of the manuscript and their excellent suggestions, which improved the paper considerably.

Registry No. PAQ, 98330-76-8; PAQ(Me)$_2$, 98330-78-0; acetonitrile, 75-05-8; propionitrile, 107-12-0; benzonitrile, 100-47-0; acetone, 67-64-1; *n*-butyl alcohol, 71-36-3; 1,2-dichloroethane, 107-06-2; methylene chloride, 75-09-2; 2-methyltetrahydrofuran, 96-47-9; 1,1,1-trichloroethane, 71-55-6; 1,2-dimethoxyethane, 110-71-4; ethyl acetate, 141-78-6; ethyl ether, 60-29-7; chlorobenzene, 108-90-7; α-chloronaphthalene, 90-13-1; chloroform, 67-66-3; 1,2-dichloromethane, 106-93-4; anisole, 100-66-3.

Modeling the Oscillatory Bromate Oxidation of Ferroin in Open Systems

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A model for the ferroin–bromate–bromide–sulfuric acid system in a continuously stirred (flow-through) tank reactor has been constructed by extending the Noyes–Field–Thompson mechanism with the following *composite processes*: (a) ferroin–bromate, (b) ferroin–bromous acid, (c) ferroin–hypobromous acid, (d) ferroin–bromine, (e) ferriin–bromide, and (f) ferriin–bromine. The calculated high-amplitude oscillations and kinetic phase diagram are in good accordance with the experiments reported earlier. By completing the scheme with a reaction step accounting for the precipitation and dissolution of a ferroin–tribromide salt, the batch oscillations found at high concentrations of reactants can also be simulated.

Introduction

The Belousov–Zhabotinsky (BZ) oscillatory reaction, the cerium(III)-catalyzed oxidation of malonic acid by acidic bromate, has been commonly applied during the last few decades for studying a wide variety of temporal and spatial instabilities in chemical systems.[1–4]

A small amount of tris(1,10-phenanthroline)iron(II), a well-known redox indicator called ferroin, is often added to a BZ mixture in order to better visualize the periodic changes. Vavilin et al.[5] observed first that ferroin itself can also catalyze the BZ reaction. Later, Beck et al.[6] found that even the simple ferroin-bromate batch reaction can oscillate at extremely high concentrations of reactants. Another necessary condition for the periodic behavior is the continuous but partial removal of the produced bromine by an inert gas stream. The cerium–bromate batch reaction shows no periodicity under the same conditions. This difference in behavior of the ferroin- and cerium–bromate systems has never been explained in terms of mechanisms. The ferroin-bromate reaction is bistable in a continuously stirred (flow-through) tank reactor (CSTR). Oscillations can emerge only by adding bromide ion to the input flow.[7] The bromide ion-controlled oscillations are similar to those observed in the analogous cerium system in a CSTR.[8,9] However, some characteristic features of oscillations in the ferroin system are different from those in the cerium system, for example, (1) During an oscillatory cycle, the total amount of ferroin is oxidized to ferriin, the iron(III) complex, and vice versa. It results in a periodic color change from red to blue and back to red, respectively. Accordingly, high-amplitude potential oscillations can be detected by a platinum electrode in phase with the color change. The cerium–bromate–bromide system possesses only small-amplitude oscillations.[8,9] (2) Oscillations occur in a much broader range of input concentrations in the ferroin-containing system than in that found with cerium.[8,9]

One may think that the acidic bromate oxidation of cerium(III) or ferroin should proceed by similar mechanisms. In this case, the ferroin system could easily be simulated on the basis of the well-established mechanism for the cerium system. Thus, one should simply change the rate constants of a few elementary steps in accordance with the different redox properties of the two catalysts. On the contrary, we failed to characterize the ferroin system within the framework of the Field–Körös–Noyes (FKN)[10] theory for the cerium-catalyzed reaction.

