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Stirring-Controlled Bifurcations in the 1,4-Cyclohexanedione−Bromate Reaction

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We report the experimental observation that stirring in a closed 1,4-cyclohexanedione−bromate reaction can induce transitions not only between oscillatory and nonoscillatory states but also between simple and period-doubled oscillations. Notably, the transition from simple to complex oscillations occurs as a result of increasing stirring rate. When illumination was employed to characterize the importance of microfluctuations of concentrations, the threshold stirring rate for inducing a bifurcation was found to increase proportionally to the intensity of the applied light. Numerical simulations with an existing model illustrate that the experimental phenomena could be qualitatively reproduced by considering effects of mixing on diffusion-limited radical reactions, namely, the disproportion reaction of hydroquinone radicals.

1. Introduction

Bromate oscillators using 1,4-cyclohexanedione (1,4-CHD) as the organic substrate have attracted increasing attention in the past decade.[1−10] The subtle response of the 1,4-CHD−bromate reaction to illumination has made it an attractive model system for exploring perturbed spatiotemporal dynamics.[11] The bubble-free, uncatalyzed 1,4-CHD−bromate oscillator was first reported by Farage and Janjic in 1982.[1,2] They also observed strong influences of mechanical stirring in this system, which showed that the amplitude of oscillation was amplified by increasing the stirring rate. Notably, when spontaneous oscillations stopped at a higher stirring rate, decreasing the stirring rate could revive the oscillatory behavior. In this study, we report new experimental phenomena regarding effects of stirring in the 1,4-CHD−bromate reaction, which include consecutive bifurcations induced by changing stirring rate and cooperative interactions of stirring and photosensitivities.

Stirring effects on nonlinear chemical dynamics have motivated many experimental and theoretical studies in a variety of chemical systems, conducted either in continuously flow stirred tank reactors (CSTR) or in batch reactors.[12−40] These effects include changes in both the frequency and the amplitude of oscillation, and quenching of spontaneous oscillations.[12−19] Most of these observed effects can be explained on the basis of concentration fluctuations. In a CSTR system, for example, incomplete mixing of fresh reactants flowing into the bulk solution led to concentration fluctuations.[20−22] In a batch reactor, despite there being no inflow of fresh chemicals, concentration fluctuations may result from interactions between fast chemical reactions and turbulent transports of substances.[23−27] Numerical investigations with cellular mixing models and probabilistic cellular automaton models, carried out independently by several research groups, have shed light on the significance of inhomogeneity in observed stirring effects.[29−31]

Depending on the properties of each reacting system, observed stirring effects had also been explained in terms of sources other than fluctuations in local concentrations. For example, gas exchange such as O_2 absorption and/or Br_2 loss in bromate oscillators with an open surface has been considered as an important factor.[13,15,24,31−35] Absorptions of intermediate reagents onto the hydrophobic walls of the reactor, Pt electrode, or stirring bar once were also considered as a possible reason.[32,36] In addition, Noszticzius and co-workers demonstrated that different stirring effects in the Belousov−Zhabotinskii (BZ) reaction could also be modeled semiquantitatively by a diffusion-controlled radical−radical reaction step in a radicalator model.[37] In the following, we demonstrate that effects of stirring in the 1,4-CHD−bromate reaction can also be qualitatively described by considering influences of mixing on diffusion-limited radical reactions. Photoillumination was also employed in this study as a means to manipulate the inhomogeneity in local reaction kinetics.

