If we have enough $D/(D+S)$ data we may write a system of m equations with n unknowns ($m \geq n$) that in matrix representation is reduced to

$$\hat{b} = \hat{A}\hat{f}$$

where the elements of $\hat{b}$ are

$$b_i = D/(D+S)$$

The coefficients of the matrix $\hat{A}$ are

$$a_{ij} = \frac{k(E_j)}{k(E_j) + \omega_i}\Delta E$$

and the unknowns of matrix $\hat{f}$ are

$$f_i = f(E_j)$$

Solving the system of linear equations, we can find the values of the energy distribution function.

Registry No. CMD, 4222-21-3; VC, 75-01-4; SF$_6$, 2551-62-4; CH$_3$I, 74-88-4; O$_2$, 7782-44-7; N$_2$, 7727-37-9; 1-chlorodiazoethane, 59712-39-9; 1-chloro-1-methylcarbene, 31304-51-5.

Supplementary Material Available: Detailed outlines of the mathematical deconvolution method used. The influence of experimental errors and collision softness on the results of the deconvolution method application is also estimated (8 pages including Figures 5–7). Ordering information is given on any current masthead page.

Bistability and Bromide-Controlled Oscillation during Bromate Oxidation of Ferroin in a Continuous Flow Stirred Tank Reactor

V. Gáspár, G. Bazsa, and M. T. Beck*

Department of Physical Chemistry, Institute of Chemistry, Kossuth Lajos University, Debrecen, Pf.7., 4010, Hungary *(Received: April 15, 1985)*

Autocatalytic oxidation of Fe(phen)$_3^{2+}$ (ferroin) by bromate has been investigated in a continuous flow stirred tank reactor (CSTR). A *closed region of bistability* exists in the plot of input stream concentrations of ferroin and bromate. The bromate–ferroin–bromide system exhibits bistability and *high amplitude oscillations* over a *broad range of concentrations*. As a first approximation a revised Oregonator type model extended by reactions of ferroin and ferriin describes the system. However, further reactions have to be taken into consideration for a quantitative description.

Introduction

Discovery of small-amplitude oscillations in a CSTR containing bromate, bromide, and cerous or manganeous ions has been reported by Orbán et al.[1] and Geiseler.[2,3] The search for these so-called minimal bromate oscillators was stimulated by computations[4] based on the Noyes–Field–Thompson (NFT) model.[5] Existence of a *very narrow region of small-amplitude oscillations* was predicted near the critical point, at which the bistability of the system disappears.

Although ferroin is a well-known catalyst of the Belousov[6]–Zhabotinsky[7] (BZ) reaction,[8] there are no reports on either the dynamics of the simple ferroin–bromate autocatalytic reaction[9-12] or the existence of a ferroin-catalyzed minimal bromate oscillator *in a CSTR*. The necessity for such investigations, however, is strongly supported by a number of experimental observations[8,13-18] which indicate differences in behavior and possibly in mechanism of metal-ion- and ferroin-catalyzed BZ oscillators.[17,18]

The *higher level of complexity* in ferroin-catalyzed systems is demonstrated by the experiments performed in our laboratory earlier.[19] It was found, surprisingly, that ferroin can react with bromate alone in an oscillatory manner. However, the continuous and partial removal of bromine and high concentrations of both reactants are the necessary conditions of oscillation. This observation strongly indicates that, at least at high concentrations, there must be basic differences in the chemistry of bromate–ferroin and bromate–metal ion (Ce^{3+}, Mn^{2+}) systems. Then in the BZ systems, in which the concentrations of catalysts are much lower, these differences can also result in some modifications.

The bromate–ferroin batch oscillatory system shows similarities to the bromate–cerous–oxalic acid system.[21] Therefore, at a very early stage of our study the differences mentioned earlier were attributed also to the possibility of a kind of bromine-controlled

---

(1) Orbán, M.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 2657.

(2) Geiseler, W. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 721.

(3) Geiseler, W. *J. Phys. Chem.* **1982**, *86*, 4394.

(4) Bar-Eli, K. In "Nonlinear Phenomena in Chemical Dynamics", Vidal, C., Pacault, A., Eds.; Springer-Verlag: West Berlin, 1981; Vol. 12, p 228.

(5) Noyes, R. M.; Field, R. J.; Thompson, R. C. *J. Am. Chem. Soc.* **1971**, *93*, 7315.

(6) Belousov, B. P. *Ref. Radiat. Med.* **1959**, *1958*, 145.

(7) Zhabotinsky, A. M. *Dokl. Akad. Nauk. SSSR* **1964**, *157*, 392.

(8) Vavilin, V. A.; Gulak, P. V.; Zhabotinsky, A. M.; Zaikin, A. N. *Izv. Akad. Nauk. SSSR Ser. Chim.* **1969**, *11*, 2618.

