The Mixed Bromate Oscillator by 1,4-Cyclohexanedione and 1,3-Cyclohexanedione in a Flow System

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We have studied the oscillatory behaviors of cyclohexanedione(CHD)-BrO_3^--Ce^{4+}-H^+ reaction in a flow system and we have found a chaotic regime if a mixture of 1,4-cyclohexanedione(1,4-CHD) and 1,3-cyclohexanedione(1,3-CHD) is used as an organic reductant in the reaction system. The mixing ratio between the two substrates of 1,4-CHD and 1,3-CHD were changed under the condition of fixed total CHD concentration. The oscillatory behaviors of the mixed system were also changed by the flow rate variations. We have obtained various oscillation patterns by the mixed substrate reaction system *i.e.*, CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in a flow condition. An attempt was also made to simulate the experimentally obtained results.

Introduction

The Belousov-Zhabotinsky (BZ) reaction,[1,2] which is understood as an oscillatory oxidation of a one-electron redox couple catalyst such as Ce^{3+}/Ce^{4+},[1] Fe^{2+}/Fe^{3+},[3] and Ru^{2+}/Ru^{3+} [4] by a bromate ion in the presence of an organic reductant in acdic condition, has been widely employed for temporal[5] and spatio-temporal[6] pattern formations. Among these reactions, the system using malonic acid as an initial reductant substrate and a cerium ion as a metal catalyst has been used most frequently and has been studied well for the oscillating reactions.

Recently, it has been studied for the modified BZ reaction systems in which malonic acid is replaced by other organic compounds.[5,7-12] The BZ reaction with malonic acid as an initial substrate has an important drawback which is producing carbon dioxide gas bubbles[7] in the oscillating reaction process. Some attempts have been made to develop gas-free versions for the BZ oscillation reaction. The diketonic compound such as cyclohexanedione (CHD)[5,7-12] is well known for being suitable for the gas-free[10] BZ oscillation systems, and the reactions using the CHD compound of 1,4-cyclohexanedione or 1,3-cyclohexanedione as an initial substrate for the BZ type reaction have been studied previously.[7-12]

Szalai *et al.*[13] have reported recently on the detailed chemical mechanism of 1,4-cyclohexanedione-Bromate-Acid oscillatory system, and they have explained the mechanistic model of the system with full rate constants in the detailed mechanism.

Jang *et al.*[14] have compared the characteristic oscillatory behaviors of 1,4-CHD/BrO_3^-/Ce^{4+}/H^+ and 1,3-CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in a batch system and also have studied varying oscillatory behaviors of CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction by a variation of an initial mixing ratio between 1,4-CHD and 1,3-CHD as a mixed substrate.

In this paper we report our investigations on varying oscillatory behaviors of the CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in a flow condition. The oscillatory behaviors have been varied by an initial mixing ratio between 1,4-CHD and 1,3-CHD with a similar method in a batch system of previous report.[14] However in this flow experimental study, we have used two experimental parameters, i.e., by coupling an initial mixing ratio value between 1,4-CHD and 1,3-CHD and the flow rate value in the continuous flow stirred tank reactor (CSTR)[2] experiments. In this system it was possible to vary the oscillation patterns of CHD/BrO_3^-/Ce^{4+}/H^+ reaction more readily than in the batch system. And we have obtained some more complex oscillation patterns including a chaotic regime than the patterns which have been obtained in the separate 1,4-CHD/BrO_3^-/Ce^{4+}/H^+ or 1,3-CHD/BrO_3^-/Ce^{4+}/H^+ reaction in the CSTR experiments.

