Simple and Complex pH Oscillations and Bistability in the Phenol-Perturbed Bromite-Hydroxylamine Reaction¹

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The unbuffered reaction between bromite and hydroxylamine at pH 3-7 has been studied under closed and open conditions. The stoichiometry of the batch system depends on the initial concentration ratio of the reactants and on the starting pH. The reaction is strongly autocatalytic in H⁺. Under flow conditions the reaction exhibits bistability between two steady states but does not oscillate. If the flow system is perturbed by an input of phenol, it shows oscillatory behavior in pH, potential of a Pt electrode, and color. A qualitative explanation of the batch and oscillatory behaviors is suggested. The bromite-hydroxylamine-phenol flow system can be characterized as a large-amplitude, long-period, pH-driven oscillator.

Introduction

The early development of nonlinear chemical dynamics was dominated by the study of a single system, the Belousov– Zhabotinsky (BZ) reaction.² A major advance took place in the 1980s with the systematic design of a variety of chlorite-based oscillating chemical reactions.³ A key species in the BZ reaction is bromous acid, HBrO₂, which is the autocatalyst in the positive feedback loop. Because bromous acid and its conjugate base bromite ion, BrO₂⁻, are unstable and difficult to prepare, relatively little is known about the chemistry of these species. The chemistry of BrO₂⁻ only superficially resembles that of its congener ClO₂⁻, the starting point for so many of the non-BZ chemical oscillators,⁴ and it is not clear whether there might be a family of bromite oscillators as well.

Recently, solid NaBrO₂·3H₂O has become commercially available, opening up the possibility of studying both the fundamental chemistry of the bromite ion and its reactions in open systems. The first bromite oscillator, the BrO_2 --I⁻ reaction⁵ was reported in 1991, but previous efforts to expand this single example to a family of oscillators in analogy to other oxyhalogen oscillators have been unsuccessful.

Chlorite, bromate, iodate, and periodate ions, all of which participate in multiple oscillatory reactions, resemble bromite in being strong oxidants that give rise to intermediates and products with several lower oxidation states. There appear, however, to be significant mechanistic differences between the oscillators these oxyhalogen ions participate in and the bromite-iodide system.⁶ Indeed, because of the much greater reactivity of HBrO₂ compared with BrO₂⁻, the BrO₂⁻-I⁻ system may be regarded as a pH-driven oscillator.

Designing new oscillators based on bromite chemistry turns out to be more than simply a matter of duplicating the analogous chlorite systems. For example, experiments with the ClO_2^- -NH₃OH⁺ reaction reveal an absence of any features likely to lead to oscillatory behavior. However, the BrO₂⁻-NH₃OH⁺ reaction, the subject of the present paper, has all the essential features to give rise to exotic phenomena in a CSTR: its shows strong autocatalysis, it can react by pathways with different stoichiometries, and several relatively stable intermediates are formed, the removal of which by different reagents allows us to perturb the system. We present here experiments in which the bromite-hydroxylamine system shows bistability in a flow reactor and behaves in an oscillatory manner when the system is perturbed with an inflow of phenol.

Experimental Section

Materials. The following chemicals have been used in our experiments: sodium bromite trihydrate (NaBrO₂·3H₂O, technical grade, Aldrich), hydroxylamine sulfate [(NH₂OH)₂·H₂-SO₄, 99%, Aldrich], phenol (C₆H₅OH, 100%, Mallinckrodt), sodium hydroxide solution (0.1 N, certified, Fisher).

Analytical Procedures. Since solid $NaBrO_2 \cdot 3H_2O$ slowly decomposes during storage and because the reagent was of technical grade, it was necessary to establish the bromite content and the concentration of the possible decomposition products, bromate, hypobromite, and bromide.

