Numerical Investigation of Photochemical Behavior in Bromate−1,4-Cyclohexanedione Reactions

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In this study, photocontrolled reaction behaviors in the uncatalyzed and catalyzed bromate−1,4-cyclohexanedione (bromate−CHD) oscillators were investigated numerically. The simulation was performed with two existing models modified to include a photoreaction step denoting the photoreduction of 1,4-benzoquinone in aqueous solution. The reproduced phenomena include photoinduced and photoquenched chemical oscillations. The scene that light with a moderate intensity favors while strong illumination quenches these spontaneous oscillations is also achieved in the simulation. The modified model also illustrates that, as the reaction evolves in time, the influence of light transforms from inhibitory to constructive. The remarkable agreement between simulation and experiment strongly suggests that 1,4-benzoquinone plays a key role in the photoreaction dynamics of the studied systems.

1. Introduction

Driven by increasing interests in the perturbed nonlinear dynamics, photosensitive chemical oscillators have attracted a great deal of attention in the past 2 decades,[1−8] as photosensitivity provides a convenient approach to implement various forcing protocols with an adjustable magnitude.[9−22] Light is generally expected to either quench or support the oscillatory behavior. Such an effect shall be independent of the intensity of the applied illumination. However, Kurin-Csörgei and co-workers reported that chemical waves in the ferroin-catalyzed bromate−1,4-cyclohexanedione (bromate−CHD) medium might exhibit opposite responses to illumination of different intensities.[23] Similar behaviors were later observed in the stirred ferroin−bromate−CHD system as well, in which both light-induced and light-inhibited oscillations were achieved.[24] A transition from light-quenched to light-induced oscillatory behavior at a constant light intensity has also been observed in the uncatalyzed bromate−CHD system.[25]

The subtle responses to illumination, coupled with the absence of gas production, have made the ferroin−bromate−CHD reaction an attractive model system to explore novel spatiotemporal behaviors.[26−30] Despite of the observation of a number of interesting photochemical phenomena in the above systems, the underlying photoreaction mechanism remains to be understood. Earlier investigations have demonstrated that ferroin could be excited by light to induce temporal oscillations or pattern formation in the ferroin−bromate−malonic acid reaction.[31] The achievement of light-induced oscillations in the uncatalyzed bromate−CHD system rules out that the metal catalyst ferroin is a key source responsible for the photocontrolled behavior in the ferroin−bromate−CHD system.[24] Recent mechanistic investigations suggested that 1,4-benzoquinone, an oxidation product of CHD, might play an important role in photoinduced oscillations in the uncatalyzed and catalyzed bromate−CHD oscillators.[24,25] To account for photoquenched oscillatory phenomenon, illumination-induced production of bromide was speculated because bromide is a known inhibitor of the autocatalysis in bromate-based oscillators.[9]

To examine the validity of our earlier hypothesis and gain further insights into the photochemistry of bromate−CHD oscillators, in this study we carried out numerical simulations via incorporating the latest experimental results into two existing models which have successfully reproduced chemical oscillations in bromate−CHD systems.[32−34] More specifically, our attention is focused on the photoreduction of 1,4-benzoquinone (1,4-Q). Investigations on the photochemistry of 1,4-Q have confirmed the partial photoreduction of 1,4-Q to 1,4-hydroquinone (H_2Q).[35,36] H_2Q is an important reagent participating the autocatalytic cycle in bromate−CHD reactions.[32−34] As presented in the following, the subtle photosensitivity observed experimentally was successfully reproduced, which includes photoinduced and photoquenched oscillatory behavior as well as their intricate dependence on light intensity.

2. Model

The aim of this research is to examine the validity of our earlier suggestion that 1,4-benzoquinone plays a critical role in the photosensitivity seen in the catalyzed and uncatalyzed bromate−CHD systems.[25] Photoreduction of benzoquinone to hydroquinone and 2-hydroxybenzoquinones in aqueous solution has been reported earlier by Görner.[35] To qualitatively account for such a photoreduction process, the following schematic reaction was proposed here:

$$2Q \rightarrow H_2Q + \text{product} \qquad (A)$$

where the rate constant is controlled by light intensity and the product denotes substances which do not participate in further reaction in bromate−CHD systems. Details of the photoreduction processes of benzoquinone have been largely omitted from the above step in an attempt to build a simple model.[35] We would like to point out that our recent exploration also shows that the presence of bromine, an intermediate reagent in