An attempt also has been made to simulate the experimental results of the CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction varying by an initial mixing ratio in the CSTR experiments. The simulations are based on the Field-Körös-Noyes (FKN) mechanism[15] of the BZ reaction in which malonic acid has been used as an organic reductant. We have used the FKN mechanism with a small modification by replacing malonic acid as a mixed substrate using 1,4-CHD and 1,3-CHD. In this simulation we have focused on the organization of a modified model in which oscillatory behaviors of CHD/BrO_3^-/Ce^{4+}/H^+ reaction system are able to be varied by an initial mixing ratio between 1,4-CHD and 1,3-CHD and by the flow rate in the CSTR experiments. From the simulational study we have obtained varying oscillatory behaviors by coupling the two parameters together. However, an elaborate result being consistent with the experimental results has not been obtained because we have used the modified FKN mechanism in which mixed CHD substrate has been used instead of malonic acid as an initial substrate and because the detailed reaction mechanism for the CHD/BrO_3^-/Ce^{4+}/H^+ reaction system has not been known well. Continuous simulation study for more elaborate result should be done by using some more detailed reaction mechanism and by adjusting the elementary rate constants accurately for the mechanism.

Experimental Section

The working solutions were prepared from stock solutions

of 0.6 M $NaBrO_3$ (Junsei Chemical, 99%), 0.2 M 1,4-cyclohexanedione (Fluka, 98%), 0.2 M 1,3-cyclohexanedione (Fluka, 97%), 2.4×10^{-3} M cerous sulfate (Fluka, 97%), and 2 M sulfuric acid (Fluka, 98%). The initial mixing amount ratios between two substrates of 1,4-cyclohexanedione and 1,3-cyclohexanedione were determined by a volume ratio of adding stock solutions or by an initial ratio of reaction concentration between the two substrates. All reagents were used in their commercial grade without further purification.

The continuous flow stirred tank reactor (CSTR) experiments were performed in a cylinder type glass beaker of 25ml capacities with four inlets and one outlet under well-stirred conditions using a magnetic stirring hot plate (Cole-Parmer, G-04812-00). The reaction temperature was controlled at 35±0.5 °C with a temperature probe (Cole-Parmer, G-04812-20). The flow rate equals to the reverse of the residence time of the mixed solution in the reacting beaker.

Two types of experimental methods have been used for variation of mixing ratio between 1,4-CHD and 1,3-CHD substrate in the flow system. A peristaltic pump of four channels (Wiz, 1610-004) in which each channel is for the injection of 1,4-CHD, 1,3-CHD, $NaBrO_3$ substrate, and mixed substrate of cerous sulfate and sulfuric acid solution was used in one kind of experiments. In this case a same flow rate for all channels has been used, thus an initial mixing ratio between the two substrates are determined by an initial concentration of each substrate being injected into the reactor. In the other complementary CSTR experiments, two syringe pumps (model No. KASP005/150MT) were used in addition with a peristaltic pump. The two substrates of 1,4-CHD and 1,3-CHD solution were injected into the reactor by the syringe pumps. An initial mixing ratio between the two substrates were varied by the flow rate of injecting solution under a fixed total flow rate. In this case it is possible to vary an initial mixing ratio at any time while the oscillation reaction progresses differently with the first CSTR system in which the mixing ratio between 1,4-CHD and 1,3-CHD could not be varied in the medium of reaction.

The oscillation was followed by monitoring the changes in the bromide ion concentration with a bromide ion-selective electrode (Orion, 9435BN), and a reference electrode (Orion, L-05710-10) which is a double junction of Ag/AgCl saturated with KCl as an inner solution and 1 M sulfuric acid as an outer solution, respectively. The potential of the electrode was monitored with a pH/ISE meter (Orion, 940) and recorded with a multi-channel recorder (Cole-Parmer, G08373-20). The overall scheme of an experimental apparatus for the CSTR experiments are well described in Figure 1.