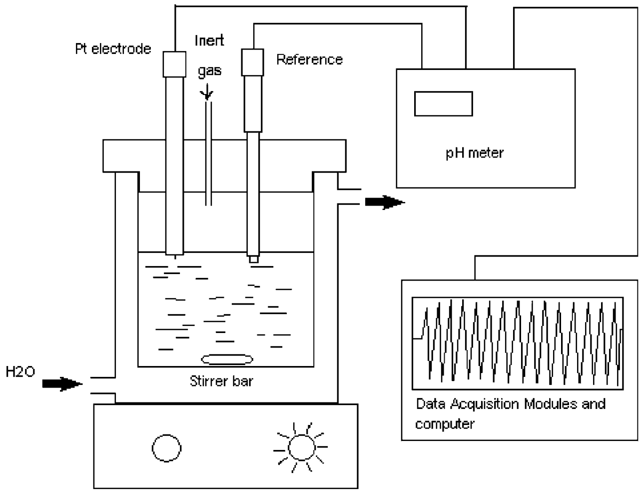

Figure 1. Schematic illustration of the experimental setup.

2. Experimental Procedure

All reactions were carried out in batch conditions under the protection of inert gases (nitrogen or argon). A schematic plot of our apparatus is presented in Figure 1. The internal diameter of the jacketed reaction beaker (purchased from ChemGlass) is 37 mm. The reaction temperature was kept at 25.0 ± 0.1 °C by a circulating water bath (Thermo NesLab RTE 7). The reaction

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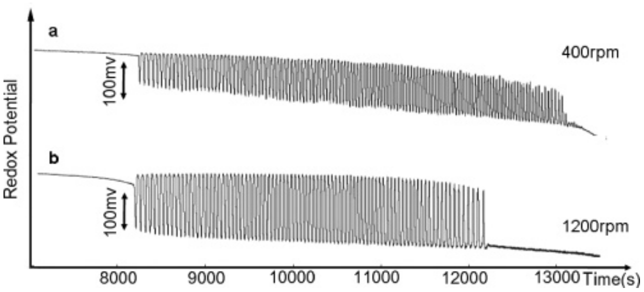

Figure 2. Time series obtained under different stirring rates: (a) 400 and (b) 1200 rpm. Other reaction conditions are $[H_2SO_4] = 0.9$ M, [1,4-CHD] = 0.06 M, and $[BrO_3^-] = 0.14$ M.

solution was stirred with an octagonal magnetic stirring bar (diameter 8 mm and length 16 mm) driven by a magnetic stirrer (Fisher Isotemp, speed ranges from 60 to 1200 rpm). The reaction was monitored by coupling a $Hg|Hg_2SO_4|K_2SO_4$ reference electrode (Radiometer Analytical XR200) with either a regular platinum electrode (length/diameter 140/1 mm) or a small platinum electrode (length/diameter 2/1 mm). A bromide-selective electrode was also employed to follow the evolution of bromide ions. To examine the influence of absorption of intermediates on Pt, a gold electrode (Radiometer, P201) was also employed. All measurements were recorded through a pH/potential meter (Radiometer PHM220) connected to a personal computer via personal Daq (USB Data Acquisition Modules, IOtech).

Stock solutions $NaBrO_3$ (Aldrich, 99%), 1.0 M, and sulfuric acid (Aldrich, 98%), 3 M, were prepared with double-distilled water. 1,4-CHD (98%, Aldrich) and 1,4-hydroquinone (99%, Aldrich) were directly dissolved in the reaction mixture. The volume of the reaction mixture was fixed at 30.0 cm^3 in all experiments. A flow meter (Cole Parmer) was used to control the flow of the inert gas. A fiber optic halogen lamp (Fisher Scientific, Model DLS-100HD, 150 W) with continuous variable light level was used as the light source, and the light perturbation was implemented by using two bifurcated fibers to illuminate the glass beaker either from opposite sides or from one side. The light intensity was measured with an optical photometer from Newport.

