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Chemical oscillations during the photoreduction of 1,4-benzoquinone in acidic bromate solution

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Abstract

The photo-mediated bromate-1,4-benzoquinone reaction was investigated systematically as a function of light intensity, reaction temperature, and concentrations of 1,4-benzoquinone, bromate, and sulfuric acid. The parameter range within which the system exhibits spontaneous chemical oscillations has been determined. The observed oscillations could be temporarily quenched by adding bromide ions, but the addition of ethanol showed irreversible influences on the oscillatory phenomenon. Examinations with narrow band filters illustrate that incident light with the wavelength of around 450 nm, which overlaps with one of the absorption peaks of 1,4-benzoquinone, favors the oscillatory behavior. Numerical simulations confirm that the coupling of the photoreduction of 1,4-benzoquinone and the autocatalytic oxidation of 1,4-hydroquinone is responsible for the observed spontaneous oscillations.

Keywords: Photoreactions; 1,4-Benzoquinone; Chemical oscillations; Nonlinear feedbacks

1. Introduction

The photoprocess of quinones and their derivatives has been an active research subject in the past two decades [1–7]. For example, Görner investigated the photoreduction of 1,4-benzoquinone in organic solvents and in aqueous solutions, and reported the formation of 1,4-hydroquinone and hydroxybenzoquinone [6,7]. A recent study showed that when the photoreduction of 1,4-benzoquinone was performed in acidic bromate solution, spontaneous chemical oscillations could be observed [8]. Such a new observation demonstrates the feasibility of designing photochemical oscillators on the basis of photoreduction of quinones, coupled with the autocatalytic oxidations of the photoreduction products (e.g. 1,4-hydroquinone). Among numerous chemical and biochemical oscillators reported [9–15], bromate-based oscillating reactions, especially the Belousov–Zhabotinsky (BZ) system, are arguably the most extensively explored nonlinear chemical media [16–24]. When acidic bromate reacts with aromatic compounds, chemical oscillations have been observed even in the absence of metal catalysts [9,12]. For example, Farage and Janjic reported in 1982 that 1,4-cyclohexanedione (CHD) could react with acidic bromate in an oscillatory manner [12], in which 200–300 high frequency temporal redox-potential and bromide-ion-concentration oscillations were recorded under optimal chemical conditions.

Notably, due to the easy manipulation of the illumination protocol and intensity, which is a great advantage in exploring interactions of external forcing and intrinsic spatiotemporal dynamics, photosensitive chemical oscillators have attracted particular attention from scientists working in different areas, and those investigations have made significant contributions toward the understanding of various complexities in nature [25–36]. Different from the vast majority of existing photosensitive chemical oscillators such as the photosensitive BZ reaction, the recently reported photochemical oscillator on the basis of photo-recycling of 1,4-benzoquinone has a number of unique features. For example, it is completely unreactive in the absence of light, which consequently offers the possibility of switching the reaction dynamics between a non-reactive state and an oscillatory or excitable state with external forcing. In this report, kinetics of the newly discovered photo-mediated bromate-1,4-benzoquinone oscillator were systematically characterized as a function of light intensity, reaction temperature, and concentrations of bromate, sulfuric acid, and 1,4-benzoquinone.

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Numerical simulations were also carried out to support that the observed oscillations were indeed arising from intrinsic reaction kinetics.

2. Materials and methods

All reactions took place in a thermostated glass vessel, where the temperature was controlled at 20.0 ± 0.1 °C with a circulating water bath. No temperature increase was detected after the reaction mixture was exposed to illumination. Evolution of the reactions was followed by a platinum electrode coupled with a $Hg|Hg_2SO_4|K_2SO_4$ reference electrode (Radiometer Analytical Inc.). A bromide selective combo electrode (Radiometer Analytical Inc.) was occasionally employed to simultaneously follow the evolution of Br^- and Pt potentials. Both the Pt and Br^- potentials were recorded with a personnel computer connected through Powerlab/4SP (ADInstrument). 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 intensity was adjusted between 0 and 100 percent of the maximum light power, I_0 (150 mW/cm^2). The absolute light intensity was measured with an optical photometer from Newport (model 1815-C). Protocols of placing the two optic fibers on the same or opposite sides of the glass reactor have been investigated and there was no difference in the oscillatory behavior, suggesting that the mixing was fast enough to generate a situation of homogeneous illumination.