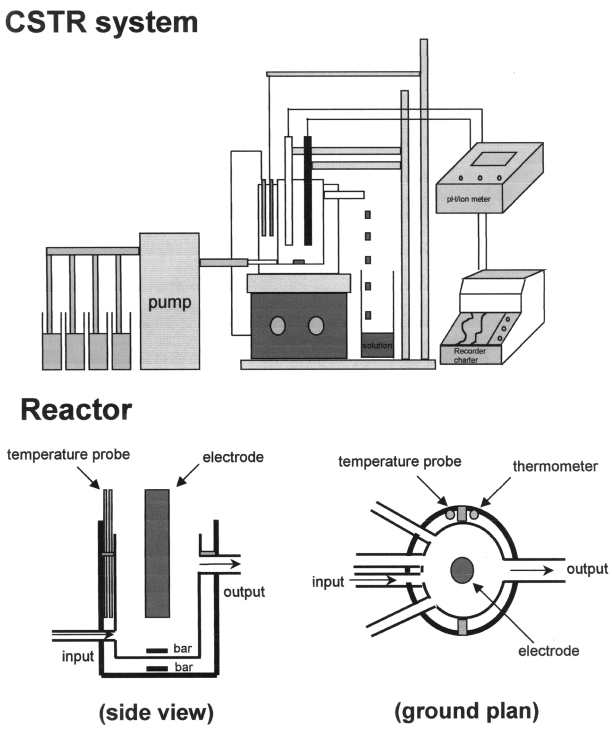

Figure 1. The overall scheme of the experimental apparatus for the continuous flow stirred tank reactor (CSTR) system.

Results and Discussion

Oscillatory Behaviors of 1,4-CHD/BrO_3^-/Ce^{4+}/H^+ and 1,3-CHD/BrO_3^-/Ce^{4+}/H^+ Reaction in a Flow System. Before we study varying oscillatory behaviors of CHD/BrO_3^-/Ce^+/H^+ oscillation reaction by an initial mixing ratio in a flow system, we have compared the two oscillatory behaviors of 1,4-CHD/BrO_3^-/Ce^+/H^+ and 1,3-CHD/BrO_3^-/Ce^+/H^+ oscillation system in a flow system. And we have studied the effect of the flow rate on each reaction system in the CSTR experiments.

Figure 2 shows some examples of the oscillatory behaviors obtained by 1,4-CHD/BrO_3^-/Ce^{4+}/H^+ and 1,3-CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in the CSTR experiments. The oscillatory behaviors being obtained by the two systems are different in the view of the oscillation period and the amplitude. Periodic or quasiperiodic time series have

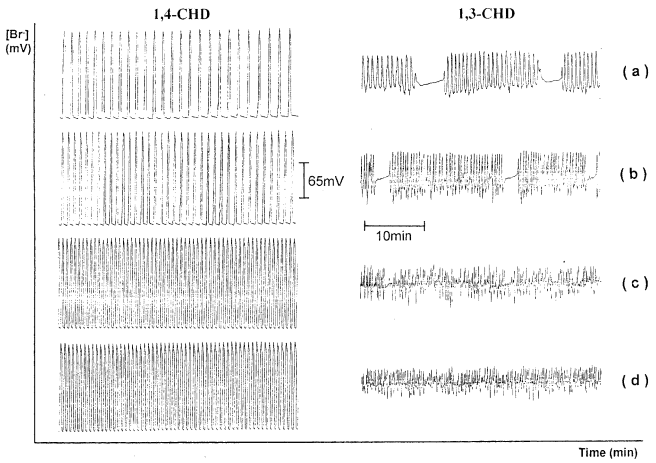

Figure 2. Time series of potential response of bromide concentration in the oscillation reaction of 1,4-CHD/BrO_3^-/Ce^{4+}/H^+ and 1,3-CHD/BrO_3^-/Ce^{4+}/H^+ in the CSTR experiments. The residence times (= 1/flow rate) of total input reactant are as follows: (a) t_{res}=104.6 min. (b) t_{res}=66.0 min. (c) t_{res}=48.2 min. (d) t_{res}=37.9 min. where $[CHD]_0 = 0.07$ M, $[BrO_3^-]_0 = 0.12$ M, $[Ce^{3+}]_0 = 6 \times 10^{-4}$ M, $[H^+]_0 = 1.0$ M.

left diagram of Figure 2. The oscillation patterns do not vary greatly by the flow rate change. The oscillation period decreases in a little by an increase of the flow rate. Bursting or more complex oscillatory behaviors have been obtained in 1,3-CHD reaction system as shown in the right diagrams of Figure 2. The amplitudes in the 1,3-CHD oscillation system are shorter than those in the 1,4-CHD system similarly with the result obtained by Jang *et al*. in the batch experiments.[14] And the oscillations by 1,3-CHD system depend large on the change of the flow rate in the CSTR experiments. The bursting pattern[16] as shown in (a) and (b) at a low flow rate have changed into a complex oscillation as shown in (c) and (d) by an increase of the flow rate.

