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Tentative Reaction Network for Bromate-Bromide-Ferroin System and Simulation of Behavior of the System under Batch Reactor and Continuous-Flow Stirred Tank Reactor Conditions

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One tentative reaction network for the bromate-bromide-tris(1,10-phenanthroline)iron(II) (ferroin) system in an acidic medium was examined by means of a simulation method, which involved the Field-Körös-Noyes scheme, the reduction of $HBrO_2$ and HOBr by ferroin via two-electron transfer processes and the reactions of $Fe(phen)_2^{2+}$ with BrO_3^-, $HBrO_2$, HOBr, and $BrO_2\cdot$. The network successfully reproduced the behavior of the system in a batch reactor. The behavior of the system in a continuous-flow stirred tank reactor (CSTR) was simulated under two CSTR conditions: 1) Bromide flowed into the CSTR, and 2) bromide did not flow into the CSTR. Under the former condition, the system exhibited bistability and sustained oscillations. The calculated oscillations were of small amplitude and high frequency. Under the latter condition, the system exhibited bistability.

The oxidation of tris(1,10-phenanthroline)iron(II) (ferroin) by bromate in an acidic medium was studied in a batch reactor and a continuous-flow stirred tank reactor (CSTR) modes. The reaction in a batch reactor can be characterized as follows:[1-3] (i) Under suitable conditions, ferroin initially decreases due to its decomposition (decomposition phase) and the phase is followed by a burst of tris(1,10-phenanthroline)-iron(III) (ferriin) formation (autocatalytic phase). During the autocatalytic phase the concentration of ferriin increases exponentially with a sharp transition to the final state of the reaction, where $[Fe(phen)_3^{2+}]$ is approximately equal to zero. The duration of the decomposition phase (induction period) is lengthened by the addition of bromide. (ii) Under the other condition, the decomposition phase is not followed by the autocatalytic phase.

The oxidation of ferroin by bromate in a sulfuric acid medium in a CSTR was studied by Gáspár et al.[4] There are some differences in the reaction behavior of the system and that of a bromate-bromide-metal ion (metal ion: cerium(III) or manganese(II)) system. These systems usually exhibit bistability and sustained oscillations under CSTR conditions.[4-9] When the systems are not supplied with bromide via feed flow, though the cerium(III) system exists in a monostable state, the ferroin system exhibits bistability. Though sustained oscillations of metal ion systems are minimal, those of the ferroin system possess a large amplitude. Ferroin, as well as cerium, catalyzes the oxidation of such organic substrates as malonic acid by bromate, called the Belousov-Zhabotinsky (BZ) reaction. These catalysts exhibit somewhat different features in BZ reactions. For example, in the cerium-catalyzed system, an induced period is observed before the onset of oscillations; in the ferroin-catalyzed system, however, there is no induced period.[10,11]

The difference in the reaction behaviors described above may result from differences in the reaction mechanisms. The reaction behavior of the bromate-bromide-metal ion system in a CSTR is fairly reproducible by using the Field-Körös-Noyes (FKN) mechanism.[12,13] On the other hand, information concerning the mechanism of ferroin-related reactions is rather scarce. Though several reaction mechanisms were proposed to explain the behavior of the bromate-bromide-ferroin reaction system and that of the ferroin-catalyzed BZ reaction, the mechanisms of the ferroin-related systems were not confirmed to date.[14-18] In this study we propose one tentative reaction network for the bromate-bromide-ferroin system and examine it by means of a simulation method in order to explain the behavior of the system in an acidic medium under batch reactor and CSTR conditions. The reaction network is based on the assumption that the FKN scheme can be applied as a first approximation, that $HBrO_2$ and HOBr are reduced by ferroin via two-electron transfer processes and that $Fe(phen)_2^{2+}$, which is formed by the decomposition of ferroin, reacts with BrO_3^-, $BrO_2\cdot$, $HBrO_2$, HOBr, and Br^-.

Reaction Network

The reaction network of the bromate-bromide-ferroin system is thought to be complex, since the behavior of the system, indeed, shows great variety. In this study, the following reaction network was tested in order to simulate the behavior of the system:

$$BrO_3^- + Br^- + 2H^+ \rightleftarrows HBrO_2 + HOBr \quad (1)$$

$$Br^- + HOBr + H^+ \rightleftarrows Br_2 + H_2O \quad (2)$$

$$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr \quad (3)$$

$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \quad (4)$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftarrows 2BrO_2\cdot + H_2O \quad (5)$$

$$Fe(phen)_3^{2+} + BrO_2\cdot + H^+ \rightleftarrows Fe(phen)_3^{3+} + HBrO_2 \quad (6)$$

$$2Fe(phen)_3^{2+} + HBrO_2 + 2H^+ \rightarrow 2Fe(phen)_3^{3+} + HOBr + H_2O \quad (7)$$

$$2\mathrm{Fe(phen)_3}^{2+} + \mathrm{HOBr} + \mathrm{H}^+ \rightarrow 2\mathrm{Fe(phen)_3}^{3+} + \mathrm{Br}^- + \mathrm{H_2O} \tag{8}$$