All reactions reported here were conducted under the protection of nitrogen. However, no significant difference was observed without the protection of nitrogen. For reactions measured with a UV/vis spectrophotometer (Ocean Optics, USB 2000), a single fiber was used to illuminate the reaction mixture from the top of the cuvette. Stock solutions $NaBrO_3$ (Aldrich, 99%), 0.6 M, NaBr (Aldrich, 99%), 0.01 M, and sulfuric acid (Aldrich, 98%), 3.0 M, were prepared with double-distilled water. Liquid bromine, ethanol (95%), and 1,4-benzoquinone (98%) were purchased from Aldrich company and were introduced by directly dissolving proper amounts into the reaction mixture. Bromate solution was added to the reaction mixture in the last step, after 1,4-benzoquinone (Q) has dissolved completely. All chemicals were commercial grade and were used without further purification.

3. Results and discussion

Fig. 1 presents time series of the bromate-Q reaction under different light intensities: (a) 100 mW/cm^2, (b) 90 mW/cm^2, (c) 80 mW/cm^2, and (d) 70 mW/cm^2. As discussed in the earlier report, in the absence of illumination Pt potential of the bromate and 1,4-benzoquinone mixture stays flat at about 600 mV, implicating that there is no reaction taking place. Periodic variations in the Pt potential are observed in Fig. 1a–c, where there is a long induction time before the oscillatory phenomenon onsets. During the induction period, bromide ion concentration increases gradually as measured with a bromide selective electrode. The induction time decreases with increasing light intensity, but eventually no oscillations could take place when the light intensity is too high, suggesting that there is an optimum intensity for supporting oscillations in this system.

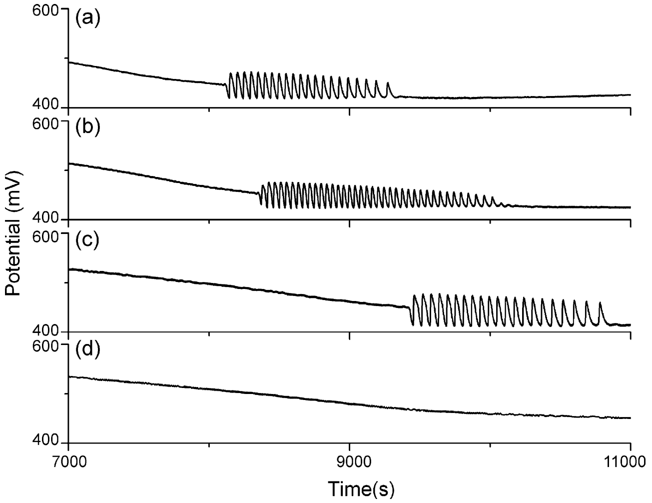

Fig. 1. Time series of the bromate-Q reaction at different illumination intensities, (a) 100 mW/cm^2, (b) 90 mW/cm^2, (c) 80 mW/cm^2, and (d) 70 mW/cm^2. Other reaction conditions are: [Q] = 0.02 M, [H_2SO_4] = 1.8 M, and [$NaBrO_3$] = 0.05 M.

Measurements of the absorption spectrum show that diluted Q solution (2.0 × 10^{-5} M) has one absorption peak at 246 nm, whereas the concentrated Q solution (0.02 M, used in most of our experiments) also has a weak absorption peak at about 440 nm. On the other hand, the power of the halogen light source concentrates within the visible region and in order to have a detectable amount of UV light the overall light intensity needs to be above 50 mW/cm^2. The mismatch between the absorptions of Q and the distribution of light power could be responsible for the intense illumination required in Fig. 1.

Fig. 2 presents the reaction behavior at different temperatures: (a) 10.0 °C, (b) 15.0 °C, (c) 17.5 °C, (d) 20.0 °C, (e) 22.5 °C, (f) 25.0 °C, (g) 27.5 °C, and (h) 30.0 °C. Other reaction conditions are [BrO_3^-] = 0.05 M, [H_2SO_4] = 1.8 M, [Q] = 0.02 M, and I = 100 mW/cm^2. Oscillations are observed for the temperature as low as 10.0 °C. Increasing temperature accelerates the over-

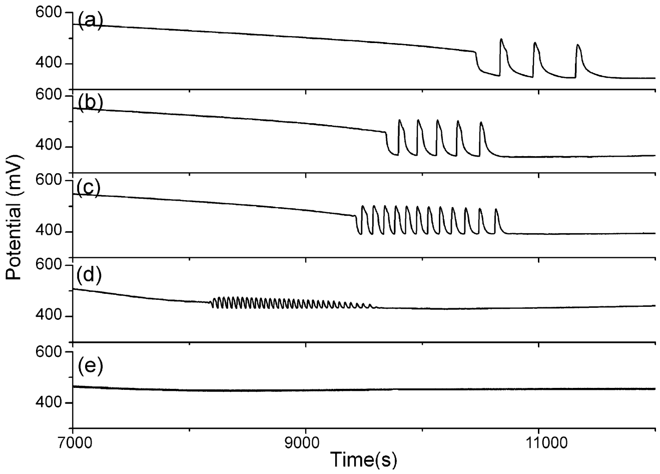

Fig. 2. Evolution of the bromate-Q reaction at different temperatures: (a) 10.0 °C, (b) 15.0 °C, (c) 20.0 °C, (d) 25.0 °C, and (e) 27.5 °C. Other conditions are [Q] = 0.02 M, [H_2SO_4] = 1.8 M, [$NaBrO_3$] = 0.05 M, and I = 100 mW/cm^2.

