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Inorganic Bromate Oscillators. Bromate–Manganous–Reductant[1]

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A family of systems containing bromate and manganous ions and an inorganic reductant such as hydrazine, sulfite, arsenite, stannous, or iodide ion exhibits sustained oscillations in a flow reactor. These systems show bistability as well. Model calculations predict limit cycle behavior if the bromide flow of the minimal bromate oscillator is replaced by a flow of a reductant which generates bromide from Br_2 and/or HOBr sufficiently rapidly.

Introduction

By far the most thoroughly studied oscillating chemical reaction is the metal-ion-catalyzed oxidation of an organic substrate by bromate ion in aqueous sulfuric acid.[3] The remarkable success of mechanistic studies[4,5] on the Belousov–Zhabotinskii (BZ) oscillator has been limited primarily by a lack of knowledge about the organic intermediates produced by the reaction. For this reason, there has been considerable interest in designing purely inorganic bromate oscillators, for which a complete mechanistic description would presumably be a more feasible task.

The first reported inorganic bromate oscillator was the "minimal bromate oscillator" discovered by Orbán et al.[6] and later by Geiseler,[7] after its existence had been predicted in a calculation by Bar-Eli[8] using a simplified model[9] of the BZ reaction. The minimal oscillator consists of bromate, bromide, and a metal ion (cerous or manganeous) in a stirred tank reactor (CSTR).

More recently it has been shown[10] that the metal ion in the minimal oscillator may be replaced by chlorite and, more suprisingly, that the bromide flow (which substitutes for the organic substrate in the BZ system) can simultaneously be replaced by a flow of any of a series of inorganic reductants.

Adamčiková and Ševčík[11] have reported oscillations in a BZ type mixture containing sodium hypophosphite in place of the organic substrate and with a nitrogen flow to drive off gaseous products. This system resembles the BZ reaction with oxalic acid[12] and is intermediate in character between the usual closed (batch) BZ configuration and the open (CSTR) system of the minimal and bromate–chlorite[10] oscillators.

In this paper we report that a group of inorganic reductants gives rise to sustained oscillation when used in place of bromide in the minimal bromate system in a CSTR. We also report on model calculations which elucidate the function of the reductant species.

Experimental Section

All reagents used were the highest grade commercially available and, with the exception of the bromate as described below, were used without further purification. All stock solutions were prepared in 1.5 M H_2SO_4, except those of hydrazine, arsenite, sulfite, and iodide, which were prepared in water. In the latter cases the manganous solution was prepared in 3 M H_2SO_4 so that the effective final acid concentration in the reactor was 1.5 M. Bromate solutions were purged with nitrogen to drive off the bromine evolved during dissolution in the sulfuric acid.

All experiments were performed at a temperature of 25.0 ± 0.1 °C in a thermally regulated Pyrex CSTR[13] with four input channels and a volume of 21.5 cm^3. The signal monitored was the potential of a Pt electrode vs. a mercury–mercurous sulfate reference electrode.

Much of the experimental work involves establishment of the so-called cross-shaped phase diagram.[14] This was accomplished as follows: For each set of input concentrations ($[BrO_3^-]_0$, $[Mn(II)]_0$, $[H^+]_0$, $[\text{reductant}]_0$), the reactor was filled by using the highest speed of the Sage 375-A peristaltic pump. The pump speed, measured as the "flow rate" k_0 (the reciprocal of the residence time τ), was then lowered through a sequence of values at each of which the steady-state or oscillatory response was recorded. After reaching zero flow rate, the pump speed was then increased stepwise to its maximum and the response followed again. Differences in response at the same k_0 value between the increasing and decreasing flow rate segments of the experiment show the existence of hysteresis and bistability at that particular set of constraints.

Results

Seven inorganic reductants (sulfite, arsenite, stannous, iodide, ferrocyanide, hydrazine, and hydroxylamine) were investigated. In each case, experiments were carried out in which the response of the system at various input flows of bromate, Mn(II), and the reductant was investigated as a function of k_0. In Figure 1, we show the results obtained with arsenite as the reductant in the form of a constraint–constraint ($[BrO_3^-]_0$–$[AsO_3^{3-}]_0$) plot. We observe the typical cross-shaped phase diagram,[14] with regions of monostability, bistability, and oscillation meeting at a critical point.

