The Variation of Oscillatory Behaviours in the Oscillating Reaction System of CHD/BrO₃⁻/Ce⁴⁺/H⁺

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The Belousov-Zhabotinskii (BZ) reaction, which is composed of a bromate-organic acid-metal catalyst and an acidic solution is a commonly employed chemical oscillating reaction system. Cyclohexanedione (CHD) has been used as an initial organic substrate in oscillation systems. We studied each system of 1,4-CHD/BrO₃⁻/ Ce⁴⁺/H⁺ and 1,3-CHD/BrO₃⁻/Ce⁴⁺/H⁺ oscillating reactions, and studied the control of oscillating characters in a CHD/BrO₃⁻/Ce⁴⁺/H⁺ batch system using a mixed substrate of 1,4-CHD and 1,3-CHD under a fixed total CHD concentration. In the mixed reactions, 1,4-CHD was used as a main substrate and small amounts of 1,3-CHD were used in order to vary the oscillatory behaviours by changing the mixing amount ratio of two substrates.

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 acidic condition, has been widely employed for temporal[5] and spatio-temporal[6] pattern formations. Among these reactions, the system using malonic acid[7] as an initial reductant substrate and a cerium ion as a metal catalyst has been used most frequently and has been studied well for oscillating reactions.

Recently, it has been studied for observing the chemical oscillation in the modified BZ reaction in which malonic acid is replaced by other organic compounds[5,8-10] since the BZ reaction with malonic acid as an initial substrate has a drawback, which is producing carbon dioxide gas bubbles[11] in the oscillating reaction process. The diketonic compounds such as cyclohexanedione (CHD)[5,8-10] are well known for being suitable for the gas-free[10] oscillating reactions, and the reactions using the CHD compound as an initial substrate for the BZ type reaction have been studied previously.

Farage and Janjic[12] have reported on the uncatalysed oscillatory oxidation of 1,4-cyclohexanedione(1,4-CHD) by a bromate ion in acidic solution. Kurin-Csörgei *et al.*[8,9] give a full explanation of the mechanism in which simple gaseous carbon dioxide can not be found among the reaction products of the 1,4-CHD-bromate ion-sulfuric acid reaction system.

L.Treindl and V.zváč[13] have reported on the effect of mechanical stirring on oscillatory behaviour using 1,3-cyclohexanedione(1,3-CHD) as an initial substrate for the BZ type reaction.

In the present paper we report our investigations of oscillatory behaviours in batch reactions of a CHD/BrO₃⁻/Ce⁴⁺/ H⁺ system using a mixed substrate of 1,4-CHD and 1,3-CHD. By mixing the two CHDs as an initial substrate for the BZ type reaction, we were able to vary the oscillatory behaviours of the CHD/BrO₃⁻/Ce⁴⁺/H⁺ system by a ratio of the initial mixing amount of 1,4-CHD and 1,3-CHD under fixed total CHD concentration.

The oscillatory behaviours of each system using 1,4-CHD and 1,3-CHD as an initial substrate were compared separately in the same experimental conditions prior to the mixed reactions. In the mixed reactions, 1,4-CHD was used as a main substrate and small amounts of 1.3-CHD were used in order to vary the oscillatory behaviours by changing the mixing ratio of two substrates.

Experimental

Materials. The working solutions were prepared from five stock solutions of 0.6 M NaBrO₃ (Junsei chemical, 99%), 0.2 M 1,4-cyclohexanedione (Fluka, 98%), 0.2 M 1,3-cyclohexanedione (Fluka, 98%), 2.4×10^{-3} M cerous ion being prepared from $Ce_2(SO_4)_3$ (Fluka, 97%), and 2 M sulfuric acid (Fluka, 98%). The initial mixing amount ratios of two substrates with 1,4-CHD and 1,3-CHD were determined by the volume ratio of adding stock solutions. All reagents were used in their commerical grade without further purification.

Procedures and Apparatus. The batch experiments were performed in cylinder type glass beakers of 30 mL capacity under well-stirred batch conditions using a magnetic stirring hot plate (Cole-Parmer, G-04812-00) and thermostated at 35 ± 0.5 °C with a temperature probe (Cole-Parmer, G-04812-20). The reactions were followed by monitoring the changes in the bromide concentration with a bromide ion-selective electrode (Orion, 9435BN) and a reference electrode which was a double junction of Ag/AgCl saturated with KCl as an inner solution and 1 M sulfuric acid as an outer solution (Orion, L-05710-10), respectively. The potential of the electrode was monitored with a pH/ISE meter (Orion, 940) and recorded with a multi-channel recorder (Cole-Parmer, G-08373-20).