First we ruled out the presence of NaOBr by taking the spectrum of a freshly prepared 10⁻² M NaBrO₂·3H₂O solution and comparing the absorbances at 296 and 330 nm with the bromite spectrum given by Lee and Lister.⁷ The ratio of absorbance values that we measured, 1.36, agrees well with the 1.37 found by Lee and Lister for a hypobromite-free sample. We analyzed for bromite with a modification of the method of Hashmi and Ayaz⁸ (no $(NH_4)_2SO_4$ was added and much less than the recommended amount of NaHCO3 was used in order to obtain reproducible results), using standard As(III), which was back titrated with standard I₂ solution. For the determination of bromite in the presence of bromate, we developed a new method: in pH 4.7 buffer (1:1 CH₃COOH/CH₃COO⁻) when excess KI is added, only the bromite produces I_2 , which is then titrated with standard $Na_2S_2O_3$. After the end point is reached, the mixture is acidified with H_2SO_4 to pH 0-1, and the additional I_2 formed in the reaction between BrO_3^- and I^- is titrated with $Na_2S_2O_3$ solution. For bromite content the average of these two methods gave $88.5 \pm 1.5\%$ NaBrO₂·3H₂O. For bromate we found 7.1 ± 1.2% NaBrO₃. The sample contained 4-5% absorbed water. No detectable Br- was found.

The hydroxylamine was determined by titration with standard I₂ solution.⁹ The purity of the Aldrich product was found to be 99.5%. The same analytical procedure was used to establish the stoichiometry of the BrO_2 --NH₃OH⁺ reaction in excess hydroxylamine.

Preparation and Stability of Stock Solutions. The NaBrO₂ stock solutions were always freshly prepared. A small amount of NaOH in the solid NaBrO₂·3H₂O caused the 10^{-2} M stock solution to have a pH of about 10.2. At this pH the decomposition of bromite is slow, but the stock solution should be used within 5 h of its preparation. Under our experimental conditions (pH

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> 3.5) the bromate impurity can be regarded as inert toward hydroxylamine and phenol.

The $(NH_2OH)_2$ ·H₂SO₄ stock solution was prepared by dissolving a weighed amount of solid in distilled water. Half the H₂SO₄ content was neutralized with the calculated amount of NaOH. The final pH of the stock solution was adjusted to 6.50 with dilute H₂SO₄. The stock solution can be used for 2–3 days with negligible decrease in the NH₃OH⁺ content.

The phenol stock solution was made by dissolving a known amount of phenol in distilled water. The solution is stable for weeks.

Apparatus and Methods. The course of the reaction between BrO_2^- and NH_3OH^+ was followed by monitoring the pH, the potential of a Pt electrode, and, in some cases, $[Br^-]$ using an ion specific electrode. The signals were simultaneously recorded on a multichannel recorder. Data were also collected and analyzed with a personal computer. For spectrophotometric analysis of the NaBrO₂-3H₂O and for monitoring changes in spectra with time of the BrO₂--NH₃OH⁺-phenol system, we used a Hewlett-Packard 8452A diode array spectrophotometer.

Experiments under flow conditions were performed in a thermostated reactor of volume 20.50 cm³. The reactants were introduced into the reactor through four inlet tubes by a fourchannel peristaltic pump (Sage Instruments, Model 375A). The effluent was removed by overflow with aspiration. The flow rate $(k_0, \text{ reciprocal of the residence time})$ could be varied between 6×10^{-4} and $1.1 \times 10^{-2} \text{ s}^{-1}$ with a precision of $\pm 1\%$. The reactor cap held two pairs of electrodes, allowing simultaneous recording of either the pH and Pt signals or the potentials of the Pt and Br-electrodes. The dynamical behavior of the system was probed by determining the steady state or oscillatory responses of the electrodes as a function of the input concentrations ([X]₀) and flow rate (k_0) .

Results

Stoichiometric Studies. To determine the most important composite reactions in the bromite oxidation of hydroxylamine, we performed stoichiometric experiments with each starting reagent in excess. Our batch and flow experiments suggested that the most interesting phenomena occur between pH 4.5 and 6.5. We therefore selected pH 6 for the bulk of our stoichiometric studies. Known amounts of BrO_2^- and NH_3OH^+ were allowed to react in KH_2PO_4 -NaOH buffer, and the resulting mixture was analyzed after completion of the reaction was established from the Pt potential vs time curves.

