

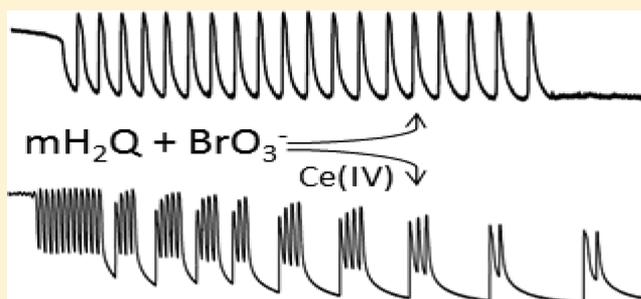
# Complex Reaction Dynamics in the Cerium–Bromate–2-Methyl-1,4-hydroquinone Photoreaction

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**S** Supporting Information

**ABSTRACT:** Spontaneous oscillations with a long induction time were observed in the bromate–2-methyl-1,4-hydroquinone photoreaction in a batch reactor, where removal of illumination effectively quenched any reactivity. A substantial lengthening of the oscillatory window and a dramatic increase in the complexity of the reaction behavior arose upon the addition of cerium ions, in which separate bifurcation regions and mixed mode oscillations were present. The complexity has a strong dependence on the intensity of illumination supplied to the system and on the initial concentrations of the reactants.  $^1\text{H}$  NMR spectroscopy measurements show that the photo-reduction of 2-methyl-1,4-benzoquinone leads to the formation of 2-methyl-1,4-hydroquinone and the compound 2-hydroxy-3-methyl-1,4-benzoquinone. Spectroscopic investigation also indicates that the presence of methyl group hinders the bromination of the studied organic substrate 2-methyl-1,4-hydroquinone, resulting in the formation of 2-methyl-1,4-benzoquinone.

**■ INTRODUCTION**

The compound 1,4-hydroquinone is capable of being autocatalytically oxidized by acidic bromate, forming quinone,<sup>1</sup> which in turn can be photoreduced to reform hydroquinone in aqueous solutions and thus create a quinone–hydroquinone cycle.<sup>2,3</sup> Chemical oscillations have recently been uncovered in the bromate–2-methyl-1,4-benzoquinone (mBQ) photoreaction.<sup>4</sup> However, no attempt was made to study the effect that addition of one-electron redox couples would have on the above nonlinear system. Introduction of metal catalysts such as ferriin or cerium ions to the reaction has the ability to generate a second autocatalytic cycle through their reactions with bromine dioxide.<sup>5–8</sup> Körös and co-workers have reported that spontaneous oscillations could be revived in the uncatalyzed bromate–aromatic compound oscillators upon the introduction of one-electron redox couples,<sup>9</sup> implicating that a nonlinear system consisting of multiple oscillatory subunits might be conveniently constructed by introducing metal ions into bromate–aromatic compound oscillators.

Exploration into the intricate nature of those coupled or perturbed nonlinear chemical systems has grown substantially over the past two decades and continues to be an area of active research.<sup>10–16</sup> Existing reports have shown that the presence of coupled autocatalytic cycles could lead to the observation of various complex chemical oscillations such as bursting, period-doubling, chaos, etc.<sup>17–20</sup> Because photosensitivity offers a convenient approach for implementing various temporal and spatiotemporal coupling and perturbation, the incorporation of illumination into nonlinear chemical dynamics has seen much study in the past two decades.<sup>21–28</sup>

In this study, the 2-methyl-1,4-hydroquinone ( $\text{mH}_2\text{Q}$ ) photoreaction was investigated with and without the presence of one-electron redox couple  $\text{Ce}^{4+}/\text{Ce}^{3+}$ . As shown in the following, depending on cerium concentration, different complex oscillations were caused to emerge in this photo-controlled oscillatory system. As the initial reactants are consumed in time, the studied chemical system gradually evolved through mixed mode oscillations (MMOs), which are characterized by a single period that contains a large amplitude and one or more small amplitude oscillations ( $L^S$  notation).<sup>29–34</sup> Under suitable conditions, sequential oscillations, which feature the coexistence of two or more isolated oscillatory regimes, were also observed in this closed reaction system. Although sequential oscillation may occur through coupling of two nonlinear feedbacks, earlier study also has suggested that this may occur if an intermediate product formed during the reaction can form an oscillator with the starting oxidant.<sup>35,36</sup> To shed light on such a question, mechanistic studies using  $^1\text{H}$  NMR spectroscopy and ultraviolet–visible (UV–vis) spectroscopic techniques were performed to measure intermediate species formed in this bromate-based photochemical oscillator.