3. Experimental Results

Figure 2 presents two time series obtained under different stirring rates: (a) 400 and (b) 1200 rpm. Other reaction conditions are $[H_2SO_4] = 0.9$ M, [1,4-CHD] = 0.06 M, and $[BrO_3^-] = 0.14$ M. The frequency of oscillation decreases in responding to the increasing stirring rate. Meanwhile, as shown in the figure, spontaneous oscillations last for a shorter period of time under higher stirring rate. Notably, there is no visible change in the induction time, which is about 8200 s under the conditions studied here. When the stirring rate was switched periodically between 400 and 1200 rpm during one reaction process, increasing the stirring rate to 1200 rpm at the earlier stage of the oscillatory window would result in a significant amplification of the amplitude of oscillation. If the stirring rate was restored to 400 rpm, the amplitude of oscillation became smaller again, but the oscillation frequency was increased greatly. Similar effects of stirring on the amplitude and frequency of oscillation were also reported by Farage and co-workers in 1982.[2] Interestingly, if the stirring rate was switched to 1200 rpm at the later stage of the oscillatory window, a quenching phenomenon was observed, where spontaneous oscillations could be restored by decreasing the stirring rate back to 400 rpm. We note that the above stirring-induced transitions between oscillatory and stationary states have only been seen at the end of the oscillatory window.

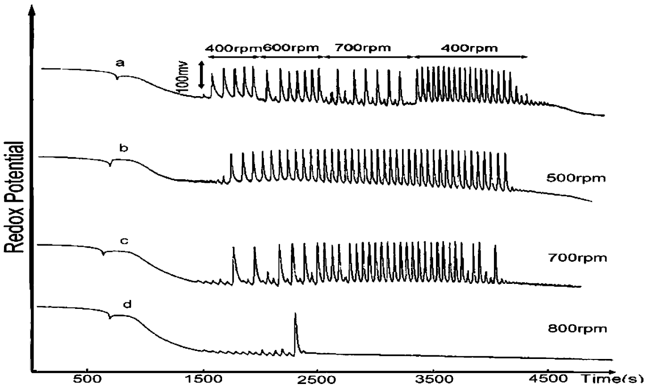

Figure 3. Time series showing dependence of oscillation pattern on stirring rates. Reaction conditions are $[H_2SO_4] = 0.9$ M, [1,4-CHD] = 0.06 M, $[H_2Q] = 0.03$ M, and $[BrO_3^-] = 0.14$ M. A small amount of hydroquinone was added here to modify the reaction dynamics, especially to shorten the induction time period.

When the flow of argon was adjusted from 1.0 to 2.0 mL/min and then to 3.0 mL/min, no variations in the above observed behavior (such as the induction time and quenching phenomenon) were recorded. These results suggest that the loss of volatile species, if there is any, does not play an important role in the above observed stirring effects because increasing the flow of gas above the solution surface at a constant stirring or increasing stirring rate at a constant gas flow would result in the same influence on the loss of volatile species. This conclusion is further supported by experiments conducted in the absence of free solution surface (i.e., the reaction mixture filled up the reactor), where the same stirring effects as presented above were observed. In those studies, we examined both PVC and Teflon lids and did not observe any difference in the overall reaction behavior.

In addition to transitions between stationary and oscillatory states, which had also been observed in the BZ reaction by Ruoff,[38] our experiments further showed that increasing the stirring rate in the 1,4-CHD−bromate reaction could induce consecutive bifurcations, leading to more complicated oscillations. An example of such a scenario is presented in Figure 3a, where reaction conditions are $[H_2SO_4] = 0.9$ M, [1,4-CHD] = 0.06 M, $[BrO_3^-] = 0.14$ M, and $[H_2Q] = 0.03$ M. Hydroquinone (H_2Q), which is an intermediate product in the studied system, was added initially as an effort to shorten the induction period. As shown in the figure, as soon as the stirring rate was increased from 400 to 600 rpm, two period-doubled oscillations appeared and then the system returned to simple oscillations of one peak per period. The reverse transition from period-2 to period-1 oscillations could be simply due to continuous variations in the reaction conditions, since no fresh reactants were supplied in a batch reactor. When the stirring rate was increased further to 700 rpm, complex oscillations were revived, in which oscillations started with one large and two small peaks per period (1^2) and then evolved to patterns of one large and one small peak per period (1^1). Later, simple oscillations were restored after the stirring rate was changed back to 400 rpm. The fact that higher stirring rates led to complicated oscillatory phenomena implicates that, in addition to microfluctuations in concentrations, there are other nontrivial mechanisms responsible for the observed stirring sensitivity in the 1,4-CHD−bromate reaction.

