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## Design of Photo-Controlled Chemical Oscillators

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**Abstract:** This article reviewed recent progresses in the design of a new class of chemical oscillators and developed a generic model that could qualitatively reproduce those photochemical oscillations seen in experiments. The two oscillators discussed in this report are based on the photolysis of 1,4-benzoquinone and its derivatives, in which external illumination is vital in initiating and sustaining the reaction processes. Nonlinear behavior in these two photo-controlled chemical oscillators are analyzed as a function of light intensity and the initial concentration of reagents including 1,4-benzoquinone, 1,4-hydroquinone, 2-methyl-1,4-benzoquinone, bromate, and sulfuric acid. A generic model proposed initially for the uncatalyzed bromate-aromatic compounds reactions was modified here to account for the photolysis of 1,4-benzoquinone or 2-methyl-1,4-benzoquinone. The modified model qualitatively reproduced chemical oscillations and their dependence on light intensity.

**Key Words:** Autocatalytic reaction; Chemical oscillations; Nonlinear feedback; Photochemistry

Nonlinear chemical behavior represents a central problem in the study of modern macroscopic chemical kinetics<sup>[1-7]</sup>. The investigation of nonlinear phenomena in chemistry has also played an important role in advancing our understanding of nonlinear dynamics, which is now recognized as a powerful tool for understanding complexity in nature<sup>[8-15]</sup>. The study of chemical waves<sup>[3,16]</sup>, for example, has provided insights into related important processes in physical and biological systems, including the development of avalanche phenomena<sup>[17]</sup>, stochastic resonance<sup>[18-21]</sup>, vulnerability and spiral formation<sup>[22]</sup>, cardiac arrhythmia<sup>[23]</sup>, nerve signal transmission<sup>[20,21]</sup>, and animal coat patterning<sup>[24]</sup>. To eventually control those complex behaviors in nature, there has been increasing interest in the study of perturbed nonlinear dynamical systems<sup>[25-39]</sup>. Due to the easy implementation of various external forcing protocols, the photosensitive ruthenium-catalyzed Belousov-Zhabotinsky (BZ) reaction<sup>[40-43]</sup> has become an archetypal model in the understanding of interactions between intrinsic dynamics and external perturbations in several disciplines, which include biologically important phenomena such as spiral activity in cardiac tissue and signal transmission in neurons<sup>[23,44]</sup>.

A number of new dynamical behaviors, which do not exist in unperturbed media, have been reported recently<sup>[25]</sup>. Petrov *et al.*<sup>[30]</sup> used a video projector to periodically drive a photosensitive BZ system at various frequencies related to the oscillation frequency of the autonomous system and found a new type of pattern formation involving phase bistability as well as spa-

tiotemporal chaos. Müller and co-workers<sup>[27,28]</sup> used illumination to create and manipulate the dynamics of spiral waves, including the formation of multi-armed spirals and feedback perturbations that govern spiral drift. Showalter and his group<sup>[18]</sup> employed spatiotemporal random forcing to manifest the constructive role of noise in sub-excitable BZ media and reported spatiotemporal stochastic resonance in a noisy BZ medium, in which the presence of random variation in external light intensity significantly improved the propagation of wave segments. Recent reports by Vanag *et al.*<sup>[32,33]</sup> showed oscillatory cluster pattern formation in the light-driven BZ medium.

As evidenced by the literature listed above, the ruthenium-BZ reaction has been extensively employed to investigate perturbed nonlinear dynamics, since the photosensitivity provides a convenient way of implementing various forcing protocols through an external illumination<sup>[17,18,26-28,35-39]</sup>. The investigation on the mechanism of the ruthenium-BZ photosensitive system has illustrated that visible light resulted in the additional production of Br<sup>-</sup> and such a process became particularly prominent in the presence of bromomalonic acid<sup>[45-47]</sup>. From a dynamic point of view, however, photosensitive chemical oscillators such as the ruthenium-BZ reaction have a limitation in the influence of imposed external forcing. More specifically, illumination can not drive the system to a non-reactive state, since the illumination implements only a parallel way of producing certain key species. To address the above constraints, we have recently thrived to develop photo-

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controlled chemical oscillators, in which light is crucial in initiating and subsequently sustaining the reactivity. In other words, the photo-controlled oscillator does not react at all in the absence of illumination.