$$2\mathrm{Fe(phen)_3}^{2+} + \mathrm{Br_2} \rightleftarrows 2\mathrm{Fe(phen)_3}^{3+} + 2\mathrm{Br}^- \tag{9}$$

$$\mathrm{Fe(phen)_3}^{3+} + \mathrm{BrO_2}\cdot + \mathrm{H_2O} \rightarrow \mathrm{Fe(phen)_3}^{2+} + \mathrm{BrO_3}^- + 2\mathrm{H}^+ \tag{10}$$

$$\mathrm{Fe(phen)_3}^{2+} \rightarrow \mathrm{Fe(phen)_2}^{2+} + \mathrm{phen} \tag{11}$$

$$\mathrm{Fe(phen)_3}^{3+} \rightarrow \mathrm{Fe(phen)_2}^{3+} + \mathrm{phen} \tag{12}$$

$$\mathrm{Fe(phen)_2}^{2+} + \mathrm{BrO_3}^- + 2\mathrm{H}^+ \rightarrow \mathrm{Fe(phen)_2}^{3+} + \mathrm{BrO_2}\cdot + \mathrm{H_2O} \tag{13}$$

$$\mathrm{Fe(phen)_2}^{2+} + \mathrm{BrO_2}\cdot + \mathrm{H}^+ \rightarrow \mathrm{Fe(phen)_2}^{3+} + \mathrm{HBrO_2} \tag{14}$$

$$2\mathrm{Fe(phen)_2}^{2+} + \mathrm{HBrO_2} + 2\mathrm{H}^+ \rightarrow 2\mathrm{Fe(phen)_2}^{3+} + \mathrm{HOBr} + \mathrm{H_2O} \tag{15}$$

$$\mathrm{Fe(phen)_2}^{2+} + \mathrm{HOBr} + \mathrm{H}^+ \rightarrow \mathrm{Fe(phen)_2}^{3+} + \mathrm{Br_2}/2 + \mathrm{H_2O} \tag{16}$$

$$\mathrm{Fe(phen)_3}^{3+} + \mathrm{Fe(phen)_2}^{2+} \rightarrow \mathrm{Fe(phen)_3}^{2+} + \mathrm{Fe(phen)_2}^{3+} \tag{17}$$

$$\mathrm{Fe(phen)_2}^{2+} + \mathrm{Br}^- \rightarrow \mathrm{Fe(phen)_2Br}^+ \tag{18}$$

$$\mathrm{Fe(phen)_2Br}^+ + \mathrm{Br}^- \rightarrow \mathrm{Fe(phen)_2Br_2} \tag{19}$$

The rate constants of these reactions are shown in Table 1 together with several rates. We assumed the FKN scheme, Reactions 1—6, as a skeleton mechanism according to Rovinsky and Zhabotinsky and used the FF set of rate constants for Reactions 1—5.[14,19,20] Reactions 6—8 correspond to a series of oxidations of ferroin by $\mathrm{BrO_2}\cdot$, $\mathrm{HBrO_2}$, and HOBr. Similar oxidation processes of Fe^{2+} and $\mathrm{Fe(CN)_6}^{4-}$ by the same bromine-related compounds take place in the oxidation of the reductants by bromate.[21—23] Though ferroin is a weaker reducing agent than the reductants, we assumed Reactions 6—8. At least, Reaction 6 was required for the appearence of an autocatalytic phase in the oxidation of ferroin by bromate. Reactions 7 and 8 were assumed to proceed via two-electron transfer according to Ganapthisubramanian and Noyes, and D'Alba and Di Lorenzo, and Gáspár et al.[15,17,18] It is presumed that the species, $\mathrm{Fe(phen)_3}^{4+}$, formed by Reactions 20 and 21 are consumed rapidly according to Reaction 22.

$$\mathrm{Fe(phen)_3}^{2+} + \mathrm{HBrO_2} + 2\mathrm{H}^+ \rightarrow \mathrm{Fe(phen)_3}^{4+} + \mathrm{HOBr} + \mathrm{H_2O} \tag{20}$$

$$\mathrm{Fe(phen)_3}^{2+} + \mathrm{HOBr} + \mathrm{H}^+ \rightarrow \mathrm{Fe(phen)_3}^{4+} + \mathrm{Br}^- + \mathrm{H_2O} \tag{21}$$

$$\mathrm{Fe(phen)_3}^{4+} + \mathrm{Fe(phen)_3}^{2+} \rightarrow 2\mathrm{Fe(phen)_3}^{3+} \tag{22}$$

