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Photocontrolled oscillatory dynamics in the bromate-1,4-cyclohexanedione reaction

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We report observations of photocontrolled oscillatory behavior in the 1,4-cyclohexanedionebromate reaction (CHD—cyclohexanedione). Experiments in a batch reactor show that illumination may exhibit qualitatively different effects on the reaction dynamics, where illumination with a moderate intensity favors oscillations while strong illumination quenches spontaneous oscillations. A transition from light-quenched to light-induced oscillations during the course of the reaction has also been observed. Investigations in a continuous flow stirred tank reactor further illustrate that the influence of light in the 1,4-CHD-bromate reaction depends not only on the intensity of the illumination but also on the phase at which the illumination is switched on. Mechanistic investigations suggest that 1,4-benzoquinone, a final product in the 1,4-CHD-bromate reaction system, plays a significant role in the occurrence of photoinduced oscillations. © 2004 American Institute of Physics. [DOI: 10.1063/1.1809111]

I. INTRODUCTION

Perturbed nonlinear dynamics had attracted increasing attention in the last two decades.¹⁻⁸ Among existing studies, the photosensitive Belousov-Zhabotinsky (BZ) reaction has played an important role because photosensitivity provides a convenient approach to implement a perturbation.9-21 A number of intriguing behaviors such as resonance phenomena had been observed when the photosensitive BZ system was subjected to an external periodic or irregular illumination.⁹⁻²¹ In general, under the same reaction conditions illumination is expected to quench or support the oscillatory behavior and such an effect shall be independent of the intensity of applied light. However, in recent reports Kurin-Csörgei and co-workers observed that chemical waves in the 1,4-cyclohexanedione-bromate-ferroin system exhibited opposite responses when the applied light intensity was adjusted (CHD—cyclohexanedione).^{22,23} A similar behavior has also been reported recently in the stirred 1,4-CHDbromate-ferroin medium, in which light-induced and lightinhibited oscillations were observed under the same reaction conditions.²⁴ The subtle response of its reaction dynamics to illumination, together with the absence of production of gases, makes the 1,4-CHD-bromate reaction an attractive model system to explore novel spatial and temporal behaviors.22-30

Despite the 1,4-CHD-bromate-ferroin reaction has received a lot of attention recently and a number of interesting photocontrolled behaviors have been observed there, its underlying photoreaction mechanism remains to be understood. Earlier investigations had demonstrated that ferroin could be excited by light to induce temporal oscillations or pattern formation in the ferroin-bromate-malonic acid reaction.^{21,31} To discriminate whether ferroin plays a similar role in the 1,4-CHD-bromate system, this paper investigated the photoreaction dynamics of the uncatalyzed 1,4-CHD-bromate system. In addition to transitions between light-enhanced and light-inhibited oscillatory phenomena, an evolution from light-quenched to light-induced oscillatory behavior has also been observed at a constant light intensity. Mechanistic investigations illustrate that 1,4-benzoquinone, a product in the above system, plays an important role in the observed photoinduced oscillations. Illumination-induced production of bromide from BrCHD, on the other hand, is the culprit for causing quenching phenomena.

II. EXPERIMENT

All reactions in a closed system were carried out in a thermostated cylindrical glass vessel, in which the temperature was maintained at (25 ± 0.1) °C by a circulating water bath (Thermo NesLab RTE 10). No temperature change has been observed when the reaction mixture was illuminated with light. Reactions were followed by a platinum electrode coupled with a double junction reference electrode which used saturated KCl as the inner solution and 1M KNO3 as the outer solution. The outer electrolyte was replaced every 12 h to avoid Cl⁻ contamination from the inner electrolyte. The redox potential was recorded with a multichannel Canlab recorder through a Corning Pinnacle pH meter. A bromide ion-selective electrode (Orion, 9435BN) coupled with the double junction reference electrode was also employed to follow the response of the reaction to illumination, which produced the same behavior as recorded by the platinum electrode. However, because the signal recorded by the bromide electrode (<30 mv) was weaker than the Pt potential (>100 mv), time series presented here were the redox potentials recorded by the platinum electrode couple. 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% of the maximum light power, I_0 (100 mW/cm²). The

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¹⁰¹³⁸

absolute light intensity was measured with an optical photometer from Newport. The optical fiber was positioned at about 2 cm above the solution surface.