Figure 3b, 3c, and 3d present three time series conducted respectively at different, but constant, stirring rates. At the

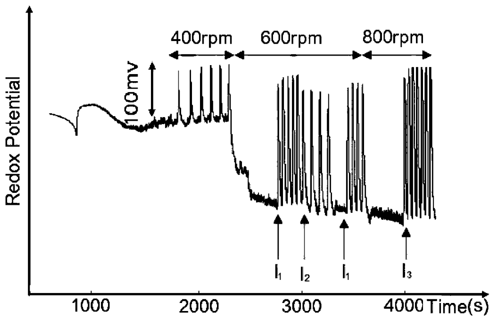

Figure 4. Effects of stirring on reaction behavior in the presence of illumination, in which the intensity of the applied light is $I_1 = 25$ mW/cm^2, $I_2 = 10$ mW/cm^2, and $I_3 = 35$ mW/cm^2. Other reaction conditions are [H_2SO_4] = 0.9 M, [1,4-CHD] = 0.06 M, [H_2Q] = 0.03 M, and [BrO_3^-] = 0.14 M. A small Pt electrode is used in this measurement.

stirring rate of 500 rpm (Figure 3b) only simple period-1 oscillations were obtained. Here, the frequency of oscillation appeared to increase in time. According to the mechanism proposed by Szalai and co-workers,[4,5] spontaneous oscillations in the 1,4-CHD−bromate reaction do not commence until the concentration of BrCHD, a precursor of Br^-, has reached a threshold level where a sufficient amount of inhibitor Br^- can be produced. Because BrCHD concentration increases in time, the production of Br^- is also accelerated accordingly, which consequently leads to an increase in the oscillation frequency. When the stirring rate was increased to 700 rpm in Figure 3c, transient complex oscillations took place. In contrast to transient complex oscillations reported in closed BZ reaction systems, which typically started from simple and then gradually evolved to more complicated patterns,[41,42] here spontaneous oscillations started with the most complicated mode (1^3) and then gradually evolved to simple oscillations. When the stirring rate was further increased to 800 rpm in Figure 3d, only one large peak, preceded by a number of small amplitude oscillations, was observed. In comparison to the results shown in Figure 2, here stirring appears to have more dramatic effects on the reaction behavior. Recall that the only difference between experiments shown in Figure 2 and Figure 3 is that 0.03 M H_2Q, an intermediate product in the studied chemical system, is added in Figure 3. This thus implies that H_2Q may have played an important role in the observed stirring sensitivity. More specifically, effects of stirring on the collective behavior of the 1,4-CHD−bromate reaction may take place through processes involving H_2Q and/or products of H_2Q.

To shed light on the importance of concentration fluctuations in the observed stirring sensitivity, illumination was introduced in the following experiments as a means to manifest the inhomogeneity in local reaction dynamics. Two protocols were investigated here: (1) a single fiber was employed to illuminate the reaction solution from one side of the reactor; (2) two bifurcated fibers were used to illuminate the solution from opposite sides of the reactor. Considering the facts that (1) the light intensity is stronger at the center of the light beam and (2) light intensity decreases along the light path due to absorption, scattering, etc., the first illumination protocol is expected to generate much stronger spatial inhomogeneity inside the reactor.

