A Simulation of Bromate-Cerium-Oxalic Acid Oscillations

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The oscillation behavior of the bromate-cerium-oxalic acid system was simulated within the FKN framework with bromine-hydrolysis control, where a radical-chain reaction of HOBr with oxalic acid and the formation of $HCO_2\cdot$ by the reduction of Ce(IV) were assumed. When $[(COOH)_2]=0.03$ mol dm^{-3} and $k_{13}=0.075$ s^{-1} (k_{13}: the rate constant of bromine removal), the oscillation behavior was qualitatively consistent with the experimental results. Excitability in the reduced and oxidized steady states, induced by a sudden change in the concentration of bromine, was simulated. No bistability was found. When $[(COOH)_2]=0.03$ mol dm^{-3}, no hysteresis near the bifurcation points was observed. However, when $[(COOH)_2]=0.001$ mol dm^{-3}, hysteresis was observed in the transition between the oxidized steady state and the oscillatory state.

The FKN mechanism seems widely accepted at present as a qualitatively adequate description of the exotic Belousov-Zhabotinskii (BZ) oscillation.[1] In the mechanism, bromide is a control intermediate, and a stoichiometric factor is used in order to simplify the complicated processes of the reduction of Ce(IV) and the formation of bromide by malonic acid and its brominated compound.[2,3] The BZ oscillation in the presence of silver ions could also be simulated within the FKN framework.[4]

Recently Noszticzius et al.[5,6] reported characteristic oscillation behavior of the bromate-cerium-oxalic acid system under batch conditions, and Gáspár and Galambosi,[7] in the CSTR mode. In this system, the bromine had to be removed physically or chemically in order to sustain the oscillations between the explicit oxidized steady state and the reduced steady state, and the time period of the oscillations depended on the magnitude of the bifurcation parameters. Moreover, excitability in the steady states and bistability were observed.

Field and Boyd simulated the oscillation of the bromate-cerium-oxalic acid-acetone system by using the Oregonator model with bromine-hydrolysis control,[8] supporting the idea that bromide is an intermediate in the system as well. Gáspár and Galambosi also reported a simulation for the bromate-cerium-oxalic acid system within a revised Oregonator model.[7] However, these simulations did not reproduce the oscillation behavior described above. The inconsistency seems to be ascribable to the excessive simplification of the reduction process of HOBr by oxalic acid. The bromate-cerium-oxalic acid system is one of the simplest BZ-type oscillations because oxalic acid cannot be brominated. Thus, when we simulate the oscillation behavior of this system, we have to take account of the processes of the reduction of Ce(IV) and of the formation of bromide in detail. Noyes,[9] as well as Field and Boyd,[8] has proposed the formation of $HCO_2\cdot$ and $Br\cdot$ radicals in the processes of the reduction of Ce(IV) by oxalic acid and the formation of bromide. In this paper, we will simulate the oscillation behavior of the bromate-cerium-oxalic acid system by using the FKN mechanism with bromine-hydrolysis control and by assuming the formation of $HCO_2\cdot$ and $Br\cdot$ radicals, according to the proposals of Noyes and of Field and Boyd.

Reaction Mechanism and Method of Calculation

Bromate and oxalic acid react in the presence of a cerium catalyst to give bromine and CO_2:[5]

$$2BrO_3^- + 5(COOH)_2 + 2H^+ \longrightarrow 10CO_2 + Br_2 + 6H_2O \quad (a)$$

In this study, the following mechanism will be assumed for Reaction a:

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

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

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

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2\cdot + H_2O \quad (4)$$

$$BrO_2\cdot + Ce(III) + H^+ \rightleftharpoons Ce(IV) + HBrO_2 \quad (5)$$

$$2HBrO_2 \longrightarrow HOBr + BrO_3^- + H^+ \quad (6)$$

$$HOBr + (COOH)_2 \longrightarrow HCO_2\cdot + Br\cdot + H_2O + CO_2 \quad (7)$$

$$Ce(IV) + (COOH)_2 \longrightarrow Ce(III) + HCO_2\cdot + CO_2 + H^+ \quad (8)$$