Experimental Results

Oscillatory Behaviours of each system, 1,4-CHD/ BrO₃⁻/Ce⁴⁺/H⁺ and 1,3-CHD/BrO₃⁻/Ce⁴⁺/H⁺. For studying and comparing the two oscillating reactions with 1, 4-CHD and 1,3-CHD as initial substrates in the system of CHD/BrO₃⁻/Ce⁴⁺/H⁺, we have followed each reaction separately in the same reaction conditions prior to the mixing systems of the two CHDs.

Figure 1 and Figure 2 show some examples of potential

recordings of time response by the bromide ion selective electrode in the reaction systems of 1,4-CHD/BrO_3^-/Ce^{4+}/H^+ and 1,3-CHD/BrO_3^-/Ce^{4+}/H^+, respectively. The two oscillating systems have shown some different oscillatory behaviours as compared in (a)-(d) of Figure 1 and Figure 2.

The initial concentration of the hydrogen ion needed for the oscillatory behaviour was about two times more in the 1,3-CHD substrate oscillating systems than in the 1,4-CHD reaction systems with the same concentrations of CHD and other reagents as compared in the reaction conditions of (a)-(d) of Figures 1 and 2. Figures 1(a) and 2(a) show the different hydrogen ion concentration needed for an oscillatory behaviour under the same concentrations of other initial reagents. However, at the hydrogen ion concentration over a limit value, the oscillatory behaviours of the 1,3-CHD and 1,4-CHD system could be obtained equally under the same hydrogen ion concentration as shown in Figure 1(b) and Figure 2(b). Figure 2(c) of the 1,3-CHD system could fully explain the result of no periodic oscillation waves in contrast to the result of the 1,4-CHD system as shown in Figure 1(c). At the lower CHD initial con-

centration, the periodic oscillation waves were also obtained under the same hydrogen ion concentration of 0.5 M as shown in Figures 1(d) and 2(d).

The oxidation rates of the CHD substrate in the FKN[7] mechanism also would be different between the two reaction systems. The different oxidation rates of the 1,3-CHD reaction and the 1,4-CHD reaction as an initial substrate would affect the induction period of the two oscillatory behaviours.

The induction period in the 1,4-CHD oscillating reaction system was very long compared to that in the 1,3-CHD reaction system in which the oscillation begins as soon as the reactants are mixed in the reactor. Periodic or quasi-periodic oscillations generally continued a long time in the 1,4-CHD reaction while the oscillations in the 1,3-CHD reaction were much briefer. The amplitude of the 1,3-CHD system diminished gradually with the reaction time and the oscillation period was short in the 1,3-CHD reaction compared to that in the 1,4-CHD system. The oscillatory behaviours of each reaction system under the same experimental
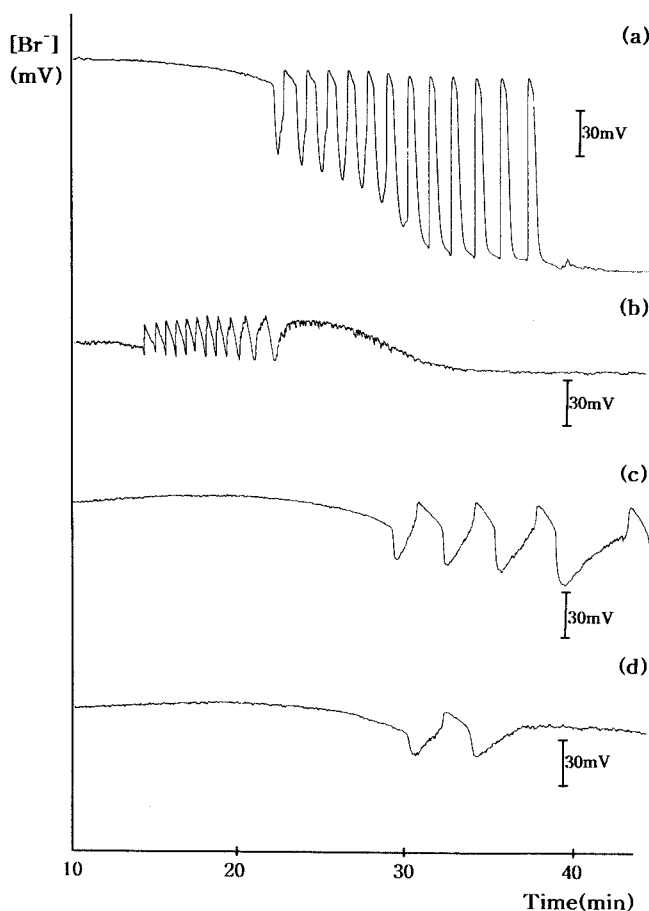