TABLE I: A Model for the Ferroin–Bromate Reaction[a]

$BrO_3^- + Br^- + \{2H^+\} \rightleftharpoons HOBr + HBrO_2$	(1)
$HBrO_2 + Br^- + \{H^+\} \rightleftharpoons 2HOBr$	(2)
$HOBr + Br^- + \{H^+\} \rightleftharpoons Br_2 + \{H_2O\}$	(3)
$BrO_3^- + HBrO_2 + \{H^+\} \rightleftharpoons 2BrO_2^\bullet + \{H_2O\}$	(4)
$2HBrO_2 \rightleftharpoons HOBr + BrO_3^- + \{H^+\}$	(5)
$Fe(phen)_3^{2+} + BrO_2^\bullet + \{H^+\} \rightarrow Fe(phen)_3^{3+} + HBrO_2$	(6)
$2Fe(phen)_3^{2+} + BrO_3^- + \{3H^+\} \rightarrow 2Fe(phen)_3^{3+} + HBrO_2 + \{H_2O\}$	(7)
$2Fe(phen)_3^{2+} + HBrO_2 + \{2H^+\} \rightarrow 2Fe(phen)_3^{3+} + HOBr + \{H_2O\}$	(8)
$2Fe(phen)_3^{2+} + HOBr + \{H^+\} \rightarrow 2Fe(phen)_3^{3+} + Br^- + \{H_2O\}$	(9)
$2Fe(phen)_3^{2+} + Br_2 \rightarrow 2Fe(phen)_3^{3+} + 2Br^-$	(10)
$2Fe(phen)_3^{3+} + 2Br^- \rightarrow 2Fe(phen)_3^{2+} + Br_2$	(11)
$Fe(phen)_3^{3+} + Br_2 \rightarrow \{[Fe(phen)_3Br_2]^{3+}\}$	(12)
$Br_2 \rightarrow \{Br_2(gas)\}$	(13)

[a] Changes in the concentrations of species in brackets are not taken into account; phen = 1,10-phenanthroline.

The standard reduction potential of the ferriin/ferroin couple (1.06 V)[11] is lower than that of cerium(IV)/cerium(III) in sulfuric acid (1.44 V).[12] Therefore, it has been speculated in several reports[12–19] that ferroin, unlike cerium(III), could directly be

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TABLE II: Rate Equations[a]

$$v_1 = d[BrO_3^-]/dt = -k_1[BrO_3^-][Br^-] + k_{-1}[HOBr][HBrO_2]$$
$$v_2 = d[HBrO_2]/dt = -k_2[HBrO_2][Br^-] + k_{-2}[HOBr]^2$$
$$v_3 = d[HOBr]/dt = -k_3[HOBr][Br^-] + k_{-3}[Br_2]$$
$$v_4 = d[BrO_3^-]/dt = -k_4[BrO_3^-][HBrO_2] + k_{-4}[BrO_2^\bullet]^2$$
$$v_5 = d[BrO_3^-]/dt = k_5[HBrO_2]^2 - k_{-5}[HOBr][BrO_3^-]$$
$$v_6 = d[HBrO_2]/dt = k_6[Fe(phen)_3^{2+}][BrO_2^\bullet]$$
$$v_7 = d[BrO_3^-]/dt = -k_7[Fe(phen)_3^{2+}][BrO_3^-]$$
$$v_8 = d[HBrO_2]/dt = -k_8[Fe(phen)_3^{2+}][HBrO_2]$$
$$v_9 = d[HOBr]/dt = -k_9[Fe(phen)_3^{2+}][HOBr]$$
$$v_{10} = d[Br_2]/dt = -k_{10}[Fe(phen)_3^{2+}][Br_2]$$
$$v_{11} = d[Br_2]/dt = (k_{11} + k_{11}'[Br^-])[Fe(phen)_3^{3+}][Br^-]$$
$$v_{12} = d[Br_2]/dt = -k_{12}[Fe(phen)_3^{3+}][Br_2]$$
$$v_{13} = d[Br_2]/dt = -k_{13}[Br_2]$$

[a] Constant concentration of H^+ has been incorporated in the rate constants.

oxidized by bromine species such as BrO_3^-, $HBrO_2$, HOBr, and Br_2 besides its known reaction with $BrO_2^\bullet$ radical. However, *standard kinetic investigations of these direct reactions have been carried out only scantly*, if at all.

In this paper, on the basis of the results of our recent kinetic studies of some of the accessible direct reactions, a model is developed for the ferroin–bromate–bromide–sulfuric acid system in a CSTR. We will show that high-amplitude oscillations and a kinetic phase diagram can be calculated in good accordance with the experimental results.[7] At the high concentration of reactants applied in the batch experiments,[6] a red precipitate is formed. If a reaction step accounting for the formation and dissolution of this precipitate is added to the scheme, the batch oscillations can also be simulated.

