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Effect of bromide concentration on the induction period of the cerium-catalysed Belousov-Zhabotinsky oscillating reaction

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ABSTRACT: Temporal oscillations of the cerium(IV)-catalysed Belousov-Zhabotinsky reaction under addition of various Br^- concentrations are investigated. The relationship between the induction period and Br^- concentration, which is a controlling species in the BZ oscillating reaction, is reported. The oscillations of the Ce(IV) catalyst are followed by using UV-Vis spectrophotometric methods under closed batch and oxygen free systems. Experimental observations demonstrate that increasing Br^- concentration decreases the induction period exponentially, whereas it increases the oscillation period linearly. The results reveal that the oscillations without induction period are observed by the addition of 1.0×10^{-2} M Br^- concentration. Addition of Br^- into the BZ solution mainly involves the process A of the FKN mechanism. Numerical results reveal that the addition of Br^- increases the production of BrMA, but decreases the induction period.

KEYWORDS: Belousov-Zhabotinsky reaction, temporal oscillations, cerium catalyst

INTRODUCTION

The Belousov-Zhabotinsky (BZ) reaction involves the oxidation of an organic compound, such as malonic acid, by an acidified bromate solution in the presence of a metal ion catalyst, such as cerium[1–5]. The reaction can exhibit the nonlinear phenomena, such as chemical waves and chemical oscillations of the intermediate species. The BZ reaction can be described via the FKN (Field Kőrös Noyes) mechanism which contains 3 main processes: (A) decrease of Br^- concentration and bromination of malonic acid, (B) the autocatalytic reaction of $HBrO_2$ with the concurrent oxidation of Ce(III) catalyst to Ce(IV), and (C) regeneration of Br^- and the oxidized state of catalyst resetting back to the reduced state. Br^- is an important intermediate species that controls the dynamics of the BZ oscillations because its concentration needs to reach a critical value in order to switch the process from A to B.

One of the main dynamical behaviour before occurring the oscillations in the cerium-catalyst BZ reaction is the induction period, which can be observed in many types of the BZ system[6–19]. In the classical BZ reaction, the induction period is explained by the time required for the brominated organic products to accumulate, e.g., bromomalonic acid needs to reach a crucial concentration for the onset of oscillations[6,8,10]. This chemical is generated via a bromination reaction between malonic acid in an enol form and bromine. Based on the FKN mechanism, the time to reach a crucial concentration of bromomalonic acid depends on the rate of formation, which strongly depends on the concentration of bromine produced in the process A and the initial concentration of malonic acid. Bromine is generated in the process A via the reaction of Br^- with hypobromous acid under acidic condition. It is consumed by the bromination reaction and its amount is reduced via hydrolysis. Malonic acid plays a dual role in the BZ reaction: reduction of the catalyst and the removal of bromine via bromination reaction[8,9].

In the bromate-malonic acid-cerium–catalysed BZ reaction, the induction period depends on the initial concentrations of the BZ reactants (cerium, malonic acid, and bromate concentrations). It becomes shorter with increasing the initial concentrations of cerium and malonic acid, but it becomes larger with increasing the initial bromate concentration[10]. Induction period can be shortened or suppressed by the addition of bromomalonic acid and the concentration of chloride ion is one parameter that can lengthen the induction period[7]. Other parameters that can enhance the length of induction period are the oxygen[11], acetonitrile[12], and $AgNO_3$ concentrations[12]. The lengthening of induction period can also be observed, when methyl ketones were added[14–16]. The increase of the methyl ketone concentration extended the time for reaching the crucial concentration of bromomalonic acid, leading to the enhancement of the induction period[14,15]. Not only induction period, other parameters, i.e., oscillation lifetime and oscillation period are affected by ketone, i.e., acetone[16]. Not only in the bromate-malonic acid-cerium-catalyst BZ system, but induction period can also be observed in other systems such as the bromate-hypophosphite-acetone-dual catalyst system[17,18] or the system of bromate-1, 4 hydroquinone photoreaction[19]. Also, quenching in dynamics of chemical oscillations can be observed under addition of Ce(IV), $HBrO_2$, HOBr, and Br^- in the BZ reaction[20,21].