Figure 1. Time series of potential response of bromide concentration in the oscillating reaction system of 1,4-CHD/BrO_3^-/Ce^{4+}/H^+. The variation of oscillatory behaviours by the initial reagent conditions are as follows: (a) [1,4-CHD]$_0$=0.05 M, [BrO_3^-]$_0$=0.15 M, [Ce^{3+}]$_0$=6×10^{-4} M, [H^+]$_0$=0.5 M. (b) [1,4-CHD]$_0$=0.05 M, [BrO_3^-]$_0$=0.15 M, [Ce^{3+}]$_0$=6×10^{-4} M, [H^+]$_0$=1.5 M. (c) [1,4-CHD]$_0$=0.02 M, [BrO_3^-]$_0$=0.15 M, [Ce^{3+}]$_0$=6×10^{-4} M, [H^+]$_0$=0.5 M. (d) [1,4-CHD]$_0$=0.015 M, [BrO_3^-]$_0$=0.15 M, [Ce^{3+}]$_0$=6×10^{-4} M, [H^+]$_0$=0.5 M.
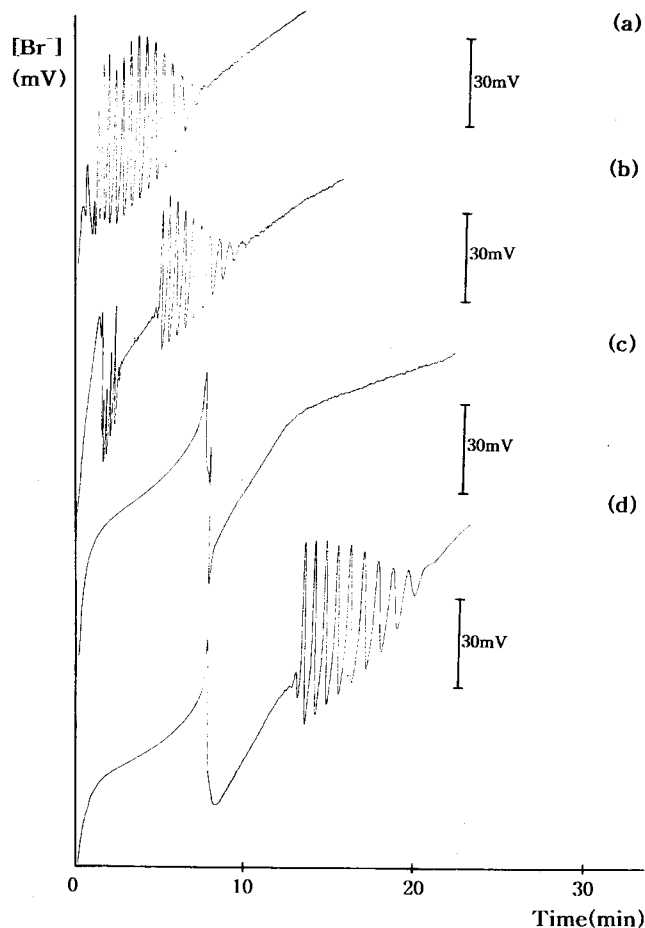
Figure 2. Time series of potential response of bromide concentration in the oscillating reaction system of 1,3-CHD/BrO_3^-/Ce^{4+}/H^+. The variation of oscillatory behaviours by the initial reagent conditions are as follows: (a) [1,3-CHD]$_0$=0.05 M, [BrO_3^-]$_0$=0.15 M, [Ce^{3+}]$_0$=6×10^{-4} M, [H^+]$_0$=2.0 M. (b) [1,3-CHD]$_0$=0.05 M, [BrO_3^-]$_0$=0.15 M, [Ce^{3+}]$_0$=6×10^{-4} M, [H^+]$_0$=1.5 M. (c) [1,3-CHD]$_0$=0.02 M, [BrO_3^-]$_0$=0.15 M, [Ce^{3+}]$_0$=6×10^{-4} M, [H^+]$_0$=0.5 M. (d) [1,3-CHD]$_0$=0.015 M, [BrO_3^-]$_0$=0.15 M, [Ce^{3+}]$_0$=6×10^{-4} M, [H^+]$_0$=0.5 M.