As the input flow of the reductant is increased from a very low value, the region of bistability narrows and shifts

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[1] Part 16 in the series Systematic Design of Chemical Oscillators. Part 15: Alamgir, M.; De Kepper, P.; Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1983**, *105*, 2641-3.

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TABLE I: Oscillatory Conditions for Bromate-Mn(II)-Reductant (R) Systems[a]

reductant	$[BrO_3^-]_0$,[b] M	$[R]_0$,[b] M	k_0,[b] 10^{-3} s^{-1}	$[BrO_3^-]_0^{crit}$,[c] M	$[R]_0^{crit}$,[c] M
SO_3^{2-}	10^{-1}	3.5×10^{-3}	2.0-3.1	1.4×10^{-1}	3.1×10^{-3}
	1.5×10^{-1}	3.5×10^{-3}	4.9-7.8		
AsO_3^{3-}	10^{-1}	10^{-3}	3.0-4.3	1.2×10^{-1}	8.7×10^{-4}
	1.5×10^{-1}	10^{-3}	7.4-10.1		
NH_2-NH_2	10^{-1}	5×10^{-4}	5.1-6.7	1.3×10^{-1}	4.0×10^{-4}
Sn(II)	10^{-1}	5×10^{-3}	4.5-5.4	1.0×10^{-1}	4.1×10^{-4}
I^-	2.5×10^{-2} [d]	6.5×10^{-4} [d]	11.2-12.0[d]	2.2×10^{-2} [d]	4.5×10^{-4} [d]
	10^{-2} [e]	10^{-2} [e]	10.3-12.1[e]	4.0×10^{-2} [e]	6.0×10^{-2} [e]

[a] $[Mn(II)]_0 = 1.0 \times 10^{-3}$ M in all cases. [b] Typical constraints in the middle of the oscillatory region (circles in Figure 1). [c] Constraints at critical point (cross point in Figure 1) with $k_0 = 9.4 \times 10^{-3}$ s^{-1}. [d] Oscillations similar to BrO_3^--Mn^{2+}-Br^- and other BrO_3^--Mn^{2+}-R systems. [e] Oscillations similar to BrO_3^--I^- system. Additional critical point for subcritical Hopf bifurcation occurs at $[BrO_3^-] = 5 \times 10^{-3}$, $[I^-]_0 = 3 \times 10^{-3}$ M.

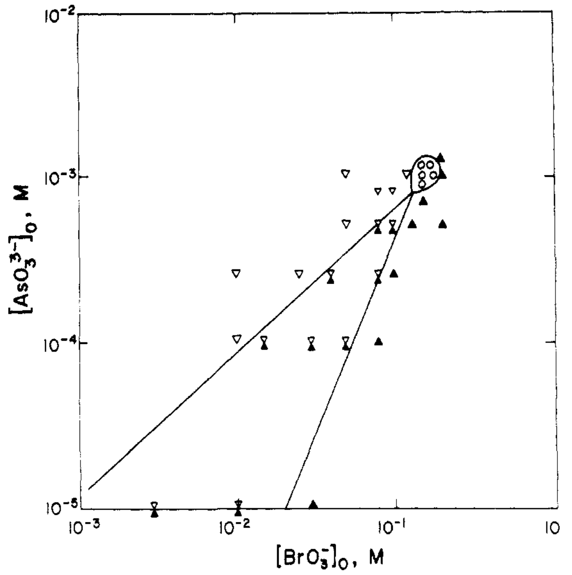

Figure 1. Phase diagram in the $[BrO_3^-]_0$-$[AsO_3^{3-}]_0$ plane. Fixed constraints: $[Mn^{2+}]_0 = 1 \times 10^{-3}$ M, $k_0 = 9.4 \times 10^{-3}$ s^{-1}, $[H_2SO_4]_0 = 1.5$ M, $T = 25$ °C. Symbols: (▽) low potential state; (▲) high potential state; (⧗) bistability; (O) oscillation.