Figure 4 presents effects of stirring on the collective reaction behavior in the presence of illumination. Other reaction conditions are identical to those used in Figure 3, except a small Pt electrode is employed here to follow the reaction. Consistent with earlier observation, when stirring was increased, spontaneous oscillations stopped. However, illuminating the system with a 25 mW/cm^2 light revived the oscillatory behavior. Decreasing the light intensity to 10 mW/cm^2 reduced both the frequency and amplitude of these light-revived oscillations. After the 10 mW/cm^2 illumination became incapable of sustaining oscillations at the stirring rate 600 rpm, adjusting the light to 25 mW/cm^2 was able to revive spontaneous oscillations. Significantly, if the stirring was increased to a higher value (800 rpm), these light-induced oscillations disappeared again; however, a further increase in the light intensity (35 mW/cm^2) was able to bring oscillatory behavior back. This experiment illustrates that the threshold stirring rate for stopping spontaneous oscillations increases proportionally to the intensity of the applied light. Such a cooperative interaction of light and stirring could arise from illumination-enhanced fluctuations in local concentrations (kinetics), which obviously requires a higher stirring rate to homogenize the solution. A recent numerical study reported spontaneous oscillations induced by inhomogeneous local kinetics in an excitable BZ medium.[43] Our further experiments showed, however, that although illumination protocol 1 generated stronger spatial inhomogeneity, the light intensity required to induce oscillations with a single fiber was exactly twice as much as that of using dual fibers in protocol 2. Such a result indicates that fluctuations in local kinetics (e.g., concentrations) are not the primary reason for the behavior seen in Figure 4.

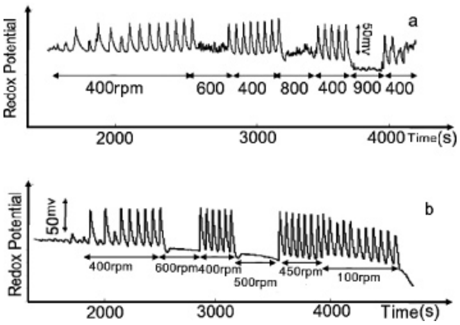

Figure 5. Stirring sensitivity of 1,4-CHD−bromate reaction investigated by (a) a small Pt electrode and (b) a gold electrode.

Alternatively, the cooperative interaction of stirring and illumination may result from their opposite kinetic influences on the reaction dynamics: the above experiments have showed that higher stirring rates drove the system toward a reduced steady state. In contrast, illumination in the 1,4-CHD−bromate reaction quenched spontaneous oscillations to an oxidized state.[44] Therefore, the apparent effects of stirring on oscillations shall be weakened or even canceled out by the presence of illumination. As a result, oscillations were retained even after the stirring rate was increased to beyond the critical value in which oscillations would otherwise have disappeared in the absence of light. In other words, the critical stirring rate is pushed up to a higher value. This hypothesis is supported by the following numerical simulations.

Figure 5 presents two results recorded respectively with a small Pt electrode and a gold electrode. Reaction conditions used here are the same as those in Figure 3, i.e., [H_2SO_4] = 0.9 M, [1,4-CHD] = 0.06 M, [BrO_3^-] = 0.14 M, and [H_2Q] = 0.03 M. Oscillation patterns in Figure 5a and 5b are qualitatively the same, suggesting that adsorption of intermediates on the Pt electrode does not play any role in the observed stirring effects.

4. Numerical Simulations

Microfluctuations in bromide ion concentrations have been suggested by Ruoff to play a leading role in the occurrence of spontaneous oscillations in a closed anaerobic classical BZ