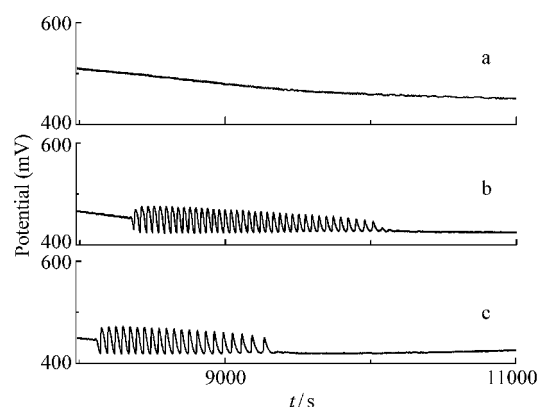
This article reviews the most recent progress in the design of photo-controlled chemical oscillators, including detailed discussion on the nonlinear chemical dynamics in the illuminated bromate-1,4-benzoquinone (BQ) and bromate-2-methyl-1,4-benzoquinone (mBQ) reactions<sup>[48-50]</sup>. The attempt of understanding how the change in the reactivity of 1,4-benzoquinone due to the presence of a function group affects the nonlinear behavior has resulted in the discovery of a new bromate-2-methyl-benzoquinone photochemical oscillators. Results presented here shall greatly facilitate the future design of new photochemical oscillators and the further investigation of perturbed nonlinear chemical dynamics.

## 1 Bromate-BQ photoreaction

The photolysis of quinones and their derivatives has been an active research subject in the past two decades<sup>[51-58]</sup>. For example, Görner<sup>[55-57]</sup> investigated the photoreduction of BQ in organic solvents and in aqueous solutions and reported the formation of 1,4-hydroquinone (H<sub>2</sub>Q) and hydroxybenzoquinone in aqueous solution. The photo production of H<sub>2</sub>Q is particular interesting to us since H<sub>2</sub>Q is a popular reducing agent that can be readily oxidized by various substances<sup>[59,60]</sup>. In particular, it can be autocatalytically oxidized by acidic bromate, satisfying a key condition in constructing a chemical oscillator<sup>[61-63]</sup>. Among numerous chemical and biochemical oscillators reported, bromate-based oscillating reactions are arguably the most extensively explored nonlinear chemical media<sup>[64-83]</sup>. In the bromate-1,4-cyclohexanedione (CHD) oscillator, 1,4-benzoquinone is detected as a final product, suggesting that there is no reaction between acidic bromate and 1,4-benzoquinone<sup>[63]</sup>.

### 1.1 Oscillations in the illuminated bromate-BQ system

Time series of the illuminated bromate-BQ reaction under different light intensities ( $I$ ): (a) 70, (b) 90, and (c) 100  $\text{mW} \cdot \text{cm}^{-2}$  are presented in Fig. 1<sup>[48]</sup>. Our characterization indicates that light from the halogen light source concentrates within the visible range between 350 and 800 nm. The portion of UV light becomes significant when the applied light intensity is larger than 60  $\text{mW} \cdot \text{cm}^{-2}$ . Details of the experimental setup can be found in an earlier publication<sup>[48]</sup>. In the absence of illumination, Pt potential of the bromate and BQ mixture stayed flat at about 600 mV, implicating that there was no reaction taking place. In Fig. 1a, Pt potential of the illuminated system decreased gradually in time and reached about 500 mV after about 9000 s, suggesting that reactions took place in this illuminated system. Significantly, periodic variations in the Pt potential emerged in Fig. 1b, where there was a long induction time before the oscillatory phenomenon occurred. The induction time decreased in Fig. 1c as a result of increasing light intensity. Meanwhile, the number of os-



**Fig. 1** Time series of the bromate-BQ reaction at different illumination intensities

$I/(\text{mW} \cdot \text{cm}^{-2})$ : (a) 70, (b) 90, (c) 100. Other reaction conditions:  $[\text{BQ}] = 0.02 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{H}_2\text{SO}_4] = 1.8 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{NaBrO}_3] = 0.05 \text{ mol} \cdot \text{L}^{-1}$