Experimental Section

All chemicals used were the highest grade commercially available. Sodium bromate was recrystallized three times. A stock solution of ferroin was prepared as described earlier.[7] An acidic stock solution of ferriin was prepared daily from the stock solution of ferroin by oxidation with solid PbO_2 followed by filtration.[26] A concentrated solution of HOBr was freshly prepared by the method of Chapin.[27]

In all kinetic measurements, the change in ferroin concentration was monitored on a Hitachi-100-60 stopped-flow spectrophotometer by following the change in absorbance at $\lambda = 513$ nm ($\epsilon = 1.1 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[11] The cell compartments were well-thermostated ($t = 25.0 \pm 0.1$ °C). For the applied ranges of initial concentrations, see the corresponding subsections.

Elemental analysis data and infrared spectral characterization of the red precipitate were provided by the Analytical Laboratory, Department of Organic Chemistry, Kossuth L. University, Debrecen, Hungary.

A Model for the Ferroin-Catalyzed Bromate Oscillator in a CSTR

A scheme for the system is given in Table I. Reactions 1–6 are based on the Noyes–Field–Thompson (NFT) mechanism[22] of the cerium–bromate–bromide system in a CSTR. Reactions 1–5 are the reversible, elementary steps of the bromate–bromide reaction in acidic solution. Reaction 6 is the irreversible, one electron oxidation of ferroin with the $BrO_2^\bullet$ radical. Rovinsky and Zhabotinsky[15,23] pointed out that the oxidation of ferroin, unlike the analogous reaction of cerium(III) with the radical, can be almost complete.

Reactions 7–10 are the proposed *direct* oxidations of ferroin with different bromine species. We suggest that these processes are irreversible, similar to reaction 6. Elementary step mechanisms have been developed[13-21] but not yet confirmed for these processes; therefore, we utilize stoichiometric equations. Consequently, overall rate equations are applied in the calculations. A similar approach based on only an empirical rate law description of the composite processes has been successfully applied by Gâspâr and Showalter[24] for modeling the oscillatory iodate oxidation of ferrocyanide and sulfite in a CSTR.[25]

Reduction of ferriin with bromide[14] can also play an important role in the dynamics. An empirical rate law is also applied for this reaction.

We have observed that a yellowish-green precipitate is formed when ferriin reacts with bromine at high concentrations. Unfortunately, the composition of the solid compound could not be unambiguously determined. Similar to our earlier report,[7] we suggest that this precipitate is a bromine adduct of ferriin. Since precipitation has not been observed in the CSTR experiments,[7] reaction 12 describes the adduct formation only in solution.

Step 13 corresponds to the physical removal of bromine by the gas stream due to a water pump, which is applied to maintain a constant volume of the system in the flow-through reactor.

Kinetics of the Composite Processes

Process a: Ferroin–Bromate Direct Reaction. During the *induction period* of the autocatalytic ferroin–bromate batch reaction, a considerable amount of ferroin (~5–10% of the initial concentration)[17-20] is oxidized to ferriin. On the contrary, only a very small amount of cerium(III) is converted to cerium(IV) during the induction period of the analogous cerium–bromate reaction. Noyes[12] and Prasad et al.[17] suggested that the difference in behavior of the two catalysts is due to the following: a direct oxidation by acidic bromate occurs with ferroin but not with cerium(III). It can be justified quantitatively on the basis of the estimated standard reduction potential of the $BrO_3^-/BrO_2^\bullet$ couple in sulfuric acidic (1.15 V).[12] This value is slightly higher than the standard reduction potential of the ferriin/ferroin couple and is much lower than that of the cerium(IV)/cerium(III) redox pair. Therefore, as Noyes[12] pointed out, a direct reaction of bromate is thermodynamically favored with ferroin but is unfavorable with cerium(III).

The FKN theory[10] predicts that after mixing acidic solutions of bromate and ferroin steady-state concentrations of other bromine species are established within a fraction of a second and remain at these low values during most part of the induction period. Based on the estimated values of steady-state concentrations and the corresponding rate equations discussed later, we concluded that the oxidation of ferroin with the intermediate bromine species could be completely neglected at the beginning of the induction period. Therefore, an empirical rate law derived from initial rate measurements could be considered as the rate equation for the ferroin–bromate direct reaction.