Varying Oscillatory Behaviors of CHD/BrO_3^-/Ce^{4+}/H^+ Oscillation Reaction by an Initial Mixing Ratio between 1,4-CHD and 1,3-CHD Substrate in a Flow System. Figure 3 shows some examples of the varying oscillatory behaviors of CHD/BrO_3^-/Ce^{4+}/H^+ system by an initial mixing ratio between 1,4-CHD and 1,3-CHD in the CSTR experiments. An initial mixing ratio is varied from (r1) to (r3) at a flow rate value and the flow rate is varied from (a) to (d) at an initial mixing ratio value. Various and complex oscillation patterns have been obtained by changing the mixing ratio and the flow rate together as shown in Figure 3.

At low flow rate, the oscillatory behaviors of the mixed system depend large on the mixing ratio of the two substrates as shown in (a) of Figure 3. The periodic oscillation of (r1) changes into a bursting oscillation as shown in (r3) by an increase of 1,3-CHD. This bursting pattern is similar with the bursting oscillations being obtained in the 1,3-CHD/BrO_3^-/Ce^{4+}/H^+ reaction as shown in Figure 2. If the flow rate increases from (a) to (d), the oscillations change gradually into an aperiodic as shown in (b) and (c). The oscillations have changed eventually into a chaotic with an increase of the flow rate as shown in (r1), (r2), and (r3) in (d) of Figure 3. We are interested with the result that the oscillation pattern in the medium ratio (r2) is affected greatly by the flow rate. The oscillation patterns of (r2) in the flow rate of (c) and (d) are more complex than the oscillation patterns of (r1) or (r3) in the same flow rate. This means that the oscillation patterns of the mixed CHD/BrO_3^-/Ce^{4+}/H^+ oscillation system are able to be varied by a new experimental parameter *i.e.*, an initial mixing ratio between 1,4-CHD and 1,3-CHD substrate.

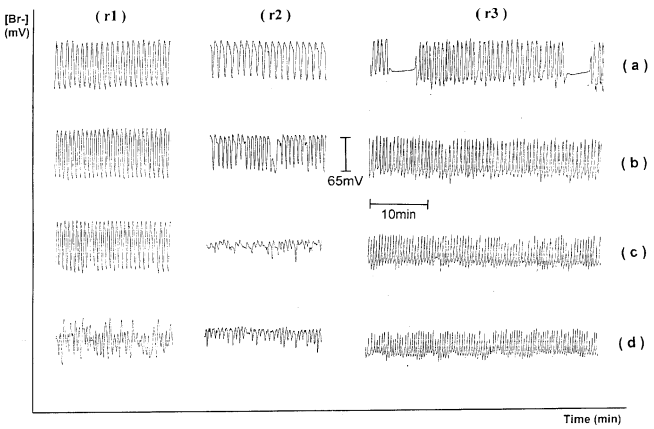

Figure 3. Time series of potential response of bromide concentration of CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in the CSTR experiments when an initial mixing ratio is varied by a concentration of 1,4-CHD and 1,3-CHD. The used condition is as follows: (r1) r_4=0.85, r_3=0.15 (r2) r_4=0.50, r_3=0.50 (r3) r_4=0.15, r_3=0.85. (a) t_{res} = 104.6 min. (b) t_{res} = 66.0 min. (c) t_{res} = 48.2 min. (d) t_{res} = 37.9 min. where $[CHD]_0$(=$[1,4\text{-CHD}]_0$+$[1,3\text{-CHD}]_0$) = 0.07 M, $[BrO_3^-]_0$ = 0.12 M, $[Ce^{3+}]_0 = 6 \times 10^{-4}$M, $[H^+]_0$ = 1.0 M.