**■ EXPERIMENTAL SECTION**

All reactions were carried out in a 50 mL thermal-jacketed glass beaker (ChemGlass) in which the reaction temperature was sustained at  $25.0 \pm 0.1$  °C by a circulating water bath (Thermo

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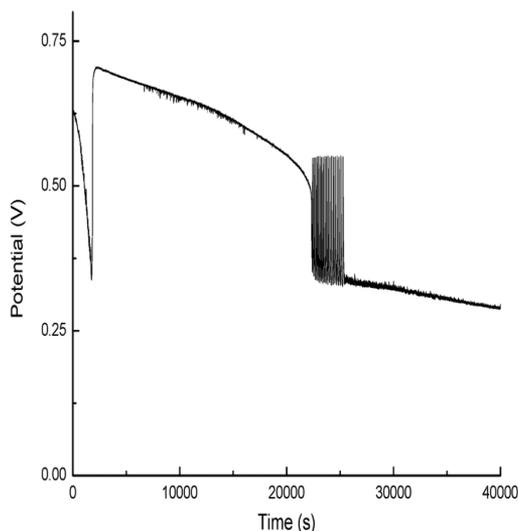
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NesLab RTE 7). A 30.0 mL volume was used for every reaction. To obtain a homogeneous system the reaction solution was stirred with a magnetic stir bar, driven by a magnetic stirrer (Fisher Isotemp) at approximately 1000 rpm. Reactions were monitored with a platinum electrode coupled with a  $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{K}_2\text{SO}_4$  reference electrode (Radiometer Analytical, XR200 and M231Pt-9), which were held in place by a Teflon cap placed on top of the thermal-jacketed beaker. All reaction profiles were recorded through a pH–potential meter (Radiometer PHM220) connected to a computer through an e-Corder 201 data logger (eDAQ company). The source of illumination was a 150 W halogen light (Fisher Scientific, Model DLS-100HD) with a continuous variable light level and was placed at a distance of 60 mm from the reaction beaker. The intensity of illumination was measured with an optical power meter (Model 1815-C, Newport).

All  $^1\text{H}$  NMR spectroscopic studies were performed using a Bruker Avance 500 MHz spectrometer, and the samples were dissolved in deuterated chloroform (Cambridge Isotope Laboratories, 99.8%). Absorption spectroscopic investigations were performed using a UV–visible spectrophotometer (Ocean Optics, 2000 USB), where a quartz cuvette (HELLMA) with a 10.0 mm light path was placed in a CUV sample holder. The cuvette was stirred continuously with a small magnetic stir bar. Illumination was supplied with a halogen lamp with the assistance of an optic fiber that was placed directly above the cuvette. Stock solutions of analytical grade sodium bromate ( $\text{NaBrO}_3$ , Aldrich, 99%), 0.6 M; sulfuric acid ( $\text{H}_2\text{SO}_4$ , Aldrich, 95–98%), 6.0 M; and cerium(IV) ( $\text{Ce}(\text{SO}_4)_2$ , Aldrich, 0.01M), were prepared with double-distilled water. The 2-methyl-1,4-hydroquinone ( $\text{C}_7\text{H}_8\text{O}_2$ , Aldrich, 98+%) was directly dissolved in the reaction mixture.