$$HCO_2\cdot + HOBr \longrightarrow Br\cdot + H_2O + CO_2 \quad (9)$$

$$Br\cdot + (COOH)_2 \longrightarrow HCO_2\cdot + Br^- + CO_2 + H^+ \quad (10)$$

$$Br\cdot + Br\cdot \longrightarrow Br_2 \quad (11)$$

$$HCO_2\cdot + HCO_2\cdot \longrightarrow (COOH)_2 \quad (12)$$

$$Br_2 \longrightarrow Br_2(gas) \quad (13)$$

Table 1. Rate Constants Used in the Calculations

k_1	$2.1\ M^{-3}\ s^{-1}$	k_6	$4.0\times10^7\ M^{-1}\ s^{-1}$
k_2	$8.0\times10^9\ M^{-2}\ s^{-1}$	k_7	$25\ M^{-1}\ s^{-1}$
k_{-2}	$110\ s^{-1}$	k_8	$27.5\ M^{-1}\ s^{-1}$
k_3	$2.0\times10^9\ M^{-2}\ s^{-1}$	k_9	$2.0\times10^7\ M^{-1}\ s^{-1}$
k_4	$1.0\times10^4\ M^{-2}\ s^{-1}$	k_{10}	$2000\ M^{-1}\ s^{-1}$
k_{-4}	$2.0\times10^7\ M^{-1}\ s^{-1}$	k_{11}	$1.0\times10^8\ M^{-1}\ s^{-1}$
k_5	$6.0\times10^5\ M^{-2}\ s^{-1}$	k_{12}	$1.2\times10^9\ M^{-1}\ s^{-1}$
k_{-5}	$5.0\times10^7\ M^{-1}\ s^{-1}$		

(1 M=1 mol dm^{-3})

The mechanism consisted of the FKN mechanism with bromine-hydrolysis control and the formation of $HCO_2\cdot$ and $Br\cdot$ radicals in a reaction between HOBr and oxalic acid. That is, HOBr reacted with oxalic acid to give $HCO_2\cdot$ and $Br\cdot$ radicals, and the radicals consumed HOBr and oxalic acid according to a radical-chain reaction composed of Reactions 9 and 10 or vanished according to Reactions 11 and 12. Reaction 14 was ignored because it was thought to make no contribution to the BrO_3^-–oxalic acid reaction:[8]

$$Br\cdot + HCO_2\cdot \longrightarrow Br^- + CO_2 + H^+ \quad (14)$$

Ce(IV) was assumed to give $HCO_2\cdot$ according to Reaction 8 and was thus explicitly concerned with the consumption of HOBr. Reaction 13 represents a process of the first order, where the bromine produced was removed from the BrO_3^-–Ce–$(COOH)_2$ system.[6,7] Reaction 15, which is a part of the FKN mechanism, is not important because it is very slow ($k_{15}=9.6\ mol^{-1}\ s^{-1}$ and $k_{-15}=1.3\times10^{-4}\ mol^{-3}\ s^{-1}$):[10]

$$Ce(IV) + BrO_2\cdot + H_2O \rightleftharpoons Ce(III) + BrO_3^- + 2H^+ \quad (15)$$

The rate constants of Reactions 1—12 are shown in Table 1. The k_1—k_{-4} and k_6 rate constants are according to Bar-Eli and Ronkin,[10] and k_5 and k_{-5}, according to Tyson.[11] The other rate constants agreed with those estimated by Field and Boyd.[8] Ce(IV) is reduced to Ce(III) by oxalic acid according to Reactions 8 and 16:[12,13]

$$Ce(IV) + HCO_2\cdot \longrightarrow Ce(III) + CO_2 + H^+ \quad (16)$$

We ignored Reaction 16 and assumed a larger k_8 value than that obtained experimentally.[8]

The numerical integration of the differential equations generated from Reactions 1—13 was performed using the Gear algorithm.[14] In the calculations we assumed that $[H^+]=1$ mol dm^{-3} and that $[Ce]_{total}(=[Ce(III)]+[Ce(IV)])=0.0005$ mol dm^{-3}, while k_{13} and $[BrO_3^-]$ were regarded as bifurcation parameters.