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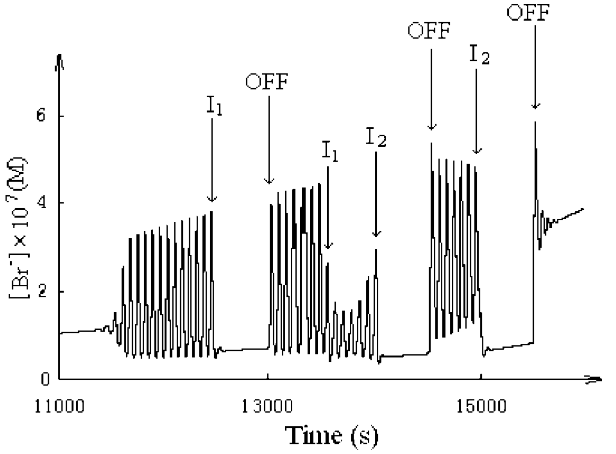

Figure 1. Time series showing light-inhibited oscillatory behavior in the uncatalyzed bromate−CHD reaction. Initial compositions of the reagents are as follows: $[BrO_3^-] = 0.15$ M, $[H_2SO_4] = 1.0$ M, $[H_2Q] = 0.02$ M, and $[CHD] = 0.048$ M. Illumination is implemented via increasing k_A from 0 to I_1 ($k_A = 2.8 \times 10^{-4}$ M^{-1} s^{-1}) and I_2 ($k_A = 6.0 \times 10^{-4}$ M^{-1} s^{-1}) Other rate constants used in the simulation are provided in Table 3.

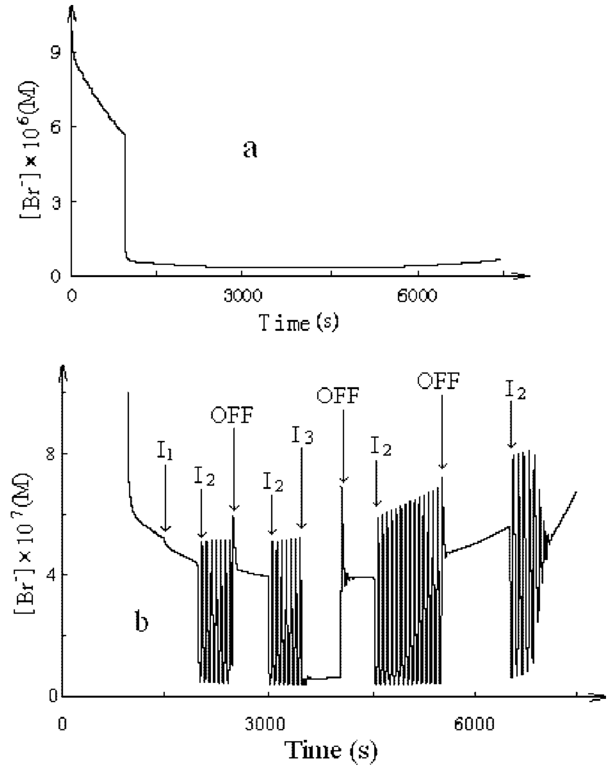

Figure 2. Simulation of light-induced oscillations in the uncatalyzed bromate−CHD reaction: (a) without illumination and (b) under illumination of various intensities. Initial compositions of the reaction solution are as follows: $[BrO_3^-] = 0.15$ M, $[H_2SO_4] = 1.0$ M, $[H_2Q] = 0.04$ M, and $[CHD] = 0.048$ M. I_1, $k_A = 2.0 \times 10^{-5}$ M^{-1} s^{-1}; I_2, $k_A = 2.5 \times 10^{-4}$ M^{-1} s^{-1}; and I_3, $k_A = 4.0 \times 10^{-4}$ M^{-1} s^{-1}.

bromate−CHD reactions,[32,33] may affect the photoreduction path of benzoquinone,[36] but the final products still consist of hydroquinones. The second-order nature of the above reaction step A reflects the correct stoichiometric relationship suggested by photoexperiments.[35] The second-order nature is not important for reproducing the following photochemical behavior as Q concentration stays almost constant.