Thus, we used Eqs. 23 and 24 as the rates of Reactions 7 and 8, respectively:

$$v_7 = k_7[\mathrm{Fe(phen)_3}^{2+}][\mathrm{HBrO_2}] \tag{23}$$

and

$$v_8 = k_8[\mathrm{Fe(phen)_3}^{2+}][\mathrm{HOBr}]. \tag{24}$$

Though Reaction 10 is unknown experimentally, we used this reaction in order to explain the behavior of a bromate-bromide-ferroin system under the CSTR condition that $[\mathrm{Br}^-]_0=0$ M (1 M=1 mol dm^{-3}); the value of $[\mathrm{Fe(phen)_3}^{2+}]_0$ is considerably large, where the subscript, 0, indicates the concentration of a chemical species in the feed flow. It was assumed that the backward step of Reaction 10 does not occur according to Rabái and Epstein.[23] Ferroin and ferriin in an acidic medium decompose slowly.[2,24] Because $\mathrm{Fe(phen)_2}^{2+}$, formed by the decomposition of ferroin, is thought to be a stronger reducing agent than ferroin, a series of oxidation processes of $\mathrm{Fe(phen)_2}^{2+}$ by $\mathrm{BrO_3}^-$, $\mathrm{BrO_2}\cdot$, $\mathrm{HBrO_2}$, and HOBr, Reactions 13—16, were assumed. Reaction 17 is a relatively fast redox process between $\mathrm{Fe(phen)_3}^{3+}$ and $\mathrm{Fe(phen)_2}^{2+}$ ions. The backward step of Reaction 17 was ignored because of the relatively high reducing power of $\mathrm{Fe(phen)_2}^{2+}$. It is reported that ill-defined red precipitates are formed in the system of bromate and ferroin of high concen-

Table 1. Rate Constants Used in This Study[a)]

Reaction	Forward	Backward	Rate	Ref.
1	2 $\mathrm{M^{-3}\,s^{-1}}$	3.2 $\mathrm{M^{-1}\,s^{-1}}$		20
2	8×10^9 $\mathrm{M^{-2}\,s^{-1}}$	110 $\mathrm{s^{-1}}$		20
3	3×10^6 $\mathrm{M^{-2}\,s^{-1}}$	—		20
4	3000 $\mathrm{M^{-1}\,s^{-1}}$	—		20
5	42 $\mathrm{M^{-2}\,s^{-1}}$	4.2×10^7 $\mathrm{M^{-1}\,s^{-1}}$		20
6	10^7 $\mathrm{M^{-1}\,s^{-1}}$	2.75×10^2 $\mathrm{M^{-1}\,s^{-1}}$	$v_6=k_6\,[\mathrm{Fe(phen)_3}^{2+}][\mathrm{BrO_2}\cdot]$	14, 15
7	600 $\mathrm{M^{-1}\,s^{-1}}$	—	$v_7=k_7\,[\mathrm{Fe(phen)_3}^{2+}][\mathrm{HBrO_2}]$	—
8	80 $\mathrm{M^{-1}\,s^{-1}}$	—	$v_8=k_8\,[\mathrm{Fe(phen)_3}^{2+}][\mathrm{HOBr}]$	—
9	2 $\mathrm{M^{-1}\,s^{-1}}$	100 $\mathrm{M^{-1}\,s^{-1}}$		4, 26
10	10^4 $\mathrm{M^{-1}\,s^{-1}}$	—		—
11	7×10^{-5} $\mathrm{s^{-1}}$	—		2, 24
12	7×10^{-5} $\mathrm{s^{-1}}$	—		24
13	5 $\mathrm{M^{-1}\,s^{-1}}$	—	$v_{13}=k_{13}\,[\mathrm{Fe(phen)_2}^{2+}][\mathrm{BrO_3}^-]$	21, 23
14	10^9 $\mathrm{M^{-1}\,s^{-1}}$	—		23, 27
15	2×10^5 $\mathrm{M^{-1}\,s^{-1}}$	—		23
16	10^5 $\mathrm{M^{-1}\,s^{-1}}$	—		23
17	4×10^4 $\mathrm{M^{-1}\,s^{-1}}$	—		28
18	5×10^6 $\mathrm{M^{-1}\,s^{-1}}$	—		—
19	5×10^6 $\mathrm{M^{-1}\,s^{-1}}$	—		—

a) 1 M=1 mol dm^{-3}.

trations.[4] In this study we regarded the red precipitate as $Fe(phen)_2Br_2$ which is synthsized easily.[25] Thus, we employed Reactions 18 and 19. The rate constants of Reactions 6—8, 10, and 13—19, and that of the backward step of Reaction 9 are unknown. The k_{-9} value was estimated on the basis of the kinetic data for the ferriin-I^--Br^- system, reported by Ige et al.[26] The magnitude of the rate constants of k_7, k_8, and k_{10} were determined by trial and error, and possible values were employed as the other rate constants. The 11-variable rate equations generated from Reactions 1—19 were examined (11 variables: the concentrations of BrO_3^-, $BrO_2\cdot$, $HBrO_2$, HOBr, Br_2, Br^-, $Fe(phen)_3^{2+}$, $Fe(phen)_3^{3+}$, $Fe(phen)_2^{2+}$, $Fe(phen)_2^{3+}$, and $Fe(phen)_2Br^+$). In a CSTR mode, the terms $k_0(C_{0i}-C_i)$ were added to the rate equations, where C_i and C_{0i} are the concentrations of species i in the solution and in the feed flow, respectively, and k_0 is the reciprocal of the residence time. The state of the system in a CSTR is dependent on the constraints: $[BrO_3^-]_0$, $[Br^-]_0$, $[H^+]_0$, $[Fe(phen)_3^{2+}]_0$, and k_0. The calculation of the steady states was performed by Newton's method. The stability of the steady states was surveyed by means of a linearized stability analysis. The temporal evolution of the system was determined by using Gear's method.