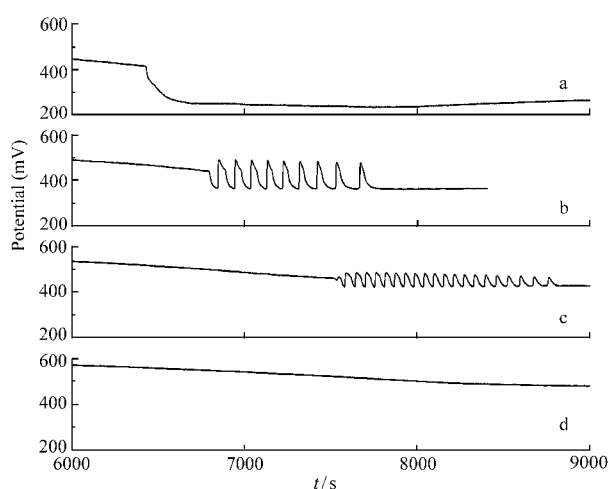
cillations also decreased. Eventually, when the light intensity became too high, no chemical oscillations could be achieved, confirming that light intensity is an effective bifurcation control parameter in this photo-controlled chemical oscillator. Measurement with a bromide selective electrode indicates that during the induction period bromide ion concentration increases gradually.

The absorption spectrum of BQ solution has three peaks, where the largest one is located at 246 nm and a rather weak one, which is indeed visible only at very high BQ concentration, lies in the visible region (ca 440 nm). The water jacket and the glass walls of the reactor cut the amount of UV light going into the reactor significantly. In order to excite BQ molecules, whether through their strong absorption in the UV region or the weak absorption of yellow light, an intensive illumination is thus required here. An improved design of the setup which can allow UV light to penetrate through without deterioration shall greatly reduce the demand on the applied light intensity.

### 1.2 Dependence on reaction conditions

Bromate concentration is known to be a key parameter in all bromate-based oscillators, in which the system stays at a reduced state at a low bromate concentration whereas an oxidized state is generally achieved at a high bromate concentration. The influence of bromate in this photo-controlled oscillator is presented in Fig. 2, where other reaction conditions were kept constant at:  $[\text{H}_2\text{SO}_4] = 1.8 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{BQ}] = 0.02 \text{ mol} \cdot \text{L}^{-1}$ , and  $I = 100 \text{ mW} \cdot \text{cm}^{-2}$ . In Fig. 2a, there was an abrupt decrease in the Pt potential at about 6000 s after mixing all reactants together, yet no spontaneous oscillations was obtained. Oscillatory behavior took place in Figs. 2b and 2c as a result of increasing bromate concentration from the level used in Fig. 2a. However, still increase of bromate concentration resulted in adverse effects, causing these spontaneous oscillations to vanish in Fig. 2d. As illustrated by the time series in Fig. 2, the transition from non-oscillatory to oscillatory evolution at the low bromate condition (from Fig. 2a to 2b) is different from that at the high bromate concentration (from Fig. 2c to 2d).

As presented in the initial report, H<sub>2</sub>SO<sub>4</sub> and BQ concentra-



**Fig.2 Reaction behavior achieved at different concentrations of NaBrO<sub>3</sub>**

[NaBrO<sub>3</sub>]/(mol·L<sup>-1</sup>): (a) 0.03, (b) 0.04, (c) 0.05, (d) 0.06. Other reaction conditions: [BQ]=0.02 mol·L<sup>-1</sup>, [H<sub>2</sub>SO<sub>4</sub>]=1.8 mol·L<sup>-1</sup>, *I*=100 mW·cm<sup>-2</sup>