Table 1. Summary and comparison of oscillation patterns between the two oscillating reactions of 1,4-CHD and 1,3-CHD in the same experimental conditions as shown in Figure 1 and Figure 2

	1,4-CHD/BrO_3^-/ Ce^{4+}/H^+	1,3-CHD/ BrO_3^-/Ce^{4+}/H^+
Induction period (τ_{ind}, min)	14.0^a-30.5^b	1.0^c-7.5^b
Oscillation preiod (1/v, min)	0.73^a-4.50^b	0.47-0.94
Amplitude (A, mV)	27.5^a-121.0^b	52.3-60.5
Duration (D, min)	8.0-17.5	7.0-8.5

^{a}[H^+]$_0$=1.5 M. ^{b}[H^+]$_0$=0.5 M. ^{c}[H^+]$_0$=2.0 M. The initial concentration ranges of reagents used in the two reaction systems are as follows:

[1,4-CHD]$_0$=0.015-0.050 M   [1,3-CHD]$_0$=0.015-0.050 M
[BrO_3^-]$_0$=0.15 M   [BrO_3^-]$_0$=0.15 M
[Ce^{3+}]$_0$=6×10^{-4} M   [Ce^{3+}]$_0$=6×10^{-4} M
[H^+]$_0$=0.5-1.5 M   [H^+]$_0$=0.5-2.0 M

conditions are compared in Figures 1 and 2, and summarized in Table 1.

By comparing the induction period, duration time, and oscillation period of the two oscillation systems, we could approximate that the rate constants of the enolization and the oxidation reaction in the FKN mechanism would be large values for the 1,3-CHD reaction system.

Mixed systems of CHD(1,4-CHD+1,3-CHD)/ BrO_3^-/Ce^{4+}/H^+. Figure 3 shows some examples of oscillatory behaviours in the oscillating reaction when 1,4-CHD and 1,3-CHD are mixed as an initial substrate. The oscillatory behaviours varied according to the initial mixing amount ratio between the two substrates as shown in (a)-(e) of Figure 3. The initial concentrations of the reagents which were used were fixed at the same values throughout all the reactions in which the ratio varied. The ratios between the two CHDs were changed under the fixed total CHD concentration of the two mixing substrates.

We used 1,4-CHD as a main substrate since the oscillatory behaviours did not occur with the small hydrogen ion concentration used in our experimental conditions if the 1,3-CHD was used as a main substrate.

We were interested in the oscillatory behaviour which divided into two oscillation patterns, as shown in the ratio (d) of Figure 3, in which the ratio of 1,4-CHD is 0.88. From the divided pattern of the ratio (d), we could see that the former would occur from the action of the 1,3-CHD in the mixed substrate and the latter from the 1,4-CHD when we regarded the characters of the two oscillatory behaviours in the case where the two were used separately. The induction period and the oscillation period of the former are similar to the behaviours of the 1,3-CHD system as shown in Figure 2, and those of the latter are similar to the 1,4-CHD system as shown in Figure 1.

Some changes in the initial mixing ratio of the two substrates brought about different oscillatory behaviours. A small decrease of the mixing ratio in the 1,4-CHD concentration from 0.88 to 0.84 as shown in ratio (c) derived only one oscillating pattern. This tendency of not dividing is more apparent in the reaction in which the 1,4-CHD concentration is decreased more as shown in ratio (b) of 0.80. We were also very interested in the periodic oscillation by
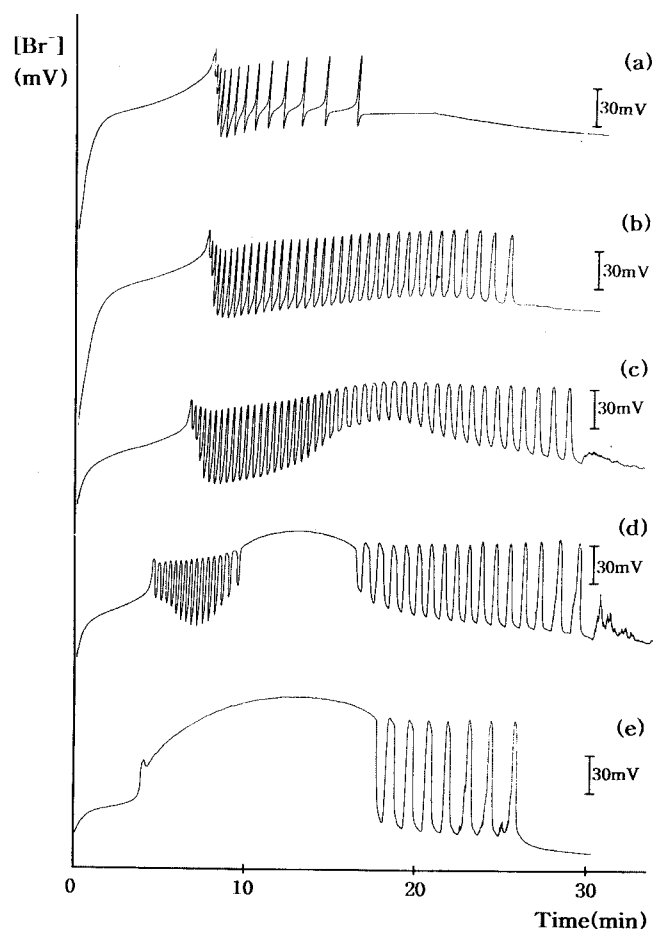