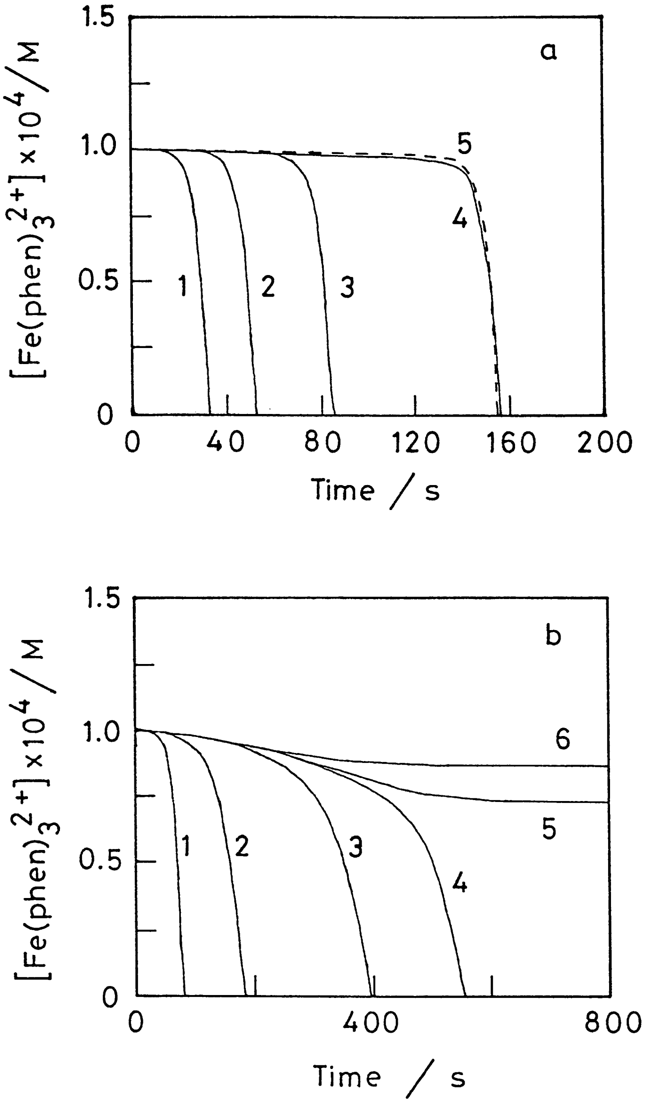

Fig. 1. Change of $[Fe(phen)_3^{2+}]$ in the oxidation of ferroin by bromate in a batch reactor.
$[Fe(phen)_3^{2+}]_{in}=10^{-4}$ M (1 M=1 mol dm^{-3}) and $[H^+]_{in}=0.83$ M. a: $[BrO_3^-]_{in}=0.01$ M, and $[Br^-]_{in}=10^{-12}$ M (1), 10^{-6} M (2), 5×10^{-6} M (3), and 1.5×10^{-5} M (4). b: $[Br^-]_{in}=10^{-12}$ M, and $[BrO_3^-]_{in}=5\times10^{-3}$ M (1), 3×10^{-3} M (2), 2.4×10^{-3} M (3), 2.34×10^{-3} M (4), 2.33×10^{-3} M (5), and 2.3×10^{-3} M (6).
The dashed line represents the experimental result by Kuhnert et al.[3]

Results and Discussion

Reaction Behavior of a Bromate-Bromide-Ferroin System in a Batch Reactor. The temporal change of $[Fe(phen)_3^{2+}]$ in the oxidation of ferroin by bromate is shown in Fig. 1. The values of the rate constants of Reactions 7, 8, and 10 were determined so as to reproduce the oxidation curve of ferroin under the batch reactor condition ($[Br^-]_{in}=1.5\times10^{-5}$ M, $[BrO_3^-]_{in}=0.01$ M: $[H^+]_{in}=0.83$ M, and $[Fe(phen)_3^{2+}]_{in}=10^{-4}$ M, where the subscript, in, indicates the initial concentration of a species), reported by Kuhnert et al. and the bistable region obtained in the CSTR condition ($[H_2SO_4]_0=0.1$ M, $[BrO_3^-]_0=0.05$ M, $[Fe(phen)_3^{2+}]_0=10^{-3}$ M, $[Br^-]_0=0$ M, and $k_0=0.01$ s^{-1}), reported by Gáspár et al.[3,4] As shown in Fig. 1-a, the reaction network examined in this paper could reproduce the features (decomposition phase, autocatalytic phase, dependency of the induction period on $[Br^-]_{in}$ and adrupt transition of the system from the autocatalytic phase to the final state) in the oxidation of ferroin by bromate. Figure 1-b shows that the reaction behavior is also influenced by the initial concentration of bromate.[#] Though the decomposition phase was followed by the autocatalytic phase in the oxidation curve of ferroin when $[BrO_3^-]_{in}$ equaled 2.4×10^{-3} M, there was no autocatalytic phase in the oxidation curve when $[BrO_3^-]_{in}$ equaled 2.3×10^{-3} M This means that there is a threshold with regard to the initial concentration of bromate and that the autocatalytic process proceeds when the $[BrO_3^-]_{in}$ value is larger than the threshold. As shown in Fig. 2, the threshold of $[BrO_3^-]_{in}$ was inversely proportional to the $[H^+]_{in}$ value. The existence of the threshold of $[BrO_3^-]_{in}$ and a similar dependency of the threshold on $[H^+]_{in}$ were observed in the oxidation of tris(2,2′-bipyridyl)iron(II), $Fe(bpy)_3^{2+}$, by bromate.[1]