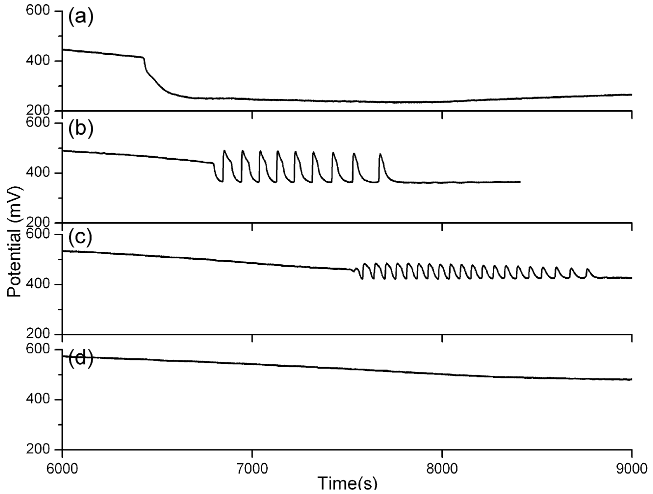

Fig. 3. Reaction behavior achieved at different concentrations of $NaBrO_3$: (a) 0.03 M, (b) 0.04 M, (c) 0.05 M, and (d) 0.06 M. Other reaction conditions are [Q] = 0.02 M, $[H_2SO_4] = 1.8$ M, and $I = 100$ mW/cm^2.

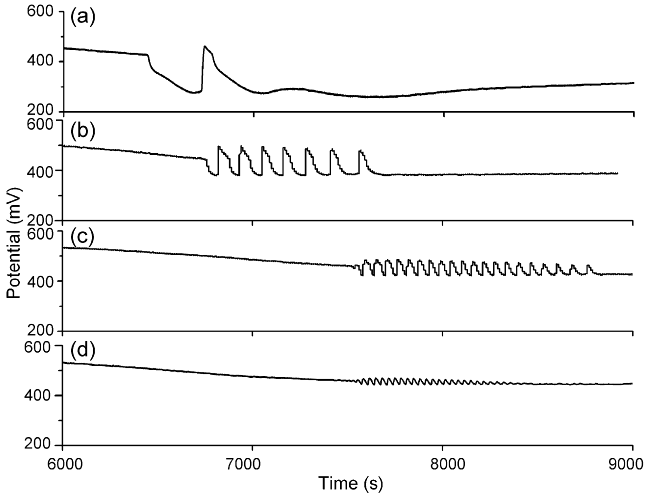

Fig. 4. Oscillatory behavior at different concentrations of H_2SO_4: (a) 1.0 M, (b) 1.4 M, (c) 1.8 M, and (d) 1.9 M. Other reaction conditions are [Q] = 0.02 M, $[NaBrO_3] = 0.05$ M, and $I = 100$ mW/cm^2.

all reaction process, as indicated by the rapid decrease of the Pt potential. Increasing the temperature reduces the induction time, but increases the oscillation frequency. No oscillations could be obtained when the temperature is higher than 27.5 °C. The above results clearly demonstrate that reaction temperature is a key parameter in achieving oscillations in this photo-mediated reaction system. Here, lowing temperature appears to favor the oscillatory behavior.

Fig. 3 presents time series at different initial concentrations of bromate: (a) 0.03 M, (b) 0.04 M, (c) 0.05 M, and (d) 0.06 M. Other reaction conditions are: $[H_2SO_4] = 1.8$ M, [Q] = 0.02 M, and $I = 100$ mW/cm^2. In Fig. 3a, there is an abrupt decrease in the Pt potential at about 6000 s after mixing all reactants together, yet no spontaneous oscillations is obtained. Increasing bromate concentration allows the oscillatory behavior to occur in Fig. 3b and c. However, still increase of bromate concentration results in adverse influences, causing the disappearance of spontaneous oscillations in Fig. 3d. The above results show that under the conditions studied here the concentration of bromate should be between 0.03 and 0.06 M in order to achieve spontaneous oscillations in this photo-driven chemical oscillator. Fig. 3 also demonstrates that the transition from non-oscillatory to oscillatory evolution at the low bromate condition (from Fig. 3a and b) is different from that at the high bromate concentration (from Fig. 3c and d).