Experiments in a continuous flow stirred tank reactor (CSTR) were followed with a platinum electrode (from London Scientific) coupled with a $Hg|Hg_2SO_4|K_2SO_4$ reference electrode. The Pt potential signal was recorded through a REC 80 Servograph recorder. The reaction temperature was maintained at (25 ± 0.1) °C by a circulating water bath (Thermo NesLab RTE 7). Here, light perturbation was applied by using two bifurcated optic fibers to illuminate the glass chamber from opposite directions. Stock solutions NaBrO₃ (Aldrich, 99%), 0.45M, and 1,4-CHD (Aldrich, 98%), 0.144M, were dissolved, respectively, in 1.5M sulfuric acid solution. Hydroquinone (Aldrich, 99%), 0.06M was directly dissolved in doubly distilled water. All three stock solutions were pumped into the CSTR by a peristaltic pump at equal flow rates. All chemicals were used in their commercial grade without further purification.

III. RESULTS IN A BATCH REACTOR

The 1,4-CHD-bromate reaction was first investigated over a broad range of conditions in order to identify a set of suitable conditions for characterizing the influence of light. A desired condition to characterize the inhibitory effect of light is that under which spontaneous oscillations last for a long time period so that multiple perturbations could be examined in one run. Our experiments illustrated that increasing the initial concentration of bromate prolonged the oscillatory window; however, the induction time of spontaneous oscillations was also significantly prolonged. Our further exploration showed that the addition of hydroquinone (H_2Q) could greatly shorten the induction period. More significantly, as shown in the following, the initial concentration of hydroquinone could also be employed as an effective dynamic control parameter (see Figs. 1 and 2) to alter the oscillatory behavior. Therefore, hydroquinone was employed throughout this study as a means of manipulating the reaction dynamics and reducing the induction period of the 1,4-CHD-bromate oscillations.

Figure 1 presents two examples of quenching phenomena. Here spontaneous oscillations occur at about 1 h after the beginning of the reaction, i.e., after mixing all reactants together. Initial compositions of the reaction solution were $[H_2SO_4] = 1.0M$, $[NaBrO_3] = 0.15M$, [1,4-CHD]= 0.048M, and $[H_2Q] = (a) 0.02M$ and (b) 0.03M. As shown in Fig. 1(a), during the earlier oscillatory stage, 25% I_0 (25 mW/cm²) successfully quenched the oscillation and caused the Pt potential to return to the same level as before the occurrence of spontaneous oscillations. After the light was turned off to allow the spontaneous oscillations to resume, another application of 25% I_0 (25 mW/cm²) could not successfully quench the system as it did in the earlier trail. Instead, the overall potential was shifted upwards while the oscillation amplitude did not appear to be affected. However, the application of 50% I_0 (50 mW/cm²) resulted in quenching of the system in two separate attempts. In Fig. 1(b), 25% I_0 (25 mW/cm²) only managed to shift the potential upwards and reduced the amplitude slightly. 50% I_0 (50 mW/cm²)



FIG. 1. Time series showing the light-inhibited oscillatory behavior at different initial concentrations of H_2Q : (a) 0.02*M* and (b) 0.03*M*. Initial compositions of other reagents are $[BrO_3^-]=0.15M$, $[H_2SO_4]=1.0M$, and [1,4-CHD]=0.048M.

managed to raise the potential significantly in both attempts, but only resulted in the decrease in the amplitudes of these oscillations. There was a noticeable difference in the rise in potential when 50% I_0 (50 mW/cm²) was used on both occasions. This difference may be attributed to the stage of the reaction. The second application of 50% I_0 (50 mW/cm²)



FIG. 2. Time series showing light-induced oscillations. Initial compositions of reaction solution are $[BrO_3^-]=0.15M$, $[H_2SO_4]=1.0M$, $[H_2Q]=0.04M$, and [1.4-CHD]=0.048M.

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FIG. 3. Time series showing a transition from light-quenched to light-induced oscillations. The initial compositions of the reaction mixture are $[BrO_3^-]=0.15M$, $[H_2SO_4]=1.0M$, $[H_2Q]=0.03M$, and [1,4-CHD]=0.04M.

was during the latter stage of the oscillatory part of the reaction, and the system seemed to have had more difficulty in raising the potential. Successful quenching was achieved after the light intensity was raised to 63% I_0 (63 mW/cm²). The above results illustrate that an increase in the initial concentration of hydroquinone reduces the negative influence of light on spontaneous oscillations. Such an effect could well be resulted from the fact that hydroquinone, a photosensitive species, absorbs increasing amounts of light to shield the influence of light on other photosensitive species.