TABLE 1: Mechanistic Model of the CHD−Bromate−Acid Oscillatory System

R1	$Br^- + HOBr + H^+ \Leftrightarrow Br_2 + H_2O$	$k_1 = 8 \times 10^9$ mol^{-2} dm^6 s^{-1}	$k_{-1} = 80$ s^{-1}
R2	$Br^- + HBrO_2 + H^+ \Leftrightarrow 2HOBr$	$k_2 = 2.5 \times 10^6$ mol^{-2} dm^6 s^{-1}	$k_{-2} = 2 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}
R3	$Br^- + BrO_3^- + 2H^+ \Leftrightarrow HOBr + HBrO_2$	$k_3 = 1.2$ mol^{-3} dm^9 s^{-1}	$k_{-3} = 3.2$ mol^{-2} dm^6 s^{-1}
R4	$HBrO_2 + H^+ \Leftrightarrow H_2BrO_2^+$	$k_4 = 2 \times 10^6$ mol^{-1} dm^3 s^{-1}	$k_{-4} = 1 \times 10^8$ s^{-1}
R5	$HBrO_2 + H_2BrO_2^+ \rightarrow HOBr + BrO_3^- + 2H^+$	$k_5 = 1.7 \times 10^5$ mol^{-1} dm^3 s^{-1}	
R6	$HBrO_2 + BrO_3^- + H^+ \Leftrightarrow Br_2O_4 + H_2O$	$k_6 = 48$ mol^{-2} dm^6 s^{-1}	
R7	$Br_2O_4 \Leftrightarrow 2BrO_2^\bullet$	$k_7 = 7.5 \times 10^4$ s^{-1}	$k_{-7} = 1.4 \times 10^9$ mol^{-1} dm^3 s^{-1}
R8	$H_2Q + BrO_2^\bullet \rightarrow HQ^\bullet + HBrO_2$	$k_8 = 8 \times 10^5$ mol^{-1} dm^3 s^{-1}	
R9	$HQ^\bullet + BrO_2^\bullet \rightarrow Q + HBrO_2$	$k_9 = 8 \times 10^9$ mol^{-1} dm^3 s^{-1}	
R10	$2HQ^\bullet \Leftrightarrow H_2Q + Q$	$k_{10} = 8.8 \times 10^8$ mol^{-1} dm^3 s^{-1}	$k_{-10} = 7.7 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}
R11	$CHD + H^+ \Leftrightarrow CHDE + H^+$	$k_{11} = 7.0 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}	$k_{-11} = 5.2 \times 10^2$ mol^{-1} dm^3 s^{-1}
R12	$CHDE + Br_2 \rightarrow BrCHD + H^+ + Br^-$	$k_{12} = 2.8 \times 10^9$ mol^{-1} dm^3 s^{-1}	
R13	$CHDE + HOBr \rightarrow BrCHD + H_2O$	$k_{13} = 2.8 \times 10^9$ mol^{-1} dm^3 s^{-1}	
R14	$BrCHD \rightarrow CHED + Br^- + H^+$	$k_{14} = 5 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}	
R15	$CHED + H^+ \rightarrow H_2Q + H^+$	$k_{15} = 1.94 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}	
R16	$H_2Q + Br_2 \rightarrow Q + 2Br^- + 2H^+$	$k_{16} = 3 \times 10^4$ mol^{-1} dm^3 s^{-1}	
R17	$H_2Q + BrO_3 + H^+ \rightarrow Q + Br^- + H^+ + H_2O$	$k_{17} = 2 \times 10^{-2}$ mol^{-2} dm^6 s^{-1}	
R18	$H_2Q + HOBr \rightarrow Q + Br^- + H^+ + H_2O$	$k_{18} = 6 \times 10^5$ mol^{-1} dm^3 s^{-1}	
R19	$CHD + BrO_3 + H^+ \rightarrow H_2Q + HBrO_2 + H_2O$	$k_{19} = 1 \times 10^{-5}$ mol^{-2} dm^6 s^{-1}	

reaction.[38] Since the 1,4-CHD−bromate oscillator is also bromide-controlled, the mechanism of microfluctuations in Br^- concentration shall also be capable of explaining the transition from oscillatory to stationary states observed above. On the other hand, our perturbation experiments with an inhomogeneous light source suggest that in addition to microfluctuations, which cannot be avoided in a mechanistically stirred reaction system, there could also be other nontrivial mechanisms responsible for the observed stirring effects. Such speculation is further supported by the result that transitions between oscillatory and stationary states only appear at the end of the oscillatory window, even though at the beginning of the oscillation window the system is also at the neighborhood of a bifurcation point and thus is equally susceptible to fluctuations in concentrations of Br^-. To explore other explanations, we turned our attention to the possible influence of mixing on those diffusion-controlled radical reactions, in particular those processes involving hydroquinone and/or products of hydroquinone, suggested by comparing experiments shown in Figures 2 and 3.