Bromite-Hydroxylamine Reaction. In the presence of excess reductant, the unreacted NH_3OH^+ was determined by back titration with I₂ solution. When the ratio of $[NH_3OH^+]$ to $[BrO_2^-]$ is 2:1 or higher, the stoichiometry is given quite accurately by eq 1. The evolution of N_2O gas is clearly noticeable.

$$BrO_{2}^{-} + 2NH_{3}OH^{+} = N_{2}O + Br^{-} + 3H_{2}O + 2H^{+}$$
 (1)

With excess oxidant ($[BrO_2^{-}]$: $[NH_3OH^+] \ge 2:1$), elementary bromine formed and was assayed iodometrically after extraction with CCl₄. We found a ratio of approximately 2:1 between the initial $[BrO_2^{-}]$ and the $[Br_2]$ formed. We had difficulties, however, in establishing the correct stoichiometry, because at pH 6 Br₂ can originate not only from the direct reaction between BrO_2^{-} and NH_3OH^+ but also from a parallel decomposition reaction of BrO_2^{-} . We have studied this process separately. The stoichiometry in excess BrO_2^{-} may be approximated by eq 2.

$$2BrO_2^{-} + NH_3OH^{+} = NO_3^{-} + Br_2 + 2H_2O$$
 (2)

Decomposition of Bromite. The decomposition of bromite in aqueous solution in various buffers, in both the presence and the absence of bromide, has been studied by several authors, particularly in alkaline solutions.^{7,10} The literature suggests that H^+ and Br^- ions significantly increase the rate of decomposition. The products at alkaline pH are Br^- , BrO_3^- , and OBr^- . At high pH the rate is slow, but below pH 6.2 the decomposition speeds up and appreciable quantities of bromine can be detected.¹⁰

Our studies of the batch and flow BrO_2 --NH₃OH⁺ system were carried out in unbuffered solution below pH 7, so we also measured the stoichiometry of the decomposition under these conditions. To obtain a qualitative picture, we prepared a set of aqueous solutions of 5×10^{-4} M bromite. We then added sufficient dilute H₂SO₄ to produce initial pH's of 6.27, 5.85, 5.35, 4.46, 3.95, and 3.50, and we followed the pH vs time for each solution. In all cases, the pH rose to a higher final value, sometimes more than one unit higher (e.g., from 4.46 to 5.50) within 5-10 min. The formation of bromine, especially at the lower pHs, was clearly detectable by smell and color.

These experimental findings are consistent with the following stoichiometry for decomposition in the acid pH range:

$$5BrO_2^- + 2H^+ = 3BrO_3^- + Br_2 + H_2O$$
 (3)

The stoichiometry in eq 3 implies a 5:3 ratio for $[BrO_2^-]$ reacted to $[BrO_3^-]$ formed and a 5:1 ratio for $[BrO_2^-]$ reacted to $[Br_2]$ formed. We undertook a quantitative assessment of this stoichiometry as follows. A weighed amount of NaBrO₂·3H₂O was dissolved in water and acidified with H₂SO₄ to pH \approx 3. After 5 min the Br₂ formed was extracted with CCl₄. The Br₂ and BrO₃⁻⁻ contents of the organic and aqueous phases, respectively, were measured by standard iodometric methods. The experimentally determined ratios were 5:3.2 for bromate and 5:0.7 for bromine, which are in reasonable agreement with the theoretical values, suggesting that reaction 3 is the predominant stoichiometry of the decomposition in acid medium.

The stoichiometry of eq 3 does not appear in the literature cited above, but it can be deduced from pseudoelementary steps (3a-c) which are suggested in those references. The combination $1/2[5 \times (3a) + (3b) + 2 \times (3c) - 5 \times (3d)]$ results in the overall process of reaction 3.

$$HBrO_2 + BrO_2^{-} \rightarrow OBr^{-} + BrO_3^{-} + H^{+} \qquad (3a)$$

$$3HOBr \rightarrow 2Br^{-} + BrO_{3}^{-} + 3H^{+}$$
(3b)

$$HOBr + Br^{-} + H^{+} \rightarrow Br_{2} + H_{2}O \qquad (3c)$$

$$HBrO_2 = H^+ + BrO_2^-$$
(3d)