(9) Körös, E.; Burger, M.; Kis, Á. *React. Kinet. Catal. Lett.* **1974**, *1*, 475.

(10) Rovinsky, A. B.; Zhabotinsky, A. M. *Teor. Eksp. Khim.* **1979**, *15*, 25.

(11) Rovinsky, A. B.; Zhabotinsky, A. M. *React. Kinet. Catal. Lett.* **1979**, *11*, 205.

(12) Yoshida, T.; Ushiki, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1772.

(13) (a) Váradi, Z. Ph.D. Thesis, Debrecen, Hungary, 1972. (b) Váradi, Z.; Beck, M. T. *J. Chem. Soc., Chem. Commun.* **1973**, 30.

(14) Körös, E.; Burger, M.; Friedrich, V.; Ladányi, L.; Nagy, Zs.; Orbán, M. *Faraday Symp. Chem. Soc.* **1974**, *9*, 28.

(15) Smoes, M. L. *J. Chem. Phys.* **1979**, *71*, 4669.

(16) Ganapathisubramanian, N.; Noyes, R. M. *J. Phys. Chem.* **1982**, *86*, 5158.

(17) Rovinsky, A. B.; Zhabotinsky, A. M. *J. Phys. Chem.* **1984**, *88*, 6081.

(18) Noyes, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 4644.

(19) (a) Beck, M. T.; Bazsa, G.; Hauck, K. In "Kinetics of Physicochemical Oscillations", Discussion Meeting at Aachen, 1979, Preprints of Submitted Papers, Vol. 1, p 123. (b) Beck, M. T.; Bazsa, G.; Hauck, K. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 408.

(20) "Oscillations and Travelling Waves in Chemical Systems", Field, R. J., Burger, M., Eds.; Wiley: New York, 1984, Chapter 2.

(21) Noszticzius, Z.; Bódiss, J. *J. Am. Chem. Soc.* **1979**, *101*, 3177.

0022-3654/85/2089-5495$01.50/0 © 1985 American Chemical Society

mechanism for the oscillation. The bromine-controlled model (the so called Explodator[22]) has recently been questioned by Noyes[23] from a theoretical point of view. Noszticzius et al.[24] report an experimental test that proves unambiguously the role of bromide ion as the only control intermediate in these systems. In the ferroin–bromate batch oscillatory system the concentration of bromine reaches a high value and thus, altogether, the bromine-hydrolysis-controlled (BHC) model of Field[20] is of prime importance. Therefore, the differences should only result from some additional reaction(s) of ferroin and ferriin.

The ferroin–bromate batch oscillatory reaction appears simple, since only two reagents are initially involved. However, modeling of the oscillation is not easy, since the exact description of the effect of gas stream is difficult and also an ill-defined red precipitate formed. Therefore, we have decided to investigate the dynamics of the ferroin–bromate–(bromide) system in a CSTR, since this set of experimental conditions is much more appropriate for modeling and provides useful results for checking mechanistic ideas both qualitatively and quantitatively.

Experimental Section

All chemicals were reagent grade products ($NaBrO_3$, BDH; NaBr and *o*-phenanthroline, Reanal; $FeSO_4 \cdot 7H_2O$, Reachim; H_2SO_4 (96%), Carlo Erba). Sodium bromate was recrystallized three times to avoid contamination from bromide ions. Ferroin solutions were freshly prepared. The acidic decomposition of ferroin[9,12] was negligible in the course of experiments.

The reactor consists of two pieces: a thermostated glass vessel and a VINIDUR (PVC-based) top. Solutions were pumped through two capillary tubings (Cole-Palmer, 6408-41, Tygon) into the CSTR with a Cole-Palmer pump at the top section. The volumes of transported solutions per unit time were measured as a function of the voltage that regulated the pump. The accuracy of stream velocity was within ±2%. The solution was stirred with a magnetic stirrer. A water pump drained the excess solution continuously from the CSTR. The top section was designed to accommodate bright-platinum and bromide-selective (Radelkis OP-Br) electrodes and a salt bridge. The common reference was a saturated calomel electrode (Radiometer K401) connected to the system by a double-junction salt bridge (saturated KNO_3–saturated KCl). The emf values were measured by Radiometer pHM 51 and Radelkis OP-208 mV meters and were recorded as a function of time with Radelkis OP-814/1 recorders.

The experiments were performed at constant acidity, 0.1 and 0.5 M H_2SO_4 in ferroin–bromate and bromate–ferroin–bromide systems, respectively. In the second system the required amount of sodium bromide was dissolved in the ferroin solution.

The standard method of the CSTR experiments was the following: The empty reactor was filled from reservoirs at a fixed flow rate ($k_0 = 1/\tau$, where τ is the mean residence time). After a steady state had been reached, the feed was continued at least for 3τ time and then the value of k_0 or one of the stream concentrations was increased or decreased, instantaneously. After approaching the new steady state the whole procedure was repeated. When, for instance, an oscillatory state evolved, the oscillation was followed also at least for 3τ time.