## RESULTS AND DISCUSSION

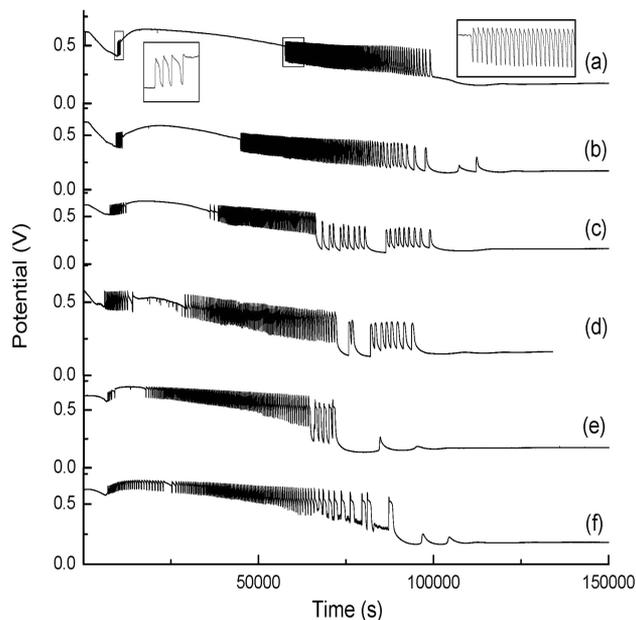
Figure 1 presents a transient oscillatory behavior of the bromate– $\text{mH}_2\text{Q}$  system. After a brief induction time, there is a redox potential spike, which signals the autocatalytic oxidation of  $\text{mH}_2\text{Q}$  to  $\text{mBQ}$ . Following the drastic potential spike, the redox potential gradually decreases for nearly 5 h. Such a



**Figure 1.** Chemical oscillations in the bromate– $\text{mH}_2\text{Q}$  photoreaction. Reaction conditions were  $[\text{mH}_2\text{Q}] = 0.075$  M,  $[\text{H}_2\text{SO}_4] = 1.5$  M,  $[\text{BrO}_3^-] = 0.1$  M, and a light intensity of  $200$   $\text{mW}/\text{cm}^2$ .

decrease in the redox potential will diminish or be significantly slowed when the applied illumination intensity is reduced, suggesting that such a process is related to the photoreduction of  $\text{mBQ}$ . Later, a group of spontaneous oscillations emerge, suggesting that the bromate– $\text{mH}_2\text{Q}$  photoreaction forms a chemical oscillator. Notably, illumination is absolutely critical in this system as removal of illumination during the oscillations causes the system to return to a nonreactive state. Despite our extensive effort of varying reaction parameters such as the concentration of each reagent, only transient simple oscillations were obtained in the bromate– $\text{mH}_2\text{Q}$  photoreaction.

The effect of introducing cerium(IV) to the bromate– $\text{mH}_2\text{Q}$  photoreaction is significant, as can be seen in Figure 2. At a

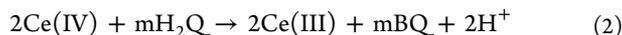


**Figure 2.** Time series of the cerium–bromate– $\text{mH}_2\text{Q}$  photoreaction carried out at different initial cerium concentrations: (a)  $8.3 \times 10^{-5}$  M, (b)  $1.7 \times 10^{-4}$  M, (c)  $2.5 \times 10^{-4}$  M, (d)  $3.3 \times 10^{-4}$  M, (e)  $4.2 \times 10^{-4}$  M, and (f)  $5.0 \times 10^{-4}$  M. Other reaction conditions were  $[\text{mH}_2\text{Q}] = 0.075$  M,  $[\text{H}_2\text{SO}_4] = 1.3$  M,  $[\text{BrO}_3^-] = 0.1$  M, and a light intensity of  $80$   $\text{mW}/\text{cm}^2$ .