Figure 3. Time series of potential response of bromide concentration in the mixed reaction system of 1,4-CHD and 1,3-CHD as an initial substrate in the reaction of CHD/BrO_3 /Ce^{4+}/H^+. The initial mixing ratio (r_i=[1,4-CHD]$_0$/[CHD]$_0$, r_j=[1,3-CHD]$_0$/[CHD]$_0$) under the fixed conditions of other reagents of [CHD]$_0$(= [1,4-CHD]$_0$+[1,3-CHD]$_0$)=0.07 M, [BrO_3^-]$_0$=0.15 M, [Ce^{3+}]$_0$=6× 10^{-4} M, [H^+]$_0$=0.5 M are as follows; (a) [1,4-CHD]$_0$=0.0504 M, [1, 3-CHD]$_0$=0.0196 M (r_i=0.72, r_j=0.28). (b) [1,4-CHD]$_0$=0.0560 M, [1,3-CHD]$_0$=0.0140 M (r_i=0.80, r_j=0.20). (c) [1,4-CHD]$_0$=0.0588 M, [1,3-CHD]$_0$=0.0112 M (r_i=0.84, r_j=0.16). (d) [1,4-CHD]$_0$= 0.0616 M, [1,3-CHD]$_0$=0.0084 M (r_i=0.88, r_j=0.12). (e) [1,4-CHD]$_0$= 0.0644 M, [1,3-CHD]$_0$=0.0056 M (r_i=0.92, r_j=0.08).

ratio (b). The oscillation period and the amplitude in ratio (b) are very periodic and the oscillation continues for a long time periodically as it would if it were derived from the reaction system using one organic substrate. However, more decreasing of the ratio from 0.88 to the ratio (a) of 0.72 resulted a different oscillation pattern in which only the former oscillation pattern was occurring.

Furthermore, with a small increase of the 1,4-CHD concentration from the value of 0.88 to the ratio (e) of 0.92, a similar oscillation pattern with the ratio (a) occured in which only one part was obtained. However, the characteristics of oscillatory behaviours are different in the two systems with ratios (a) and (e). The oscillation pattern in ratio (e) is similar to the characteristics in the 1,4-CHD reaction system, and the pattern in ratio (a) with the 1,3-CHD system. The oscillatory behaviours of Figure 3 are summarized in Table 2.

746 *Bull. Korean Chem. Soc.* **1998**, Vol. 19, No. 7

Young-Joon Jang et al.

Table 2. The varying of oscillation patterns by the mixing ratio of 1,4-CHD and 1,3-CHD as an initial substrate as shown in Figure 3

Ratio of initial		τ_{ind}	$1/v$	A	D
$[1,4\text{-CHD}]_0$	$[1,3\text{-CHD}]_0$	(min)	(min)	(mV)	(min)
0.80	0.20	8.5	0.69	55.0-60.5	24.0
0.84	0.16	8.0	0.67	33.0-60.5	29.5
0.88	0.12	6.0	0.81	38.5-71.5	33.5
0.92	0.08	22.5	1.71	88.0-93.5	12.0
0.72	0.28	9.0	0.88	49.5-55.0	11.5

The initial concentrations of reagents used are the same throughout all the reaction systems and as follows: $[\text{CHD}]_0(=[1,4\text{-CHD}]_0+[1,3\text{-CHD}]_0)=0.07$ M. $[\text{BrO}_3^-]_0=0.15$ M. $[\text{Ce}^{3+}]_0=6\times10^{-4}$ M. $[\text{H}^+]_0=0.5$ M