The actual values of the reactor volume, flow rate, and input concentrations of the components are listed in the figures. The temperature was constant ($T = 298 \pm 0.1$ K).

Results and Discussion

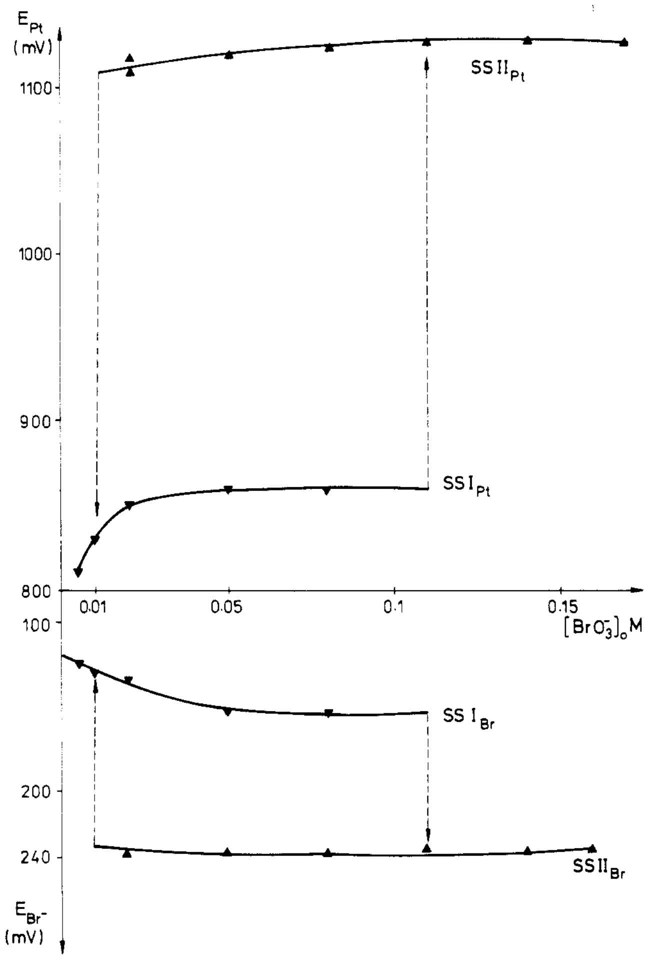

Figure 1. Hysteresis in the potentials of platinum and bromide-selective electrodes by changing $[NaBrO_3]_0$: $[\text{ferroin}]_0 = 2 \times 10^{-4}$ M, $[H_2SO_4]_0 = 0.1$ M, $V = 35.0$ mL, $k_0 = 10^{-2}$ s^{-1}. (Reference: saturated calomel electrode.) $[x]_0$, concentrations are given in the reactor after mixing but before any reaction takes place.

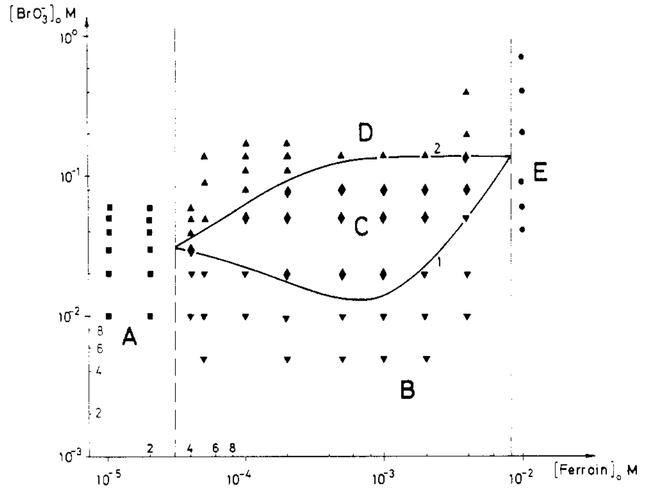

Figure 2. Bifurcation diagram for the ferroin–bromate system. $[H_2SO_4]_0 = 0.1$ M, $V = 35.0$ mL, $k_0 = 10^{-2}$ s^{-1}. The symbols are explained in Table I.