Bromine-Hydroxylamine Reaction. In reactions 2 and 3 elementary bromine is formed. The reaction between Br_2 and NH_3OH^+ is likely to play a significant role in the $BrO_2^--NH_3^ OH^+$ system. Only a single short communication treats the kinetics of the Br_2 oxidation of NH_3OH^+ at pH 6, but no stoichiometry is presented.¹¹ The concentration of NH_3OH^+ can be measured quantitatively¹² using BrO_3^- in the presence of $Br^$ and H^+ . In this reaction the oxidant is Br_2 , and the products are NO_3^- and Br^- , implying the following stoichiometry:

$$3Br_2 + NH_3OH^+ + 2H_2O = NO_3^- + 6Br^- + 8H^+$$
 (4)

Batch Experiments. Our stoichiometric studies demonstrate that the course of the reaction between BrO_2^- and NH_3OH^+ is influenced primarily by the initial composition and the starting pH. If either of the two reactants is in significant excess, one of the two limiting stoichiometries, reactions 1 and 2, prevails. If the initial concentrations are comparable, however, a mixed stoichiometry is found, and this stoichiometry varies with the initial pH.



Figure 1. Platinum electrode potential (dotted line) and pH (solid line) vs time in the bromite-hydroxylamine reaction. $pH_0 = 6.60$, T = 25 °C. (a) r = 1 ([BrO₂-] = [NH₃OH⁺] = 1 × 10⁻³ M); (b) r = 0.5 ([BrO₂-] = 5×10^{-4} M, [NH₃OH⁺] = 1×10^{-3} M).

To evaluate the effect of the initial composition, we set the starting pH at 6.60 and varied r, the ratio of $[BrO_2^{-}]$ to $[NH_3-OH^+]$. Depending on the initial composition, two types of pH and Pt traces could be distinguished (Figure 1). Type I (Figure 1a) consists of an S-shaped curve for the Pt potential accompanied by a pH curve with a sharp minimum. Curves of this type are obtained when $r \ge 0.8$ (when r approaches 5, the reaction is too fast to follow). A pale yellow color indicates the presence of Br₂ as an end product. Type II curves (Figure 1b) consist of an S-shaped pH drop and a maximum in the Pt potential vs time. This behavior occurs when $r \le 0.7$ (when r approaches 0.3, the curves lose their characteristic shape and become monotonic). No Br₂ was detected under these conditions, but formation of bubbles indicated N₂O evolution.

Figure 2 shows the time evolution of the reaction when r is fixed at 1 and the starting pH of the solution, pH₀, is varied. We see that curves of type I are replaced by type II curves when the initial pH is lowered.

Besides the pH and the Pt potential, we monitored the time evolution of the end product bromide. The bromide-sensitive electrode was somewhat responsive to the reactant $[BrO_2^{-}]$ as well, so only qualitative data could be obtained. The bromide is formed autocatalytically. When bromite is in excess, a cusp appears in $[Br^{-}]$ before it reaches its final value. The final $[Br^{-}]$ approaches but does not attain the initial concentration of NH₃-OH⁺. If NH₃OH⁺ is in excess, $[Br^{-}]$ goes monotonically to saturation after the autocatalytic rise, and its final value is close to the initial $[BrO_2^{-}]$.

Flow Experiments with the BrO₂--NH₃OH⁺ System. Both the batch (Figure 2) and flow experiments are extremely sensitive to the initial pH, and this quantity must be carefully controlled if reproducible results are to be obtained. The starting pH in our flow experiments in the absence of an inflow of NaOH was always close to 6.5, since the pH of the stock NH₃OH⁺ had been adjusted to 6.50 (see Experimental Section) and the hydroxylamine solution constitutes a buffer with pK = 6.



Figure 2. Platinum electrode potential and pH at fixed r = 1 ([BrO₂⁻] = [NH₃OH⁺] = 5 × 10⁻⁴ M). Initial pH: (a) 7.80, (b) 6.97, (c) 6.64, (d) 6.35, (e) 5.93.