The dependence of the *initial rate* of the ferroin–bromate reaction was determined in the induction period by varying the initial concentrations of bromate, ferroin, sulfuric acid, and bromide. Experiments[28] were carried out in the following range of concentrations: $[Br^-]_0 = (0.2\text{–}2.0) \times 10^{-5}$ M, $[BrO_3^-]_0 = 0.03\text{–}0.1$ M, $[Fe(phen)_3^{2+}]_0 = (0.5\text{–}2.0) \times 10^{-4}$ M, and $[H^+]_0 = 0.07\text{–}0.15$ M. By taking into account the stoichiometry defined by reaction 7 in Table I, the results obeyed empirical rate law α:

$$v_\alpha = -\tfrac{1}{2}\, d[Fe(phen)_3^{2+}]/dt = k_\alpha[Fe(phen)_3^{2+}][BrO_3^-][H^+]^2 \qquad (\alpha)$$

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TABLE III: Values of Rate Constants

$k_1 = 8.75 \times 10^{-1}$ M^{-1} s^{-1}	$k_{-1} = 3.2$ M^{-1} s^{-1}
$k_2 = 1.5 \times 10^{6}$ M^{-1} s^{-1}	$k_{-2} = 2 \times 10^{-5}$ M^{-1} s^{-1}
$k_3 = 4 \times 10^{8}$ M^{-1} s^{-1}	$k_{-3} = 1.1 \times 10^{2}$ s^{-1}
$k_4 = 2.5 \times 10^{1}$ M^{-1} s^{-1}	$k_{-4} = 4.2 \times 10^{7}$ M^{-1} s^{-1}
$k_5 = 3 \times 10^{3}$ M^{-1} s^{-1}	$k_{-5} = 5 \times 10^{9}$ M^{-1} s^{-1}
$k_6 = 1 \times 10^{9}$ M^{-2} s^{-1}	
$k_7 = 1 \times 10^{-1}$ M^{-1} s^{-1}	
$k_8 = 1$ M^{-1} s^{-1}	
$k_9 = 5 \times 10^{-3}$ M^{-1} s^{-1}	
$k_{10} = 1 \times 10^{2}$ M^{-1} s^{-1}	
$k_{11} = 4 \times 10^{-4}$ M^{-1} s^{-1}	$k_{11}' = 1.8 \times 10^{-2}$ M^{-2} s^{-2}
$k_{12} = 5 \times 10^{2}$ M^{-1} s^{-1}	
$k_{13} = 5 \times 10^{-1}$ s^{-1}	

where $k_\alpha = (3.8 \pm 0.6) \times 10^{-1}$ M^{-3} s^{-1}. Notice that no bromide ion dependence was found. Rate law α is in complete agreement with a rate law determined earlier by Prasad et al.[17] In the calculations, $k_\alpha = 0.4$ M^{-3} s^{-1} was applied.

Process b: Ferroin–Bromous Acid Direct Reaction. No kinetic investigation of this reaction was carried out, since the fast disproportionation of bromous acid did not allow unambiguous experiments. On the basis of similarities between reactions 7 and 8, the following rate law has been constructed:

$$v_\beta = -\tfrac{1}{2}\, d[\mathrm{Fe(phen)_3^{2+}}]/dt = k_\beta[\mathrm{Fe(phen)_3^{2+}}][\mathrm{HBrO_2}][\mathrm{H^+}] \qquad (\beta)$$

Following D'Alba and DiLorenzo,[16] k_β has been chosen larger than k_α by a factor of 5.

Process c: Ferroin–Hypobromous Acid Direct Reaction. A large excess of hypobromous acid was applied for a measurable initial rate. Experiments were carried out in the following range of concentrations: $[\mathrm{HOBr}]_0 = (0.75\text{–}2.0) \times 10^{-1}$ M, $[\mathrm{Fe(phen)_3^{2+}}]_0 = (0.02\text{–}1.0) \times 10^{-3}$ M, and $[\mathrm{H^+}]_0 = 0.01\text{–}2.0$ M. Under these conditions, an autocatalytic decrease in the ferroin concentration has been observed. This feature is attributed to the secondary oxidation of ferroin by bromine, which is formed autocatalytically in a sequence of reactions (9, 3, and 10) in Table I. A series of experiments performed with the same sample of hypobromous acid always showed that the initial rate is linearly dependent on the concentration of both reactants. Since no hydrogen ion dependence was found, the following rate equation has been defined:

$$v_\gamma = -\tfrac{1}{2}\, d[\mathrm{F(phen)_3^{2+}}]/dt = k_\gamma[\mathrm{Fe(phen)_3^{2+}}][\mathrm{HOBr}] \qquad (\gamma)$$

The experimental results showed, in agreement with the proposal of D'Alba and DiLorenzo,[16] that the oxidation of ferroin by hypobromous acid is a slow process. However, a well-defined value for the rate constant could not be determined, since the results greatly varied from sample to sample. Due to the applied procedure,[27] the freshly prepared hypobromous acid solution always contains bromate and bromous acid in a small amount—not more than 1% of the HOBr concentration. The much faster reactions of ferroin with these species greatly affect the accuracy of the measurements. For an estimated value of k_γ, consult Table III.