Influences of H_2SO_4 concentration on the bromate-Q photochemical reaction are presented in Fig. 4, in which $[H_2SO_4]$ = (a) 1.0 M, (b) 1.4 M, (c) 1.8 M, and (d) 1.9 M. The optimum H_2SO_4 concentration at which the system generates the largest number of oscillation peaks is around 1.8 M. Oscillations become barely visible at $[H_2SO_4] = 1.9$ M and disappear completely when H_2SO_4 concentration is above 2.0 M. Fig. 4 shows that both the oscillation frequency and induction time increase with H_2SO_4 concentration.

Fig. 5 presents responses of the bromate-Q oscillator to a pulse Br^- perturbation, in which both Pt and Br^- potentials were recorded. Our calibrations indicate that a lower potential reading in Fig. 5b corresponds to a higher bromide concentration. During the long induction time period (which is not shown here), bromide concentration increases slowly. A temporal increase of Br^- concentration, which is seen as an abrupt drop in the Br^- potential, quenches the oscillatory behavior. During the non-oscillatory recovery process the Br^- concentration decreases and oscillations resume once Br^- concentration becomes low enough. Interestingly, Fig. 5b indicates that for the oscillatory behavior to revive the system does not require Br^- concentration to return to the original level. Depending on the concentration and phase at which Br^- is added, the spontaneous oscillations recover through several peaks with gradually decreasing or increasing amplitudes, a typical feature seen in earlier quenching experiments [37]. It suggests that this photo-mediated bromate-Q oscillator is bromide-controlled.

Fig. 6 shows responses of the bromate-Q oscillator to perturbations of ethanol. The presence of ethanol clearly reduces the amplitude of oscillation, in which the larger the amount of ethanol added, the smaller the oscillation amplitude became. When the ethanol concentration is too high, these spontaneous oscillations are completely quenched. Different from pertur-

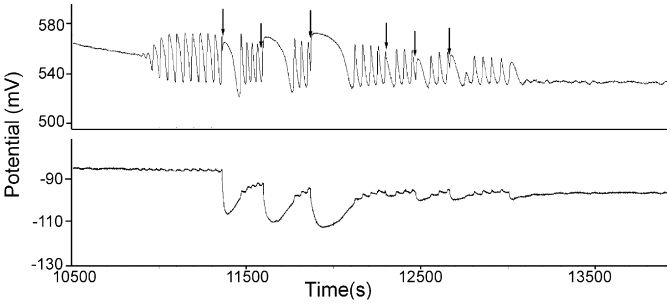

Fig. 5. Quenching of the bromate-Q oscillations with bromide: (a) monitored by a Pt electrode, and (b) monitored by a Br selective electrode. Arrows indicate the time when 10.0 μL (the first three injections) or 2.0 μL (the last three injections) of 0.01 M NaBr solution is injected into the reaction mixture. Other reaction conditions are [Q] = 0.02 M, $[H_2SO_4] = 1.8$ M, $[NaBrO_3] = 0.05$ M, and $I = 100$ mW/cm^2.

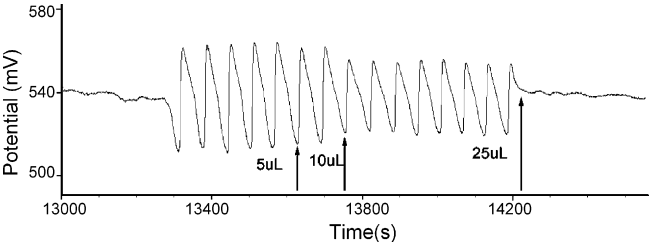

Fig. 6. Responses of the bromate-Q oscillations to perturbations of ethanol. Arrows indicate where a small volume of diluted ethanol (20%) is injected into the reaction mixture. Reaction conditions are [Q] = 0.02 M, $[H_2SO_4]$ = 1.8 M, $[NaBrO_3]$ = 0.05 M, and I = 100 mW/cm^2.

bations of Br^-, influences of adding ethanol are irreversible, implicating that during the reaction process ethanol is not consumed like Br^-. Such a kinetic effect suggests that the major role of ethanol is a radical scavenger, although there are reports that ethanol reacts with acidic bromate [38,39]. Working out from the above perspective, result in Fig. 6 suggests that the bromate-Q photochemical oscillator is also radical-controlled. The radical interactions may arise from several sources: As suggested in earlier investigations on the bromate-1,4-CHD reaction [40,41], H_2Q reacts with bromine dioxide radicals to form H_2Q radicals which undergo subsequent reactions with bromine dioxide radicals to build the autocatalytic cycle. The presence of ethanol may remove H_2Q and bromine dioxide radicals or radicals formed during the photoreduction of Q to hinder the overall autocatalytic cycle.