Another type of oscillators that lack of induction period are the bromine-hydrolysis-controlled (BHC) reactions[9]. The main characteristics of BHC are (i) the absence of an easily brominated organic compound, (ii) Br^- concentration is controlled by hydrolysis of bromine, (iii) absence of an induction period. The BHC oscillators strongly require the removal of Br_2 to start the oscillations. Br_2 can be removed by addition of acetone or bubbling an inert gas. However, the induction period can be observed in the BHC system under addition of ketone[13]. Hence the time necessary for the bromomalonic acid to accumulate is not the unique explanation for the presence of an induction period in all type of the BZ reaction. However, the concept of crucial concentration of bromomalonic acid for the induction period can be only used in the classical BZ reaction, i.e., bromate-malonic acid-H_2SO_4-cerium-catalysed BZ oscillating reaction[6,8,14].

Although many investigations have reported the effect of various chemicals on the induction period[6–19], the effect of Br^- concentration on the induction period of the cerium-catalysed Belousov-Zhabotinsky oscillating reaction has not been directly reported. In this study various Br^- concentrations are initially added in the BZ solution to investigate their effect on the induction and oscillation periods. The experimental results are discussed based on the rate of bromine and bromomalonic acid production involved in the process A of the FKN mechanism. This study will be one additional piece of information to understand the oscillation dynamics of the cerium-catalysed BZ reaction under Br^- addition.

MATERIALS AND METHODS

The temporal oscillations were studied in a closed batch system under nitrogen gas atmosphere. The stock solutions are 0.12 M sodium bromate (Fluka) dissolved in deionized water, 0.40 M malonic acid (Fluka) dissolved in 2 M H_2SO_4 (96%, Carlo Erba), 1.6×10^{-3} M cerium(IV) sulphate tetrahydrate (Riedel-deHaën) dissolved in 2 M H_2SO_4. The BZ reaction is mixed and studied in a reactor equipped with quartz cuvette cells (path length 1 cm). The solution was continuously stirred at a constant rate (300 rpm). The temperature in the cell will be kept constant at $25.0 \pm 0.2\,^\circ C$ by using the Peltier temperature control unit.

To generate the BZ oscillations, 0.75 cm^3 of deionized water, 0.75 cm^3 of 0.12 M sodium bromate, and 0.75 cm^3 of 0.40 M malonic acid are mixed in a cuvette cell. Then the solution was bubbled with nitrogen gas for 15 min. Subsequently, 0.75 cm^3 of 1.6×10^{-3} M cerium(IV) sulphate tetrahydrate was pipette into the mixed solution and the absorbance was recorded. The total volume of the BZ solution is 3.00 cm^3. The initial concentrations were 0.1 M malonic acid, 0.03 M sodium bromate, 4.0×10^{-4} M cerium(IV) sulphate tetrahydrate, and 1 M H_2SO_4. During the BZ reaction proceeds, nitrogen gas was purged over the BZ solution. All experimental data were recorded in a computer. The spectra for kinetic measurements were taken on Agilent 8453 diode array spectrophotometers. For the investigation of effects of various Br^- concentrations, the concentrations of KBr (UNILAB) were varied in the range of 1.0×10^{-6} to 1.0×10^{-2} M.

RESULTS AND DISCUSSION

When all reactants of the BZ reaction are mixed, the colour of solution is yellow (oxidized form of cerium catalyst). Then the alternate change of Ce(IV) (yellow) to Ce(III) (colourless) is observed. Temporal oscillations of the Ce(IV) catalyst is detected by UV-Vis spectrophotometer at 400 nm ($A_{400\,\mathrm{nm}}$). A typical temporal trace of the BZ oscillations without Br^- is shown in Fig. 1. The absorbance value (corresponding to the concentration of Ce(IV)) sharply decrease to the minimum value at point a. Then the absorbance increases a bit and slightly decreases to

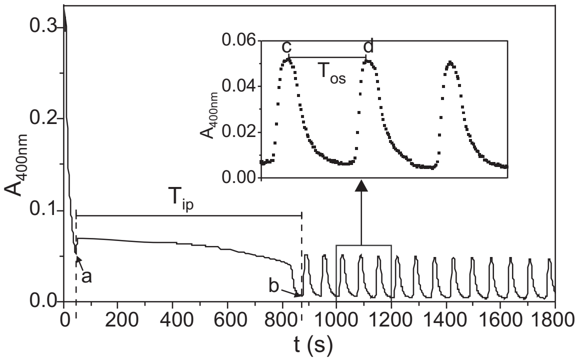

Fig. 1 Temporal trace of oscillations of the cerium-catalysed BZ reaction without addition of Br^-. Initial concentrations: 0.03 M $NaBrO_3$, 0.10 M malonic acid, 4.0×10^{-4} M Ce(IV), and 1.00 M H_2SO_4. The stirring rate and temperature are 300 rpm and $25.0 \pm 0.2\,°C$, respectively.