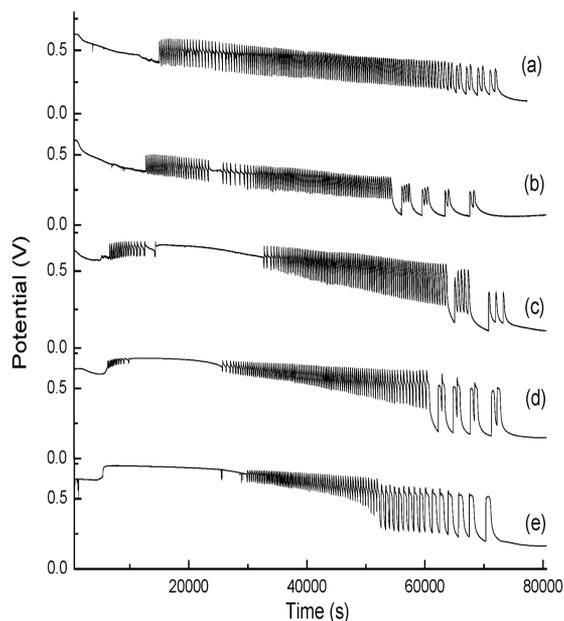
cerium(IV) concentration of  $8.3 \times 10^{-5}$  M (Figure 2a), sequential oscillations were present with a quiescent period of approximately 5 h. Notably, the second set of high-frequency oscillations lasted over 11 h. Increasing the concentration of cerium proved to increase the number of oscillations in both oscillatory windows while decreasing the time interval between them. Complexity at the end of the reaction, in the form of mixed mode oscillations, arose at a cerium concentration of  $2.5 \times 10^{-4}$  M (Figure 2c). In Figure 2f, when the concentration of cerium was  $5.0 \times 10^{-4}$  M, the two oscillatory windows converge, giving rise to a single oscillatory window with aperiodicity emerging near the end of the oscillatory window. Here, the variation of cerium concentration was performed with initial reactant concentrations of  $[\text{mH}_2\text{Q}] = 0.075$  M,  $[\text{BrO}_3^-] = 0.1$  M, and  $[\text{H}_2\text{SO}_4] = 1.3$  M. The supplied light intensity is  $80$   $\text{mW}/\text{cm}^2$ , which allowed for a slow evolution of the system. The addition of cerium introduces the following reaction:



in which the bromine dioxide radicals that were also autocatalytically generated and consumed in the uncatalyzed bromate–mH<sub>2</sub>Q reaction implement the desired coupling. Note that couplings may also take place through the reaction between Ce(IV) and the organic reductants, such as



In the cerium–bromate–mH<sub>2</sub>Q system, at a sulfuric acid concentration of 1.0 M (Figure 3a), only one long-lasting



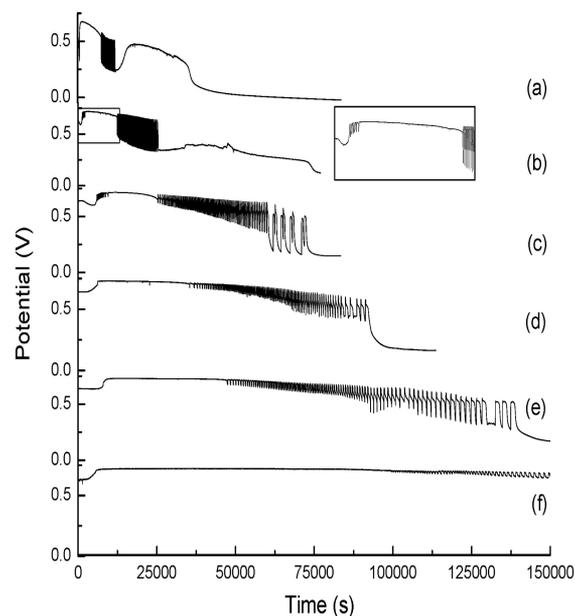
**Figure 3.** Time series of the cerium–bromate–mH<sub>2</sub>Q photoreaction carried out at different initial sulfuric acid concentrations: (a) 1.0 M, (b) 1.1 M, (c) 1.2 M, (d) 1.5 M, and (e) 1.8 M. Other reaction conditions were [mH<sub>2</sub>Q] = 0.075 M, [Ce(IV)] =  $3.3 \times 10^{-4}$  M, [BrO<sub>3</sub><sup>−</sup>] = 0.1 M, and a light intensity of 80 mW/cm<sup>2</sup>.

sequence of oscillations occurs. In Figure 3b, increasing the acid concentration to 1.1 M causes two oscillatory windows to form with a brief quiescent period. At the end of the oscillatory window, mixed mode oscillations occur and transition from 1<sup>3</sup> to 1<sup>1</sup> can be seen. An increase in H<sub>2</sub>SO<sub>4</sub> concentration further, from 1.2 to 1.5 M (panels c and d in Figure 3, respectively), gives an increase in the quiescent time period between oscillatory windows as well as mixed mode oscillations. At an even higher acid concentration of 1.8 M, the primary set of oscillations is no longer present and two distinct oscillatory frequencies emerge in the second window. This time series highlights that variation in the concentration of sulfuric acid had a profound influence on the mH<sub>2</sub>Q system catalyzed by cerium.