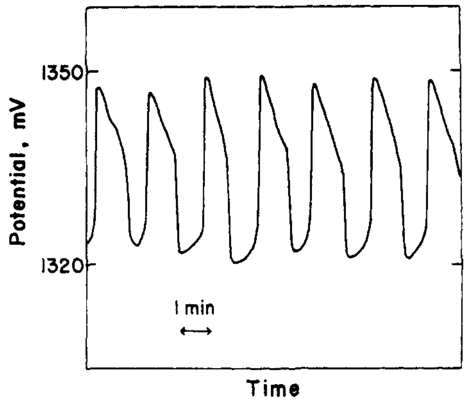

Figure 2. Oscillations in the potential of a platinum electrode (vs. Hg/Hg_2SO_4 reference electrode) with $[Mn^{2+}]_0 = 1 \times 10^{-3}$ M, $[BrO_3^-]_0 = 0.125$ M, $[SO_3^{2-}]_0 = 3 \times 10^{-4}$ M, $k_0 = 9.26 \times 10^{-3}$ s^{-1}. Other constraints as in Figure 1.

toward higher $[BrO_3^-]_0$, until it vanishes at the critical point, beyond which the system begins to oscillate. Similar results are obtained with sulfite, hydrazine, or stannous in place of arsenite, and an oscillatory potential trace for sulfite is shown in Figure 2. The shape of the oscillatory region and the wave form, amplitude, and period of oscillation greatly resemble those of the minimal bromate oscillator,[6] suggesting a close relation between these systems and that one. The measured redox potential is certainly a mixed one, responding both to the $[Mn^{3+}]/[Mn^{2+}]$ ratio and also to the ratio of unreacted to reacted reductant (e.g., $[SO_3^{2-}]/[SO_4^{2-}]$). The conditions which give rise to oscillation are summarized in Table I.

Iodide also produces similar oscillations when combined with flows of bromate and manganous ions. However, as reported in detail elsewhere,[1] at appropriate k_0 and $[BrO_3^-]_0$ values, an iodide flow can generate oscillations even in the total absence of Mn(II). These latter oscillations are closer in wave form and period to those seen in the chlorite–iodide system[15] than to the minimal bromate oscillations.

We were unable to find oscillatory conditions with either $Fe(CN)_6^{4-}$ or NH_2OH as the reductant. In an attempt to establish a correlation between the rate of reaction of the reductant with bromate and its ability to generate oscillation, we carried out a series of batch experiments. Each of the reductants was reacted with bromate in 1.5 M H_2SO_4 in the absence of manganous ion, and the reaction was followed with a bromide-sensitive electrode. The rates of bromide ion production were in the order

$$Fe(CN)_6^{4-} > SO_3^{2-} > Sn(II) \gg NH_2OH > AsO_3^{3-} > N_2H_4 > I^- \quad (1)$$

There is thus no simple correlation of the type sought. We shall return to this point in the Discussion.

We also attempted to generate "batch" oscillations with the above reductants using N_2 as a carrier gas as Adamčiková and Ševčík[11] had done with hypophosphite. Although we were able to reproduce their results (and to get oscillations with hypophosphite as the reductant in a CSTR), we were unable to find any set of conditions which gave sustained oscillation with any of the other reductants. A wide range of bromate (10^{-5}–10^{-2} M), reductant (10^{5}–10^{-1} M), and Mn(II) (10^{-4}–10^{-2} M) concentrations as well as N_2 flow rates (10–50 L/h) were investigated. Bromine evolution was rapid in all cases. Once the pink Mn(III) color and high Pt electrode potential appeared, no further change could be observed, even on drastically lowering the N_2 flow. However, with Mn(II) in the range 10^{-3}–10^{-2} M and a reductant concentration a bit above the stoichiometric amount, if one starts with a gas flow of about 10 L/h and then increases the flow to about 35 L/h, several potential oscillations of increasing amplitude are observed before a low potential state is reached. This behavior is illustrated in Figure 3.

Calculations

In ref 10 it was shown that the observed bistability and oscillations in the bromate–chlorite–bromide reaction could be accounted for by a nine-step mechanism which combines Bar-Eli's model[8] for the reaction of bromate, cerium,

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(15) Orbán, M.; Dateo, C.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 5911–8.