Varying Oscillatory Behaviors of CHD/BrO_3^-/Ce^{4+}/H^+ Oscillation Reaction in Complementary CSTR Experiments. In order to verify the dependency of the oscillatory behaviors of the CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction by an initial mixing ratio between 1,4-CHD and 1,3-CHD, we have carried out another type of CSTR experiments. Two syringe pumps were used in addition with a peristaltic pump for the injection of 1,4-CHD and 1,3-CHD substrate into the reactor with different flow rate. An initial mixing ratio between the two substrates were varied by the flow rate differency between the two substrates under the fixed total flow rate condition. In the CSTR experiments for the results as shown in Figure 3, only one four channel peristaltic pump was used and therefore the ratio between the two substrates should be controlled by the initial concentration differency. Figure 4 shows some examples of the oscillatory behaviors obtained by this complementary CSTR system. The arrows indicate the beginning points of flow rate change between 1,4-CHD and 1,3-CHD under a fixed total flow rate. The oscillatory behavior changes into a different pattern some minutes after the flow rate variation has been carried out as shown in (a)-(d) of Figure 4. The time difference between a point of the flow rate change and a point of the oscillation

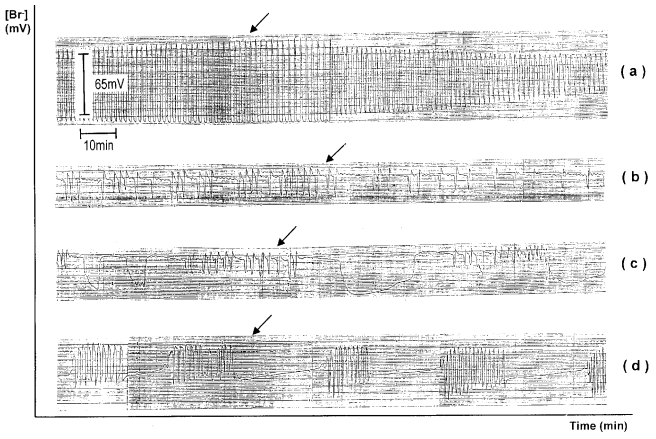

Figure 4. The variation of oscillatory behaviors in the CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in the CSTR experiments when an initial mixing ratio between 1,4-CHD and 1,3-CHD is changed by a flow rate value between the two substrates. The total flow rate of the reacting solution is under a fixed value. The experiments were done at a total flow rate being consistent with t_{res}= 48.2 min. The changing values of mixing ratio at indicated points are as follows: (a) 1.0:0.0 → 0.9:0.1. (b) 0.7:0.3 → 0.6:0.4. (c) 0.5:0.5 → 0.4:0.6. (d) 0.3:0.7 → 0.2:0.8. where the ratio mean the flow rate between 1,4-CHD and 1,3-CHD, and the used initial concentration of reactants are [1,4-CHD] = 0.07 M, [1,3-CHD] = 0.07 M, $[BrO_3^-]$ = 0.10 M, $[Ce^{4+}] = 6 \times 10^{-4}$, and $[H^+]$ = 0.70 M.

pattern change is able to be explained by the time gap needed for the concentration change in the reactor by the flow rate regulation in the injecting system. From these results which have been obtained by this complementary system, we are able to confirm for the facts that the oscillation patterns of CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction have been varied by the control of an initial mixing ratio between 1,4-CHD and 1,3-CHD in the flow system. We have also found that it is possible to vary some oscillation patterns into another patterns while the oscillation reaction is on progressing.