The Ferroin–Bromate System. A typical hysteresis curve is presented in Figure 1. In this experiment the $NaBrO_3$ concentration is increased or decreased in the inlet stream at a fixed flow rate and input concentration of ferroin and acid. Below a critical value of $NaBrO_3$ input concentration the system is characterized by a low potential at the platinum electrode (SSI_{Pt})—high concentration of ferroin—and by a low potential at the bromide-selective electrode (SSI_{Br})—high concentration of bromide ion—at the same time. This branch of steady states is designated SSI. When the critical $NaBrO_3$ input concentration is reached, the system jumps to SSII. It corresponds to a high potential at the platinum electrode ($SSII_{Pt}$)—low concentration of ferroin–and a high potential at the bromide electrode ($SSII_{Br}$)—very low concentration of bromide ion. Transitions from one state to the other may be generated by perturbations, e.g. injection of a small

---

[22] Noszticzius, Z.; Farkas, H.; Schelly, Z. A. *J. Chem. Phys.* **1984**, *80*, 6062.

[23] Noyes, R. M. *J. Chem. Phys.* **1984**, *80*, 6071.

[24] Noszticzius, Z.; Gáspár, V.; Försterling, H. D. *J. Am. Chem. Soc.* **1985**, *107*, 2314.

TABLE I: Characteristic Features of Different Regions in the Bifurcation Diagram for the Ferroin-Bromate System (Figure 2)

region	symbol in Figure 2	range of input concn, M	electrode potential values
A	■	$[\text{ferroin}]_0 < 3 \times 10^{-5}$	$SSI_{Pt} \leftrightarrow SSII_{Pt}$; SSI_{Br}
B, SSI	▼	$3 \times 10^{-5} < [\text{ferroin}]_0 < 10^{-2}$ $[BrO_3^-]_0$ below curve 1	SSI_{Pt}; SSI_{Br}
C, bistability	♦	$3 \times 10^{-5} < [\text{ferroin}]_0 < 10^{-2}$ $[BrO_3^-]_0$ between curves 1 and 2	SSI_{Pt}, $SSII_{Pt}$; SSI_{Br}, $SSII_{Br}$
D, SSII	▲	$3 \times 10^{-5} < [\text{ferroin}]_0 < 10^{-2}$ $[BrO_3^-]_0$ above curve 2	$SSII_{Pt}$; $SSII_{Br}$
E, Br_2 production	●	$[\text{ferroin}]_0 > 10^{-2}$	$SSI_{Pt} \leftrightarrow SSII_{Pt}$; $SSII_{Br}$

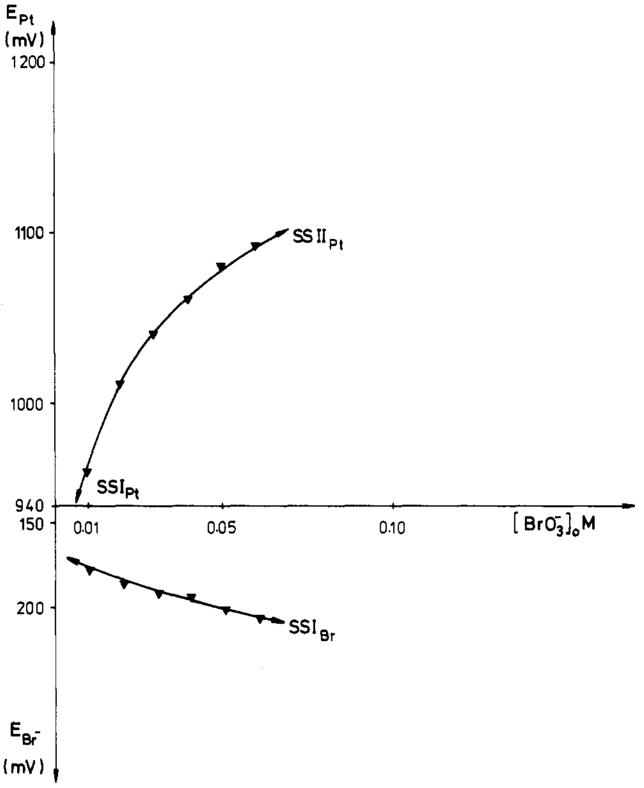

Figure 3. Reversible changes of steady-states potentials in region A of Figure 2, $[\text{ferroin}]_0 = 10^{-5}$ M. Other parameters are the same as in Figure 2.

amount of ferroin, sulfuric acid, or sodium bromide. The system is *bistable*.

The bifurcation diagram for ferroin-bromate system (Figure 2) was measured by repeating the above procedure (Figure 1) at different input concentrations of ferroin. It was found that the *region of bistability is closed* (region C in Figure 2). Curves 1 and 2 correspond to transitions from SSII to SSI and back, respectively. The intersections of the curves were drawn by extrapolating the curves. These points equal the critical points, at which the multistable behavior of the system evolves or disappears. Regions B and D are the SSI and SSII branches described earlier. These are the flow and thermodynamic regions, respectively.

No hysteresis has been detected in regions A and E. In region A the potential of the platinum electrode changes continuously from SSI_{Pt} to $SSII_{Pt}$ and back on the same curve increasing and then decreasing the $NaBrO_3$ concentration in the stream (Figure 3). Consequently, the solution turns from red to blue and back to red. However, the potential of the bromide-selective electrode does not change from SSI_{Br} to $SSII_{Br}$. It remains in the SSI_{Br} region.