TABLE II: Mechanism for Bromate-Manganous-Reductant[a] Systems

no.	reaction	rate constants	
B1	$BrO_3^- + Br^- + 2H^+ \rightleftarrows HBrO_2 + HOBr$	$k_{B_1} = 2.1\ M^{-2}\ s^{-1}$	$k_{-B_1} = 1 \times 10^4\ M^{-1}\ s^{-1}$
B2	$HBrO_2 + Br^- + H^+ \rightleftarrows 2HOBr$	$k_{B_2} = 2 \times 10^9\ M^{-2}\ s^{-1}$	$k_{-B_2} = 5 \times 10^{-5}\ M^{-1}\ s^{-1}$
B3	$HOBr + Br^- + H^+ \rightleftarrows Br_2 + H_2O$	$k_{B_3} = 8 \times 10^9\ M^{-2}\ s^{-1}$	$k_{-B_3} = 110\ s^{-1}$
B4	$BrO_3^- + HBrO_2 + H^+ \rightleftarrows 2BrO_2 + H_2O$	$k_{B_4} = 1 \times 10^4\ M^{-2}\ s^{-1}$	$k_{-B_4} = 2 \times 10^7\ M^{-1}\ s^{-1}$
B5	$Mn^{2+} + BrO_2 + H^+ \rightleftarrows Mn^{3+} + HBrO_2$	$k_{B_5} = 6.5 \times 10^5\ M^{-2}\ s^{-1}$	$k_{-B_5} = 2.4 \times 10^7\ M^{-1}\ s^{-1}$
B6	$Mn^{3+} + BrO_2 + H_2O \rightleftarrows Mn^{2+} + BrO_3^- + 2H^+$	$k_{B_6} = 9.6\ M^{-1}\ s^{-1}$	$k_{-B_6} = 1.3 \times 10^{-4}\ M^{-3}\ s^{-1}$
B7	$2HBrO_2 = BrO_3^- + HOBr + H^+$	$k_{B_7} = 4 \times 10^7\ M^{-1}\ s^{-1}$	$k_{-B_7} = 2.1 \times 10^{-10}\ M^{-2}\ s^{-1}$
R1	$BrO_3^- + SO_3^{2-} + H^+ \rightarrow HBrO_2 + SO_4^{2-}$	$k_{R_1} \leqslant 10^1\ M^{-2}\ s^{-1}$ (see text)	
R2	$HOBr + SO_3^{2-} \rightarrow Br^- + SO_4^{2-} + H^+$	$k_{R_2} \geqslant 10^8\ M^{-1}\ s^{-1}$ (see text)	
R3	$Br_2 + SO_3^{2-} + H_2O \rightarrow 2Br^- + SO_4^{2-} + 2H^+$	$k_{R_3} \geqslant 10^6\ M^{-1}\ s^{-1}$ (see text)	

[a] Sulfite chosen as a typical two-electron reductant.

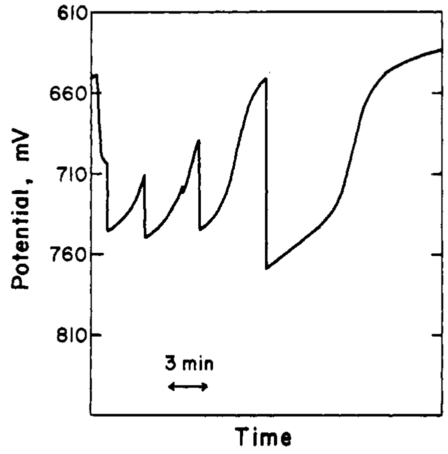

Figure 3. Transient oscillations in a batch reactor with a nitrogen carrier gas flow. At small maximum near vertical axis, the gas flow is increased from 10 to 35 L/h. Initial reactant concentrations: $[AsO_3^{3-}] = 0.17$ M, $[Mn^{2+}] = 0.0017$ M, $[BrO_3^-] = 0.06$ M, $[H_2SO_4] = 1.5$ M.

and bromide in a CSTR with Thompson's scheme[16] for the batch reaction between bromate and chlorite. It was further suggested that the ability of other bromate-chlorite-reductant systems to oscillate results from the generation of bromide by reaction(s) of the reductant with bromate and/or with lower oxidation states of bromine. Since the BrO_3^--Mn(II) system also oscillates with a variety of different reductants, we undertook a set of calculations to test the hypothesis that limit cycle behavior can be observed if the bromide flow in the minimal bromate oscillator is replaced by a flow of reductant capable of reducing BrO_3^-, HOBr, and/or Br_2.[17]