Process d: Ferroin–Bromine Direct Reaction. Excess bromine was applied for pseudo-first-order conditions. (The reference sample was always a bromine solution of the same concentration as that used initially in the reacting mixture.) Initial rates have been determined in the following range of initial concentrations: $[\mathrm{Br_2}]_0 = (0.5\text{–}3.0) \times 10^{-3}$ M, $[\mathrm{Fe(phen)_3^{2+}}]_0 = (0.2\text{–}1.5) \times 10^{-4}$ M, and $[\mathrm{H^+}]_0 = 0.1\text{–}1.0$ M. By taking into account the stoichiometry of reaction 10, the data obeyed rate law δ:

$$v_\delta = -\tfrac{1}{2}\, d[\mathrm{Fe(phen)_3^{2+}}]/dt = k_\delta[\mathrm{Fe(phen)_3^{2+}}][\mathrm{Br_2}] \qquad (\delta)$$

The value of k_δ varied around 10^2 M^{-1} s^{-1} with 10% error. We applied the rounded value in the calculations. Ige et al.[29] reported an identical rate law; however, there is 2 orders of magnitude difference in the value of the rate constants. A direct comparison is difficult, since they applied perchloric acid.

Process e: Ferriin–Bromide Direct Reaction. Initial rates were determined as a function of initial concentrations within the following range: $[\mathrm{Br^-}]_0 = 0.1\text{–}1.0$ M, $[\mathrm{Fe(phen)_3^{3+}}]_0 = (0.1\text{–}5.0) \times 10^{-3}$ M, and $[\mathrm{H^+}]_0 = 0.5\text{–}2.0$ M. By considering the stoichiometry of the reaction, the experimental data resulted in rate law ϵ:

$$v_\epsilon = \tfrac{1}{2}\, [\mathrm{Fe(phen)_3^{2+}}]/dt = (k_{\epsilon 1} + k_{\epsilon 2}[\mathrm{Br^-}])[\mathrm{Fe(phen)_3^{3+}}][\mathrm{Br^-}]/[\mathrm{H^+}] \qquad (\epsilon)$$

where $k_{\epsilon 1} = (2.0 \pm 0.5) \times 10^{-4}$ s^{-1} and $k_{\epsilon 2} = (9.0 \pm 1.0) \times 10^{-3}$ M^{-1} s^{-1}.

Appearance of two terms in this rate law indicates the complexity of an underlying mechanism for the ferriin–bromide reaction. The following parallel reaction paths could be considered:

path I

$$2\mathrm{Fe(phen)_3^{3+}} + \mathrm{Br^-} + \{\mathrm{H_2O}\} \rightarrow 2\mathrm{Fe(phen)_3^{2+}} + \mathrm{HOBr} + \{\mathrm{H^+}\} \qquad (\mathrm{Ia})$$

$$\mathrm{HOBr} + \mathrm{Br^-} + \{\mathrm{H^+}\} \rightleftharpoons \mathrm{Br_2} + \{\mathrm{H_2O}\} \qquad (\mathrm{Ib})$$

path II

$$2\mathrm{Fe(phen)_3^{3+}} + 2\mathrm{Br^-} \rightarrow 2\mathrm{Fe(phen)_3^{2+}} + \mathrm{Br_2} \qquad (\mathrm{II})$$

The first-order dependence on bromide concentration might be the result of path I, which proceeds through the intermediate hypobromous acid. The second-order dependence might originate from path II, most preferably by the formation of the $\mathrm{Br_2^-}$ intermediate species. Nevertheless, the first-order dependence on ferriin concentration indicates that the rate-determining elementary step should involve only one ferriin molecule in both cases. The reciprocal dependence on hydrogen ion concentration is not fully understood. An explanation based on the reverse of reaction Ia cannot be justified for conditions applied in initial rate measurements for the forward direction. In addition, the initial rate of the ferroin–hypobromous acid reaction has been found to be independent on the hydrogen ion concentration—see Process c subsection. It has been suggested, however, that in acidic water solutions there exists a fast equilibrium between ferriin and its so-called "pseudohydrate" derivative.[40] Formation of the pseudohydrate is less favorable with higher acidity. Therefore, if the derivative is more reactive than the ferriin itself, the reciprocal dependence of the initial rate on the hydrogen ion concentration can be explained.