Figure 2 presents the time series of light-induced oscillatory behavior in the uncatalyzed 1,4-CHD-bromate reaction. As shown in Fig. 2(a), the system did not oscillate in the absence of illumination. This nonoscillatory behavior was obtained by increasing the initial concentration of hydroquinone to 0.04*M*. Together with the results shown in Fig. 1, it illustrated that the concentration of hydroquinone was an effective bifurcation control parameter. Although no spontaneous oscillations occurred here, there was still a sharp drop in the Pt potential after a short time period (<30 min) and light-induced oscillations could be achieved after the abrupt drop in the Pt potential took place. Later, the redox potential returned to its initial level (i.e., before the potential drop) and no light-induced oscillations could be obtained afterwards. As shown in Fig. 2(b), 50% I_0 (50 mW/cm²) was able to induce oscillations most effectively. What is interesting to note is that when the light was turned off after the first application of 50% I_0 (50 mW/cm²), smaller amplitude (and lower frequency) oscillations continued at a lower potential for several minutes. This implies that the species created through use of light would eventually be used up in the reaction some time after the light was stopped; thus "residual

TABLE II. Photocontrolled reaction behavior under different concentrations of hydroquinone (H₂Q). Other initial compositions are [1,4-CHD] = 0.048M, [H₂SO₄] = 1.0M, and [BrO₃⁻] = 0.15M.

$[H_2Q](M)$	Spontaneous/ No oscillation	Light induced/inhibited
0	No oscillations	No activity
0.01	No oscillations	No activity
0.02	Spontaneous	Inhibited; quenching at above 25% I_0 early on, 50% at later stage.
0.03	Spontaneous	Inhibited, quenching at above $62.5\% I_0$
0.04	No oscillations	Induced; oscillations at above 30% I_0
0.05	No oscillations	Induced; oscillations at above 50% I_0
0.06	No oscillations	Induced; oscillations at above 63% I_0
0.07	No oscillations	Induced; oscillations at above 75% I_0

oscillations" were bound to occur for some time after the light supply was cut off.

Time series shown in Fig. 3 illustrates a transition from light-inhibited (at the earlier stage of the reaction) to lightinduced oscillatory behavior (at the later stage of the batch reaction). Here the initial concentration of 1,4-CHD is 0.04M, slightly lower than that in Fig. 1(b), while other reaction conditions are kept constant. The use of light (25 and 50 mW/cm^2) resulted in an upward shift in the potential and the frequency of oscillations was also increased dramatically upon the application of light. Use of 63% I_0 (63 mW/cm²) was required to quench oscillations. Surprisingly, application of 50% I_0 (50 mW/cm²) after spontaneous oscillations disappeared resulted in a "revival" of oscillations. Such a qualitative change in responding to illumination provides a set of unique information for deciphering the underlying photoreaction mechanisms. We would like to note that the above revival phenomena could also be achieved under other initial conditions. However, the time period over which revival oscillations can be achieved is quite narrow (<5 min).

To gain more insight into the appearance of the above observed light-induced and light-quenched oscillations, experiments were carried over a broad range of 1,4-CHD and hydroquinone concentrations. The results were summarized in Tables I and II, where initial concentrations of sulfuric acid and bromate were held constant at 1.0*M* and 0.15*M*, respectively. As listed in Table I, an increase in the initial concentration of 1,4-CHD favored the occurrence of spontaneous oscillations and the system also required stronger illumination for a successful quenching. When hydroquinone

TABLE I. Photocontrolled reaction behavior at different initial concentrations of 1,4-CHD. Other initial conditions are $[H_2Q]=0.03M$, $[H_2SO_4]=1.0M$, and $[BrO_3]=0.15M$.

[1,4-CHD](<i>M</i>)	Spontaneous/No oscillation	Light induced/inhibited
0.01	No oscillations	No activity at all
0.02	No oscillations	No activity at all
0.03	No oscillations	Induced; oscillations at above 25% I_0
0.04	Spontaneous	Inhibited; quenching at 63% I_0
0.05	Spontaneous	Inhibited; quenching at 50% I_0
0.06	Spontaneous	Inhibited; quenching at 63% I_0
0.07	Spontaneous	Inhibited; quenching at 75% I_0
	-	

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TABLE III. Photocontrolled reaction behavior at different initial concentrations of H_2SO_4 . Other initial conditions are $[H_2Q]=0.03M$, [1,4-CHD]= 0.06*M*, and $[BrO_3^-]=0.15M$.