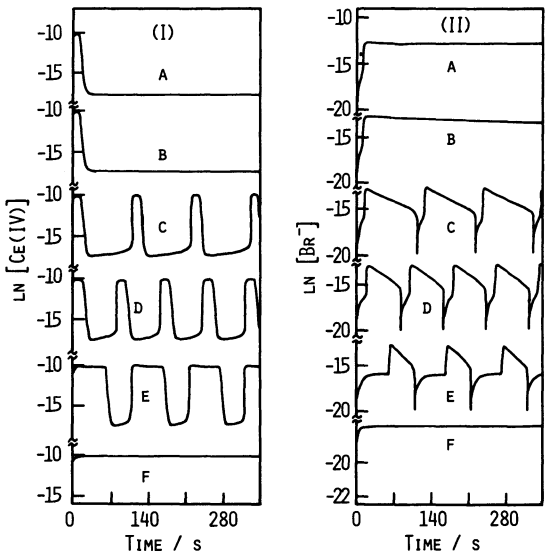

Fig. 1. The change in the oscillation pattern with k_{13}. $[BrO_3^-]=0.03$ mol dm^{-3}, $[(COOH)_2]=0.03$ mol dm^{-3}. k_{13} A: 0.001 s^{-1}, B: 0.005 s^{-1}, C: 0.05 s^{-1}, D: 0.075 s^{-1}, E: 0.1 s^{-1}, F: 0.25 s^{-1}.

Results and Discussion

When $[(COOH)_2]=0.03$ mol dm^{-3}. Figure 1 shows the change in the oscillation pattern with k_{13}. When $k_{13}=0.001\ s^{-1}$, the bromate–cerium–oxalic acid system stayed at a reduced steady state (steady-state LO by Noszticzius et al.[6]) characterized by a small concentration of Ce(IV). On the other hand, when $k_{13}=0.25\ s^{-1}$, the system stayed at an oxidized steady state (steady-state HI) characterized by a large concentration of Ce(IV). When $0.005\ s^{-1}\leq k_{13}\leq 0.1\ s^{-1}$, the system exhibited sustained oscillations between the two steady states. The time period of the oscillations, T, and the time that the system spent in either steady state, τ, depended on the value of k_{13}.

Figure 2 shows the relationship between the oscillation pattern and the concentration of bromate. When $[BrO_3^-]=0.006$ mol dm^{-3}, the system existed in a reduced steady state, and when $[BrO_3^-]=0.045$ mol dm^{-3}, in an oxidized steady state. When 0.007 mol $dm^{-3}\leq[BrO_3^-]\leq 0.0425$ mol dm^{-3}, the sustained oscillations between the two steady states appeared. T and τ depended on the value of $[BrO_3^-]$, but the amplitude of the oscillations was approximately constant. Hysteresis was not observed in the transitions from the monostable steady states to the oscillatory state, or vice versa.

Figure 3 shows the excitability of a reduced steady state induced by a sudden decrease in the concentration of bromine. The value of $[Br_2]$ at the steady state was 1.2857×10^{-8} mol dm^{-3}. When $[Br_2]=1.02\times10^{-8}$ mol dm^{-3}, the system returned to the reduced steady state with a damped oscillation. When $[Br_2]=1.01\times$

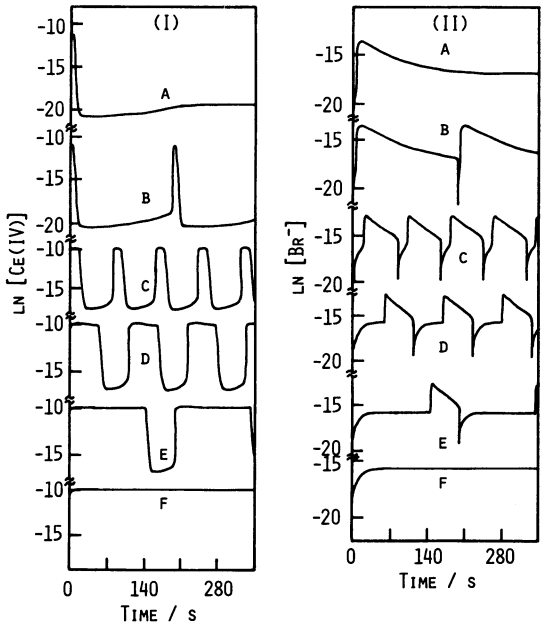

Fig. 2. The change in the oscillation pattern with $[BrO_3^-]$.
$[(COOH)_2]=0.03$ mol dm^{-3}, $k_{13}=0.075$ s^{-1}. $[BrO_3^-]$ A: 0.006 mol dm^{-3}, B: 0.007 mol dm^{-3}, C: 0.03 mol dm^{-3}, D: 0.04 mol dm^{-3}, E: 0.0425 mol dm^{-3}, F: 0.045 mol dm^{-3}.