Table 3. The simple FKN mechanism considered for the mixed substrate in the $\text{CHD/BrO}_3^-/\text{Ce}^{4+}/\text{H}^+$ oscillating reaction systems[7,14]

| Reaction mechanism |
|---|
| (R1) $\text{Br}^- + \text{HBrO}_2 + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O}$ |
| (R2) $\text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightarrow 2\text{HOBr}$ |
| (R3) $\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \rightarrow \text{HBrO}_2 + \text{HOBr}$ |
| (R4) $2\text{HBrO}_2 \rightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+$ |
| (R5) $\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightarrow 2\text{BrO}_2\cdot + \text{H}_2\text{O}$ |
| (R6) $\text{BrO}_2\cdot + \text{Ce}^{3+} + \text{H}^+ \rightarrow \text{HBrO}_2 + \text{Ce}^{4+}$ |
| (R7) $1,4\text{-CHD} + \text{Br}_2 \rightarrow 1,4\text{-BrCHD} + \text{Br}^- + \text{H}^+$ |
| $\quad\quad 1,3\text{-CHD} + \text{Br}_2 \rightarrow 1,3\text{-BrCHD} + \text{Br}^- + \text{H}^+$ |
| (R8) $1,4\text{-CHD} + \text{Ce}^{4+} \rightarrow \text{Ce}^{3+} + \text{other products}$ |
| $\quad\quad 1,3\text{-CHD} + \text{Ce}^{4+} \rightarrow \text{Ce}^{3+} + \text{other products}$ |
| (R9) $1,4\text{-BrCHD} + \text{Ce}^{4+} \rightarrow \text{Ce}^{3+} + \text{Br}^- + \text{other products}$ |
| $\quad\quad 1,3\text{-BrCHD} + \text{Ce}^{4+} \rightarrow \text{Ce}^{3+} + \text{Br}^- + \text{other products}$ |

Discussions

We have studied the characteristics of oscillatory behaviours for the reaction systems of $1,4\text{-CHD/BrO}_3^-/\text{Ce}^{4+}/\text{H}^+$ and $1,3\text{-CHD/BrO}_3^-/\text{Ce}^{4+}/\text{H}^+$, and we have considered oscillatory behaviours of a mixed system which depends on the initial mixing amount ratio of the two mixed substrates of 1,4-CHD and 1,3-CHD in the batch oscillating system of $\text{CHD/BrO}_3^-/\text{Ce}^{4+}/\text{H}^+$.

The FKN mechanism is considered equally with the 1,4-CHD and 1,3-CHD oscillating reaction systems for comparing the oscillatory behaviours of the two systems as shown in Table 3 and the different ketonic structures of the two substrates are compared in the reaction processes of (R 7), (R8), and (R9). We have neglected the detailed reaction mechanism.[7] We have focused on the initial mixing amount ratio of the two substrates. The simulation results considering the detailed mechanism and accurate rate constants will be considered in subsequent studies. The initial mixing amount ratio is an easy adjustable parameter in the experiments.

The different oscillatory behaviours of 1,3-CHD and 1,4-CHD reaction systems can be explained by the different ketonic structure between the two substrates. In the 1,4-CHD compound ( ), only one enolization process is possible since four carbons which do not have a ketone group are in

the same position; *i.e.*, . On the other hand, in the 1,3-CHD compound ( ), two enolization processes, and , are possible. Among the two enolization processes of the 1,3-CHD substrate, the process for the would depend largely on the initial hydrogen ion concentration. Thus, the needed hydrogen ion concentration for the oscillating reaction would be much more for the 1,3-CHD system under the same substrate concentration. The enolization process is closely connected with the partial bromination reaction of (R7) in Table 3 in the FKN mechanism of BZ oscillating reaction. The reaction rate difference of the enolization process between the two CHDs is compared in the induction period of the two oscillating reactions. The total rate by the two enolization processes in the 1,3-CHD reaction would be somewhat more rapid than only one process in the 1,4-CHD reaction for the oscillatory behaviour. Two enolization processes of 1,3-CHD appear well in the experimental results of bursting structure as shown in (a)-(d) of Figure 2.

In conclusion, we were able to vary the oscillatory behaviours of the mixing systems easily in the oscillation characteristics, including induction period and oscillation pattern by the fine control of the mixing ratio between 1,4-CHD and 1,3-CHD in the $\text{CHD/BrO}_3^-/\text{Ce}^{4+}/\text{H}^+$ system.

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