The model employed here to simulate photocontrolled behavior in the uncatalyzed bromate−CHD system is constructed by adding the above reaction step A to a mechanism proposed by Körös and co-workers (see Table 1). The model listed in Table 1 is very successful in reproducing chemical oscillations in the uncatalyzed bromate−CHD system.[32,37] The core of this mechanism is the autocatalytic production of $HBrO_2$ via the reaction between H_2Q and bromine dioxide radicals, implementing a nonlinear feedback necessary for any chemical oscillator. Discussions about the selection of these reaction steps as well as the corresponding rate constants (see Table 3) can be found in the original report.[32]

The simulation of photochemical behavior in the ferroin−bromate−CHD system was performed on the basis of a model listed in Table 2, which is an extended version of the mechanism of the uncatalyzed bromate−CHD system.[34] This extended mechanism, consisting of 22 reactions and 15 species, simulates satisfactorily the behavior of the ferroin−bromate−CHD oscillator at increasing concentration of ferroin and at the concentration of [ferroin] = 0.[33] Our simulation merely incorporates the reaction step A into the above model.

To get chemical oscillations under the initial compositions reported in the corresponding experiments, our calculations show that the rate constants k_{11} and k_{-11} for the reaction CHD + H^+ $\Leftrightarrow$ CHDE + H^+ have to be adjusted from 2.1×10^{-4} M^{-1} s^{-1} and 5.2×10^{2} M^{-1} s^{-1} to 3.0×10^{-4} M^{-1} s^{-1} and 1.0×10^{2} M^{-1} s^{-1}, respectively. Otherwise, all rate constants used in our simulation are the same as reported in literature.[32,33] Integration of the corresponding mass rate laws was performed with the Berkely Madonna program from IBM.

3. Photoreaction Behavior in the Uncatalyzed System

Figure 1 presents quenching phenomena calculated with the model listed in Table 1 plus the reaction step A. To mimic changes in the light intensity in experiments, rate constant k_A was adjusted arbitrarily here with $k_A = 0$ representing no illumination. Initial conditions used in the calculation are the same as those used in experiments;[25] i.e., $[H_2SO_4] = 1.0$ M, $[NaBrO_3] = 0.15$ M, $[CHD] = 0.048$ M, and $[H_2Q] = 0.02$ M. The initial presence of H_2Q in the experimental investigation was to reduce the induction time of spontaneous oscillations.[25] As shown in Figure 1, during the earlier oscillatory stage illumination successfully quenched the oscillation, causing the bromide concentration to return to a level similar to that before the occurrence of spontaneous oscillations. Upon turning off the illumination, these spontaneous oscillations resumed. Another application of the same magnitude illumination failed to quench the oscillation. Such a result is in excellent agreement with experiments.[25] On the other hand, the application of a stronger illumination (i.e., a larger k_A value) resulted in quenching behavior on two separate attempts. This result suggests that quenching phenomenon in uncatalyzed bromate oscillators could be caused by light-induced production of H_2Q, although such a process does not produce the inhibitor of the autocatalytic reaction. Figure 1 also illustrates that as reactants are consumed continuously, the system eventually evolves out of the oscillatory window. The scene that oscillations diminish with gradually decreasing amplitudes implicates that a reverse supercritical Hopf bifurcation may have taken place here.

Figure 2 presents two time series calculated without (a) and with (b) the influence of light. In Figure 2a, the system does not produce any spontaneous oscillation, although there is an abrupt drop in the concentration of bromide after a brief reaction time. The existence of such an abrupt change in the reaction behavior is similar to the scenario reported in experiments.[25]