tions also showed great influences on the occurrence of spontaneous oscillations in the bromate-BQ photochemical system. Under the conditions listed in Fig.2b, an optimum H<sub>2</sub>SO<sub>4</sub> concentration at which the system generated the largest number of oscillation peaks was around 1.8 mol·L<sup>-1</sup>. Oscillations became barely visible at [H<sub>2</sub>SO<sub>4</sub>]=1.9 mol·L<sup>-1</sup> and disappeared completely when H<sub>2</sub>SO<sub>4</sub> concentration became higher than 2.0 mol·L<sup>-1</sup>. Both the oscillation frequency and induction time increased monotonically with H<sub>2</sub>SO<sub>4</sub> concentration. Similarly, the concentration of BQ must also be within a moderate range in order to achieve spontaneous oscillations in the bromate-BQ photoreaction and the suitable range appeared to be between 0.02 and 0.07 mol·L<sup>-1</sup>. We would like to point that the suitable BQ concentration depends on the applied light intensity. The existence of a narrow concentration for spontaneous oscillations indicates the challenge faced in the development of new chemical oscillators.

### 1.3 Mechanistic study

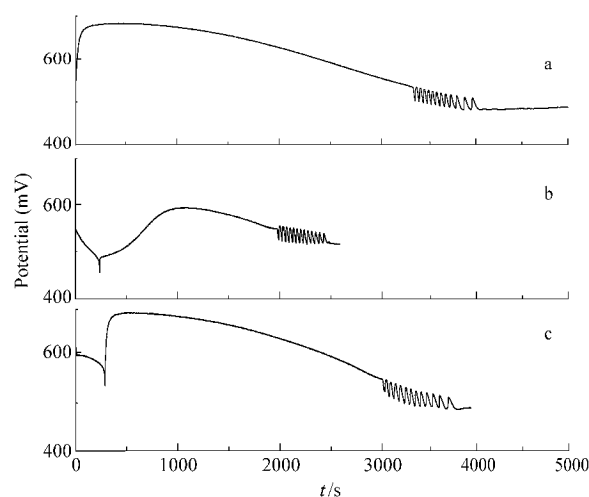
As opposed to the BZ reaction<sup>[84,85]</sup>, which is also a bromate-based chemical oscillator, oscillatory mechanism of the uncatalyzed bromate-aromatic compound reactions remains elusive, especially how the autocatalytic production of HBrO<sub>2</sub> and the formation of bromide ions are harmonized to allow the periodic evolution<sup>[86-88]</sup>. To shed light on this critical issue, measurements with bromide ion selective electrode have been performed and illustrated that during the non-oscillatory evolution Br<sup>-</sup> concentration decreased gradually. Chemical oscillations commenced after Br<sup>-</sup> concentration became low enough. A pulse addition of bromide ion solution could also temporarily quench the oscillatory behavior. Depending on the amount of and phase at which Br<sup>-</sup> was added, the spontaneous oscillations might recover through several peaks with gradually decreasing or increasing amplitudes, a typical feature seen in the BZ quenching experiments. It thus suggests that this bromate-BQ photochemical oscillator is also bromide-controlled. To gain more insight and conclusively information, the above quenching experiments need to be per-

formed in a continuously flow stirred tank reactor (CSTR)<sup>[40,42,43]</sup>, in which the continuous supply of fresh chemicals can keep dynamics of the system at a stable, but far from thermodynamic equilibrium state.

One of the challenges in understanding the mechanism of the bromate-BQ reaction is why there is a long induction time. Does the long induction time arise from the desired accumulation of certain intermediate reagents? To address the above concern, in Fig.3 influences of brominated substrates on the induction time was tested, where compositions of the reaction solution in Fig.3a were [H<sub>2</sub>SO<sub>4</sub>]=1.8 mol·L<sup>-1</sup>, [NaBrO<sub>3</sub>]=0.05 mol·L<sup>-1</sup> and [BQ]=0.02 mol·L<sup>-1</sup>. The induction time is about 3200 s in Fig.3a. In the experiment shown in Fig.3b, Br<sub>2</sub> solution (ca 0.001 mol·L<sup>-1</sup>) was first mixed with 0.02 mol·L<sup>-1</sup> H<sub>2</sub>Q to react for 3600 s, and then 0.05 mol·L<sup>-1</sup> NaBrO<sub>3</sub> and 1.8 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> were added to the mixture and the illumination was turned on at the same time. The first Pt potential dip seen in Fig.3b corresponded to the autocatalytic oxidation of H<sub>2</sub>Q to BQ by the acidic bromate, which occurred even in the absence of illumination. The presence of brominated species in Fig.3b significantly reduced the induction time (ca 2000 s in Fig.2b). To examine whether the decrease in the induction time is due to the usage of H<sub>2</sub>Q as the starting reactant, a parallel experiment with [H<sub>2</sub>SO<sub>4</sub>]=1.8 mol·L<sup>-1</sup>, [NaBrO<sub>3</sub>]=0.05 mol·L<sup>-1</sup>, and [H<sub>2</sub>Q]=0.02 mol·L<sup>-1</sup> was run in Fig.3c, where the induction time was significantly longer than that in Fig.3b and was indeed comparable to that in Fig.3a. Given that the only difference between reactions of 3b and 3c was that Br<sub>2</sub> was added to reaction 3b to produce brominated species, the above result strongly suggested that the accumulation of brominated substrates could be responsible for the induction time.

