2]\) oscillates as that used in the experimental phase diagram, Figure 5. Figure 6a shows the calculated pH oscillation. The broader peak width, which distinguishes this system from its iodate analogue, \([\text{Br}_2]\) shows very sharp peaks to a maximum of \( 5 \times 10^{-4} \text{ M} \), coincident with the pH drop. The minimum concentration for \([\text{Br}_2]\) to be observed by eye is \( 10^{-4} \text{ M} \). The calculated result thus explains the absence of \([\text{Br}_2]\) color during the experimental oscillation, in contrast to the EOE oscillator, where \([\text{I}_2]\) is much higher and the iodine is clearly visible.

A calculated phase diagram in the flow rate \((k_0)-[\text{SO}_2\text{O}_3^-]_0\) plane is shown in Figure 6, using exactly the same set of parameters as that used in the experimental phase diagram, Figure 5. Figure 6a resembles the experimental results at \( 30 \degree\text{C} \) (Figure 5b) without any systematic attempt to simulate the temperature effect. The same calculation with \( k_0 = 57.5 \text{ M}^{-2} \text{s}^{-1} \) is shown in Figure 6b. The oscillatory region is broadened and shifted as occurs in the experiments when the temperature is increased from 30 to 40 \degree\text{C}. The small decrease in the peak width of the oscillation that accompanies this increase in \( k_0 \) was also observed on raising the temperature. Apparently, this 70% increase in \( k_0 \) can account for much of the effect seen in response to a 10 \degree\text{C} increase in temperature.

In addition to the satisfying agreement between the calculated and the experimental results, our mechanism also predicts some features that have not yet been experimentally observed. One example is bistability between oscillation and SSII. At \([\text{SO}_2\text{O}_3^-]_0 = 0.075 \text{ M} \), if the flow rate is decreased gradually starting from SSII, the system will have an oscillatory region before it falls into SSII, as shown in Figure 6a. If, however, the flow rate is scanned in the other direction, increasing from SSII, the system would stay in that steady state until \( k_0 \) reaches the critical value for SSII. No oscillation appears. Since this region is predicted to be quite narrow, it is possible that it escaped experimental observation.

**Discussion**

The proposed mechanism does an excellent job in reproducing the major dynamical features of the system with reasonable rate constants and at the parameter values actually employed in the experiments.

Much in the tradition established by Noyes in his study of the BZ system, our mechanistic investigation of the bromate–sulfite–ferrocyanide reaction has already led us into deeper insights into the component processes of this system as well as into the mechanisms of related systems. Further experimental study of the kinetics of the reduction of \( \text{BrO}_3^- \) by \( \text{Fe(CN)}_6^{4-} \), covering the same pH range as in the oscillation, reveals that the reaction is far more complex than expected. The order of \([\text{H}^+]\) dependence is between 0 and 1, and the observed autocatalysis is not due to the reaction of \( \text{BrO}_3^- \) and \( \text{Br}^- \). The full mechanism involves at least four steps and several fast equilibria. However, the simple rate law, eq 3, employed in this study can be a limiting case of the full rate law under certain conditions. Future refinement of the present mechanism to take into account the above detailed study of reaction 9 may well prove worthwhile, given the considerable importance of the negative feedback process in generating the oscillations. A reinvestigation of the EOE mechanism, inspired by some of the differences between the present mechanism and those proposed earlier, has also proved profitable and will be published shortly.

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**Registry No.** \( \text{BrO}_3^- \), 15541-45-4; \( \text{SO}_2\text{O}_3^- \), 14265-45-3; \( \text{Fe(CN)}_6^{4-} \), 13408-63-4.

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