Changing the concentration of mH<sub>2</sub>Q also had a significant impact. The quiescent period between oscillations decreased when the concentration of mH<sub>2</sub>Q was increased, and at 0.12 M, the two oscillatory windows merged into a single regime. Mixed mode oscillations were present between 0.09 and 0.065 M mH<sub>2</sub>Q when the other reactant concentrations were [H<sub>2</sub>SO<sub>4</sub>] = 1.0 M, [BrO<sub>3</sub><sup>−</sup>] = 0.1 M, and [Ce(IV)] =  $3.3 \times 10^{-4}$  M. When the concentration of bromate was varied, sequential oscillations were present between 0.09 and 0.12 M bromate, and the two oscillatory regimes were seen to merge at 0.08 M. A drastic shortening of the overall oscillatory window was observed when

the concentration of bromate was low, presumably due to the lack of available oxidant.

Altering the intensity of the supplied illumination also proved to have a significant effect on the cerium–bromate–mH<sub>2</sub>Q reaction. Figure 4 shows the time series when the intensity of



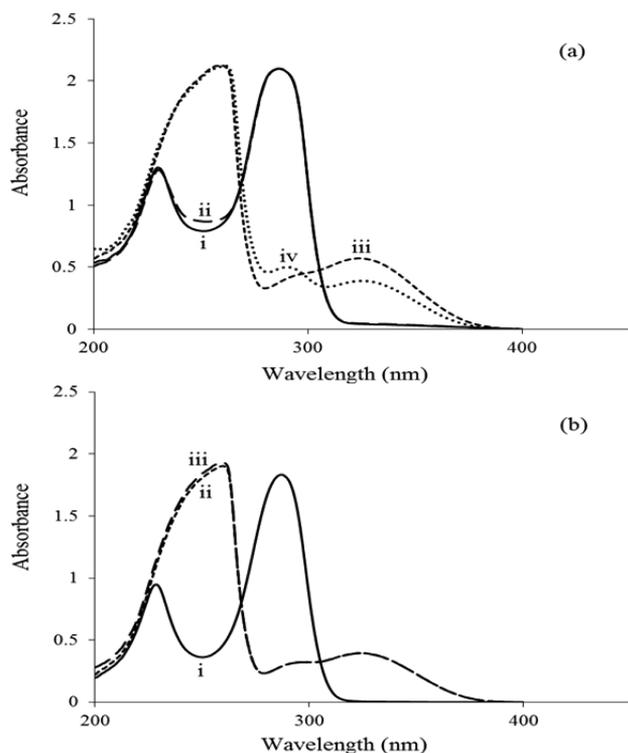
**Figure 4.** Time series of the cerium–bromate–mH<sub>2</sub>Q photoreaction carried out at different initial light intensities: (a) 250 mW/cm<sup>2</sup>, (b) 150 mW/cm<sup>2</sup>, (c) 80 mW/cm<sup>2</sup>, (d) 65 mW/cm<sup>2</sup>, (e) 40 mW/cm<sup>2</sup>, and (f) 20 mW/cm<sup>2</sup>. Other reaction conditions were [mH<sub>2</sub>Q] = 0.075 M, [H<sub>2</sub>SO<sub>4</sub>] = 1.5 M, [Ce(IV)] =  $3.3 \times 10^{-4}$  M, and [BrO<sub>3</sub><sup>−</sup>] = 0.1 M.

illumination is decreased from 250 mW/cm<sup>2</sup> to 20 mW/cm<sup>2</sup>. When 250 mW/cm<sup>2</sup> illumination is supplied to the reaction, only high-frequency oscillations occur (Figure 4a). Two separate oscillatory windows emerge when the intensity has been decreased to 150 mW/cm<sup>2</sup> (Figure 4b), and mixed mode oscillations occur during the second oscillatory window when the intensity is further decreased to 80 mW/cm<sup>2</sup> (Figure 4c). Further decreasing the intensity eliminates the first set of oscillations, and the induction time increases with decreasing intensity. At 40 mW/cm<sup>2</sup>, oscillations occur after a lengthy induction time of approximately 13 h and last for about 25 h (Figure 4e). An induction time of about 30 h occurs at an intensity of 20 mW/cm<sup>2</sup> (Figure 4f), but the system maintains oscillations for over 55 h.