### 1.4 The coexistence of BQ and H<sub>2</sub>Q

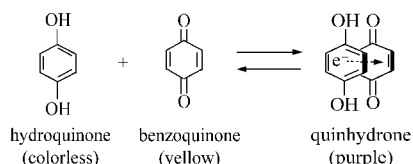
It is well documented that colorless H<sub>2</sub>Q and yellow BQ can readily form dark colored complexes as shown in Scheme 1. In the bromate-BQ photochemical system, both H<sub>2</sub>Q and BQ pre-



**Fig.3 Influences of the initial presence of brominated species on the induction time**

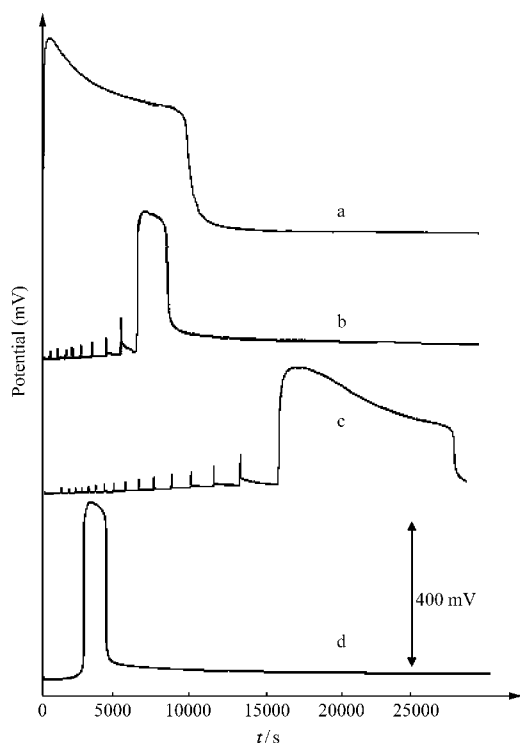
Compositions of the reaction solution are [H<sub>2</sub>SO<sub>4</sub>]=1.8 mol·L<sup>-1</sup>, [NaBrO<sub>3</sub>]=0.05 mol·L<sup>-1</sup>, (a) [Q]=0.02 mol·L<sup>-1</sup>, (b) [H<sub>2</sub>Q]=0.02 mol·L<sup>-1</sup> and [Br<sub>2</sub>]=0.001 mol·L<sup>-1</sup>, (c) [H<sub>2</sub>Q]=0.02 mol·L<sup>-1</sup>; *I*=140 mW·cm<sup>-2</sup>.

sent, whether  $\text{H}_2\text{Q}$ -BQ complexes are formed and the formation and dissociation of such complexes play an important role in the oscillatory kinetics represents an interesting subject. The above topic could also be critical in deciphering mechanisms of several closely related chemical oscillators such as the bromate-CHD system in which  $\text{H}_2\text{Q}$  and BQ are intermediates. Notably, the bromate-CHD oscillators have exhibited various interesting nonlinear behaviors which could not be interpreted based on the current mechanisms<sup>[89]</sup>.