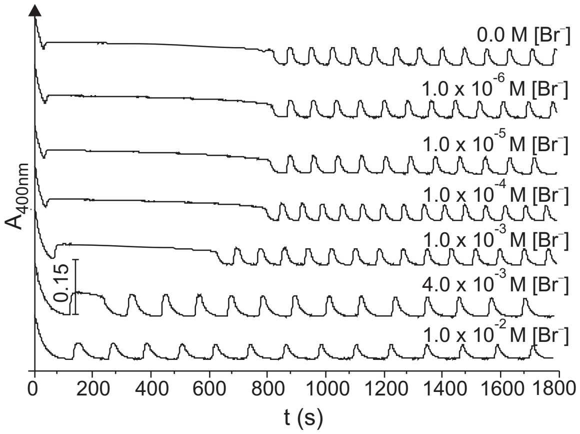

Fig. 2 Temporal trace of oscillations under addition with various Br^- concentrations. Initial concentrations of other chemicals are 0.03 M $NaBrO_3$, 0.10 M malonic acid, 4.0×10^{-4} M Ce(IV), and 1.00 M H_2SO_4.

point b. Time interval between a and b in Fig. 1 indicates the first oxidation and reduction of the cerium catalyst and will be defined as an induction period (T_{ip}). The value of T_{ip} for the recipe without addition of Br^- shown in Fig. 1 is 810 ± 2 s (mean of two experiments). After this time interval, the system shows regular oscillations of absorbance (see the inset of Fig. 1). It is noted that the interval between data points in the inset is 1 s. The amplitude of the oscillation peak slightly decreases with time. The oscillation period (T_{os}), which is time interval between maximum absorbance values of two consecutive peaks is quite constant during the observation time. The value of T_{os} for the recipe without Br^- is 80 ± 2 s.

The oscillations of bromate-malonic acid-cerium(IV)-catalysed BZ reaction in one cycle (point c to d in the inset of Fig. 1) can be divided into 3 processes, corresponding to the field-Kőrös-Noyes (FKN) mechanism[1–5]: process A—the decrease of Br^- to a critical concentration and bromination of malonic acid; process B—the autocatalytic reaction of $HBrO_2$ with the concurrent oxidation of Ce(III) catalyst to Ce(IV); process C—the regeneration of Br^- and reduction of Ce(IV) to Ce(III) by the organic substrates, i.e., $CH_2(COOH)_2$, and $BrCH(COOH)_2$. Oscillation period (T_{os}) is the sum of time interval in these three processes (see the inset of Fig. 1). Interval at point a to b represents the induction period (T_{ip}), which is the time for accumulating of bromomalonic acid ($BrCH(COOH)_2$) for a crucial concentration[6,7].

The effect of various Br^- concentrations on the oscillations profile is summarized in Fig. 2. Addition of low Br^- concentration (1.0×10^{-6} and 1.0×10^{-5} M) results a small decrease in both induction period (T_{ip}) and oscillation period (T_{os}). The values of T_{ip} for 1.0×10^{-6} and 1.0×10^{-5} M Br^- concentration are 808 ± 2 and 806 ± 2 s, respectively (mean of two experiments). The values of T_{os} are 81 ± 2 and 80 ± 2 s, respectively, for 1.0×10^{-6} and 1.0×10^{-5} M Br^- concentration (mean of two experiments). However, the results show that the induction period clearly shortens with increasing of Br^- concentration in the range 1.0×10^{-4}–4.0×10^{-3} M. The suppression of induction period can be observed at 1.0×10^{-2} M Br^- concentration. In the range of 1.0×10^{-4}–1.0×10^{-2} M Br^- concentration, the distance between two consecutive peaks which represented the oscillation period clearly increases with increasing Br^- concentration.