According to the reaction network tested in this study, the threshold of $[BrO_3^-]_{in}$ in the batch reactor mode is generated due to competition between Reactions 4 and 5 when the concentration of bromide is

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[#] The small value of $[Br^-]_{in}$ used in the calculations did not affect the results of calculations.

low. The threshold, $[BrO_3^-]_{in(th)}$, is represented by Eq. 25 on the basis of several assumptions (Appendix):

$$[BrO_3^-]_{in(th)}=k_4[HBrO_2]_{max}/(k_5[H^+])+\Delta A, \qquad (25)$$

where $[HBrO_2]_{max}$ is the maximum in the concentration of $HBrO_2$, which is formed autocatalytically according to Reactions 5 and 6, and ΔA is the decrease in the concentration of bromate ($[BrO_3^-]_{in}-[BrO_3^-]$). Because the magnitude of ΔA is smaller than that of $k_4[HBrO_2]_{max}/(k_5[H^+])$ in Eq. 25, the threshold of $[BrO_3^-]_{in}$ is inversely proportional to $[H^+]$, which is approximately equal to $[H^+]_{in}$. When $[BrO_3^-]_{in} \approx [BrO_3^-]_{in(th)}$, the oxidation curve of ferroin deviates from its typical shape (4 and 5 in Fig. 1-b). In this case, it is thought that the decomposition and autocatalytic phases are not defined experimentally. Such an intermediate region is also observed in the oxidation of $Fe(bpy)_3^{2+}$ by bromate.[1] When the $[BrO_3^-]_{in}$ value is larger than the threshold and $[Br^-]$ is high, bromide is oxidized by bromate according to Reactions 1—3. If $[Br^-]$ becomes sufficiently low, Reaction 5 proceeds: The system goes from the decomposition phase to the autocatalytic phase (Fig. 1-a).

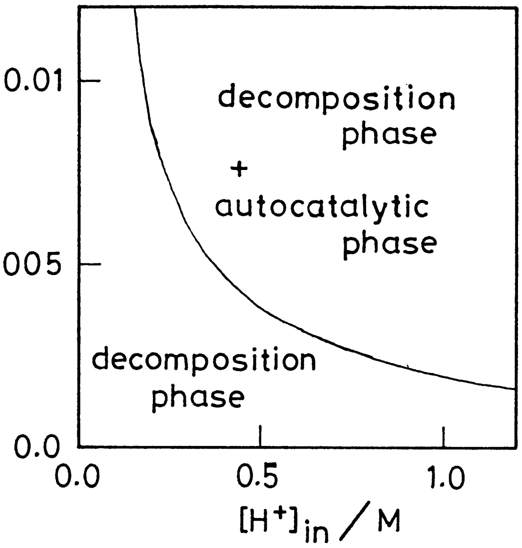

Fig. 2. Phase diagram in the oxidation of ferroin by bromate in a batch reactor.
$[Fe(phen)_3^{2+}]_{in}=10^{-4}$ M and $[Br^-]_{in}=10^{-12}$ M.

Reaction Behavior of a Bromate-Bromide-Ferroin System in a CSTR. Figure 3 shows the relationship between the value of $[BrO_3^-]_0$ and the steady-state values of $Fe(phen)_3^{3+}$ and Br^- when $[H^+]_0=0.2$ M, $[Fe(phen)_3^{2+}]_0=10^{-3}$ M, $[Br^-]_0=0$ M, and $k_0=0.01$ s^{-1}. If the concentration of BrO_3^- in the feed flow was low, the system stayed in SSI, which was a steady state characterized by a low concentration of $Fe(phen)_3^{3+}$ and a high concentration of Br^-. On the other hand, when the concentration of BrO_3^- in the feed flow was high, the system existed in SSII, which was a steady state characterized by a high concentration of $Fe(phen)_3^{3+}$ and a low concentration of Br^-. Then, the system was bistable in the $[BrO_3^-]_0$ range of 0.0238—0.0817 M. Because the system in a steady state suddenly moved to the other steady state at a critical value of $[BrO_3^-]_0$, we obtained a hysteresis loop. The bistable region of the system exists in a five-dimensional space of $[H^+]_0$, $[BrO_3^-]_0$, $[Fe(phen)_3^{2+}]_0$, $[Br^-]_0$, and k_0. Figure 4 shows the bistable region projected on the $[Fe(phen)_3^{2+}]_0$—