Fig. 7 shows influences of brominated substrates on the induction time. Here, in order to shorten the induction time the applied light intensity is higher than that used in the above experiments. Compositions of the reaction solution in Fig. 7a are $[H_2SO_4]$ = 1.8 M, $[NaBrO_3]$ = 0.05 M, and [Q] = 0.02 M, in which the induction time is about 3200 s. In the experiment shown in Fig. 7b, Br_2 solution (c.a. 0.001 M) was first mixed with 0.02 M H_2Q to react for an hour, and then 0.05 M $NaBrO_3$ and 1.8 M H_2SO_4 were added to the mixture and the illumination was turned on at the same time. The first Pt potential dip seen in Fig. 7b corresponds to the autocatalytic oxidation of H_2Q to Q by the acidic bromate, which occurs even in the absence of illumination. The presence of brominated species in Fig. 7b significantly reduces the induction time (ca. 2000 s in Fig. 7b). To examine whether the decrease of the induction time is due to the usage of H_2Q as the starting reactant, a parallel experiment with $[H_2SO_4]$ = 1.8 M, $[NaBrO_3]$ = 0.05 M, and $[H_2Q]$ = 0.02 M was run in Fig. 7c. The induction time in Fig. 7c is significantly longer than that in Fig. 7b, and is indeed comparable to that in Fig. 7a. Given that the only difference between reaction 7b and 7c is that Br_2 was added to reaction 7b to produce brominated species, this result strongly suggests that the accumulation of brominated substrates is responsible for the observed long induction time.

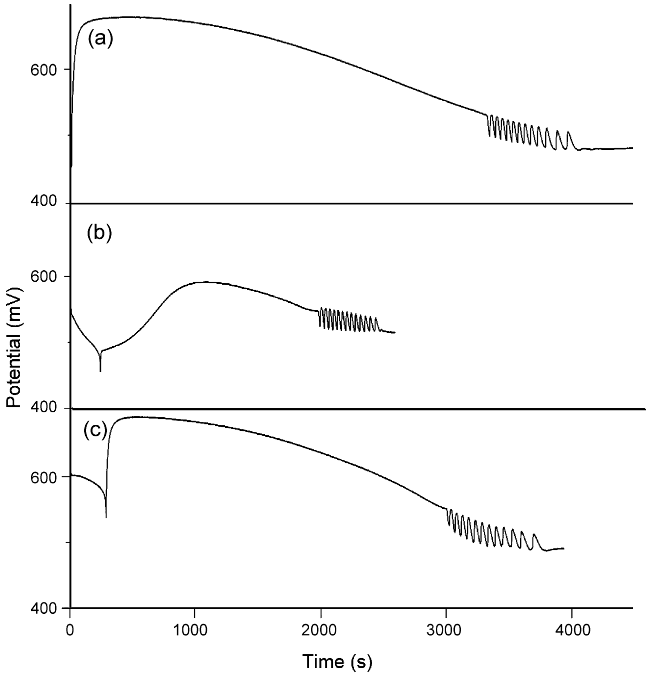

Fig. 7. Influences of the initial presence of brominated species on the induction time. Compositions of the reaction solution are $[H_2SO_4]$ = 1.8 M, $[NaBrO_3]$ = 0.05 M, and (a) [Q] = 0.02 M; (b) $[H_2Q]$ = 0.02 M and $[Br_2]$ = 0.001 M; and (c) $[H_2Q]$ = 0.02 M. Light intensity I = 140 mW/cm^2.

Fig. 8a presents the absorption spectra of the bromate-Q reaction at different times. As is shown in the figure, the initial reaction mixture has a broad absorption peak around 430 nm. This peak becomes visible only under high initial concentration of Q (>0.005 M), indicating that it is the absorption of Q. The magnitude of the absorption at 430 nm decreases continuously in time, indicating the consumption of Q. The spectrum recorded at t = 3000 s shows that a new substance with a maximum absorption wavelength of 350 nm was produced. Unfortunately, we have not been able to determine this product with GC/MS method. The Q concentration used in Fig. 8a is 0.01 M. Increasing Q concentration to 0.02 M, while all other conditions were