Reactions 10 and 11 in Table I appear as the reverse of each other, but the corresponding rate equations do not obey microscopic reversibility at equilibrium. This might be subject to serious concern. However, empirical rate laws derived from initial rate measurements can be incomplete. Thus, empirical rate equations do not obviously reflect the kinetics of a complex reacting system all the way from an initial state to an equilibrium. For the same reason, rate equations for the forward and reverse directions derived from independent initial rate measurements may not reflect microscopic reversibility at equilibrium. The point in our case is that the experimentally determined initial rate equations and rate constants are *not the ones that apply when the system is at equilibrium*.

We emphasize that the proposed scheme in Table I is not an elementary step mechanism since experimentally determined initial rate equations were applied for the composite processes. Thus, reaction 11 describes the conversion of ferriin and bromide to ferroin and bromine, respectively, and the rate of this overall process in the forward direction is approximated by rate law ϵ.

Process f: Ferriin–Bromine Adduct Formation. No kinetic study of the reaction has been performed. For the applied rate law and rate constant, see Tables II and III.

Modeling the CSTR Experiments

Calculations were based on reactions 1–13 in Table I by applying the rate equations in Table II and rate constants in Table III. Changes in the concentrations of species in brackets were not taken into account. The concentration of the hydrogen ion

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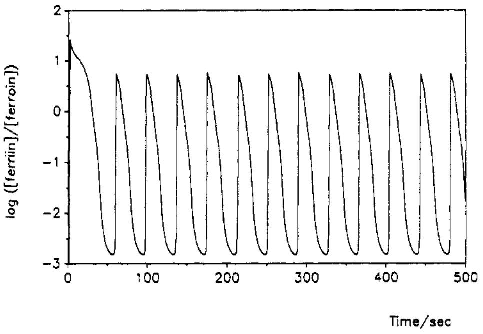

Figure 1. High-amplitude oscillations calculated by the proposed model for the ferroin–bromate–bromide system in a CSTR at $k_0 = 10^{-2}$ s^{-1}. Input concentrations: $[BrO_3^-]_0 = 0.16$ M, $[\text{ferroin}]_0 = 3 \times 10^{-4}$ M, $[H^+]_0 = 0.5$ M, and $[Br^-]_0 = 7 \times 10^{-4}$ M.

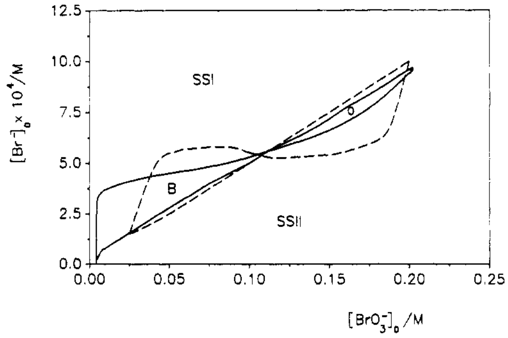

Figure 2. Calculated (solid) and experimental (dashed) kinetic phase diagrams at $k_0 = 10^{-2}$ s^{-1}. Fixed input concentrations are $[\text{ferroin}]_0 = 3 \times 10^{-4}$ M and $[H^+]_0 = 0.5$ M: SSI, red state; SSII, blue state; B, bistability; O, oscillations.

(0.5 M) at the corresponding power has been incorporated in the values of the rate constants. Rate constants of reactions 1–5 were chosen according to Field and Försterling.[30] Following the method of Rovinsky and Zhabotinsky,[31] the value of k_6 in Table III is set much higher than that of the rate constant of an analogous reaction with cerium(III). The first-order rate constant of bromine removal was taken from our earlier study.[7] The flow terms have been added to the differential equations, but input has been considered only for ferroin, bromate, and bromide.

The numerical integrations resulted in periodic changes in the concentration of ferroin at certain values of input concentrations and flow rates. The period of high-amplitude oscillations in the calculations is shorter than that in the experiments by only a factor of 2. Figure 1 shows that the conversion from ferroin to ferriin and back to the reduced state is almost complete during an oscillatory cycle. It is likely that similar alterations in a real system would result in periodic color changes.