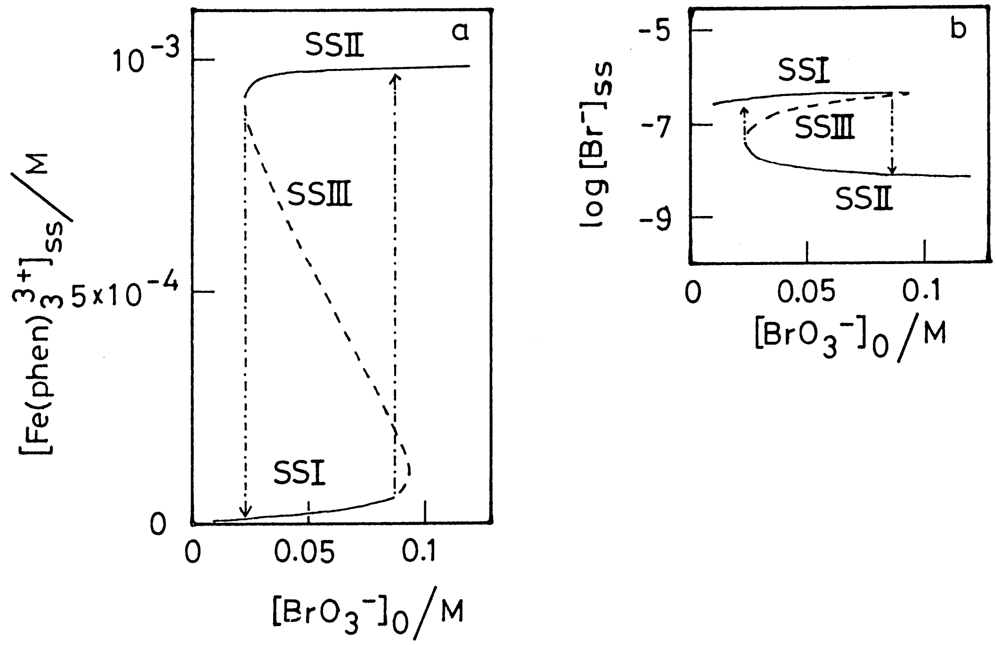

Fig. 3. Hysteresis of the bromate-bromide-ferroin system in a CSTR.
$[Fe(phen)_3^{2+}]_0=10^{-3}$ M, $[Br^-]_0=0$ M, $[H^+]_0=0.2$ M, and $k_0=0.01$ s^{-1}.

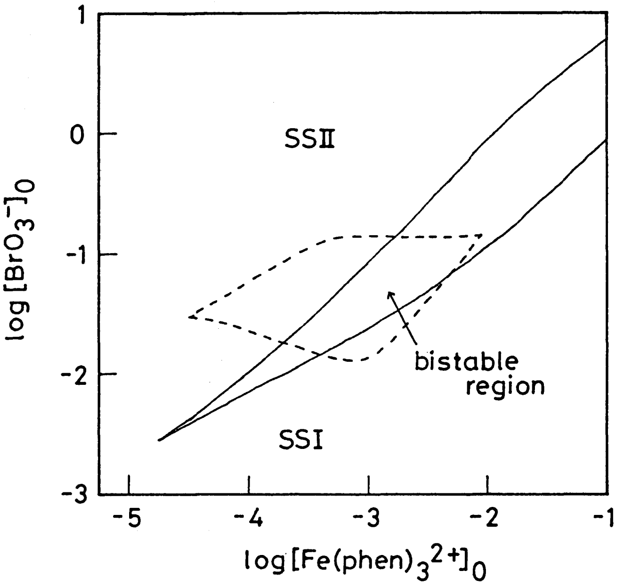

Fig. 4. Hysteresis limit of the bromate-bromide-ferroin system in a CSTR.
$[H^+]_0$=0.2 M, $[Br^-]_0$=0 M, and k_0=0.01 s^{-1}.
The dashed line represents the experimental result by Gáspár et al. ($[H_2SO_4]_0$=0.1 M, $[Br^-]_0$=0 M, and k_0=0.01 s^{-1}).[4]

$[BrO_3^-]_0$ subspace when $[H^+]_0$=0.2 M, $[Br^-]_0$=0 M, and k_0=0.01 s^{-1}. The bistable region calculated is open. However, the region observed experimentally is closed.[4]