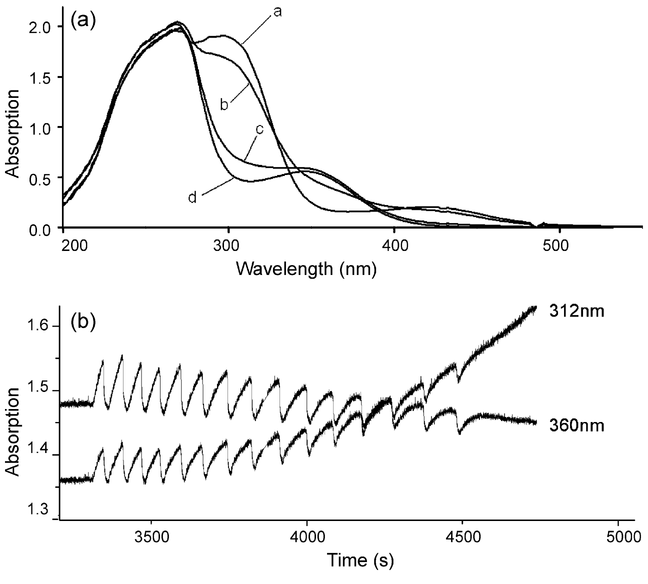

Fig. 8. (a) Absorption spectra of the illuminated bromate-Q system at different reaction times—(a): 5 s, (b): 600 s, (c): 3000 s, and (d): 4200 s; (b) Time series collected at different wavelengths. Reaction conditions are $[H_2SO_4]$ = 1.8 M, $[NaBrO_3]$ = 0.05 M, I = 50 mW/cm^2, and [Q] = 0.01 M in (a) and 0.02 M in (b) volume of the reaction solution is 2.5 mL.

Table 1
The oscillation magnitude and number of peaks when the system is illuminated with light of different wavelengths

Wavelength (nm)	Peak numbers	Amplitude (mV)
400 (±10 nm)	16	39
450 (±10 nm)	30	28
650 (±10 nm)	27	26
500 (±40 nm)	34	24
550 (±40 nm)	30	28
600 (±40 nm)	40	27

kept the same, did not induce qualitative change in the result shown in Fig. 8a, except that the recorded spectra became noisy within the UV range. Under high Q concentrations such as 0.02 M, however, the system could exhibit spontaneous oscillations, which is illustrated in Fig. 8b with two time series collected simultaneously at 312 and 360 nm. Large amplitude temporal oscillations at 312 and 360 nm suggest the periodic formation of semiquinone species. Results in Fig. 8 indicate that the new substance (with absorption at 350 nm) is formed well before the system reaches the oscillatory window. Its accumulation may be related to the long induction time and needs to be investigated further. Table 1 summarizes the dependence of the bromate-Q oscillations on the wavelength of the incident light. These experiments were conducted by placing a narrow band filter in front of the optic fibers. These measurements show that the incident light within 450 ± 10 nm has constructive effects on the oscillatory behavior, in agreement with that Q solution has an absorption peak within the same wavelength range. Because those narrow band filters also significantly cut the intensity of the incident light, we were unable to see oscillations with the filters centered within the UV regime where Q has a large absorption.

4. Numerical simulations

Design of the bromate-Q photochemical oscillator is based on the light-induced conversion of 1,4-benzoquinone to 1,4-hydroquinone. While the conversion of Q to H_2Q in aqueous solution is a rather complicated process involving multiple steps [6,7], in this study we use the following schematic step to represent the complicated photoreduction of Q:

$$\mathrm{Q} + h\nu \rightarrow \mathrm{H_2Q} \tag{1}$$

The above schematic reaction does not consider the production of hydroxybenzoquinone as proposed by Gorner [7]. Whether hydroxybenzoquinone also reacts with acidic bromate will be examined in the future research. Rate constant of reaction (1) is adjusted arbitrarily in this study to reflect effects of light intensity on such a process. Earlier investigations on the bromate-1,4-CHD oscillator have suggested that H_2Q and bromate in acidic solution undergo the following reactions [40,41].

$$\mathrm{Br^-} + \mathrm{HOBr} + \mathrm{H^+} \leftrightarrow \mathrm{Br_2} + \mathrm{H_2O} \tag{2}$$

$$\mathrm{Br^-} + \mathrm{HBrO_2} + \mathrm{H^+} \rightarrow 2\mathrm{HOBr} \tag{3}$$

$$\mathrm{Br^-} + \mathrm{BrO_3}^- + 2\mathrm{H^+} \leftrightarrow \mathrm{HOBr} + \mathrm{HBrO_2} \tag{4}$$

$$2\mathrm{HBrO_2} \rightarrow \mathrm{HOBr} + \mathrm{BrO_3}^- + \mathrm{H^+} \tag{5}$$

$$\mathrm{HBrO_2} + \mathrm{BrO_3}^- + \mathrm{H^+} \leftrightarrow 2\mathrm{BrO_2}* + \mathrm{H_2O} \tag{6}$$