In region E the situation is somewhat similar to region A. The differences are that the change in the potential of the platinum electrode is more sharp and the potential of the bromide-selective electrode remains in the $SSII_{Br}$ region. (Not indicated here.) In this case the formation of bromine has been observed.

The characteristic features of different regions in the bifurcation diagram for the ferroin-bromate system are summarized in Table I.

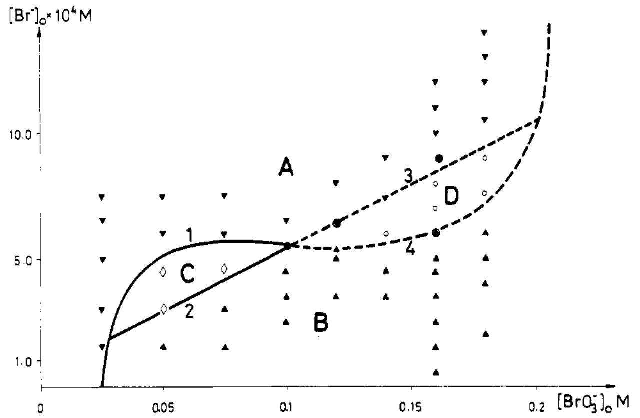

Figure 4. Bifurcation diagram for the bromate-ferroin-bromide system: $[\text{ferroin}]_0 = 3 \times 10^{-4}$ M, $[H_2SO_4]_0 = 0.5$ M, $k_0 = 10^{-2}$ s^{-1}, $V = 30.0$ mL.

To our knowledge this is the first example in the field of bromate chemistry, in which the complete closed region of bistability has been determined *experimentally*. It is also an interesting observation that applying the same concentrations as in the batch experiment no oscillation can be detected in the CSTR. It indicates that bromine removal by flow is perhaps not as effective as it is by stream in the batch experiment. This fact would indicate that the region of bistability does not become an oscillatory region.

The Bromate-Ferroin-Bromide System. The bifurcation diagram for the bromate-ferroin-bromide system is shown in Figure 4, at a fixed flow rate and input concentration of ferroin and acid. The procedure applied was the same as in the ferroin-bromate system but the input concentration of the bromide ion was changed systematically in different runs. There are four parts in the plot of the constraints. Regions A and B correspond to the monostable states SSI and SSII, respectively. SSI is characterized by high concentrations of ferroin and bromide, while in SSII both concentrations are low. Curves 1 and 2 indicate the transitions from one steady state to the other. The bistability region is designated C. It was found, as in cases of metal-ion-catalyzed minimal bromate oscillators, that over the range of bistability the system bifurcates to an oscillatory system (region D). Curves 3 and 4 correspond to transitions from the monostable states to the oscillatory state and back. During these transitions a kind of hysteresis occurs. As it is indicated in Figure 4, there are some points near the borders of region D at which both the oscillatory and one of the monostable states were detected. This observation is not unique. Similar points were found experimentally by Masełko[25] in the bromate-manganeous-citric acid system. The computations of Kumpinsky et al.[32] based on the NFT mechanism[5] resulted also in such points in a phase diagram of the manganeous-catalyzed minimal bromate oscillator under special conditions. The amplitudes are high (Figure 5): more than 300 mV in Pt potential and about 120 mV in Br^--selective electrode potential. These values are higher by a factor of 6-10 than the analogous values of the metal-ion-catalyzed minimal bromate oscillators.[1-3] The amplitude and period of oscillations are constant within experimental uncertainty over the whole region D. By these results and applying the classification method of Masełko,[25] the bifurcation on both sides of region D may be related to type II,

---

(25) Masełko, J. *J. Chem. Phys.* **1982**, *67*, 17.