TABLE 1: Model for the Bromate−CHD System

$$\mathrm{Br^- + HOBr + H^+ \Leftrightarrow Br_2 + H_2O} \tag{R1}$$

$$\mathrm{Br^- + HBrO_2 + H^+ \Leftrightarrow 2HOBr} \tag{R2}$$

$$\mathrm{Br^- + BrO_3{}^- + 2H^+ \Leftrightarrow HOBr + HBrO_2} \tag{R3}$$

$$\mathrm{HBrO_2 + H^+ \Leftrightarrow H_2BrO_2{}^+} \tag{R4}$$

$$\mathrm{HBrO_2 + H_2BrO_2{}^+ \rightarrow HOBr + BrO_3{}^- + 2H^+} \tag{R5}$$

$$\mathrm{HBrO_2 + BrO_3{}^- + H^+ \Leftrightarrow Br_2O_4 + H_2O} \tag{R6}$$

$$\mathrm{Br_2O_4 \Leftrightarrow 2BrO_2{}^*} \tag{R7}$$

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

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

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

$$\mathrm{CHD + H^+ \Leftrightarrow CHDE + H^+} \tag{R11}$$

$$\mathrm{CHDE + Br_2 \rightarrow BrCHD + H^+ + Br^-} \tag{R12}$$

$$\mathrm{CHDE + HOBr \rightarrow BrCHD + H_2O} \tag{R13}$$

$$\mathrm{BrCHD \rightarrow CHDE + Br^- + H^+} \tag{R14}$$

$$\mathrm{CHDE + H^+ \rightarrow H_2Q + H^+} \tag{R15}$$

$$\mathrm{H_2Q + Br_2 \rightarrow Q + 2Br^- + 2H^+} \tag{R16}$$

$$\mathrm{H_2Q + H^+ + BrO_3{}^- \rightarrow Q + HBrO_2 + H_2O} \tag{R17}$$

$$\mathrm{H_2Q + HOBr \rightarrow Q + Br^- + H^+ + H_2O} \tag{R18}$$

$$\mathrm{CHD + BrO_3{}^- + H^+ \rightarrow H_2Q + HBrO_2 + H_2O} \tag{R19}$$

TABLE 2: Model for the Bromate−CHD−Ferroin Oscillatory System

$$\mathrm{Br^- + HOBr + H^+ \Leftrightarrow Br_2 + H_2O} \tag{R1}$$

$$\mathrm{Br^- + HBrO_2 + H^+ \Leftrightarrow 2HOBr} \tag{R2}$$

$$\mathrm{Br^- + BrO_3{}^- + 2H^+ \Leftrightarrow HOBr + HBrO_2} \tag{R3}$$

$$\mathrm{HBrO_2 + H^+ \Leftrightarrow H_2BrO_2{}^+} \tag{R4}$$

$$\mathrm{HBrO_2 + H_2BrO_2{}^+ \rightarrow HOBr + BrO_3{}^- + 2H^+} \tag{R5}$$

$$\mathrm{HBrO_2 + BrO_3{}^- + H^+ \Leftrightarrow Br_2O_4 + H_2O} \tag{R6}$$

$$\mathrm{Br_2O_4 \Leftrightarrow 2BrO_2{}^*} \tag{R7}$$

$$\mathrm{H_2Q + 2BrO_2{}^* \rightarrow Q + 2HBrO_2} \tag{R20}$$

$$\mathrm{Fe(phen)_3{}^{2+} + BrO_2{}^* + H^+ \rightarrow Fe(phen)_3{}^{3+} + HBrO_2} \tag{R21}$$

$$\mathrm{CHD + H^+ \Leftrightarrow CHDE + H^+} \tag{R11}$$

$$\mathrm{CHDE + Br_2 \rightarrow BrCHD + H^+ + Br^-} \tag{R12}$$

$$\mathrm{BrCHD + H^+ \rightarrow CHED + Br^- + 2H^+} \tag{R22}$$

$$\mathrm{CHED + H^+ \rightarrow H_2Q + H^+} \tag{R15}$$

$$\mathrm{CHD + BrO_3{}^- + H^+ \rightarrow H_2Q + HBrO_2 + H_2O} \tag{R19}$$

$$\mathrm{CHD + HBrO_2 \rightarrow HOBr + H_2Q + H_2O} \tag{R23}$$

$$\mathrm{H_2Q + H^+ + BrO_3{}^- \rightarrow Q + HBrO_2 + H_2O} \tag{R17}$$

$$\mathrm{H_2Q + HOBr \rightarrow Q + Br^- + H^+ + H_2O} \tag{R18}$$

$$\mathrm{H_2Q + Br_2 \rightarrow Q + 2Br^- + 2H^+} \tag{R16}$$

$$\mathrm{2Fe(phen)_3{}^{3+} + CHD \rightarrow 2Fe(phen)_3{}^{2+} + H_2Q + 2H^+} \tag{R24}$$

$$\mathrm{2Fe(phen)_3{}^{3+} + BrCHD \rightarrow Q + Br^- + 3H^+ + 2Fe(phen)_3{}^{2+}} \tag{R25}$$

$$\mathrm{2Fe(phen)_3{}^{3+} + H_2Q \rightarrow 2Fe(phen)_3{}^{2+} + Q + 2H^+} \tag{R26}$$

$$\mathrm{2Fe(phen)_3{}^{2+} + BrO_3{}^- + 3H^+ \rightarrow 2Fe(phen)_3{}^{3+} + HBrO_2 + H_2O} \tag{R27}$$

Same as achieved in experiments, here the nonoscillatory behavior was obtained by increasing the initial concentration of hydroquinone to 0.04 M from 0.03 M. Simulation in Figure 2b illustrates that an above-threshold light intensity is required to generate light-induced oscillations, where no oscillations could be induced when $k_A = 1.0 \times 10^{-5}\ \mathrm{M^{-1}\ s^{-1}}$. On the other