Since it cannot be postulated that the potential of a platinum electrode E_{Pt} is directly determined by the ferriin/ferroin couple (the bromine/bromide couple could be at least as important), a direct comparison of the calculated time traces with the experimental ones is not easy. If we still approximate E_{Pt} on the basis of the [ferriin]/[ferroin] ratio only, the calculated potential oscillates between 0.9 and 1.1 V in excellent agreement with the measurements.[7] In addition, the shape of potential vs time curves in the calculations is similar to that in the experiments.

Calculated and experimental kinetic phase diagrams showing closed regions of bistability and oscillations are compared in Figure 2. The crossing point of the two regions in the calculations is remarkably close to that determined in the experiments.

Modeling the Oscillations in the Ferroin–Bromate Batch Reaction

The results of calculations based on reactions in Table I quantitatively describe the dynamics of the ferroin–bromate–bromide system in a CSTR. In order to apply the same model for batch oscillations at high concentrations of bromate and ferroin, one has to consider the presence of three phases: solid (a red precipitate), liquid (the reaction mixture), and gas (bromine). The removal of bromine from the solution is included in the differential equations. However, the effect of the precipitate has yet to be defined in terms of rate laws.

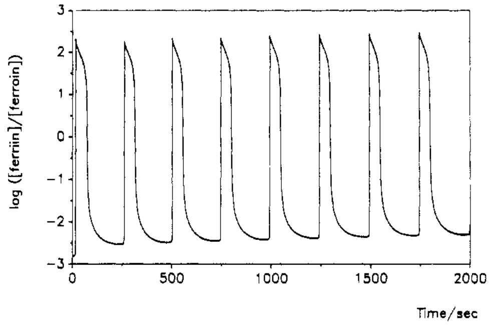

Figure 3. Calculated high-amplitude oscillations under batch conditions at $k_{13} = 2.0$ s^{-1}. Initial concentrations: $[BrO_3^-] = 0.05$ M, $[Br^-] = 2 \times 10^{-5}$ M, $[Br_2] = 1 \times 10^{-6}$ M, [ferroin] $= 1 \times 10^{-4}$ M, [ferriin] $= 2 \times 10^{-3}$ M, and $[H^+] = 0.5$ M.

By analyzing the red precipitate, we have found the bromine/iron ratio to be 5.4. Since bromination of the phenanthroline ligand could not be detected in an infrared spectrum, we suggest that the main component of the solid compound is a ferroin–tribromide salt formed by the following equation:

$$\text{Fe(phen)}_3^{2+} + 2Br^- + 2Br_2 \rightleftharpoons \text{Fe(phen)}_3(Br_3)_2 \qquad (P)$$

The rate of precipitate formation (v_π) can be defined by rate law π:

$$v_\pi = -d[\text{Fe(phen)}_3^{2+}]/dt = k_\pi[\text{Fe(phen)}_3^{2+}][Br_2]^2[Br^-]_2 \qquad (\pi)$$

The red precipitate is slightly soluble in water. Therefore, it can partially dissolve as the reaction proceeds in the solution phase. As a first approximation, we suppose that the dissolution rate v_σ is constant:

$$v_\sigma = d[\text{Fe(phen)}_3^{2+}]/dt = k_\sigma \qquad (\sigma)$$

The solubility product $L = [\text{Fe(phen)}_3^{2+}][Br_2]^2[Br^-]^2$ can easily be expressed as the ratio of rate constants k_σ and k_π. An approximate value of L ($\approx 10^{-13}$ M^5) has been determined by titration of the solutions of ferroin and bromide with bromine solution until precipitate formation.

Values of rate constants k_σ and k_π are not known. We have arbitrarily chosen a value of 10^{-6} M s^{-1} for k_σ, expressing that dissolution is generally a slow process. Taking into account the value of L, k_π is equal to 10^7 M^{-4} s^{-1}.

Kinetic equations π and σ were added to the differential equations applied earlier but with the flow terms excluded. Oscillations could be calculated only in a limited range of the bromine removal rate (k_{13}), which is in qualitative agreement with that of the experiments. Calculated high-amplitude oscillations in a ferroin–bromate batch reaction are shown in Figure 3. Because of the nature of the system, initial concentrations had to be chosen arbitrarily, and no quantitative agreement with the experiments can be expected.

No oscillations could be calculated without the kinetic terms describing the formation and dissolution of the ferroin–tribromide precipitate. These processes play an essential role in the periodic behavior for the following reason. Once the precipitate is formed at the very beginning of the reaction, it acts like a reservoir. Thus, the reacting system in the solution is continually resupplied with ferroin, bromine, and bromide ion so that the solubility equilibrium is always established. Without precipitate formation, however, such a reservoir is not available, and the total amount of ferroin is simply converted to ferriin by the autocatalytic reaction sequence in Table I. Since such a precipitate cannot be formed in the cerium–bromate system, the difference in behavior of the two

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systems can now be understood in terms of the mechanism.