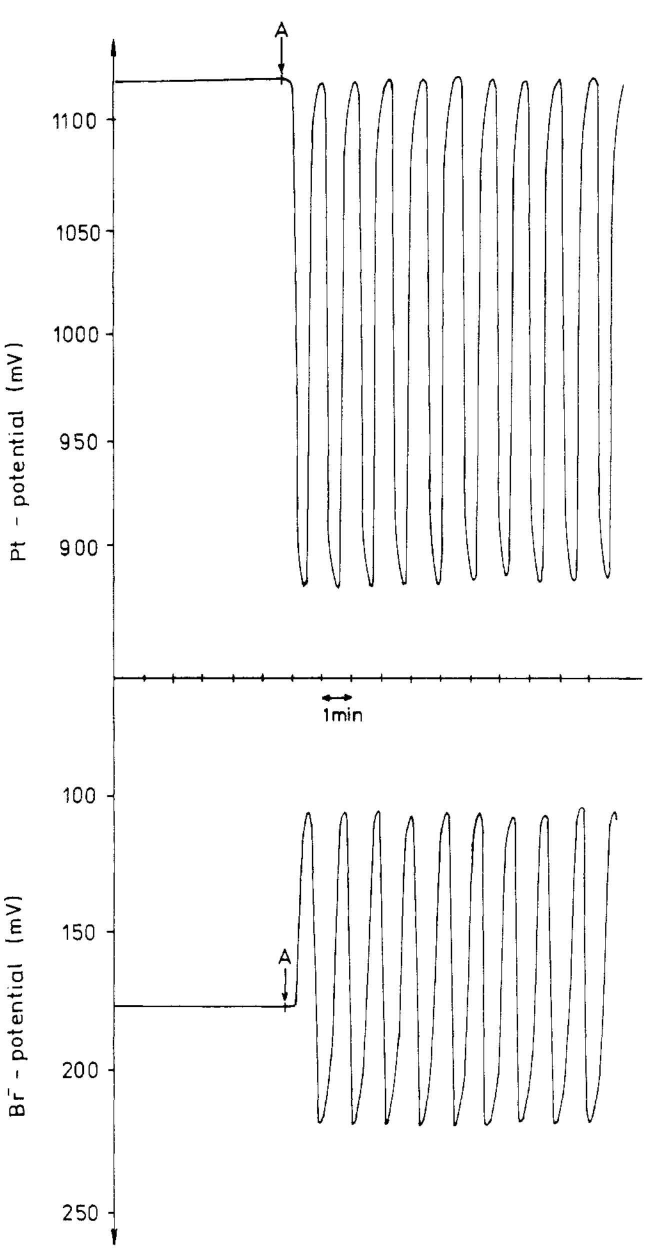

Figure 5. High amplitude oscillations in both potentials measured in the ferroin-catalyzed minimal bromate oscillator in a CSTR: $[BrO_3^-]_0$ = 0.16 M, $[\text{ferroin}]_0 = 3 \times 10^{-4}$ M, $[H_2SO_4]_0$ = 0.5 M, $k_0 = 10^{-2}$ s^{-1}, V = 30.0 mL. At point A the concentration of bromide ($[Br^-]_0$) was adjusted to 7×10^{-4} from 6×10^{-4} M.

that is a subcritical Hopf bifurcation.

Search for the Mechanism. Since the crossed-shape diagram of the ferroin–bromate–bromide system shows a lot of similarities to the diagrams of the metal-ion-catalyzed systems, it is evident that the mechanism for ferroin-catalyzed systems might be based also on the well-known NFT model.[5] However, there are two observations that can be explained only by additional reactions of ferroin and ferriin. These observations are the formation of bromine in the ferroin–bromate system at high initial concentration of ferroin and the extremely high amplitude of oscillations in ferroin–bromate–bromide system (at low initial concentration of ferroin).

There are different explanations for the origin of bromine. In an early paper Noyes[18] proposed the occurrence of the reactions

$$\text{Fe(phen)}_3^{2+} + \text{HOBr} + \text{H}^+ \rightleftharpoons \text{Fe(phen)}_3^{3+} + \text{Br}\cdot + \text{H}_2\text{O} \qquad \text{(A1)}$$

$$2\text{Br}\cdot \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \text{Br}_2 \qquad \text{(A2)}$$

The net stoichiometric process is 2(A1) + (A2):

$$2\text{Fe(phen)}_3^{2+} + 2\text{HOBr} + 2\text{H}^+ \rightleftharpoons 2\text{Fe(phen)}_3^{3+} + \text{Br}_2 + 2\text{H}_2\text{O}$$

The problem with reaction A1 is that it is thermodynamically unfavorable by at least 0.3 V. Therefore, Ganapathisubramanian and Noyes[16] have recently proposed an alternative reaction pathway. It consists of a two-electron pseudoelementary process

$$\text{Fe(phen)}_3^{2+} + \text{HOBr} + \text{H}^+ \rightleftharpoons \text{Fe(phen)}_3^{4+} + \text{Br}^- + \text{H}_2\text{O} \qquad \text{(B1)}$$

followed by the rapid equilibrium

$$\text{Fe(phen)}_3^{2+} + \text{Fe(phen)}_3^{4+} \overset{\text{fast}}{\rightleftharpoons} 2\text{Fe(phen)}_3^{3+} \qquad \text{(B2)}$$

The net stoichiometric change is (B1) + (B2):

$$2\text{Fe(phen)}_3^{2+} + \text{HOBr} + \text{H}^+ \rightleftharpoons 2\text{Fe(phen)}_3^{3+} + \text{Br}^- + \text{H}_2\text{O}$$

The formation of bromine is attributed to

$$\text{HOBr} + \text{Br}^- + \text{H}^+ \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O} \qquad \text{(C)}$$

which is a pseudoelementary process of the revised Oregonator model[23] too. Although the proposal of an Fe(IV) species with a two-electron reduction potential of about 1.2–1.3 V can explain a number of puzzling observations, the existence of such a species is by no means proved experimentally and seems to be a kind of strange theoretically.