[H ₂ SO ₄]	Spontaneous/No scillations	Light induced/inhibited
0.4M	No oscillations	N/A
0.5M	No oscillations	Induced at 25% I_0
0.6M	No oscillations	Induced at 25% I_0
0.7M	Spontaneous	Quenching at 50% I_0
0.8M	Spontaneous	Quenching at 50% I_0
0.9M	Spontaneous	Quenching at 50% I_0
1.0M	Spontaneous	Quenching at 50% I_0
1.1M	Spontaneous	Quenching at 50% I_0
1.2 <i>M</i>	No oscillations	No response to light

was adjusted as a variable, its overall effects on the oscillatory dynamics were not monotonic, where spontaneous oscillations were obtained only within a narrow parameter window. Also shown in Table II was that light of higher intensity was required to initiate oscillations when the concentration of hydroquinone was increased.

How the photocontrolled reaction dynamics response to the variation of the concentration of sulfuric acid has also been examined here. Experiments illustrated that spontaneous oscillations could be achieved when $[H_2SO_4]$ was between 0.7M and 1.2M while initial concentrations of other reactants were [1,4-CHD] = 0.060M, $[H_2Q] = 0.030M$, and $[BrO_3] = 0.15M$. When the concentration of sulfuric acid was below 0.7M, no spontaneous oscillations could be achieved and the reaction exhibited qualitatively the same type of Pt potential curve as that shown in Fig. 2(a). Under these nonoscillatory reaction conditions, if the intensity of the applied illumination was above 25 mW/cm² but below 50 mW/cm², light-induced oscillations could be obtained. Successful quenching behavior was observed when the light intensity was above 50 mW/cm². However, same as observed in Fig. 1(b), illuminations of lower intensity only resulted in an increase in the frequency of oscillations, exhibiting constructive effects on the oscillatory dynamics. In the case that $[H_2SO_4] > 1.2M$, the system became nonoscillatory again; but, the system only stayed at the low potential state of the U-shaped curve for a very short time period and no lightinduced oscillations were obtained there. Table III provided a summary of the effects of the initial concentration of sulfuric acid on the photoreaction dynamics. Thresholds for lightinduced and light-quenched oscillations seemed to remain constant within the concentration range investigated here. Such a result implied that hydrogen ions were not the limiting reagent here or were not involved in the photoreaction processes.

IV. RESULTS IN A CSTR

The influence of light on the 1,4-CHD-bromate reaction is also characterized in a CSTR, in which fresh reactants are continuously pumped into the reaction chamber to keep the reaction at a stable yet far from thermodynamic equilibrium state. As opposed to that the slowly but continuously decreasing concentration of reagents is the bifurcation parameter in a batch system, flow rate, which can be kept steady, is



FIG. 4. Time series showing the influence of light on the 1,4-CHD-bromate oscillation in a CSTR. Concentrations of the stock solutions are provided in the experimental section. The volume of the reactor is 40 ml and the mean resident time of the reaction solution is 90 min. The light intensity $I_0 = 100 \text{ mW/cm}^2$.

the bifurcation control parameter in a CSTR. The result that spontaneous oscillations in Fig. 1 do not appear until 60 min after mixing all reactants together suggests that the mean resident time of the reaction solution in the CSTR should be larger than 60 min in order to obtain oscillations. In addition, the short-lived spontaneous oscillations in a batch reactor indicate that spontaneous oscillations could only be obtained within a narrow range of flow rate in the CSTR when the same reaction conditions are employed. Our following experimental results are consistent with the above analysis.

Figure 4 presents an example of quenching behavior in the CSTR. Here, the mean resident time of the reaction solution in the reactor $(V=40 \text{ cm}^3)$ is 90 min, which is larger than the induction time period observed in the batch system. Spontaneous one peak per period oscillations were observed under the above conditions. When a constant illumination of the intensity of 25 mW/cm² was applied, the oscillation merely shifted upward while the frequency of oscillation becomes a bit smaller. No quenching was obtained under the perturbation of 25 mW/cm². Successful quenching was observed after the intensity of the illumination was increased to 50 mW/cm². Note that the system was driven toward bottom by the perturbation of 50 mW/cm². The illumination was kept on until the Pt potential became flat. Surprisingly, the system remained at the low Pt potential state even after the illumination was turned off. Indeed, the system could return to the oscillatory state only after the flow rate was briefly changed from 0.44 to 0.3 ml/min for about 1.0 s. This scenario indicates that the 1,4-CHD-bromate system actually has two coexisting steady states, i.e., a limit cycle and a stable steady state. The observed quenching behavior is because illumination pushed the system from the limit cycle to the steady state.