We investigated the BrO_2 -NH₃OH⁺ reaction in a flow reactor to search for bistability or oscillations. The reactants were introduced into the reactor at high flow rate. After a steady state was attained, the flow rate was changed incrementally by $\Delta k_0 \approx$ 5×10^{-4} s⁻¹. Under certain conditions, this small change in flow rate induced changes in the responses of the electrodes similar to those shown in Figure 1a,b, i.e., a transition from one steady state to another. The $BrO_2^--NH_3OH^+$ system supports two steady states: a high-pH, low-potential steady state (SSI) at high flow rates, and a low-pH, high-potential steady state (SSII) at low flow rates. Bistability between steady states occurs if hysteresis in the transitions is observed as the flow rate is varied first in one direction and then in the other. We observed bistability at many compositions in the BrO₂--NH₃OH⁺ system. For example, for $[NH_3OH^+]_0$ (a subscript zero denotes the concentration of the input solution) taking the values 5×10^{-3} , 2×10^{-3} , 5×10^{-4} , 2.5 $\times 10^{-4}$, and 10^{-4} M at fixed $[BrO_2^{-1}]_0 = 10^{-3}$ M, only one steady state appears at the highest and lowest [NH3OH+]0, but bistability is found at all intermediate $[NH_3OH^+]_0$ values. Bistability occurs over a wide range of flow rates, depending on input concentrations, from $k_0 = 1 \times 10^{-3} \text{ s}^{-1}$ to at least $1.5 \times 10^{-2} \text{ s}^{-1}$, the fastest flow rate attainable with our pump. Transition from SSI to SSII can be induced by acid perturbation and from SSII to SSI by NaOH perturbation. An example of such an experiment is shown in Figure 3. If a perturbation of $\Delta pH < 0.5$ is imposed on a steady state, the system relaxes back to the original state but a $\Delta pH \ge$ 1 in the correct direction induces transition to the other steady state.

Our inability to induce transition from SSII to SSI by flow rate changes alone demonstrates that the H⁺ produced and maintained by reactions 1 and 4 cannot be washed out of the reactor by flows attainable with our pump. In an effort to narrow the range of flow rates over which bistability occurs, we added an input flow of NaOH. As a result of the higher initial pH, the transition time lengthened significantly and the range of bistability shifted toward lower flow rates, through it remained quite wide. The NaOH input alone was not enough to shrink the region of bistability to the point where the bistable BrO_2 --NH₃OH⁺ flow system could be transformed to an oscillatory system.

Flow Experiments with the BrO_2 --NH₃OH+-NaOH-Phenol System. Considerations outlined below suggested that by adding phenol as an auxiliary reagent, we might be able to convert the



Figure 3. Transitions between steady states induced by injection of dilute H₂SO₄ and NaOH solutions in the BrO₂⁻-NH₃OH⁺ flow system. Fixed constraints: [BrO₂⁻] = [NH₃OH⁺] = 1×10^{-3} M, $k_0 = 3 \times 10^{-3}$ s⁻¹, T = 25 °C.



Figure 4. Complex and simple oscillations in pH at different flow rates. $[BrO_2^{-}]_0 = 2.5 \times 10^{-3} \text{ M}, [NH_3OH^+]_0 = 2.0 \times 10^{-3} \text{ M}, [phenol]_0 = 2.5 \times 10^{-3} \text{ M}, [NaOH]_0 = 5.0 \times 10^{-4} \text{ M}.$ $k_0 = (a) 1.5 \times 10^{-3} \text{ s}^{-1}$, (b) 2.6 $\times 10^{-3} \text{ s}^{-1}$, (c) $3.0 \times 10^{-3} \text{ s}^{-1}$.

bistable BrO₂--NH₃OH⁺ flow system into an oscillator. By varying the input concentrations, we succeeded in finding largeamplitude pH oscillations within a relatively narrow range of flow rates. The oscillations in pH can be as large as two units within the range 4.2 < pH < 6.6. The potential of a Pt electrode oscillates with amplitude as large as 120 mV. We also observe a weak color change from pink to pale yellow at the sharp pH minimum. The color change is most visible at high phenol concentrations. The period of oscillation lies between 15 and 45 min under our conditions. In most cases the oscillations have a complex character: a large-amplitude pH spike is followed by one to eight small oscillations. As the flow rate increases the number of small peaks decreases until only the single large peak remains. Examples of complex and simple oscillations in pH at different flow rates with fixed input concentrations are shown in Figure 4.