## MECHANISTIC CHARACTERIZATION

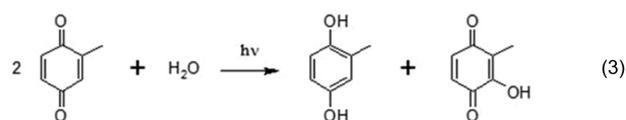
Compositions of the reaction solution were analyzed shortly after the potential spike seen in Figure 1, where the formation of mBQ ( $\delta = 6.77$ , 1/2 AB,  $J = 10.5$  Hz; 6.73 doublet of 1/2 AB,  $J = 2.5$ , 10.5 Hz; 6.62, doublet of quartets,  $J = 2.5$  Hz, 1.6 Hz; 2.07,  $A = 3$ , doublet,  $J = 1.6$  Hz) was confirmed using <sup>1</sup>H NMR spectroscopy (Supporting Information, Figure S1). Another compound was found to emerge before spontaneous oscillations take place and remain throughout the reaction giving spectral resonances of  $\delta = 7.11$  and 7.17 with a distinct AB coupling pattern ( $J = 10.8$  Hz) and  $\delta = 2.03$  (singlet,  $A = 3$ ), indicative of a 2,3-disubstituted benzoquinone, of which 2-bromo-3-methyl-1,4-benzoquinone is the most likely candidate (Supporting Information, Figure S2).

Bromine is an important intermediate in bromate-based chemical reactions and plays a critical role in modulating the concentration of bromide ion, which is known as the inhibitor of bromate-based chemical oscillations. The reaction between bromine and  $mH_2Q$  was studied here using UV–visible spectroscopy. The reaction was first examined while illuminated. In Figure 5a, absorption spectrum (i) is of 0.001 M



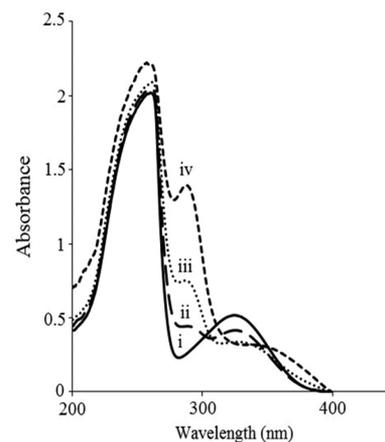
**Figure 5.** Absorption spectra of (a) the illuminated (b) the unilluminated  $mH_2Q$ –bromine reaction. In (a), absorption spectrum (i) shows  $mH_2Q$  at  $t = 0$ , (ii)  $t = 600$  s, (iii) 15 s after the addition of bromine, and (iv) 600 s after the addition of bromine. In (b), absorption spectrum (i) shows  $mH_2Q$  before the addition of bromine, (ii) 15 s after the addition of bromine, and (iii) 600 s after the addition of bromine. The concentration of  $mH_2Q$  in (a) and (b) is 0.001 M.

$mH_2Q$  before illumination is present and (ii) is collected after 600 s of illumination; no observable change in the  $mH_2Q$  peak at 290 nm was observed. Once bromine was introduced to the system, the peak associated with  $mH_2Q$  (290 nm) immediately disappears and a peak indicative of the presence of  $mBQ$  appears at 259 nm (spectrum (iii)). Spectrum (iv) was collected 600 s after the introduction of bromine, where the absorbance of  $mH_2Q$  again begins to grow. This observation is consistent with an earlier report that  $mBQ$  can be photo-reduced to  $mH_2Q$ .<sup>37</sup>  $^1H$  NMR spectroscopy of the reaction solution (Supporting Information, Figure S3) was conducted in order to determine the products, i.e., whether bromination and oxidation occurred concurrently. However, no evidence of bromination of the organic substrate was found in addition to  $mH_2Q$  and  $mBQ$ .  $^1H$  NMR spectral resonances of  $\delta = 6.98$ , s, 1H; 6.74, 1/2 AB,  $J = 10.1$  Hz, 1H; 6.73, 1/2 AB,  $J = 10.1$  Hz, 1H; and 1.96, s, 3H are identical with earlier reports for the chemical shifts of 2-hydroxy-3-methyl-1,4-benzoquinone,<sup>38,39</sup> the product from the photoreduction of  $mBQ$  which does not participate in the autocatalytic cycle. The above process can be described by