Fig. 3 summarizes the value of T_{ip} as a function of Br^- concentration. We found that T_{ip} exponentially decreases with increasing Br^- concentration as follows: $T_{ip} = 101.7 + 716\, e^{-413[Br^-]}$. Fig. 4 shows the plot of T_{os} as a function of Br^- concentration. For low Br^- concentration (1.0×10^{-6}–1.0×10^{-5} M), the values of T_{os} are not different significantly (the values of T_{os} are 79 ± 2, 81 ± 2, and 80 ± 2 s, respectively, for 0.0, 1.0×10^{-6}, and 1.0×10^{-5} M Br^- concentrations). However, T_{os} linearly increases with increasing Br^- concentration in the range of 1.0×10^{-4}–1.0×10^{-2} M (see the inset of Fig. 4). The linear relation between T_{os} and Br^- concentration is shown by $T_{os} = 4737.1\,[Br^-] + 76.0$ with R^2 of 0.92.

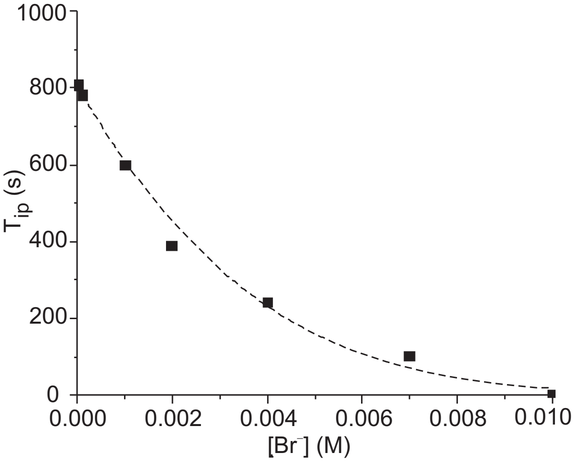

Fig. 3 Induction period (T_{ip}) as a function of $[\mathrm{Br}^-]$.

For the classical bromate-malonic-cerium-catalysed BZ reaction, it has been experimentally demonstrated that the induction period occurs until a crucial concentration of the organic brominated species, i.e., bromomalonic acid (BrMA) is reached[6,8,10,14,15,23]. It is well known that BrMA is produced via bromination reaction[8]. Based on the Gyorgyi-Turanyi-Field (GTF) model[22], the reaction mechanism involved the bromination reaction is summarized and presents in Table 1. Form the reaction mechanism, the production rates of BrMA and Br_2 are given by

$$\frac{\mathrm{d}[\mathrm{BrMA}]}{\mathrm{d}t} = k_8[\mathrm{MA_{Enol}}][\mathrm{Br_2}] + k_9[\mathrm{MA_{Enol}}][\mathrm{HOBr}] \tag{1}$$

$$\frac{\mathrm{d}[\mathrm{Br_2}]}{\mathrm{d}t} = k_1[\mathrm{HOBr}][\mathrm{Br^-}][\mathrm{H^+}] - k_{-1}[\mathrm{Br_2}] - k_8[\mathrm{MA_{Enol}}][\mathrm{Br_2}]. \tag{2}$$

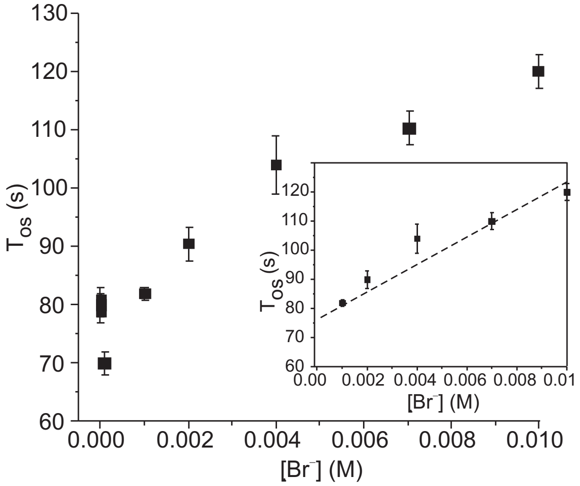

Fig. 4 Oscillation period (T_{os}) as a function of $[\mathrm{Br}^-]$. The inset picture presents the linear relation of T_{os} and $[\mathrm{Br}^-]$.