10^{-8} mol dm^{-3}, the system started to vary after ca. 15 s and then returned to the reduced steady state after ca. 240 s. When $[Br_2]=5.0\times10^{-9}$ mol dm^{-3}, the system immediately started to vary.

Figure 4 shows the excitability of an oxidized steady state induced by a sudden increase in the concentration of bromine. When $[Br_2]=1.3079\times10^{-4}$ mol dm^{-3}, the system returned to the oxidized steady state with a damped oscillation. When $[Br_2]=1.3080\times10^{-4}$ mol dm^{-3}, the system started to vary after ca. 8 s and returned to the oxidized steady state after ca. 150 s.

Figures 3 and 4 reveal that, when the change in the concentration of bromine is below a certain threshold, [Ce(IV)] and $[Br^-]$ undergo modest changes, while the change in $[Br_2]$ exceeds the threshold, [Ce(IV)] and $[Br^-]$ undergo major changes.

When $[(COOH)_2]=0.001$ mol dm^{-3}. As is shown in Fig. 5, when $[BrO_3^-]=0.002$ mol dm^{-3}, [Ce(IV)] gave rise to a jagged oscillation. When $[BrO_3^-]=0.0003$ mol dm^{-3}, the system stayed much larger in the reduced steady state. The time period of the oscillations was much larger than that when $[(COOH)_2]=0.03$ mol dm^{-3}. The amplitude of the oscillations depended on the concentration of bromate.

Figure 6 depicts the bifurcation diagram of the system studied here. The system could exist in both

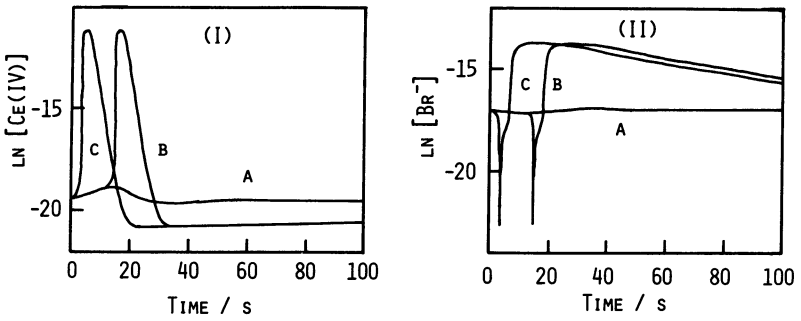

Fig. 3. The excitability of the reducd steady state induced by the changes in $[Br_2]$.
$[BrO_3^-]=0.006$ mol dm^{-3}, $[(COOH)_2]=0.03$ mol dm^{-3}, $k_{13}=0.075$ s^{-1}, $[Br_2]_{ss}=1.2857\times10^{-8}$ mol dm^{-3}. $[Br_2]$ A: 1.02×10^{-8} mol dm^{-3}, B: 1.01×10^{-8} mol dm^{-3}, C: 5.00×10^{-9} mol dm^{-3}.