The 1,4-CHD−bromate reaction mechanism has been developed by Szalai and co-workers.[4,5] The mechanism, listed in Table 1, contains 19 reaction steps and is closely related to the FKN mechanism proposed by Field, Noyes, and Körös for the BZ reaction.[45] According to the above mechanism, H_2Q reacts with bromine dioxide radicals to produce bromous acid and hydroquinone radicals (see (R8)), and hydroquinone radicals then undertake two different reactions as shown by (R9) and (R10).

$$H_2Q + BrO_2^\bullet \rightarrow HQ^\bullet + HBrO_2 \tag{R8}$$

$$HQ^\bullet + BrO_2^\bullet \rightarrow Q + HBrO_2 \tag{R9}$$

$$2HQ^\bullet \Leftrightarrow H_2Q + Q \tag{R10}$$

Whether a hydroquinone radical is going to take (R9) or (R10) is determined by the availability of its counterparts. Within the scope of a cellular model, in which the reaction solution is divided into an infinite number of small cells with each cell being governed by the same mechanism as listed in Table 1, only one hydroquinone radical is produced within each cell after the system undergoes an autocatalytic cycle (R6 + R7 + R8). Therefore, the fast disproportionation of a hydroquinone radical relies on transportations that allow it to meet with another hydroquinone radical from neighboring sites. Consequently, increasing the stirring rate would effectively result in an increase in the reaction R10. Working from this perspective, in the following simulations the rate constant k_{10} was simply adjusted to account for the influence of stirring.

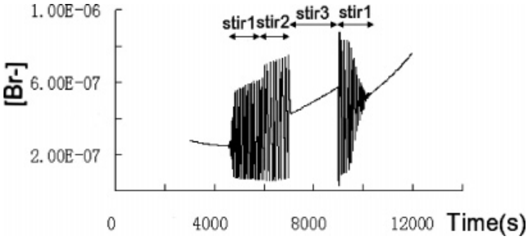

Figure 6. Stirring sensitivity of 1,4-CHD−bromate reaction calculated with the model listed in Table 1. Different stirrings correspond to the following values of k_{10}: stir1, $k_{10} = 8.8 \times 10^8$; stir2, $k_{10} = 2.0 \times 10^{11}$; stir3, $k_{10} = 2.0 \times 10^{12}$. Other reaction conditions are $[H_2SO_4] = 0.9$ M, [1,4-CHD] = 0.06 M, $[H_2Q] = 0.03$ M, and $[BrO_3^-] = 0.14$ M.

Figure 6 presents a time series calculated from the model listed in Table 1. Just as was observed in experiments, there was a long induction time. After spontaneous oscillations began, the stirring rate was increased slightly, which was implemented via increasing the rate constant k_{10}. Similar to what took place in experiments, the amplitude of oscillation was increased while the frequency of oscillation was decreased. If the stirring rate was increased still, which was again achieved by further increasing the rate constant k_{10}, a quenching phenomenon was seen there. After the system stayed at the nonoscillatory period for a while, adjusting the rate constant k_{10} back to its original value (i.e., restoring the stirring rate) revived spontaneous oscillations. The above scenario is the same as what happened in experiments (see Figure 5), illustrating that effects of stirring in the 1,4-CHD−bromate reaction could arise from impacts of mixing on diffusion-limited radical reactions. So far, no complex oscillations have been seen in the modeling.