According to the reaction network tested in this study, Reactions 6, 7, 11, and 13 are essential to the appearance of SSI under the CSTR condition that $[Br^-]_0$=0 M. On the other hand, in SSII the autocatalytic formation of $HBrO_2$, Reactions 5 and 6, is superior to Reaction 7. Comparing the rates of Reactions 5 and 7,

$$v_7/v_5=(k_7/k_5)\{[Fe(phen)_3{}^{2+}]/([H^+][BrO_3{}^-])\}. \qquad (26)$$

Equation 26 suggests that the system exists in SSI when $[Fe(phen)_3{}^{2+}]_0$ is high and that the system exists in SSII when $[BrO_3^-]_0$ is high. This is consistent with the behavior of the system, as shown in Figs. 3 and 4. Thus, the bistability of the system occurs in the region where Reactions 5 and 7 compete with each other. Under the CSTR condition that $[Br^-]_0$=0 M, the competetion between Reactions 3 and 5 does not occur because the $[Br^-]$ value is small. Equation 26 also shows that the system can possess bistability, even when the $[Fe(phen)_3{}^{2+}]_0$ value is large; the bistable region calculated is open. Though we expected that Reaction 10 would destroy the bistable structure in a high $[Fe(phen)_3{}^{2+}]_0$ region, the reaction caused only the steady state value of SSII vary slightly. Moreover, we simulated on the basis of the assumption that the red precipitate observed experimentally was the ion pair of ferroin and Br_3^- ($Fe(phen)_3(Br_3)_2$).[18,29] However, we could not obtain a closed region of bistability.

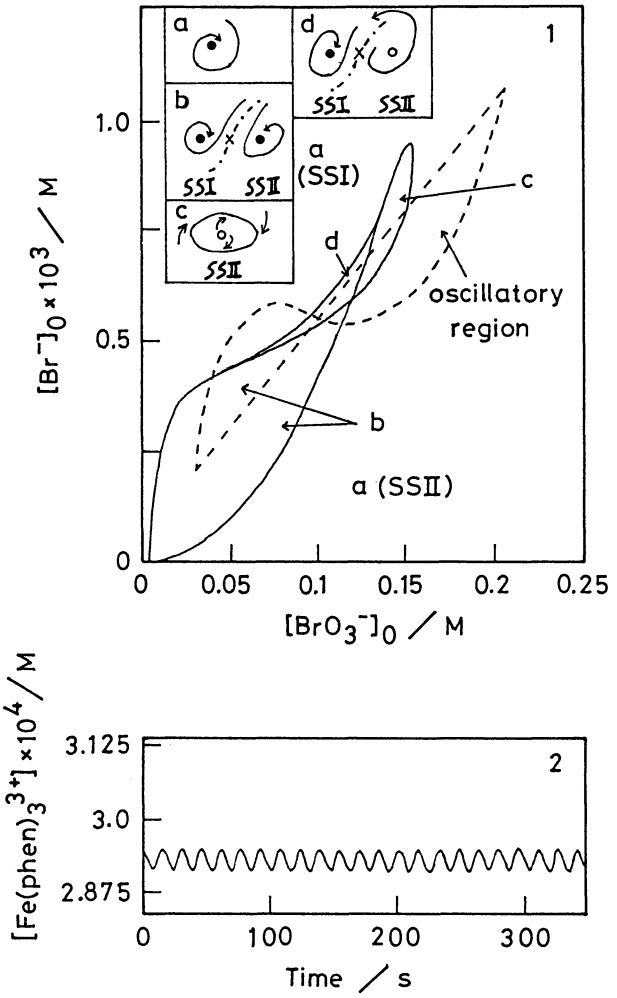

Fig. 5. Phase diagram and sustained oscillations of the bromate-bromide-ferroin system in a CSTR.
$[Fe(phen)_3{}^{2+}]_0$=3×10^{-4} M, $[H^+]_0$=1.0 M, and k_0=0.01 s^{-1}.
a: monostability, b: bistablility, c: oscillation, and d: region having one stable and two unstable solutions.
●: stable focus (node), O: unstable focus (node) and x: saddle point.
The dashed line represents the experimental result by Gáspár et al. ($[Fe(phen)_3{}^{2+}]_0$=3×10^{-4} M, $[H_2SO_4]_0$=0.5 M and k_0=0.01 s^{-1}).[4] 2: $[BrO_3^-]_0$=0.15 M and $[Br^-]_0$=8.5×10^{-4} M.

Figure 5 shows a phase diagram of the system in the $[BrO_3^-]_0$–$[Br^-]_0$ subspace when $[Fe(phen)_3{}^{2+}]_0$=3×10^{-4} M, $[H^+]_0$=1 M, and k_0=0.01 s^{-1} and sustained oscillations under the CSTR conditions ($[BrO_3^-]_0$=0.15 M, $[Br^-]_0$=8.5×10^{-4} M, $[H^+]_0$=1 M, k_0=0.01 s^{-1}, and $[Fe(phen)_3{}^{2+}]_0$=3×10^{-4} M). In Fig. 5-1, a, b, and c represent monostable, bistable, and oscillatory regions, respectively. The system was also monostable in the region d, since the rate equations possessed one stable (SSI) and two unstable equilibrium solutions in that region. The bistable and the oscillatory regions calculated in this study were in considerable agreement with those obtained experimentally.[4] This may mean that the rate constants for Reactions 1—5 are valid. The oscillatory state of this system was brought about owing to an unstabilization of SSII. Therefore, the concentration of ferriin oscillated with a small amplitude around the steady state value of $Fe(phen)_3^{3+}$. However, the amplitude of the oscillations observed experimentally is large (more than 300 mV in Pt potential).[4]