The production rate of BrMA strongly depends on concentration of $\mathrm{MA_{Enol}}$, Br_2, and HOBr. $\mathrm{MA_{Enol}}$ is an important intermediate species in the bromination reaction. The rate of change of $\mathrm{MA_{Enol}}$ can be written as follows:

$$\frac{\mathrm{d}[\mathrm{MA_{Enol}}]}{\mathrm{d}t} = k_7[\mathrm{MA}] - k_{-7}[\mathrm{MA_{Enol}}] - k_8[\mathrm{Br_2}][\mathrm{MA_{Enol}}] - k_9[\mathrm{HOBr}][\mathrm{MA_{Enol}}]. \tag{3}$$

The steady-state approximation for the enol form ($\mathrm{d}[\mathrm{MA_{Enol}}]/\mathrm{d}t = 0$) was employed to prove the bromination reaction[8]. By using this approximation, the concentration of $\mathrm{MA_{Enol}}$ equals $(k_7[\mathrm{MA}])/(k_{-7} + k_8[\mathrm{Br_2}] + k_9[\mathrm{HOBr}])$. $\mathrm{MA_{Enol}}$ is substituted in (1) and the production rate of BrMA

Table 1 Chemical reactions involved bromination in process A of the FKN mechanism.

Reaction			Rate constants		Ref
			k_{forward}	k_{backward}	
$\mathrm{HOBr} + \mathrm{Br^-} + \mathrm{H^+}$	$\longrightarrow$	$\mathrm{Br_2} + \mathrm{H_2O}$	$k_1 = 2.3 \times 10^9\ \mathrm{M^{-2}\ s^{-1}}$	$k_{-1} = 2.0\ \mathrm{s^{-1}}$	22
$\mathrm{Br^-} + \mathrm{HBrO_2} + \mathrm{H^+}$	$\longrightarrow$	$2\mathrm{HOBr}$	$k_2 = 2 \times 10^6\ \mathrm{M^{-2}\ s^{-1}}$	$k_{-2} = 2 \times 10^{-5}\ \mathrm{M^{-1}\ s^{-1}}$	22
$\mathrm{BrO_3}^- + \mathrm{Br^-} + 2\,\mathrm{H^+}$	$\longrightarrow$	$\mathrm{HBrO_2} + \mathrm{HOBr}$	$k_3 = 2.0\ \mathrm{M^{-3}\ s^{-1}}$	$k_{-3} = 3.3\ \mathrm{M^{-1}\ s^{-1}}$	22
$2\,\mathrm{HBrO_2}$	$\longrightarrow$	$\mathrm{BrO_3}^- + \mathrm{HOBr} + 2\,\mathrm{H^+}$	$k_4 = 3 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$	$k_{-4} = 7.5 \times 10^{-9}\ \mathrm{M^{-2}\ s^{-1}}$	22
$\mathrm{BrO_3}^- + \mathrm{HBrO_2} + \mathrm{H^+}$	$\longrightarrow$	$\mathrm{Br_2O_4} + \mathrm{H_2O}$	$k_5 = 33\ \mathrm{M^{-2}\ s^{-1}}$	$k_{-5} = 2200\ \mathrm{s^{-1}}$	22
$\mathrm{Br_2O_4}$	$\longrightarrow$	$2\,\mathrm{BrO_2}^\bullet$	$k_6 = 7.4 \times 10^4\ \mathrm{s^{-1}}$	$k_{-6} = 1.4 \times 10^9\ \mathrm{s^{-1}}$	22
MA	$\longrightarrow$	$\mathrm{MA_{Enol}}$	$k_7 = 3 \times 10^{-3}\ \mathrm{s^{-1}}$	$k_{-7} = 200\ \mathrm{s^{-1}}$	22
$\mathrm{MA_{Enol}} + \mathrm{Br_2}$	$\longrightarrow$	$\mathrm{BrMA} + \mathrm{Br^-} + \mathrm{H^+}$	$k_8 = 1.91 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$		22
$\mathrm{MA_{Enol}} + \mathrm{HOBr}$	$\longrightarrow$	$\mathrm{BrMA} + \mathrm{H_2O}$	$k_9 = 6.70 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$		23

MA: $\mathrm{CH_2(COOH)_2}$; $\mathrm{MA_{Enol}}$: $\mathrm{(HOOC)CH{=}C(OH)_2}$; BrMA: $\mathrm{BrCH(COOH)_2}$.