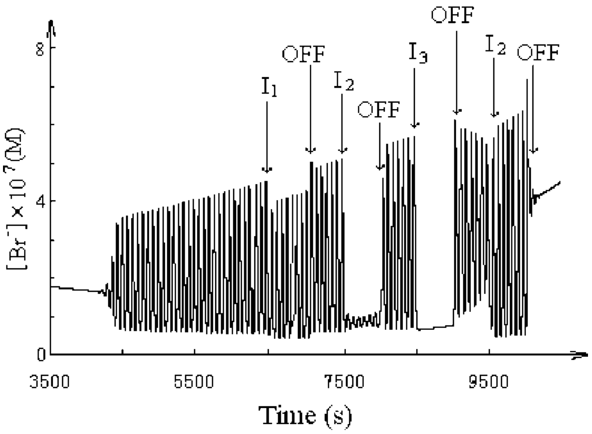

Figure 3. Time series showing transition from light-quenched to light-induced oscillations. Initial compositions of the reaction mixture are as follows: $[BrO_3^-] = 0.15$ M, $[H_2SO_4] = 1.0$ M, $[H_2Q] = 0.03$ M, and $[CHD] = 0.048$ M. Illumination is implemented via increasing rate constant k_A. I_1, $k_A = 1.0 \times 10^{-4}$ M^{-1} s^{-1}; I_2, $k_A = 2.2 \times 10^{-4}$ M^{-1} s^{-1}; and I_3, $k_A = 3.6 \times 10^{-4}$ M^{-1} s^{-1}.

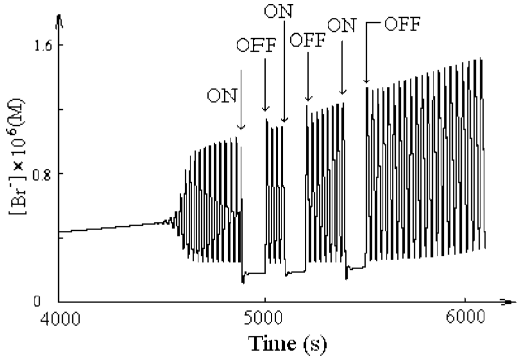

Figure 4. Time series showing light-inhibited oscillatory behavior in the ferroin-catalyzed bromate−CHD reaction. Initial compositions of the solution are as follows: $[BrO_3^-] = 0.15$ M, $[H_2SO_4] = 1.0$ M, $[H_2Q] = 0.02$ M, $[CHD] = 0.048$ M, and $[\text{ferroin}] = 2.0 \times 10^{-6}$ M. Illumination is implemented via increasing k_A from 0 to 2.0×10^{-3} M^{-1} s^{-1}. Other rate constants used in the simulation are provided in Table 4.

hand, when k_A is too large, such as $k_A = 4.0 \times 10^{-4}$ M^{-1} s^{-1}, no oscillations could be induced either. The concentration of bromide in Figure 2b drops immediately to a lower level upon turning on the illumination. This is due to the enhanced production of hydroquinone by light, which consequently accelerates the production of $HBrO_2$ which consumes Br^- rapidly.[32] Notably, the above simulation also reproduced that when light was turned off, oscillations with decreasing amplitudes continued for a few times.[25] This implies that the species created through photochemical reactions would gradually be used up in the reaction some time after the light was stopped; thus, "residual oscillations" were bound to occur for some time after the light supply was cut off.

A transition from light-inhibited at the earlier stage of the reaction to light-induced oscillatory behavior at the later stage of the batch reaction was also reproduced here. As presented in Figure 3, the use of a low-intensity illumination (e.g., $k_A = 1.0 \times 10^{-4}$ M^{-1} s^{-1}) merely resulted in a decrease in the amplitude of oscillation. The suppression on the spontaneous oscillations becomes more pronounced when k_A is increased to 2.0×10^{-4} M^{-1} s^{-1}. Further increase of k_A completely quenches the oscillatory phenomenon. At the later stage of the reaction; on the other hand, the application of illumination exhibits constructive influence, where the oscillation amplitudes are significantly amplified by light. The above success in reproducing the qualitative change in the photochemical responses by the inclusion of the above reaction process A supports an earlier conclusion that hydrogen ions were not a limiting reagent in the photoreaction processes in the bromate−CHD system.[25]