Figure 5 presents quenching phenomena achieved when the same illumination (50 mW/cm²) was applied at different phases of oscillation. Significantly, qualitatively different behaviors were observed here: When the illumination was switched on at around the top of the oscillation, the perturbation quenched these oscillations and drove the system upward. Notably, as soon as the illumination was turned off, spontaneous oscillations were restored. In contrast, if the light was switched on at around the bottom part of the oscil-



FIG. 5. Time series showing the dependence of the influence of light on the phase of oscillation. Reaction conditions here are the same as that in Fig. 4. The intensity of the applied light, which is 50 mW/cm^2 , is kept constant through out this experiment.

lation, spontaneous oscillations were also quenched; however, the system would then be driven downward and, more significantly, the system continuously evolved toward the lower potential state even after the illumination was turned off. The oscillatory behavior could be restored only after a perturbation was applied to the flow rate. The above phase dependence of the influence of light has not been observed in a batch reactor, which is presumably because no bistability has been achieved there. So far, no light-induced oscillations were obtained in the CSTR even though the same reaction conditions as used in the batch reactor had been employed.

V. MECHANISTIC INVESTIGATIONS

Same as in the BZ reaction,^{32–34} oscillations studied here could also be quenched by adding small amounts of bromide. It prompts us to wonder whether quenching phenomena in the bromate-1,4-CHD reaction is also resulted from lightinduced additional production of Br⁻. To examine the above hypothesis, we first investigated the influence of illumination on the decomposition of BrCHD. According to the mechanism proposed by Körös and co-workers,²⁹ BrCHD is the major source of the reproduction of Br⁻ in the 1,4-CHDbromate oscillator. To prepare the BrCHD solution, BrO_3^- , Br⁻, and 1,4-CHD acidic solutions are mixed in a sealed beaker according to the 1:2:3 stoichiometric relationship. The bromination process took about 35 min to complete, indicated by the disappearance of the orange color (i.e., bromine). Once the reaction mixture becomes transparent, a bromide ion-selective electrode coupled with a double junction reference electrode is inserted into the beaker to follow the variation of Br⁻ concentration. Continuous decrease in the bromide potential is recorded, which is due to the production of bromide ions. In Fig. 6, the directly measured potentials were converted to the concentration of bromide according to a standard curve obtained earlier. In this experiment, illumination was switched on and off periodically (every 5 min). As shown in the figure, the variation in the concentration of bromide was indeed slightly accelerated under illumination, although this effect became less pronounced in time. We have also tried to make BrCHD directly from 1,4-CHD and bromine; however, because of the presence of larger amounts of Br⁻, a byproduct in the above reaction, the potential measurement became less sensitive (i.e., our calibration illustrates that the potential reading has a linear relationship



FIG. 6. Time series showing the influence of illumination on the production of Br⁻ from BrCHD. Compositions of the reaction solution consist of $0.5M H_2SO_4$ and 0.03M BrCHD, prepared by mixing $0.01M BrO_3$, $0.02M Br^-$, and 0.03M 1,4-CHD in a sealed beaker. The light was kept on between 5 and 10, 15 and 20, and 25 and 30 min. The intensity of the applied light is 90 mW/cm².

with the logarithm of the concentration of bromide). We also used light to illuminate a diluted bromine solution (ca. 0.001M) in order to examine whether light-induced decomposition of bromine played any significant role here. Our bromide selective electrode did not record any change, implying that such a factor is not as important as light-induced decay of BrCHD.

To shed light on the mechanism of photoinduced oscillations, in Fig. 7 we investigated the reaction between acidic bromate and hydroquinone with or without light illumination. The solid line is the result obtained in the absence of light, whereas the dashed curve (plotted by hand after overlapping the two results) represents the reaction taken place under a constant illumination (90 mW/cm²). According to the mechanism proposed by Körös and co-workers,²⁹ following reactions are expected to take place:

$$H_2Q + BrO_3^- \rightarrow Q + HBrO_2, \qquad (1)$$

$$BrO_{3}^{-} + HBrO_{2} + H^{+} \rightarrow 2BrO_{2}^{\bullet} + H_{2}O, \qquad (2)$$

$$H_2Q + BrO_2^{\bullet} \rightarrow HQ^{\bullet} + HBrO_2, \qquad (3)$$

$$HQ^{\bullet} + BrO_{2}^{\bullet} \rightarrow Q + HBrO_{2}, \qquad (4)$$

$$2HQ^{\bullet} \rightarrow H_2Q + Q.$$
 (5)