The bistability in Fig. 5-1 occurs in the region where Reactions 3 and 5 compete with each other. The unstabilization of SSII in regions c and d (Fig. 5-1) may result from the backward step in Reaction 6, since the step is thought to be the only process having a possibility to destroy a stable SSII structure in the reaction network tested in this study. In a bromate-bromide-cerium(III) system, the backward step of Reaction 27 plays an important role in generating the minimal oscillations of the system:[13,30]

$$Ce^{3+} + BrO_2\cdot + H^+ \rightleftarrows Ce^{4+} + HBrO_2 \qquad (27)$$

and

$$k_{27} = 8\times10^4\ M^{-2}\,s^{-1} \text{ and } k_{-27} = 8.9\times10^3\ M^{-1}\,s^{-1}. \qquad (28)$$

The step is also the only process which can destroy a stable SSII structure in the FKN scheme. Because Reaction 27 is substantially reversible, the system exhibiting the oscillations is thought to be able to relax from SSII to SSI.[20] On the other hand, the equilibrium of Reaction 6 is shifted to the oxidized state $Fe(phen)_3^{3+}$ due to the lower redox potential of ferroin/ferriin (1.06 V in 1 M H_2SO_4) than that of $HBrO_2/(BrO_2\cdot + H^+)$ (1.33 V). This may lead to the situation that it is difficult for the bromate-bromide-ferroin system to relax from SSII to SSI. We believe that oscillations with a small amplitude and high frequency obtained in this study is due to the reason mentioned above. In order to reproduce oscillations with large amplitude in the bromate-bromide-ferroin system, there should be a reduction process of ferriin in the reaction network.[##] Reaction 17 was not effective because of the low concentration of $Fe(phen)_2^{2+}$. Reaction 29 was also not effective:

$$Fe(phen)_3^{3+} + Fe(phen)_2Br_2 \rightarrow Fe(phen)_3^{2+} + Fe(phen)_2^{3+} + 2Br^- \qquad (29)$$

Birk and Kozub reported the occurrence of a layer of $Fe(bpy)_3^{2+}$ along the walls of a spectrophotometer cell in the oxidation of $Fe(bpy)_3^{2+}$ by bromate.[1] Melicherčík and Treindl observed an autoreduction of ferriin in an acidic medium.[31] These puzzling phenomena may play an important role in the bromate-bromide-ferroin system in a CSTR.

Reactions 13—16, where bromate is reduced to bromine by $Fe(phen)_2^{2+}$, were available for an accumulation of bromide during the initial stage of the oxidation of ferroin by bromate; they were not effective for the appearance of SSI under the CSTR condition that $[Br^-]_0 = 0$ M.

In this study, it is concluded that the behavior of the bromate-bromide-ferroin system in a batch reactor is thoroughly explained within the framework of the FKN scheme. Though Reaction 7 in the reaction network tested here, which is unknown experimentally, was effective on reproducing the bistability of the bromate-bromide-ferroin system under the CSTR condition that bromide did not flow into a CSTR, other reactions should also be added to the FKN scheme in order to explain the puzzling observations of the bromate-bromide-ferroin system in a CSTR.

Appendix

We consider the case that Reaction 4 is competitive with Reaction 30, which is based on a combination of Reactions 5 and 6:

$$BrO_3^- + HBrO_2 + 3H^+ + 2Fe(phen)_3^{2+} \rightarrow 2HBrO_2 + 2Fe(phen)_3^{3+} + H_2O \qquad (30)$$

We assume that the rate of Reaction 30 is represented by

$$v_{30} = k_5[H^+][HBrO_2][BrO_3^-]. \qquad (31)$$

If Reaction 30 is superior to Reaction 4, $HBrO_2$ is formed exponentially. Then the system comes to a final state where a major portion of ferroin is consumed; the concentration of $HBrO_2$ reaches a maximum ($[HBrO_2]_{max}$). We assume that Reaction 30 is superior to Reaction 4 under the condition that

$$v_{30}/v_4 > \alpha, \qquad (32)$$

where $v_4 = k_4[HBrO_2]^2$ and α is represented in terms of the contribution by various reactions. In this study, we assume that $\alpha = 1$. Considering that $[BrO_3^-] = [BrO_3^-]_{in} - \Delta A$, we obtain the condition under which the system can go to the final state:

$$[BrO_3^-]_{in} > k_4[HBrO_2]_{max}/(k_5[H^+]) + \Delta A. \qquad (33)$$

Thus, the equation representing the threshold of the initial concentration of bromate is yielded as Eq. 25.

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