The oscillatory domain in this four-component system is rather narrow. In Table 1 we give an example when the concentrations of the major components, BrO_2^- and NH_3OH^+ , are fixed at the values in Figure 4, and we vary the concentrations of phenol and NaOH. At fixed [NaOH]₀ the concentration of phenol can be varied within an order of magnitude while maintaining oscillatory behavior. When the input of phenol is fixed, oscillatory behavior disappears with even smaller changes in [NaOH]₀. The oscillatory behavior is even more sensitive to changes in the input [BrO_2^-]₀

TABLE 1:	Effects of	Input P	henol and	NaOH
Concentrati	ons on Dyr	uamical H	Sehavior of	of the
BrO ₂ NH ₃	OH+-Phen	ol-NaOH	H Flow S	ystem*

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	Fixed $[NaOH]_0 = 5 \times 10^{-4} M$	
[phenol] ₀ , M	state of system ^b	
10-3	SS only, EX	
2.5×10^{-3}	$OSC(C)$ if $k_0 = 0.001 - 0.002 \text{ s}^{-1}$	
	SS if $k_0 \ge 0.003 \text{ s}^{-1}$	
5 × 10-3	SS if $k_0 \ge 0.0005 \text{ s}^{-1}$	
	OSC(C) if $k_0 = 0.0010 - 0.0015 \text{ s}^{-1}$	
	SS if $k_0 \ge 0.002 \text{ s}^{-1}$	
10-2	SS if $k_0 \ge 0.0005 \text{ s}^{-1}$	
	$OSC(S)$ if $k_0 = 0.001 \text{ s}^{-1}$	
	SS if $k_0 \ge 0.0015 \text{ s}^{-1}$	
	Fixed [phenol] ₀ = 2.5×10^{-3} M	
[NaOH] ₀ , M	state of system ^b	
2.5×10^{-4}	SS if $k_0 \le 0.003 \text{ s}^{-1}$	
	BS if $k_0 \ge 0.004 \text{s}^{-1}$	
3.75 × 10−4	SS if $k_0 \le 0.001 \text{ s}^{-1}$	
	$OSC(C)$ if $k_0 = 0.0015 - 0.0025 \text{ s}^{-1}$	
	OSC(S) if $k_0 = 0.003 \text{s}^{-1}$	
	SS if $k_0 \ge 0.004 \text{s}^{-1}$	
6 × 10-4	SS if $k_0 \le 0.00075 \text{s}^{-1}$	
	$OSC(C)$ if $k_0 = 0.0010 - 0.0016 \text{ s}^{-1}$	
	OSC(S) if $k_0 = 0.0017 - 0.0020 \text{ s}^{-1}$	
	SS if $k_0 \ge 0.0025 \text{ s}^{-1}$	
7.5 × 10−4	SS only	
10-3	SS only	

^a Fixed concentrations: $[BrO_2^-]_0 = 2.5 \times 10^{-3} \text{ M}, [NH_3OH^+]_0 = 2 \times 10^{-3} \text{ M}.$ ^b Abbreviations: SS, steady state; OSC, oscillatory state; BS, bistability; EX, excitability; (C), complex; (S), simple.

and $[NH_3OH^+]_0$. For example, with $[BrO_2^-]_0$, $[phenol]_0$, and $[NaOH]_0$ as in Figure 4, changing $[NH_3OH^+]_0$ from 2×10^{-3} to 1×10^{-3} or 3×10^{-3} M destroys the oscillatory behavior. We can regain the oscillation only by readjusting $[NaOH]_0$ and k_0 . Outside the oscillatory region bistability may also occur (see Table 1).