To simulate the cooperative effects of stirring and illumination on oscillatory behavior, the following abstract reaction has been added to the above model to account for the kinetic influences of light.

$$Q + h\nu \rightarrow H_2Q \tag{R20}$$

The above process was suggested by Görner in a recent study on photoprocesses of *p*-benzoquinone in aqueous solution.[46] In this study, the rate constant k_{20} was adjusted arbitrarily to reflect the influence of light, in which increasing k_{20} corresponds to an increase in the intensity of the applied light. The only difference between Figure 7a and 7b was the rate constant k_{10},

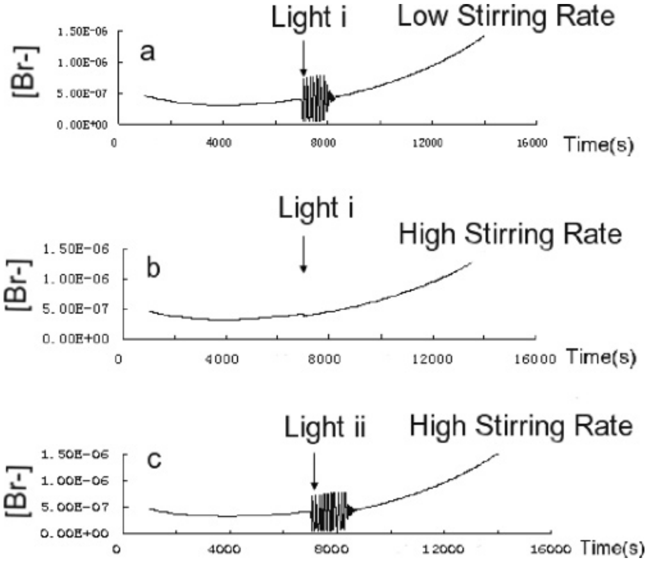

Figure 7. Cooperative effects of stirring and illumination in 1,4-CHD−bromate reaction calculated from the model listed in Table 1 and reaction R20 in the text. Other reaction conditions are $[H_2SO_4] = 0.9$ M, $[1,4\text{-CHD}] = 0.06$ M, $[H_2Q] = 0.03$ M, and $[BrO_3^-] = 0.14$ M. Rate constants in the three time series are (a) $k_{10} = 6 \times 10^{11}$, $k_{20} = 6 \times 10^{-7}$; (b) $k_{10} = 2 \times 10^{12}$, $k_{20} = 6 \times 10^{-7}$; and (c) $k_{10} = 2 \times 10^{12}$, $k_{20} = 2 \times 10^{-6}$.

which was higher in Figure 7b to account for an increase in the stirring rate. Again, the same as observed in experiments, oscillatory behavior was quenched there. Then, increasing the intensity of illumination (accomplished by merely increasing the rate constant k_{20}) in Figure 7c revived spontaneous oscillations. Such a scenario is qualitatively the same as the cooperative interaction of stirring and illumination seen in experiments, suggesting that the opposite kinetic influences of light and stirring could be responsible for the phenomena seen in Figure 4.

5. Conclusions

Complementing existing investigations on stirring effects in nonlinear reaction systems, which have showed stirring-induced transitions between stationary and oscillatory states,[1,2,38] this study demonstrates that stirring could induce consecutive bifurcations, leading to more complicated oscillatory behavior. Notably, the transition from simple to complex oscillations occurs as a result of increasing stirring rate, where faster mixing is supposed to lead to a more homogeneous medium and thus suppress fluctuation-caused irregular behavior. The occurrence of complex behavior at higher stirring rates therefore implies that in addition to microfluctuations there are other nontrivial mechanisms responsible for the observed effects of stirring. Numerical simulations with an existing model illustrate that effects of mixing on radical reactions could be a source of the observed stirring effects.

When the 1,4-CHD−bromate reaction is exposed to light, the stirring rate required to quench spontaneous oscillations is found to increase proportionally with respect to the intensity of the applied light. Our experiments with two different illumination protocols indicate that inhomogeneous local kinetics does not play a leading role in the cooperative interaction of stirring and light. Simulations by accounting for the kinetic effects of light on the production of hydroquinone from 1,4-benzoquinone qualitatively reproduce experimental results. In summary, although one cannot preclude the presence of microfluctuations in concentrations, this study illustrates that the observed stirring effects as well as the cooperative interaction of stirring and light could arise from the influence of mixing on chemical processes such as diffusion-limited hydroquinone radical reactions. This information is important for future investigations of 1,4-CHD−bromate (ferroin) oscillators.

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