Discussion

A model for the ferroin–bromate–bromide oscillatory system in a CSTR has been constructed by extending the NFT mechanism with direct reactions between ferroin (ferriin) and different bromine species. In the calculations, the proposed composite reactions have been taken into account by overall rate equations that were determined experimentally or constructed by analogy. The calculated high-amplitude oscillations and the kinetic phase diagram are in good accordance with the experiments. We have demonstrated that by completion of the scheme with just one more step, accounting for the precipitation and dissolution of a ferroin–tribromide salt, the peculiar batch oscillations can also be simulated.

Oscillations cannot be calculated if the oxidation of ferroin with $BrO_2^\bullet$ radical is neglected. It shows that the NFT-type core of the model is essential for the appearance of periodic solutions. The small-amplitude oscillations generated by the NFT mechanism in a CSTR, however, are amplified by the additional reactions, and high-amplitude oscillations emerge.

Establishing an elementary step mechanism for the ferroin system requires further experiments. A deeper understanding of the mechanism of the composite processes, especially the ferroin–hypobromous acid and the ferriin–bromide reactions, is essential.

Melichercik and Treindl[32] have recently shown that it would be easier to quantitatively describe even the acidic oxidation of ferroin with cerium(IV), if disproportionation of ferriin were allowed. It would result in the simultaneous formation of iron(IV) and iron(II) complexes. Existence of the iron(IV) ion as an intermediate was postulated by Bray and Gorin[33] as early as 1932. Conocchioli et al.[34] repeated this proposal in the 1960s. Formation of iron(IV) complexes in solution has been reported recently.[35,36] There is experimental evidence of the existence of iron(IV) in the solid state.[37] It was also suggested in several reports[14,16,18–21] that ferroin could be oxidized by the different bromine-containing species in two-electron processes, resulting in an iron(IV) complex as an intermediate. However, it is important to point out that the experimentally determined rate laws could equally be derived on the basis of either one- or two-electron elementary step mechanisms.

In the proposed scheme, we neglected the dissociation of ferroin, which is a slow process.[38–41] Consequently, the oxidation of dissociated ferroin with different bromine species[18,19,21] was not considered. Since ferroin is always resupplied by the inflow, the exclusion of these reactions is justifiable for the flow-through system. However, they might be of importance for a quantitative description of the batch experiments.

In order to learn the important species and composite reactions in determination of the characteristic behavior of the ferroin–bromate system, the sensitivity analysis of the model is in progress.

We conclude that the difference in behavior of the ferroin– and cerium–bromate systems is, in fact, related to the reactivity of ferroin (and ferriin) toward bromine species other than the $BrO_2^\bullet$ radical, while such reactivity of the cerium(III)/(IV) ions is not known. What was predicted by thermodynamic argumentations[12,14] is supported by the results of kinetic investigations reported here.

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

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Hydrogen Bond Donor Acidity Parameters for Kinetics Studies in Nonaqueous Solvents

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Several multiterm linear solvation energy models which incorporate directly or indirectly hydrogen bond donor–acceptor parameters were compared experimentally. These included the Kamlet–Taft α_{KT} scale, the Abraham α_2^H scale, and the acceptor (AN*) parameter of Riddle and Fowkes. An enlarged data base for a range of hydrogen bonding, hydrogen bonding–strongly associated, and weakly hydrogen bonding aprotic solvents was developed for this analysis. Although the α_{KT} and α_2^H parameters are fundamentally parallel in their origins, the latter is less responsive to the differentiation of structural characteristics of the donor species. The AN* quantity is shown to be a coupled mixture of solvent properties in which hydrogen bond donor acidity appears to dominate for the strongly self-associated solvents.

Some of the most troublesome aspects in the problem of modeling kinetic influences of solvents for very rapid reactions arise with media which are hydrogen bonded (HBD). Because such solvents cover the structural range from the simplest monomolecular species within weak HBD liquids (i.e. $CHCl_3$) to complex molecular equilibria among several polymeric species in the self-associated liquids (i.e. carboxylic and other protonic acids), the quantitative scaling and meaning of "hydrogen bond donor acidity" as a single universal variable appears to be fundamentally ambiguous.

Two different approaches have been used in the development of predictive models for the description of effects of the medium

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