Discussion

With the exception of a brief mention by Jhanji and Gould¹³ that in the reaction of BrO_2^- (10⁻² M) with NH₂OH·HCl (10⁻² and 2×10^{-2} M) at pH 9 the ratio of reacted NH₂OH·HCl to BrO₂⁻ is close to 2, no previous stoichiometric or kinetics investigations have been reported of the BrO2-NH3OH+ reaction. Many studies are available of the oxidation of hydroxylamine by other oxidants, such as IO₃⁻ and IO₄^{-,14} I₂,¹⁵ Fe(III),¹⁶ Ce(IV),¹⁷ S₂O₈^{2-,18} H₂O₂,¹⁹ and Fe(CN)₆^{3-,20} Analysis of these reactions shows that the oxidation of hydroxylamine may proceed with several stoichiometries, depending upon such factors as the redox potential of the oxidant, the number of electrons the oxidant can transfer in a single step, the initial ratio of reactant concentrations and the pH. Oxidation with one-electron oxidants usually yields N_2 , but two-electron oxidants can give rise to N_2O , NO_2^- , or NO3⁻. With two-electron oxidants, one often encounters two limiting stoichiometries depending on the initial concentration ratio. In excess hydroxylamine nitrogen is oxidized to the +1 state (N₂O), while in excess oxidant NO₃⁻ or NO₂⁻ is formed. Usually, a mixed stoichiometry representing a combination of the two limiting cases is observed. Bromite ion transfers two electrons in its reaction with hydroxylamine and fits in with the above limiting stoichiometries, since reaction 1 prevails in excess hydroxylamine, while reaction 2 gives the approximate stochiometry in excess bromite.

For a qualitative description of the batch and flow behavior of the unbuffered BrO_2 --NH₃OH⁺ system one must consider reactions 1-4 as well as the protonation equilibria of bromite and hydroxylamine. The curves shown in Figure 1a,b can be interpreted as follows: when $r \ge 0.8$ the reaction proceeds mainly

via eqs 2 and 4 with a small contribution from eq 1. After a slow start, the reaction speeds up autocatalytically, because the acid formed in eq 4 protonates the bromite ($pK_a = 3.43 \pm 0.05^{21}$) and the protonated oxyanion reacts much faster than the unprotonated bromite. When all the NH₃OH⁺ is consumed, the pH reaches its minimum, but some unreacted bromite remains. The acid induces the decomposition of bromite according to eq 3. The resulting consumption of H⁺ causes the pH to rise, and the potential of the Pt electrode attains its maximum, constant value owing to the presence of bromine. Figure 1b was recorded in excess NH₃OH⁺ at r = 0.5. Now (and whenever $r \le 0.7$) the predominant stoichiometry is eq 1, and the bromite is completely consumed. Reaction 1 produces acid, causing H⁺ to build up autocatalytically, but in the absence of reaction 3 no H⁺ is consumed, so the pH attains a constant low value. Reaction 2 may also proceed to some extent, but the excess NH₃OH⁺ scavenges the bromine formed, and the potential of the Pt electrode, after an overshoot, settles down to a value determined primarily by the unreacted NH₃OH⁺.

The shapes of the curves shown in Figure 2 at different initial pH values with r = 1 can also be explained in terms of eqs 1-4. At this concentration ratio the BrO₂⁻ can consume all of the NH₃OH⁺ with a stoichiometry corresponding to $3 \times (2) + (4)$:

$$3BrO_2^- + 2NH_3OH^+ \rightarrow 2NO_3^- + 3Br^- + 2H_2O + 4H^+$$
(5)

At $pH_0 > 6.6$, process 5 should be the major reaction. The higher the initial pH, the slower is the reaction, because the quantity of protonated bromite decreases with increasing pH. As reaction 5 proceeds, the rate at which acid is formed increases autocatalytically, and the ensuing pH and potential curves have shapes resembling those in Figure 1a for $r \ge 0.8$. If pH₀ is low (Figure 2, curves d and e), the decomposition reaction (3) immediately competes with reaction (5), transforming part of the reagent bromite into unreactive bromate. The actual concentration ratio of BrO₂⁻ to NH₃OH⁺ drops below r = 0.7, and curves of the type shown in Figure 1b appear.

Our batch experiments on the BrO_2 --NH₃OH⁺ system show strong autocatalysis in the production of H⁺. Autocatalytic reactions often exhibit bistability when carried out in a flow reactor. Since the autocatalytic species here is H⁺, we expect, and find, bistability between a high-pH and a low-pH steady state. In the high-pH (6-7) steady state (SSI), which appears at high flow rates, the extent of the reaction is small, and the composition is largely determined by the input flows. In the low-pH (3-4) steady state (SSII) the concentrations of the input reagents BrO_2 - and NH₃OH⁺ are very low, and the responses of the electrodes are determined primarily by the concentrations of the products H⁺ and Br₂ formed in eqs 1-4.