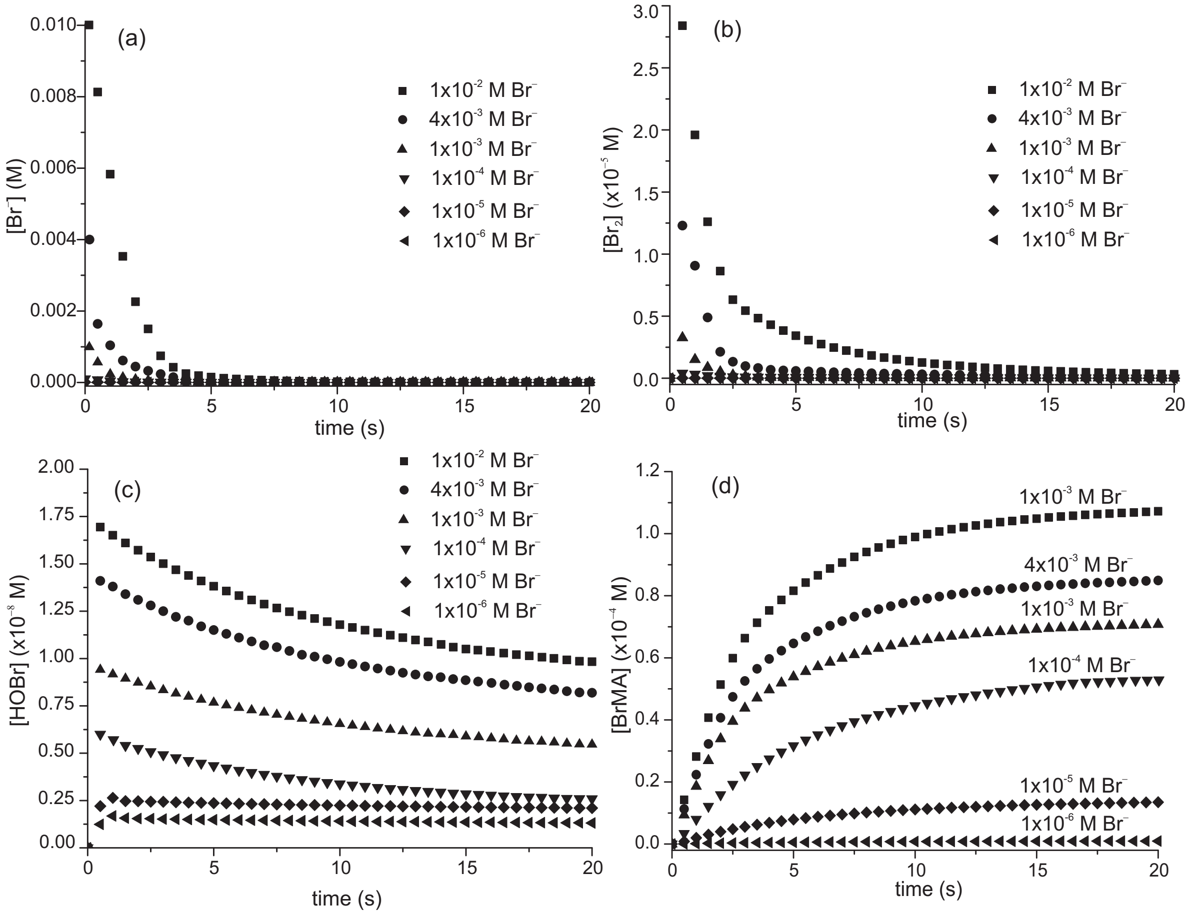

Fig. 5 Numerical results presented the concentration of (a) Br^-, (b) Br_2, (c) HOBr, and (d) BrMA as a function of time under addition of different initial Br^- concentrations ranged of 10^{-6}–10^{-2} M. Initial concentrations of other reactants: $[\mathrm{BrO}_3{}^-]_0 = 0.03$ M, $[\mathrm{MA}]_0 = 0.10$ M, $[\mathrm{H}_2\mathrm{SO}_4]_0 = 1.00$ M.

can be expressed as follows:

$$\frac{\mathrm{d}[\mathrm{BrMA}}{\mathrm{d}]}t = \frac{k_7k_8[\mathrm{MA}][\mathrm{Br}_2]+k_7k_9[\mathrm{MA}][\mathrm{HOBr}]}{k_{-7}+k_8[\mathrm{Br}_2]+k_9[\mathrm{HOBr}}].$$

The steady-state approximation reveals that the production of BrMA strongly depends on the concentration of MA, Br_2 and HOBr.