$$\mathrm{H_2Q} + \mathrm{BrO_2}* \rightarrow \mathrm{HQ}* + \mathrm{HBrO_2} \tag{7}$$

$$\mathrm{HQ}* + \mathrm{BrO_2}* \rightarrow \mathrm{Q} + \mathrm{HBrO_2} \tag{8}$$

$$2\mathrm{HQ}* \rightarrow \mathrm{H_2Q} + \mathrm{Q} \tag{9}$$

$$\mathrm{H_2Q} + \mathrm{Br_2} \rightarrow \mathrm{QBr} + \mathrm{Br^-} + \mathrm{H^+} \tag{10}$$

$$\mathrm{H_2Q} + \mathrm{BrO_3}^- + \mathrm{H^+} \rightarrow \mathrm{Q} + \mathrm{HBrO_2} + \mathrm{H_2O} \tag{11}$$

$$\mathrm{H_2Q} + \mathrm{HOBr} \rightarrow \mathrm{Q} + \mathrm{Br^-} + \mathrm{H^+} \tag{12}$$

$$\mathrm{QBr} \rightarrow \mathrm{Q} + \mathrm{Br^-} \tag{13}$$

in which reactions (6)–(8) together build an autocatalytic cycle, a key element in designing chemical oscillators [16,24]. The net outcome of reactions (2)–(13) is the oxidation of H_2Q to produce Q. Rate constants used in the following simulations are $k_1 = 7 \times 10^{-4}\,\mathrm{s^{-1}}$, $k_2 = 8.0 \times 10^9\,\mathrm{M^{-2}\,s^{-1}}$, $k_{2-} = 80\,\mathrm{s^{-1}}$, $k_3 = 2.5 \times 10^6\,\mathrm{M^{-2}\,s^{-1}}$, $k_4 = 1.2\,\mathrm{M^{-3}\,s^{-1}}$, $k_{4-} = 3.2\,\mathrm{M^{-1}\,s^{-1}}$, $k_5 = 3400\,\mathrm{M^{-1}\,s^{-1}}$, $k_6 = 48\,\mathrm{M^{-2}\,s^{-1}}$, $k_{6-} = 6.4 \times 10^7\,\mathrm{M^{-1}\,s^{-1}}$, $k_7 = 8.0 \times 10^5\,\mathrm{M^{-1}\,s^{-1}}$, $k_8 = 8.0 \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$, $k_9 = 8.8 \times 10^8\,\mathrm{M^{-1}\,s^{-1}}$, $k_{10} = 3.0 \times 10^4\,\mathrm{M^{-1}\,s^{-1}}$, $k_{11} = 2.0 \times 10^{-2}\,\mathrm{M^{-2}\,s^{-1}}$, $k_{12} = 6.0 \times 10^5\,\mathrm{M^{-1}\,s^{-1}}$, and $k_{13} = 3.0 \times 10^{-6}\,\mathrm{s^{-1}}$.

Simulations were carried out by integrating reaction rate laws derived from reactions (1)–(13). To mimic experiments, no H_2Q was presented initially in the system. Under such a configuration, the system did not exhibit any reactivity with $k_1 = 0$, i.e. in the absence of light. Fig. 9 presents time series of $\mathrm{Br^-}$ concentration calculated under different k_1 values: (a) $1.2 \times 10^{-3}\,\mathrm{s^{-1}}$, (b) $7.0 \times 10^{-4}\,\mathrm{s^{-1}}$, (c) $4.0 \times 10^{-4}\,\mathrm{s^{-1}}$, and (d) $2.0 \times 10^{-4}\,\mathrm{s^{-1}}$. Similar to the experimental results, spontaneous oscillations with a long induction time (>8000 s) are achieved at larger k_1. Again, increasing k_1 in the simulation corresponds to an increase of the applied light intensity in experiments. In consistent with experimental measurements, the $\mathrm{Br^-}$ concentration increases