Next, the experiment was performed without illumination. Spectrum (i) in Figure 5b shows the absorbance of  $mH_2Q$  before bromine was added, and spectrum (ii) is 15 s after the addition of bromine. As can be seen, the conversion of  $mH_2Q$  to  $mBQ$  occurs; therefore the oxidation of  $mH_2Q$  is not illumination-dependent. Spectrum (iii) was collected 600 s after the addition of bromine, which essentially overlaps with spectrum (ii). Therefore, the main difference caused by the lack of illumination in the  $mH_2Q$ –bromine reaction is the absence of the photoconversion from  $mBQ$  to  $mH_2Q$ . The reaction between bromine and  $mBQ$  was also studied under both illuminated and nonilluminated conditions; however, no formation of brominated  $mH_2Q$  or brominated  $mBQ$  was found after 45 min of reaction time.

To further examine the photoreduction of  $mBQ$ , absorption spectra of 0.001 M  $mBQ$  solution under constant illumination were acquired (Figure 6). Spectrum (i) was collected at the



**Figure 6.** Absorption spectra showing the photoreduction of  $mBQ$  to  $mH_2Q$  under  $35 \text{ mW/cm}^2$  intensity of illumination: (i) before illumination, (ii) after 300 s of illumination, (iii) after 1200 s of illumination, and (iv) after 3600 s of illumination. The concentration of  $mBQ$  is 0.001 M.

start of the experiment, where two absorption peaks were seen at 259 and 325 nm. This result provides support that the new peaks seen in Figure 5 are from  $mBQ$ . As can be seen in spectrum (ii), the absorption at approximately 290 nm, representative of  $mH_2Q$ , begins to grow after 300 s of illumination time. After 1200 s (spectrum (iii)) the  $mH_2Q$  peak has grown substantially and after 1 h of illumination  $mH_2Q$  peak has grown even more (see spectrum (iv)).  $^1H$  NMR spectroscopic analysis showed that the resulting product mixture was composed of  $mBQ$ ,  $mH_2Q$ , and 2-hydroxy-3-methyl-1,4-benzoquinone, in agreement with eq 3.

## CONCLUSIONS

The one-electron redox couple  $Ce^{4+}/Ce^{3+}$  was introduced to the bromate–2-methyl-1,4-hydroquinone photochemical reaction to study coupled autocatalytic cycles. Cerium proved to exhibit a prevalent effect on the system and was capable of substantially lengthening the oscillatory window. Two bifurcation regimes were found to exist when the two

autocatalytic cycles were effectively balanced, which was achieved through manipulation of the individual reaction parameters. Mixed mode oscillations were also present when cerium(IV) was utilized. The systems' sensitivity to illumination was significant as removal of illumination during an oscillatory regime completely quenched the systems' reactivity. Analysis with  $^1\text{H}$  NMR spectroscopy indicates that the presence of methyl group prevents bromination during the  $\text{mH}_2\text{Q}$ -bromine reaction. However, 2-bromo-3-methyl-1,4-benzoquinone was detected with  $^1\text{H}$  NMR spectroscopic analysis during the bromate- $\text{mH}_2\text{Q}$  photoreaction.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

$^1\text{H}$  NMR spectra illustrating (Figure S1) the formation of 2-methyl-1,4-benzoquinone before oscillations begin; (Figure S2) the formation of a product with a distinct AB coupling pattern, of which 2-bromo-3-methyl-1,4-benzoquinone is the most likely candidate; and (Figure S3) reaction between bromine and  $\text{mH}_2\text{Q}$  under illumination showing both the oxidation and photoreduction products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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