The experimental results in Fig. 3 reveal that the induction period decreases with the increase of Br^- concentration. The assumption for explaining the results is that the direct addition of Br^- will enhance the production of Br_2 and HOBr, consequently increases the production of BrMA. To prove this assumption, a simulation by numerical calculation based on the reaction mechanism shown in Table 1 is carried out. The numerical results shown in Fig. 5a reveal that the added Br^- concentration decreases with time due to it acts as a reactant for production of Br_2 and HOBr. The concentrations of Br_2 and HOBr increase with increasing of Br^- as shown in Fig. 5b,c. Br_2 sharply decreases, but HOBr slowly decreases with time. The concentration of BrMA clearly increases with increasing the Br^- concentration as presented in Fig. 5d. The numerical results confirm that the increase of Br^- concentration enhances the production of BrMA, which can shorten the induction period of the bromate-malonic-cerium-catalysed BZ reaction. However, a simulation by numerical integration using all chemical reactions in either the GTF model[22] or the MBM model[23] that would give a solid interpretation about the effect of Br^- on the induction period will be carried out in further work. Some reactions between Ce(IV) and organic species in such models[22, 23] have to be proved before using the model to explain the oscillation dynamics under Br^- addition.

The results in Fig. 4 shows that the values of T_{os} are not significantly different for low Br^- con-

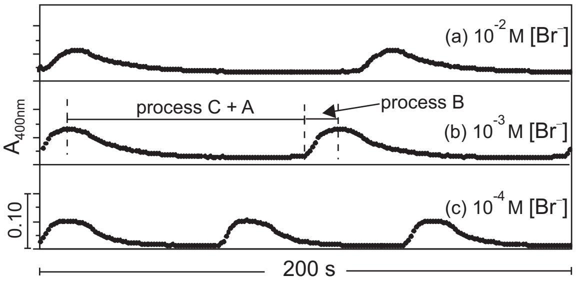

Fig. 6 Effects of Br$^-$ concentration on each process of the FKN mechanism. Initial concentrations of other chemicals are 0.03 M $NaBrO_3$, 0.10 M malonic acid, 4.0×10^{-4} M Ce(IV), and 1.00 M H_2SO_4.

centration, it linearly increases with increasing Br$^-$ concentration in the range of 1.0×10^{-3}–1.0×10^{-2} M Br$^-$ concentration. The experimental results can be explained by considering the fact that the direct addition of Br$^-$ into the BZ reaction will enhance the amount of Br$^-$ in the BZ solution. Addition of Br$^-$ into the BZ system makes a longer time for removing Br$^-$ in the process A because the BZ oscillating reaction requires the decrease in Br$^-$ concentration to the critical Br$^-$ concentration for switching the reaction process from A to B[5]. Consequently, the oscillation period is lengthened. Fig. 6a–c shows the length of each process for different Br$^-$ concentration. The results in Fig. 6 reveal that time in process C and A increases with increasing the Br$^-$ concentration, whereas durations in the process B of each Br$^-$ concentration are not significantly different. It is consistent with previous report that the oscillation in one cycle of the BZ oscillation takes time in the process A higher than other processes[16]. This indicates that the oscillation period strongly depends on the duration in the process A, which is the decrease of Br$^-$ concentration. This result confirms that addition of Br$^-$ mainly affects on the process A, resulting in the lengthening of the oscillation period.

CONCLUSIONS

Br$^-$ is one of the most important chemical species controlling the dynamics of the bromate-malonic acid-cerium–catalyst BZ oscillating reaction. Our experimental results demonstrate that the induction period of temporal oscillations in the cerium-catalysed BZ reaction are significantly shorter and finally suppressed, when the Br$^-$ concentration is increased. Introduction of Br$^-$ into the BZ solution mainly involves on the process A of the FKN mechanism. Addition of Br$^-$ clearly affects the induction period and oscillation period. The numerical results agree with the hypothesis that the addition of Br$^-$ can enhance the production of BrMA, resulting in the decrease of induction period. The increase of Br$^-$ concentration in the BZ solution results in the enhancement of oscillation period. Under addition of Br$^-$, the BZ reaction would take longer time in the process A to reduce Br$^-$ concentration, causing the increase of oscillation period. Our experimental observation is one additional piece of information to understand the induction period. Also, our recipe will be useful for analytical field using oscillating reaction for determining interested analytes since it provides the oscillations without induction period.

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