The Bar-Eli model[8,9] for the minimal bromate oscillator consists of reactions B1-B7 in Table II. We employed the rate constants as given in ref 8, though more recent calculations[18] suggest that a somewhat lower value for k_{B5} may be appropriate when manganese is used in place of cerium. With the exception of iodide, which, as discussed above, is a special case, all of the oscillatory reductants are two-electron species. For specificity, we choose sulfite as the reductant, and first supplement reactions B1-B7 with the reduction of bromate by sulfite: Williamson and King[19]

$$BrO_3^- + H_2SO_3 = HBrO_2 + HSO_4^- \qquad (R1)$$

investigated the bromate-sulfite reaction, though at much

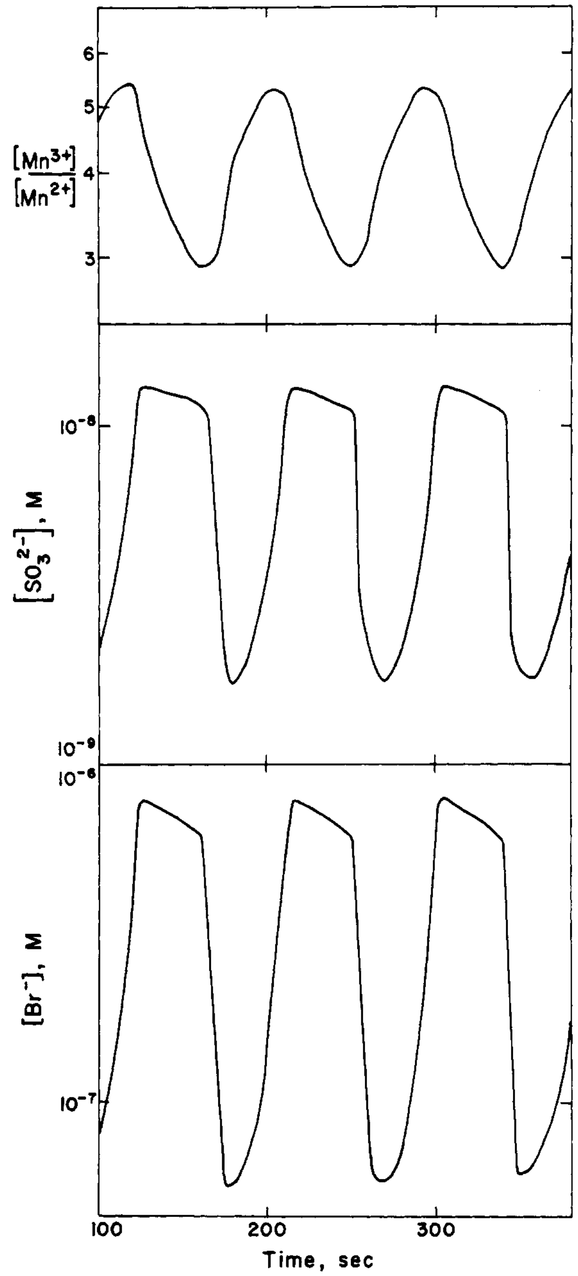

Figure 4. Concentration oscillations calculated with the mechanism of Table II. Rate constants: $k_{R1} = 1 \times 10^1\ M^{-1}\ s^{-1}$, $k_{R2} = 1 \times 10^8\ M^{-1}\ s^{-1}$, $k_{R3} = 1 \times 10^6\ M^{-1}\ s^{-1}$. Input concentrations: $[BrO_3^-]_0 = 8 \times 10^{-2}$ M, $[SO_3^{2-}]_0 = 1.4 \times 10^{-4}$ M, $[Mn^{2+}]_0 = 1.5 \times 10^{-4}$ M, $[H^+]_0 = 1.5$ M. Flow rate $k_0 = 8 \times 10^{-3}\ s^{-1}$.

higher pH's than employed in our studies, and obtained a rate law for the reduction of bromate to bromide.

$$3H_2SO_3 + BrO_3^- = 3HSO_4^- + Br^- + 3H^+ \qquad (2)$$

with

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(16) Thompson, R. C. *Inorg. Chem.* **1973**, *12*, 1905-9.

(17) We do not consider the possible reduction of intermediate bromine species ($HBrO_2$, BrO_2) by the reductant, since other reactions from the set B1-B7 reduce these species to Br(I) or Br(0) sufficiently rapidly to generate oscillation.

(18) Bar-Eli, K.; Geiseler, W., unpublished results.

(19) Williamson, F. S.; King, E. L. *J. Am. Chem. Soc.* **1957**, *79*, 5392-400.

$$\frac{d[S(IV)]}{dt} = \frac{k_1 + k_2[H^+]}{K_1^{-1}[H^+] + 1 + K_2[H^+]^{-1}}[BrO_3^-][S(IV)] \quad (3)$$

From their values of the parameters in eq 3, we estimated a starting value for k_{R1} in our calculations of 10^3 M^{-2} s^{-1}.