Simulational Results. An attempt also has been made to simulate the experimental results of the CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction varying by an initial mixing ratio between the two substrates of 1,4-CHD and 1,3-CHD in a flow system. We have used the FKN mechanism of the BZ reaction with a small modification. The modified mechanism is introduced in Table 1. The rate constants of for the reactions (R1)-(R6) are referred from the high values of Field-Forstering rate constants. The rate constants of the bromination reaction (R7) and oxidation reaction (RO-4) for the 1,4-CHD substrate are referred from the mechanistic model in the CHD-Bromate-Acid oscillating system reported by Szalai *et al*. recently.[13] The competitive rate constants in the 1,3-CHD substrate *i.e.*, (R8) and (RO-3) have been estimated from the rate constants (R7) and (RO-4) of the 1,4-CHD substrate. A detailed mechanism for the 1,3-CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction has not been known well and the rate constants of the bromination and oxidation reaction also have not been reported. We have considered the structural difference between the two CHDs for the estimation of the rate constants of 1,3-CHD. Only one enolization process is possible for the 1,4-CHD substrate ( ) since four carbons which do not have a ketone group ar ı same position, *i.e.*, , while two processes, and , are possible ir e 1,3-CHD substrate (The er-

Table 1. The modified FKN mechanism for the simulation of oscillatory behaviors of CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in a mixed system of 1,4-CHD and 1,3-CHD as an organic reductant

Reaction	Rate Constants[a]
R1) $Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O$	$k_1 = 8 \times 10^9 M^{-2}s^{-1}$
(R2) $HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$	$k_2 = 2 \times 10^8 M^{-2}s^{-1}$
(R3) $BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr$	$k_3 = 2M^{-3}s^{-1}$
(R4) $2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+$	$k_4 = 4 \times 10^8 M^{-1}s^{-1}$
(R5) $BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2 + H_2O$	$k_5 = 2 \times 10^3 M^{-2}s^{-1}$
(R6) $BrO_2 + Ce^{3+} + H^+ \rightarrow HBrO_2 + Ce^{4+}$	$k_6 = 6 \times 10^5 M^{-2}s^{-1}$
(R7) 1,4-CHD + $Br_2 \rightarrow$ 1,4-BrCHD + $Br^- + H^+$	$k_7 = 1.24 \times 10^3 M^{-1}s^{-1}$
(R8) 1,3-CHD + $Br_2 \rightarrow$ 1,3-BrCHD + $Br^- + H^+$	$k_8 = 4 \times 10^4 M^{-1}s^{-1}$
(RO-4) $2Ce^{4+}$ + 1,4-CHD + 1,4-BrCHD $\rightarrow f_4\ Br^-$	$k_{o4} = 5 \times 10^{-5} M^{-1}s^{-1}$
(RO-3) $2Ce^{4+}$ + 1,3-CHD + 1,3-BrCHD $\rightarrow f_3\ Br^-$	$k_{o3} = 5 \times 10^{-3} M^{-1}s^{-1}$

[a]The rate constants of (R1)-(R6) are referred from the "Hi" values of Field-Forstering rate constants of the FKN mechanism, the rate constants of the bromination reaction (R7) and oxidation reaction (RO-4) for 1,4-CHD substrate are referred from the report by Szalai *et al.*[14] and the rate constants of (R8) and (RO-3) are estimated values.

tion process is related with the partial l ination reaction and oxidation reaction in the BZ type reaction. The experimental results for the oscillatory behaviors of 1,4-CHD/BrO_3^-/Ce^{4+}/H^+ and 1,3-CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in a batch system reported by Jang et al. also support the structural relationship between the two substrates. They have reported a result for a short induction and duration time in the 1,3-CHD oscillation system than in the 1,4-CHD system in same experimental systems. Thus we have used some higher values for the rate constants of the bromination and oxidation reaction in the 1,3-CHD than in the 1,4-CHD reaction.