A bistable system may be converted to an oscillatory one if the autocatalytic species that accumulates after a transition from one steady state to the other is removed at a carefully adjusted rate by a reagent that does not interfere with the main reaction(s). In the BrO_2 - NH_3OH^+ flow system, H^+ is the species that needs to be removed. Reaction 3, the decomposition of bromite ion, consumes H^+ on the right time scale, i.e., relatively slowly and after the autocatalytic portion of the reaction. Under the conditions of the flow reaction, however, reaction 3 combines with reaction 2 to produce Br_2 . Bromine is a major source of H^+ formation via reaction 4, so removal of Br_2 is essential if the steady state maintained before the transition to the low-pH state is to be restored.

We chose to remove the bromine with phenol. Phenol reacts with bromine to yield *p*-bromophenol and HBr at a rate comparable to that of the $NH_3OH^+-Br_2$ reaction. In excess phenol the reaction is In reaction 6 H⁺ is also formed, but in only three-eighths of the quantity that would be produced if the bromine were removed by NH_3OH^+ in eq 4.

We also tested the effect of added phenol on the batch behavior of the bromite-hydroxylamine system. As expected from the above analysis, addition of phenol causes the S-shaped Pt potential curve of Figure 1a to turn back after the inflection point, yielding a maximum in the curve. The rise in pH after the minimum was more pronounced in the presence of phenol. A pale pink color develops before the pH minimum and then turns to pale yellow as the pH starts to rise. Spectra of the mixture taken at 20-s time intervals for 20 min reveal that the pink color truly vanishes at the pH minimum, but the intensity of the yellow color continues to increase even after the pH minimum. The pink and yellow colors correspond to absorption maxima at 490 and 410 nm. respectively. We were unable to assign these colors to any organic compound. The yellow product, which could not be extracted with CCl₄, is not bromine. We believe that these colors arise from unknown side reactions, perhaps between traces of quinones formed in the bromite oxidation of phenol and hydroxylamine to yield aromatic oximes. Since these side reactions appear not to interfere with the bromination of the phenol, we have ignored the color change in interpreting our results.

The reaction between bromine and hydroxylamine in a flow reactor shows long-period, large-amplitude pH oscillations if auxiliary reagents phenol and sodium hydroxide are introduced and the input bromite is in excess over hydroxylamine. We suggest that the oscillatory cycle arises as follows. At high pH (6-7) the bromite is almost completely $(pK_a = 3.4)$ deprotonated, and the hydroxylamine is partially $(pK_a = 6.0)$ deprotonated. The reactivity of unprotonated NH₂OH is known to be much higher than that of the protonated form.¹⁴⁻¹⁸ Therefore the reaction between BrO₂⁻ and NH₂OH can proceed slowly, largely via eq 2 and partly by eq 1. The bromine formed in eq 2 reacts rapidly with hydroxylamine by eq 4. The parallel reactions 4 and 1 (and possibly 2 if the unprotonated hydroxylamine reacts) produce H⁺, gradually lowering the pH. At lower pH a larger fraction of the bromite is protonated and reacts more rapidly with hydroxylamine, resulting in autocatalytic production of H⁺ until all hydroxylamine is consumed. At the lower pH values (pH 3.5-5) the unreacted bromite decomposes in reaction 3, and the pH starts to rise after the sharp minimum. The phenol now consumes the bromine formed, and at this stage of the oscillatory cycle the reaction mixture is nearly free of bromite, hydroxylamine and bromine. The continuous inflow of BrO₂- and NH₃OH+ gradually replenishes the reagents, and the NaOH input restores the pH to its initial high value. As the original composition is regenerated the reaction between the bromite and unprotonated hydroxylamine initiates the cycle again.

The above qualitative picture of how the oscillations arise will need to be supplemented with quantitative simulations once plausible values are available for some of the key rate constants. It already seems clear, however, from the discovery of the bromiteiodide and bromite-hydroxylamine oscillators and from the mechanistic analysis presented above, that there should indeed be a family of bromite-based oscillators. Preliminary experiments in our laboratories support this suggestion, and we look forward to the further development of this subject and to the new light that such investigations are likely to shed on the chemistry of the prototype BZ reaction.

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