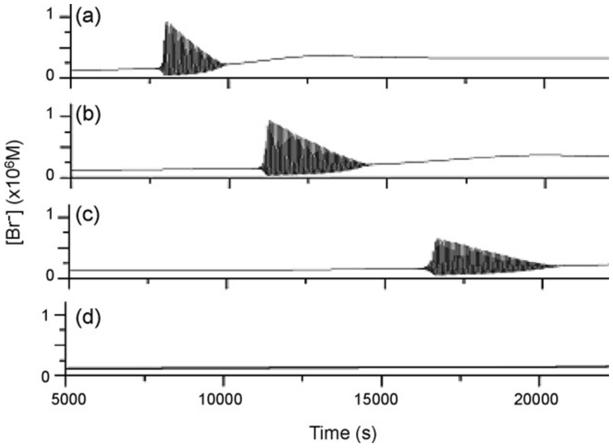

Fig. 9. Simulation results under different k_1 values: (a) $1.2 \times 10^{-3}\,\mathrm{s^{-1}}$, (b) $7.0 \times 10^{-4}\,\mathrm{s^{-1}}$, (c) $4.0 \times 10^{-4}\,\mathrm{s^{-1}}$, and (d) $2.0 \times 10^{-4}\,\mathrm{s^{-1}}$. Other initial conditions are $[\mathrm{Q}] = 0.02\,\mathrm{M}$, $[\mathrm{H_2SO_4}] = 1.8\,\mathrm{M}$, $[\mathrm{NaBrO_3}] = 0.05\,\mathrm{M}$, and $[\mathrm{Br^-}] = 10^{-7}\,\mathrm{M}$. Concentrations of other intermediates are set to 0.

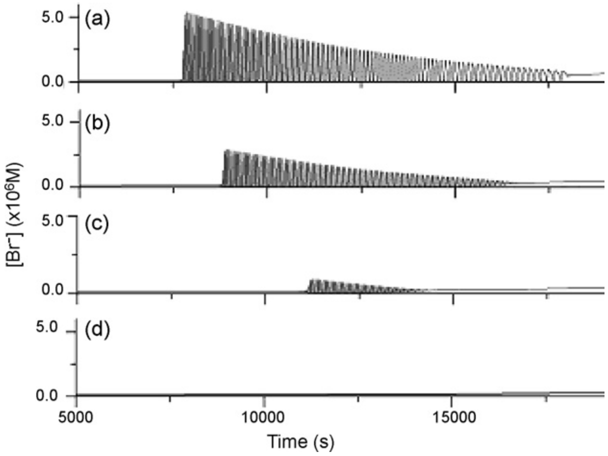

Fig. 10. Simulations of the bromate-Q reaction at different Q concentrations: (a) 0.03 M, (b) 0.025 M, (c) 0.02 M, and (d) 0.015 M. Other initial conditions are, $k_1 = 7.0 \times 10^{-4}$ s^{-1}, $[H_2SO_4] = 1.8$ M, $[NaBrO_3] = 0.05$ M and $[Br^-] = 10^{-7}$ M. Concentrations of other intermediates are set to 0.

slowly during the induction time and then oscillates. When a small amount of QBr is included initially in our modeling, the induction time is decreased greatly, in good agreement with the scenario seen in Fig. 7. Yet the formation of QBr as well as other possible brominated substances in the illuminated bromate-Q reaction needs to be explored further.

Fig. 10 presents time series calculated under different initial concentrations of Q: (a) 0.03 M, (b) 0.025 M, (c) 0.02 M, and (d) 0.015 M. The same as seen in experiments, this figure illustrates that no photo-induced oscillations could be obtained under low Q concentrations. The largest number of oscillation peaks is obtained at a moderate Q concentration. The existence of an upper and lower concentration limit of sulfuric acid and bromate for the occurrence of spontaneous oscillations could also be qualitatively reproduced with this model. However, varying the concentration of Q, sulfuric acid or bromate exhibits stronger effects on the induction time than seen in experiments. These discrepancies might arise from the simplified consideration of light-induced conversion of Q to H_2Q and the unknown processes leading to the production of brominated substances.

5. Conclusions

Kinetics of the photo-mediated bromate-1,4-benzoquinone reaction were explored in this study as a function of light intensity, reaction temperature, and concentrations of bromate, Q, and sulfuric acid. Parameter ranges with which the system exhibits spontaneous oscillations are determined. Similar to what was reported in other uncatalyzed bromate-aromatic compound oscillators [12,40], the bromate-Q photochemical oscillator has a long induction time which is greatly affected by the presence of brominated species. Perturbation experiments with bromide ions suggest that nonlinear feedbacks in this system may arise from the autocatalytic production of bromous acid, where 1,4-hydroquinone is oxidized by bromine dioxide radicals [40,41]. Meanwhile, the irreversible effects of ethanol on the oscillatory phenomenon illustrate that radical reactions also play an important role in the bromate-Q photoreaction.

Numerical simulations support that the observed spontaneous oscillations are due to the coupling of the photoreduction of Q and the autocatalytic oxidation of 1,4-hydroquinone. In addition, the simulation shows that the formation of brominated species is critical in affecting the induction time. Deciphering the formation of those brominated species in the future is essential in improving our understanding of this as well as other uncatalyzed bromate oscillators. Despite the underlying reaction mechanism remains largely unknown, the systematic exploration performed in this research offers valuable insights into the design of novel photochemical oscillators on the basis of photoreduction of quinones.

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