The other puzzling observation of Ganapathisubramanian and Noyes[16] is that excess bromide ion reduces ferriin in a relatively fast reaction, while cerium(IV) reacts with bromide in a much slower process.[26] Net reaction B1 + B2 explains this experience, but supposing only one-electron elementary steps the following thermodynamically unfavorable process should be taken into account:

$$\text{Fe(phen)}_3^{3+} + \text{Br}^- \rightleftharpoons \text{Fe(phen)}_3^{2+} + \text{Br}\cdot \qquad \text{(A3)}$$

The net stoichiometric process is 2(A3) + A(2):

$$2\text{Fe(phen)}_3^{3+} + 2\text{Br}^- \rightleftharpoons 2\text{Fe(phen)}_3^{2+} + \text{Br}_2$$

It can be shown easily that neglecting the radical–radical recombination A2 and summarizing process A1 and the reverse A3, the net stoichiometric reaction resulted equals to net reaction B1 + B2. Thus, the formation of bromine could be explained by reaction C, even if only one-electron elementary processes were supposed.

Both proposals (one- or two-electron steps) lead to the same rate law (r1) for ferroin–HOBr reaction:

$$\text{rate} = k[\text{Fe(phen)}_3^{2+}][\text{HOBr}][\text{H}^+] \qquad \text{(r1)}$$

However, depending on the proposals for the origin of bromine, the rate law for the ferriin–bromide reaction can be different.

If net reaction B1 + B2 is proposed for either one- or two-electron processes then thermodynamics would require the rate law

$$\text{rate} = k'[\text{Fe(phen)}_3^{3+}]^2[\text{Br}^-]/[\text{Fe(phen)}_3^{2+}] \qquad \text{(r2)}$$

If the ferroin–HOBr and ferriin–Br$^-$ reactions run independently, that is the radical–radical recombination process A2 cannot be neglected on the reaction time scale, the rate law (r3) should be

$$\text{rate} = k''[\text{Fe(phen)}_3^{3+}][\text{Br}^-] \qquad \text{(r3)}$$

taken into account. Our preliminary kinetic investigation of the ferriin–bromide reaction has confirmed the validity of rate law r3. (A similar rate law was found for the ferriin–OH$^-$ reaction (k_{obsd} is about 400 mol^{-1} dm^3 s^{-1}) by Nord et al.[33] Note that this process is also thermodynamically unfavorable considering one-electron steps only.) Therefore, we have constructed the following skeleton as a first and very plausible approximation for the mechanism of the ferroin-catalyzed minimal bromate oscillator *in CSTR*:

---

(26) King, E. L.; Pandow, M. L. *J. Am. Chem. Soc.* **1953**, *75*, 3063.

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr \tag{1}$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \tag{2}$$

$$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O \tag{3}$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2\cdot + H_2O \tag{4}$$

$$Fe(phen)_3^{2+} + BrO_2\cdot + H^+ \rightarrow Fe(phen)_3^{3+} + HBrO_2 \tag{5}$$

$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \tag{6}$$

$$Fe(phen)_3^{2+} + HOBr + H^+ \rightarrow Fe(phen)_3^{3+} + {}^1/_2Br_2 + H_2O \tag{7}$$

$$Fe(phen)_3^{3+} + Br^- \rightarrow Fe(phen)_3^{2+} + {}^1/_2Br_2 \tag{8}$$

$$Br_2 \rightarrow Br_2(g) \tag{9}$$

This simplest model is based on the revised Oregonator model of Noyes[23] and also the bromine-hydrolysis-control theory of Field.[20] The reactions of phenanthroline ligand in either free or coordinated forms were neglected because of the fairly low concentration of ferroin (and ferriin) in CSTR experiments. Note that the third step of the revised Oregonator has been replaced by two steps (reactions 4 and 5) according to Showalter et al.[31] and reaction 5 has been made irreversible by the results of Rovinsky et al.[10,11]

Preliminary calculations have indicated that reaction sequence 1–8 does not produce oscillations under the experimental conditions. Therfore, an independent bromine removal process (reaction 9) was included in the model. This removal is proposed due to spontaneous evaporation or the gas stream caused by water pump applied. (The inclusion of a first-order evaporation term in modeling a CSTR experiment is not unique. This was applied by De Kepper et al.[28] for describing the bistability in the arsenite–iodate reaction.[28,29])