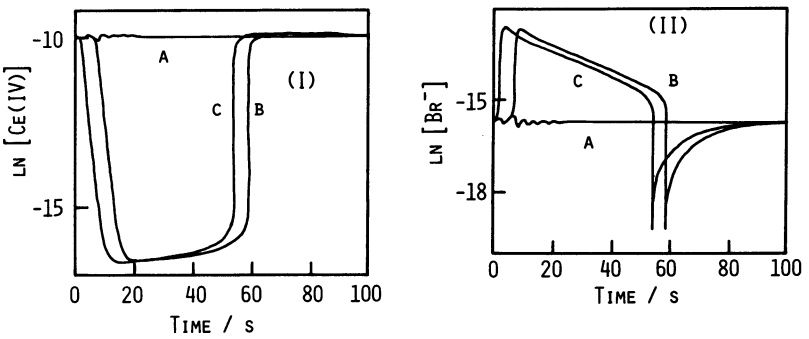

Fig. 4. The excitability of the oxidized steady state induced by the changes in $[Br_2]$.
$[BrO_3^-]=0.045$ mol dm^{-3}, $[(COOH)_2]=0.03$ mol dm^{-3}, $k_{13}=0.075$ s^{-1}, $[Br_2]_{ss}=1.2751\times10^{-4}$ mol dm^{-3}. $[Br_2]$ A: 1.3079×10^{-4} mol dm^{-3}, B: 1.3080×10^{-4} mol dm^{-3}, C: 1.3250×10^{-4} mol dm^{-3}.

reduced and oxidized steady states and in the oscillatory state, but no bistability was found in the system.

Figure 7 shows the relationship between the concentration of bromate and the time period of the oscillations. Up to now, the bromate-cerium-oxalic acid system has been simulated by using Reactions 17 and 18 instead of Reactions 7—12:[7,8]

$$HOBr + (COOH)_2 \longrightarrow Br^- + 2CO_2 + H_2O + H^+ \quad (17)$$

$$Ce(IV) + (COOH)_2 \longrightarrow Ce(III) + \text{inert products} \quad (18)$$

The model did not reproduce the characteristic oscillations of the system. That is, it has been reported that the experimental value of τ is dependent on the bifurcation parameters, such as k_{13} and $[BrO_3^-]$,[6,7] but the τ estimated from the model depended little on the parameters. Figure 7(A), which was obtained according to the model, was also not consistent with the experimental results reported by Gáspár and Galambosi.[7] Figures 7 (B) and 7 (C) were obtained on the basis of Reactions 1—13. The dependency of the time period of the oscillations on $[BrO_3^-]$ (Fig. 7(B)), as well as that of τ on the bifurcation parameters (Figs. 1 and 2) and the excitability (Figs. 3 and 4), were qualitatively consistent with the experimental results. However, the bistability could not be reproduced, and the rate constant of the bromine removal (k_{13}) and the amplitudes of the oscillations in Figs. 1 and 2 were larger than the values obtained experimentally. The failure to reproduce the bistabi-

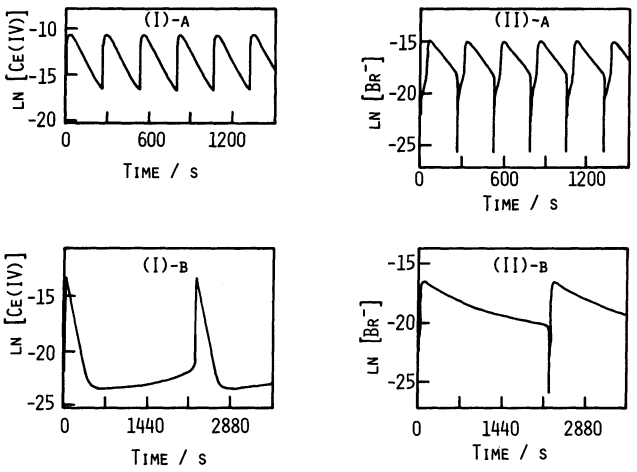

Fig. 5. The oscillations when $[(COOH)_2]=0.001$ mol dm^{-3} and $k_{13}=0.075$ s^{-1}.
A: $[BrO_3^-]=0.002$ mol dm^{-3}, B: $[BrO_3^-]=0.0003$ mol dm^{-3}.

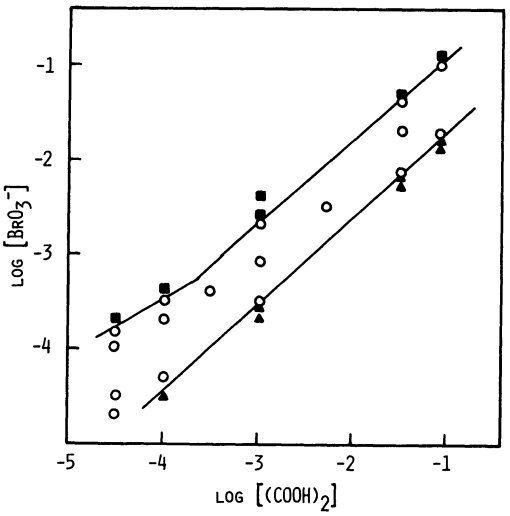

Fig. 6. The bifurcation diagram when $k_{13}=0.075$ s^{-1}.
■: oxidized steady state, ▲: reduced steady state, O: oscillatory state.