Then we have constituted a modified Oregonator model for the simulation of oscillatory behaviors of the mixed CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in the CSTR system. The derivation process for three dimensional differential equation used in the simulation is summarized in Appendix (A). The simulation was conducted by the program of *Scientist* using *Episode* integrator. A simulational result for the oscillatory behaviors of the CHD/BrO_3^-/Ce^{4+}/H^+ reaction being varied by the flow rate and by the mixing ratio is shown in (a) and (b) of Figure 5. The initial mixing ratio is varied from (r1) to (r4) and is biased for 1,3-CHD

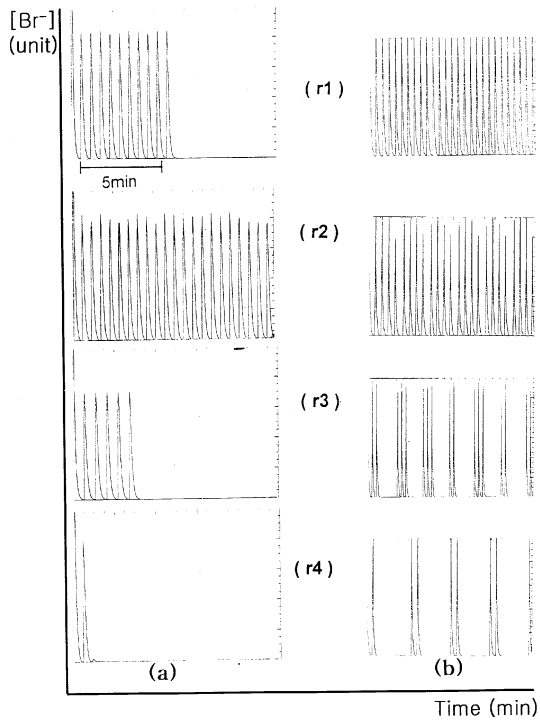

Figure 5. The varying oscillatory behaviors obtained by the simulation of the mixed CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in the CSTR system. The used conditions for an initial mixing ratio are as follows: (r1) r_4=0.70, r_3=0.30 (r2) r_4=0.40, r_3=0.60. (r3) r_4=0.25, r_3=0.75 (r4) r_4=0.10, r_3=0.90. where r_4 and r_3 mean the initial mixing ratio between 1,4-CHD and 1,3-CHD, *i.e.*, r_4=[1,4-CHD]$_0$/[CHD]$_0$, and [1,4-CHD]$_0$ and [CHD]$_0$ mean the initial concentration of 1,4-CHD and total CHD being injected into the reactor. The used total flow low rate in this simulation is t_{res} = 100.0 in case of (a) and t_{res} = 73.5 min in case of (b).

from (r1) to (r4). As shown in the simulational results, the oscillation patterns are affected much by the mixing ratio in the high flow rate condition as shown in (b) of Figure 5. Unperiodic or bursting patterns have been obtained by the variations of an initial mixing ratio from (r1) to (r4) in high flow rate as shown in (b) of Figure 5 while small pattern variation has been shown in (a). However, in the case of (a) *i.e*., in the low flow rate condition the period of oscillation duration decreased greatly when the mixing ratio is biased for 1,3-CHD from (r2) to (r4). This simulational result is similar with the previous experimental result in a batch condition[14] in which the duration of oscillation in 1,3-CHD oscillation reaction is shorter than that in the 1,4-CHD reaction. After all, the simulation results show qualitatively depending oscillation patterns of the CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction on the two experimental parameters *i.e*., initial mixing ratio and flow rate in a flow system. An accurate result being consistent with the experimental behaviors have not been obtained by this simulational study since the used conditions for the simulational studies are not correspondent with the experimentals and since the detailed mechanism has not been known well for the mixed reaction of CHD/BrO_3^-/Ce^{4+}/H^+. However we expect some more elaborate result for the oscillation reaction system of CHD/BrO_3^-/Ce^{4+}/H^+ by adjusting the reaction mechanism in detail and by using an accurate rate constants for elementary mechanistic reactions.

Conclusions

We have studied on varying oscillatory behaviors of CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction by a fine control of an initial mixing ratio between 1,4-CHD and 1,3-CHD and by a variation of the flow rate in the CSTR system. Various oscillation patterns from a periodic to a chaotic are obtained by a change of an initial mixing ratio between 1,4-CHD and 1,3-CHD substrate. An attempt was also made to simulate the experimentally obtained results.

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Appendix (A). The derivation of modified Oregonator model for the mixed CHD/BrO_3^-/Ce^{4+}/H^+ oscillation reaction in the CSTR system.