This simple model was tested by computations. The differential equation system according to reaction sequence 1–9 was solved by the method of Gear.[27] The applied rate constants were chosen from the "0" set of rate constants.[5,30] (The "0" set gave the best results in computations for modeling the cerous-catalyzed minimal bromate oscillator, Bar-Eli et al.[30]) The value of k_9 was determined experimentally ($k_{9,\mathrm{expt}} = 5 \times 10^{-3}$ s^{-1}) by a potentiometric method developed by Noszticzius et al.[34] The unknown values of k_7 and k_8 were estimated by trial. It is interesting to note that reaction 7 does not appear to be essential for the oscillation in a CSTR. (The value a k_7 can even be zero.) For calculating oscillation under experimental conditions, however, some of the constants had to be modified. The value of k_2 had to be decreased by less than a factor of 2 ($k_2 = 1.3 \times 10^9$ mol^{-2} dm^6 s^{-1}) and k_9 had to be increased to 0.05 s^{-1}. The appropriate value of k_8 had to be between 10^3 and 10^4 mol^{-1} dm^3 s^{-1}.

Although the shapes of the calculated oscillating curves were similar to the experimental curves, the model does not describe the system completely. The calculated frequency is higher than the experimental value by a factor of 2–3. The amplitudes of oscillations are much smaller than the measured amplitudes and are very similar to the amplitudes found in the metal-ion-catalyzed minimal bromate oscillators. Neither modification of different rate constants nor changing other parameters (input concentrations) resulted in high amplitude oscillations. (We also tried to apply rate laws r1 and r2 according to the net stoichiometric change (B1) + (B2) instead of reactions 7 and 8. However, we were unable to find a set of parameters that resulted even in small amplitude oscillations.

The fact that the value of k_9 had to be increased and also the absence of high amplitude oscillations indicate that perhaps *even* at low concentrations of ferroin (and ferriin) some other processes should be taken into consideration, most likely the reactions of the ligand. One of such processes would be the bromination of the ligand. We tried to include this reaction into the model, but it does not result in high amplitude oscillations. The high amplitude oscillations found experimentally are very similar to the oscillations in the complete BZ system in a CSTR.[35] Therefore, it appears that *even* at low concentrations of ferroin (and ferriin) the formation and reactions of a compound which would play a role analogous to bromomalonic acid should be included in the model.

Some of the discrepancies could also have resulted from the values of the rate constants used. There are new experimental observations[36] which confirm the "LO" set of the rate constants. It is also a problem that the k_5 value for ferroin is not known. We applied the k_5 value of the analogous reaction with cerous ion, as in some earlier cases for modeling ferroin-containing systems.[31,17] Rovinsky and Zhabotinsky[17] have recently demonstrated the changes in the amplitude and shape of the oscillating curves by increasing the k_5 value in a model for the bromate–ferroin–bromomalonic acid system.

We believe that it has no meaning to suggest different extended models, since we have not enough detailed informations on either ferroin–HOBr and ferriin–Br$^-$ reactions or the possible role of the ligand as a substrate in this system. Therefore, a complete and quantitative modeling of the dynamic behavior of the ferroin–bromate–(bromide) system in a CSTR *awaits* for detailed investigations of these reactions. Such experiments are in progress in our laboratory. We hope that these investigations can give us also the possibility to explain the batch–oscillatory reaction, since the formation of the red precipitate appears to be strongly correlated with the reactions of the coordinated ligand.

Acknowledgment. We thank Professors Kenneth Showalter and Zoltán Noszticzius for helpful discussions and Professor Richard M. Noyes and the other reviewers for their useful recommendations.

Registry No. BrO_3^-, 15541-45-4; ferroin, 14708-99-7.

---

(27) Gear, C. W. "Numerical Initial Value Problems in Ordinary Differential Equations"; Prentice Hall: Englewood Cliffs, NJ, 1971, p 209.

(28) De Kepper, P.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* **1981**, *103*, 6121.

(29) Papsin, G.; Hanna, A.; Showalter, K. *J. Phys. Chem.* **1981**, *85*, 2575.

(30) Bar-Eli, K.; Ronkin, J. *J. Phys. Chem.* **1984**, *88*, 2844.

(31) Showalter, K.; Noyes, R. M.; Bar-Eli, K. *J. Chem. Phys.* **1978**, *69*, 2514.

(32) Kumpinsky, E.; Epstein, I. R. *J. Phys. Chem.* **1985**, *89*, 688.

(33) Nord, G.; Wernberg, O. *J. Chem. Soc., Dalton Trans.* **1975**, *10*, 845.

(34) Noszticzius, Z.; Stirling, P.; Wittman, M. submitted to *J. Phys. Chem.*

(35) De Kepper, P.; Bar-Eli, K. *J. Phys. Chem.* **1983**, *87*, 480.

(36) Ariese, F.; Ungvárai-Nagy, Zs., private communication.