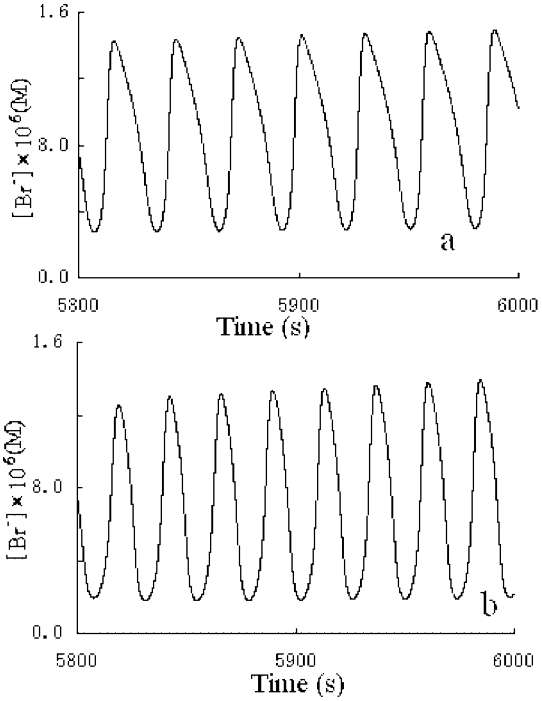

Figure 5. Time series of (a) nonilluminated and (b) illuminated ferroin−bromate−CHD reactions. Here, the oscillation frequency in b is increased due to the employment of a moderate $k_A = 8.0 \times 10^{-4}$ M^{-1} s^{-1}. All other conditions are the same as those used in Figure 4.

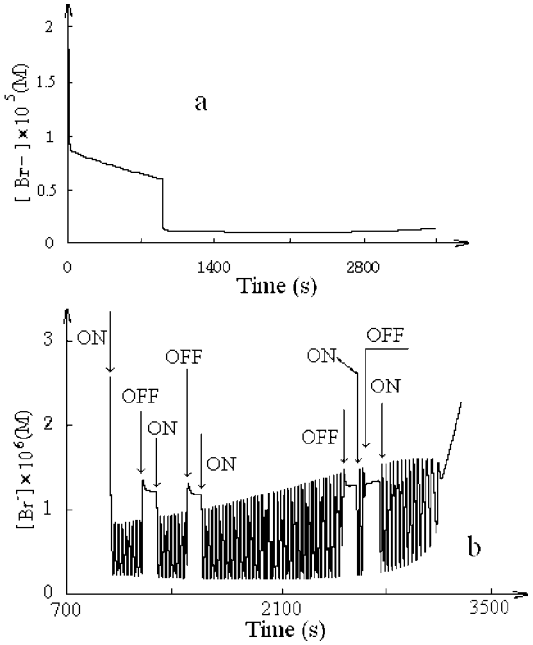

Figure 6. Simulation of light-induced oscillations in the ferroin−bromate−CHD reaction: (a) without illumination and (b) under illumination with $k_A = 2.0 \times 10^{-3}$ M^{-1} s^{-1}. Initial compositions of the reaction solution are as follows: $[BrO_3^-] = 0.2$ M, $[H_2SO_4] = 1.0$ M, $[H_2Q] = 0.02$ M, $[CHD] = 0.09$ M, and $[\text{ferroin}] = 2.0 \times 10^{-6}$ M.