The Oregonator model for the modified FKN mechanism in the Table 1 is able to be simplified as followings:

$$\begin{aligned}
&A + Y + 2H \rightarrow X + P && \text{rate} = k_3H^2AY\\
&X + Y + H \rightarrow 2P && \text{rate} = k_2HXY\\
&A + X + H \rightarrow 2X + 2Z && \text{rate} = k_5HAX\\
&2X \rightarrow A + P && \text{rate} = k_4X^2\\
&B_4 + Z \rightarrow f_4Y && \text{rate} = k_{o4}B_4Z\\
&B_3 + Z \rightarrow f_3Y && \text{rate} = k_{o3}B_3Z
\end{aligned} \qquad \text{(A-1)}$$

where A=[BrO_3^-], Y=[Br^-], H=[H^+], X=[$HBrO_2$], P=[HOBr], B_4=[1,4-CHD+1,4-BrCHD], B_3=[1,3-CHD+1,3-BrCHD], and Z=[Ce^{4+}], and k_{o4} and k_{o3} equal to the oxidation reaction rate constants of 1,4-CHD and 1,3-CHD including a brominated and an unbrominated compound. The f_4 and f_3 mean the stoichiometric factors for the Br^- regeneration in the oxidation reaction of 1,4-CHD and 1,3-CHD in the oscillation reaction process.

The differential equation for this model with three variables in the CSTR system is written as followings:

$$\begin{aligned}
dX/dT &= k_3H^2AY - k_2HXY + k_5HAX - 2k_4X^2 - k_fX\\
dY/dT &= -k_3H^2AY - k_2HXY + f_4k_{o4}B_4Z + f_3k_{o3}B_3Z + k_f(Y_i - Y)\\
dZ/dT &= 2k_5HAX - k_{o4}B_4Z - k_{o3}B_3Z + k_f(Z_i - Z)
\end{aligned} \qquad \text{(A-2)}$$

where k_f is the flow rate of reaction solution which equals to the reverse value of the residence time in the reactor, and Y_i and Z_i are input concentrations of Br^- and Ce^{4+} in the CSTR experiments.

Then, the scaled differential equation is summarized as followings:

$$\begin{aligned}
dx/dt &= \varepsilon\,(y - xy + x - qx^2 - k_{fx}x)\\
dy/dt &= 1/\varepsilon\,[-y - xy + \{1 + (f_rk_{or} - 1)r_3\}z + k_{fy}(y_i - y)]\\
dz/dt &= \omega\ [2x - \{1 + (k_{or} - 1)r_3\}z + k_{fz}(z_i - z)]
\end{aligned} \qquad \text{(A-3)}$$

the scaling factors used in the scaled differential equation are

$$t = \frac{T}{T_0},\quad T_0 = \frac{1}{(k_3k_5H^3A^2)^{1/2}}$$

$$x = \frac{X}{X_0},\quad X_0 = \frac{k_3HA}{k_2}$$

$$y_i = \frac{Y_i}{Y_0},\ y = \frac{Y}{Y_0},\ Y_0 = \frac{k_5 A}{k_2}$$

$$z_i = \frac{Z_i}{Z_0},\ Z_0 = \frac{k_3 k_5 H^2 A^2}{f_4 k_2 k_{o4} B}$$

$$\varepsilon = \left(\frac{k_5}{k_3 H}\right)^{1/2},\ q = \frac{2k_3 k_4}{k_2 k_5}$$

$$\omega = \left(\frac{f_4^2 k_{o4}^2 B^2}{k_3 k_5 H^3 A^2}\right)^{1/2}$$

$$k_{fx} = \frac{k_f}{k_5 HA},\ k_{fy} = \frac{k_f}{k_3 H^2 A},\ k_{fz} = \frac{k_f}{k_4 k_{o4} B}$$

$$f_r = \frac{f_3}{f_4},\ k_{or} = \frac{k_{03}}{k_{04}},\ r_3 = \frac{B_3}{B}$$

$B = B_4 + B_3$, k_f = flow rate = 1/(residence time).