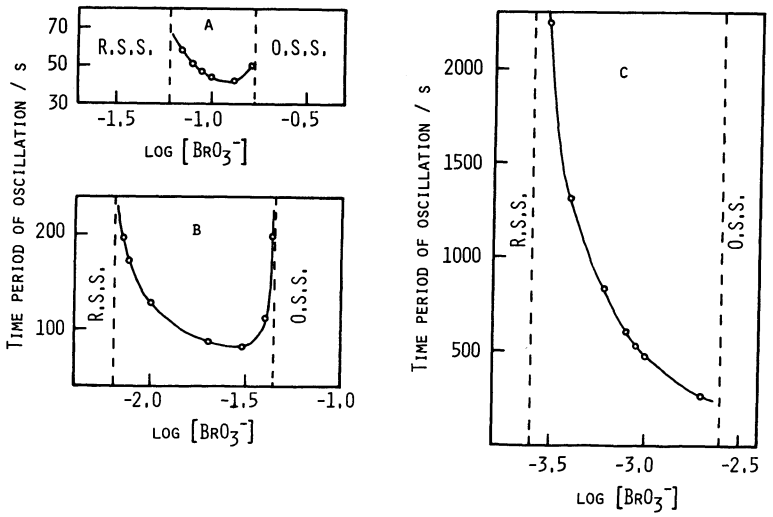

Fig. 7. The relationship between the time period of the oscillations and $[[BrO_3^-]$.
A: $[(COOH)_2]=0.05$ mol dm^{-3}, $k_{13}=0.13$ s^{-1}. Calculated by using Reactions 1—6, 13, 17, and 18.
B: $[(COOH)_2]=0.03$ mol dm^{-3}, $k_{13}=0.075$ s^{-1}. C: $[(COOH)_2]=0.001$ mol dm^{-3}, $k_{13}=0.075$ s^{-1}.

lity may be ascribed to inaccuracy in the rate constants in Table 1, for it seems difficult to determine the values of all the rate constants precisely. For the FKN mechanism, a revised set of the rate constants was developed.[15]

Maselko proposed four fundamental possibilities for bifurcation, leading from a steady state to a stable periodic orbit, and vice versa, in chemical systems.[16] There is a controversy as to the bifurcations in the classical BZ reaction.[17,18] In the bromate-cerium-oxalic acid system, the transitions from the monostable steady states to the oscillatory state have been reported to occur via saddle-node infinite-period (SNIPER) bifurcation.[6,7] The simulation in this study gave suggestions as to the bifurcations in the system. That is, the results in Figs. 1, 2, and 7(B) (the time period and the amplitude of the oscillations), and the fact that there is no hysteresis near the bifurcation points when $[(COOH)_2]=0.03$ mol dm^{-3}, were consistent with SNIPER bifurcation. On the other hand, when $[(COOH)_2]=0.001$ mol dm^{-3}, hysteresis was observed in the transition between the oxidized steady state and the oscillatory state, and not in the transition between the reduced steady state and the oscillatory state. These and the oscillation patterns in Fig. 5 suggest that the former transition occurs via subcritical Hopf bifurcation, and the latter transition, via SNIPER bifurcation.

In the reaction mechanism used in this study, HOBr is reduced by oxalic acid through both Reactions 17 and 19, under the stationary-state approximation for $HCO_2\cdot$ and $Br\cdot$ radicals:[19]

$$2HOBr + (COOH)_2 \longrightarrow Br_2 + 2CO_2 + 2H_2O \quad (19)$$

It is interesting that we can simulate the oscillation patterns of the bromate-cerium-oxalic acid system when the mechanism presented here is used, but not when Reactions 17 and 18 are used instead of Reactions 7—12. In bromate-cerium-oxalic acid-cyclohexanone system, more complicated bifurcation phenomena were observed.[20] Thus, the oscillation behavior in the bromate-cerium-oxalic acid system seems to be sensitive to the feed-back part of the reaction mechanism.

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