TABLE 3: Rate Constants for the Uncatalyzed System

reaction no.	rate constants	
R1	$K_1 = 8 \times 10^9$ mol^{-2} dm^6 s^{-1}	$K_{-1} = 80$ s^{-1}
R2	$K_2 = 2.5 \times 10^9$ mol^{-2} dm^6 s^{-1}	$K_{-2} = 2 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}
R3	$K_3 = 1.2$ mol^{-3} dm^9 s^{-1}	$K_{-3} = 3.2$ mol^{-2} dm^6 s^{-1}
R4	$K_4 = 2 \times 10^6$ mol^{-1} dm^3 s^{-1}	$K_{-4} = 1 \times 10^8$ s^{-1}
R5	$K_5 = 1.7 \times 10^5$ mol^{-1} dm^3 s^{-1}	
R6	$K_6 = 48$ mol^{-2} dm^6 s^{-1}	$K_{-6} = 3.2 \times 10^3$ s^{-1}
R7	$K_7 = 7.5 \times 10^4$ s^{-1}	$K_{-7} = 1.4 \times 10^9$ mol^{-1} dm^3 s^{-1}
R8	$K_8 = 8$ mol^{-1} dm^3 s^{-1}	
R9	$K_9 = 8 \times 10^9$ mol^{-1} dm^3 s^{-1}	
R10	$K_{10} = 8.8 \times 10^8$ mol^{-1} dm^3 s^{-1}	$K_{-10} = 7.7 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}
R11	$K_{11} = 3 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}	$K_{-11} = 1 \times 10^2$ mol^{-1} dm^3 s^{-1}
R12	$K_{12} = 2.8 \times 10^9$ mol^{-1} dm^3 s^{-1}	
R13	$K_{13} = 2.8 \times 10^9$ mol^{-1} dm^3 s^{-1}	
R14	$K_{14} = 5 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}	
R15	$K_{15} = 1.94 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}	
R16	$K_{16} = 3 \times 10^4$ mol^{-1} dm^3 s^{-1}	
R17	$K_{17} = 2 \times 10^{-2}$ mol^{-2} dm^6 s^{-1}	
R18	$K_{18} = 6 \times 10^5$ mol^{-1} dm^3 s^{-1}	
R19	$K_{19} = 1 \times 10^{-5}$ mol^{-2} dm^6 s^{-1}	

TABLE 4: Rate Constant for the Ferroin−Bromate−CHD System[a]

reaction no.	rate constants	
R1	$K_1 = 8 \times 10^9$ mol^{-2} dm^6 s^{-1}	$K_{-1} = 80$ s^{-1}
R2	$K_2 = 2.5 \times 10^9$ mol^{-2} dm^6 s^{-1}	$K_{-2} = 2 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}
R3	$K_3 = 1.2$ mol^{-3} dm^9 s^{-1}	$K_{-3} = 3.2$ mol^{-2} dm^6 s^{-1}
R4	$K_4 = 2 \times 10^6$ mol^{-1} dm^3 s^{-1}	$K_{-4} = 1 \times 10^8$ s^{-1}
R5	$K_5 = 1.7 \times 10^5$ mol^{-1} dm^3 s^{-1}	
R6	$K_6 = 48$ mol^{-2} dm^6 s^{-1}	$K_{-6} = 3.2 \times 10^3$ s^{-1}
R7	$\mathrm{K}_7 = 7.5 \times 10^4$ s^{-1}	$\mathrm{K}\text{-}_7 = 1.4 \times 10^9$ mol^{-1} dm^3 s^{-1}
R20	$K_{20} = 2 \times 10^6$ mol^{-1} dm^3 s^{-1}	
R21	$K_{21} = 1 \times 10^7$ mol^{-1} dm^3 s^{-1}	
R11	$K_{11} = 3 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}	$K_{-11} = 1 \times 10^2$ mol^{-1} dm^3 s^{-1}
R12	$K_{12} = 2.8 \times 10^9$ mol^{-1} dm^3 s^{-1}	
R22	$K_{22} = 5 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}	
R15	$K_{15} = 1.9 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}	
R19	$K_{19} = 2 \times 10^{-5}$ mol^{-2} dm^6 s^{-1}	
R23	$K_{23} = 5$ mol^{-2} dm^6 s^{-1}	
R17	$K_{17} = 2 \times 10^{-2}$ mol^{-2} dm^6 s^{-1}	
R18	$K_{18} = 6 \times 10^5$ mol^{-1} dm^3 s^{-1}	
R16	$K_{16} = 1 \times 10^4$ mol^{-1} dm^3 s^{-1}	
R24	$K_{24} = 0.14$ s^{-1}	
R25	$K_{25} = 0.051$ mol^{-1} dm^3 s^{-1}	
R26	$K_{26} = 6 \times 10^3$ mol^{-1} dm^3 s^{-1}	
R27	$K_{27} = 2 \times 10^{-2}$ mol^{-3} dm^9 s^{-1}	

[a] [H_2O] = 55 M is included in the rate constant.