We are not aware of any experimental studies of reaction R2. However, the reaction between elementary bromine and sulfite has been investigated by Halban and Eisner[20] in 0.1 M HCl. With both reactants in reaction R3 at concentrations of 0.1 M, the reaction is complete in $<1.5 \times 10^{-3}$ s, suggesting a rate constant $k_{R3} > 10^5$ M^{-1} s^{-1}.

Reaction R1 alone turns out to be insufficient to generate enough bromide to sustain oscillations or bistability, regardless of the value assigned to k_{R1}. The system of equations B1–B7 plus R1 has only a single, low-bromide ($<10^{-7}$ M) steady state. In order to allow for direct bromide production by the reductant, we introduced two additional reactions:

$$HOBr + H_2SO_3 = Br^- + HSO_4^- + 2H^+ \quad (R2)$$

$$Br_2 + H_2SO_3 + H_2O = 2Br^- + HSO_4^- + 3H^+ \quad (R3)$$

In the presence of reactions R2 and R3, the initial value chosen for reaction R1 is too high, apparently because too much sulfite is consumed in this step, leaving too little for reactions R2 and R3. However, if k_{R1} is lowered to 10^1 M^{-1} s^{-1} or less, then the experimentally observed cross-shaped phase diagram and oscillations can be produced by the model with appropriate values of k_{R2} and k_{R3}, though the calculated region of bistability tends to be significantly narrower than that found experimentally. (See Figure 4.)

Oscillations are obtained for k_{R2} values greater than or equal to 10^8 M^{-1} s^{-1} with $k_{R1} = 10^1$ M^{-2} s^{-1} and $k_{R3} = 0$. Holding k_{R1} fixed and setting $k_{R2} = 0$, we find oscillations with $k_{R3} > 10^6$ M^{-1} s^{-1}. If k_{R2} and k_{R3} are both set equal to 10^6 M^{-1} s^{-1}, then k_{R1} can be set to zero and the oscillations still persist. Thus, the calculations show that the reductant must generate bromide directly from HOBr and/or Br_2, but they are unable to distinguish between reactions R2 and R3 as the key step in producing oscillations. Initial reduction of bromate by the reductant is unnecessary, apparently because of the effectiveness of steps B1 and B4.

Discussion

Given the existence of the minimal bromate oscillator,[6] the ability of the present systems to oscillate comes as no surprise, though the results of the calculations give us further confidence that the mechanistic understanding of inorganic bromate oscillators is on a solid footing. The oscillators reported here fit nicely into the classification scheme proposed by Epstein et al.[21] as a subset of the bromate–bromide–metal ion–inorganic reductant group. That scheme goes beyond the earlier taxonomy of Noyes[22] and allows for a wider range of bromate oscillators while encompassing iodate and chlorite systems as well.

It is tempting to seek correlations between the results of our batch experiments and the ability of the various reductants to produce oscillations. The calculations suggest that a species which reacts too rapidly with bromate or too slowly with hypobromous acid and bromine will be incapable of generating oscillations. The rates summarized in expression 1 are rates of overall bromide production, i.e., of the reactions analogous to eq 2. Thus, it is not obvious that a direct correlation is appropriate, and the two nonoscillatory reductants, $Fe(CN)_6^{4-}$ and NH_2OH, rank first and fourth, respectively, in their rates.

An alternative interpretation is that the oscillatory reductants are all, with the exception of I^-, two electron reductants, while ferrocyanide and hydroxylamine are one-electron species. Iodide because of the possible role of intermediate oxidation states such as HOI and HIO_2, must be considered a special case. It may be, then, that the inability of the other one-electron reductants to give oscillatory behavior is a result of the one-electron analogues of reactions R2 and R3 being too slow. More detailed experimental and mechanistic studies of the BrO_3^-–Mn(II)–I^- system are in progress and will be reported elsewhere.

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Registry No. Mn^{2+}, 16397-91-4; BrO_3^-, 15541-45-4; N_2H_4, 302-01-2; SO_3^{2-}, 14265-45-3; AsO_3^{3-}, 15502-74-6; I^-, 20461-54-5; Sn(II), 22541-90-8.

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(20) Halban, H.; Eisner, H. *Helv. Chim. Acta.* **1935**, *18*, 724–33.

(21) Epstein, I. R.; Kustin, K.; De Kepper, P.; Orbân, M. *Sci. Am.* **1983**, *248*, 96–108.

(22) Noyes, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 4644–9.