FIG. 7. Times series showing the influence of illumination on the reaction between bromate and hydroquinone. Initial compositions of the reaction mixture are $[H_2SO_4]=0.1M$, $[H_2Q]=0.01M$, and $[BrO_3^-]=0.06M$. The intensity of the applied light is 90 mW/cm².



FIG. 8. Times series showing the influence of illumination on the reaction between bromate and 1,4-benzoquinone. Initial compositions of the reaction mixture are $[H_2SO_4]=0.5M$, [Q]=0.01M, and $[BrO_3^-]=0.06M$. Illumination of the intensity of 90 mW/cm² was turned on at about 600 s and then off at 750 s. The same illumination was switched on again at about 900 s.

Consistent with the above mechanism, time series shown in Fig. 7 illustrates that the reaction between hydroquinone and bromate is autocatalytic. Remarkably, there is no change in the induction time of the autocatalytic reaction when the system is exposed to light. Such a result suggests the following: (1) Unlike in the BZ reaction, here there is no lightinduced production of HBrO₂ as otherwise the induction period should be shortened by light; (2) hydroquinone, despite being a photosensitive reagent, is not involved in the above light-induced oscillations. Note that the concentration of sulfuric acid is decreased to 0.1M here in order to have a longer induction period. If $[H_2SO_4] = 1.0M$, the autocatalytic reaction would take place within a few seconds after mixing bromate and hydroquinone solutions together.

The fact that light-induced oscillations do not occur until the reaction has started for a while suggests that products of the 1,4-CHD-bromate reaction may be responsible for lightinduced oscillations. According to the mechanism proposed in earlier studies,²⁹ 1,4-benzoquinone (Q) is a stable final product in the studied system. A recent report by Görner suggested that 1,4-benzoquinone could be excited by light to produce hydroquinone,³⁵ a species which is involved in the autocatalytic reactions in the 1,4-CHD-bromate reaction. To examine the possible role of 1,4-benzoquinone, in Fig. 8 we studied the reaction between 1,4-benzoquinone and bromate in acidic solution. Reaction conditions are $[H_2SO_4]$ =0.5M, [Q]=0.01M, and $[BrO_3]=0.06M$. As shown in the figure, as soon as the light is switched on (at about t=600 s), a sharp decrease in the Pt potential is observed, followed by a quick return to the state of a high Pt potential. We would like to point that although the occurrence of the large excursion is independent of the time when the illumination is applied (i.e., 100 or 1000 s after mixing those species together), the large amplitude excursion could only take place once and afterward only a small amplitude variation could be obtained when another pulse illumination is applied (see t = 900 s). This could be because the first explosion produced a large quantity of Br⁻, Br₂, etc., which prevented the occurrence of another autocatalytic reaction. The swift response of the 1,4-benzoquinone-bromate reaction to illumination is the same as that observed in the 1,4-CHD-bromate system, suggesting that 1,4-benzoquinone could be responsible for light-induced oscillations.

VI. CONCLUSIONS

When the 1,4-CHD-bromate reaction is exposed to light, a variety of interesting dynamical behaviors have been observed, which include both light-induced and light-inhibited oscillations and transitions from light-inhibited to lightinduced oscillatory dynamics. Significantly, under the same reaction conditions, light could either enhance or quench the oscillating dynamics, depending on its intensity. Since the ferroin-bromate-1,4-CHD reaction exhibits similar effects of light,^{23,24} this study suggests that ferroin does not play a significant role in the photosensitivity of the ferroin-bromate-1,4-CHD reaction. Our preliminary mechanistic investigations further suggest that light-enhanced production of bromide from BrCHD is likely to be responsible for the quenching phenomena. Meanwhile, although hydroquinone is a well-known photosensitive reagent, it does not play an active role in the observed photoinduced oscillations. In accord with a recent report by Görner, which suggests that 1,4-benzoquinone could be excited by light to produce hydroquinone,³⁵ result shown in Fig. 8 illustrates that 1,4benzoquinone plays a significant role in the onset of photoinduced oscillations in the 1,4-CHD-bromate reaction.

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