4. Results in the Ferroin−Bromate−CHD Oscillator

The ferroin-catalyzed bromate−CHD medium has been reported to exhibit strong and intricate responses to illumination in both stirred and reaction-diffusion media.[23,24] A kinetically significant difference from the ruthenium-catalyzed BZ reaction is that the photoreaction behavior in ferroin−bromate−CHD systems depends on light intensity, making its interpretation more difficult. In the following calculations we attempted to examine whether reaction step A is sufficient to qualitatively reproduce those experimental results.[23] Figure 4 presents a time series calculated with the model presented in Table 2 plus reaction step A. Initial conditions employed here are [ferroin] = 1.0×10^{-6} M, [H_2SO_4] = 1.0 M, [$NaBrO_3$] = 0.2 M, [CHD] = 0.09 M, and [H_2Q] = 0.02 M. The simulation shows that spontaneous oscillations commence at about 4500 s after the reaction starts. The illumination, implemented by setting $k_A = 2.0 \times 10^{-3}$ M^{-1} s^{-1}, is able to quench those spontaneous oscillations at different occasions. This inhibitory effect of light is similar to what was reported in experiments.[23]

The effect of light with a moderate intensity is presented in Figure 5, where only spontaneous oscillations between 5800 and 6000 s are shown for a better comparison. Spontaneous oscillations in the absence of illumination are presented in Figure 5a. The moderate light intensity in Figure 5b is implemented by decreasing k_A to 8.0×10^{-4} M^{-1} s^{-1} from 2.0×10^{-3} M^{-1} s^{-1} used in Figure 4. Different from what occurred in Figure 4, in Figure 5b there is no quenching behavior. Instead, the number of peaks within the same time frame is increased by roughly 10% when compared with the illumination-free situation in Figure 5a, suggesting that light exhibits a constructive effect here. In spatially extended media, it would correspond to a decrease in wavelength.[24] This result demonstrates that the inclusion of reaction process A is adequate to account for the qualitative change in the photoresponse seen in the catalyzed bromate−CHD reaction.[23,24]

Figure 6 presents light-induced oscillatory behavior in the ferroin−bromate−CHD oscillator, in which the initial conditions are [ferroin] = 2.0×10^{-6} M, [H_2SO_4] = 1.0 M, [$NaBrO_3$] =

0.2 M, [CHD] = 0.09 M, and [H_2Q] = 0.02 M. Figure 6a confirms that under the above conditions the nonilluminated system does not produce spontaneous oscillations. When illumination is turned on in Figure 6b, there is a great drop in the concentration of bromide ions due to the enhanced production of H_2Q, which is followed by spontaneous oscillations. As soon as the illumination is switched off, the oscillatory behavior stops and bromide concentration returns to the original, high level. The above process can be repeated several times until the system eventually evolves out of the suitable time frame. Such a scene is qualitatively the same as reported in earlier experiments.[24]

5. Conclusions

As demonstrated in the above, the inclusion of photoreduction of benzoquinone successfully reproduces various photocontrolled nonlinear behaviors observed in both uncatalyzed and ferroin-catalyzed bromate−CHD reactions.[23−25] Notably, the inclusion of step A is also sufficient to reproduce the subtle dependence of the oscillatory behavior on light intensity, where illumination could either enhance or quench the oscillatory behavior. Same as in the BZ reaction, nonlinear feedbacks in the bromate−CHD oscillators are formed through the autocatalytic production of $HBrO_2$.[32] Therefore, it is natural to wonder whether quenching phenomena in the bromate−CHD reactions could also be resulting from light-induced additional production of Br^-, similar to the photosensitivity in the ruthenium-catalyzed BZ reaction.[38,39] This paper shows that a reaction step which does not involve the production of bromide ions is capable of causing the quenching phenomenon. Indeed, the reaction process A proposed here produces H_2Q, a reagent which enhances the autocatalytic cycle. The coupling of the proposed photocontrolled chemical process A and reaction R2 listed in Tables 1 and 2 in turn causes a net decrease of bromide concentration.

Understanding the recycle of bromide ions has represented a great challenge in the study of uncatalyzed bromate oscillators. The above simulation unveils that bromide concentration must be within a suitable range for oscillations to occur in the bromate−CHD system. For the conditions at which the system does not produce spontaneous oscillations, the concentration of bromide is high, as shown in Figures 2 and 6. Illumination decreases the bromide concentration to the level where the system supports spontaneous oscillations. However, further enhancing illumination could drive the system out of the oscillatory window due to an excessive decrease in bromide concentration. This accounts for the light-induced quenching behavior in Figures 1 and 4, where when the system exhibits spontaneous oscillations, the concentration of bromide ion is moderate, but there is a great decrease in bromide concentration due to illumination, dropping below the threshold concentration. In summary, the great success in reproducing those photocontrolled nonlinear reaction behaviors suggests that the photoreduction of benzoquinone plays an important role in the uncatalyzed and catalyzed bromate−CHD systems. This result is significant for future experimental study and the development of a simplified model for the above systems, which will in turn play an important role in exploring perturbed nonlinear dynamics.

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