**Scheme 1** The formation of benzoquinone hydroquinone complex

Fig.4 presents time series of the bromate-BQ- $\text{H}_2\text{Q}$  photoreaction, where different amounts of  $\text{H}_2\text{Q}$  were added initially to the bromate-BQ system<sup>[90,91]</sup>. Earlier theoretical investigation suggests that 1:1 BQ and  $\text{H}_2\text{Q}$  mixture forms a favorable dimer structure. For the 1:1  $\text{H}_2\text{Q}$ -BQ complex, in the presence of light an electron may be donated from  $\text{H}_2\text{Q}$  to BQ, forming a charge-transfer complex to give the characteristic purple color (see the above schematic illustration)<sup>[92]</sup>. As shown in Fig.4a, the system only exhibited a very broad peak in the absence of  $\text{H}_2\text{Q}$ , in which the

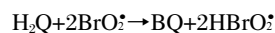
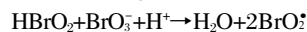


**Fig.4** Reaction behavior under different concentrations of  $\text{H}_2\text{Q}$

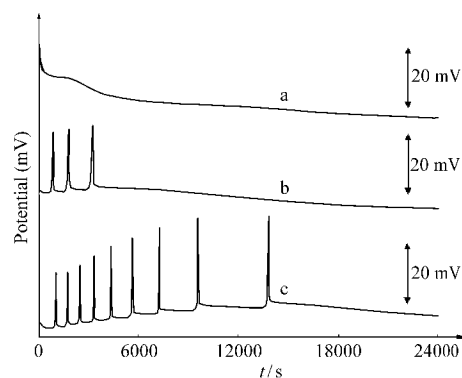
$[\text{H}_2\text{Q}]/(\text{mol}\cdot\text{L}^{-1})$ : (a) 0.0, (b) 0.0025, (c) 0.005, (d) 0.01. Other reaction conditions:  $[\text{BQ}] = 0.015 \text{ mol}\cdot\text{L}^{-1}$ ,  $[\text{NaBrO}_3] = 0.06 \text{ mol}\cdot\text{L}^{-1}$ ,  $[\text{H}_2\text{SO}_4] = 0.1 \text{ mol}\cdot\text{L}^{-1}$ ,  $I = 70 \text{ mW}\cdot\text{cm}^{-2}$ .

sudden decrease in the Pt potential at about 8000 s was consistent with the behavior of the bromate-BQ photoreaction. When  $0.0025 \text{ mol}\cdot\text{L}^{-1}$   $\text{H}_2\text{Q}$  was added (see Fig.4b), eight sharp peaks with increasing amplitudes were achieved, which were followed by a broad oscillation peak. Further increase of  $\text{H}_2\text{Q}$  concentration led to more oscillations in Fig.4c. If the concentration of  $\text{H}_2\text{Q}$  was increased still, however, the system then stopped exhibiting these sharp oscillations. Fig.4d shows that there was only one broad peak at  $0.01 \text{ mol}\cdot\text{L}^{-1}$  of  $\text{H}_2\text{Q}$ . The above scenario suggests that  $\text{H}_2\text{Q}$  may form complexes with BQ and these complexes have a prominent kinetic role in the bromate-BQ photochemical oscillator and, possibly, in other related oscillators such as bromate-CHD system as well.

It is important to note that since  $\text{H}_2\text{Q}$  is a very strong reducing agent and is quickly oxidized by acidic bromate via the autocatalytic process  $\text{H}_2\text{Q} + 2\text{BrO}_3^- \rightarrow \text{BQ} + 2\text{HBrO}_2$ , it is necessary to perform the reaction at a low acidic environment under which  $\text{H}^+$  slows down the above autocatalytic process *via* influencing the reaction  $\text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + 2\text{BrO}_2^-$ . In other words, only under low acid concentration  $\text{H}_2\text{Q}$  may have a chance to form complexes with BQ before being oxidized. Time series in Fig.5 illustrate how the dynamics of the bromate- $\text{H}_2\text{Q}$ -BQ photoreaction responds to the change of  $\text{H}_2\text{SO}_4$  concentration. Fig.5a shows that at  $[\text{H}_2\text{SO}_4] = 0.03 \text{ mol}\cdot\text{L}^{-1}$  the system did not exhibit any oscillatory behavior at all. At  $[\text{H}_2\text{SO}_4] = 0.06 \text{ mol}\cdot\text{L}^{-1}$  in Fig.5b, the system exhibited three sharp oscillations. Further increase of sulfuric acid concentration led to more sharp oscillations with increasing amplitude but decreasing frequency. This trend, especially the increase in oscillation frequency, is likely due to that high acid concentration favored the nonlinear feedback loop implemented through the reactions:



When the concentration of sulfuric acid was increased to  $0.2 \text{ mol}\cdot\text{L}^{-1}$ , only one sharp oscillation took place before the broad peak. Notably, after the broad peak there was another small amplitude oscillation at about 13000 s and this small peak largely



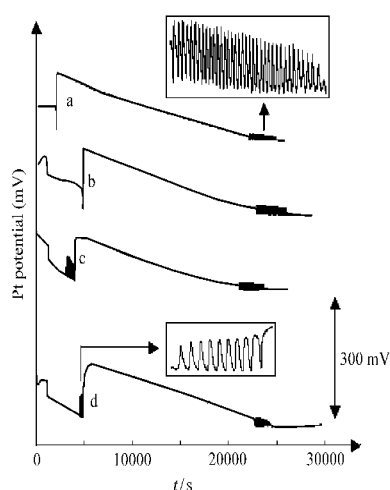
**Fig.5** Reaction behavior under different sulfuric acid concentrations

$[\text{H}_2\text{SO}_4]/(\text{mol}\cdot\text{L}^{-1})$ : (a) 0.03, (b) 0.06, (c) 0.08. Other reaction conditions are  $[\text{Q}] = 0.015 \text{ mol}\cdot\text{L}^{-1}$ ,  $[\text{H}_2\text{Q}] = 0.005 \text{ mol}\cdot\text{L}^{-1}$ ,  $[\text{NaBrO}_3] = 0.06 \text{ mol}\cdot\text{L}^{-1}$ , and  $I = \text{mW}\cdot\text{cm}^{-2}$ .

resembled the behavior seen in the bromate-BQ photochemical oscillator. The optimum  $\text{H}_2\text{SO}_4$  concentration appeared to be around  $0.1 \text{ mol}\cdot\text{L}^{-1}$ , in which a series of small, sharp oscillations could be obtained. Such a concentration is significantly lower than the value used commonly in the bromate-based chemical oscillators.

### 1.5 Reaction behavior in the presence of ferroin

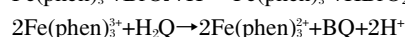
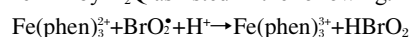
Interactions of metal catalyst ferroin with the bromate-BQ and bromate- $\text{H}_2\text{Q}$  photoreactions are investigated in this section as an attempt of providing the first model system of photo-controlled oscillator for the research of pattern formation<sup>[72]</sup>. The selection of ferroin is largely based on the fact that there is a distinct color difference between ferroin and ferriin, offering a convenient way to observe the development of spatiotemporal behavior. Time series of the bromate- $\text{H}_2\text{Q}$  photoreaction, presented in Fig.6, were obtained at under different concentrations of ferroin: (a)  $0.0 \text{ mol}\cdot\text{L}^{-1}$ , (b)  $2.0\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ , (c)  $1.5\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  and (d)  $6.0\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ . At the ferroin free conditions in Fig. 6a, the Pt potential stayed flat for about 2000 s and then exhibited a sharp jump, which was followed by a gradual decrease and then oscillatory evolution. The insertion illustrates how the oscillatory waveform looks like. The sharp Pt potential jump in Fig.6a signaled that most of the  $\text{H}_2\text{Q}$  has been oxidized to BQ through an autocatalytic process. In the presence of  $2.0\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ , as shown in Fig.6b, Pt potential of the system exhibited a sharp decrease at about 1000 s after the start of the reaction and then underwent a sharp increase after evolving flatly at a low potential for about 3000 s. After the abrupt increase in the Pt potential at around 5000 s, the reaction behavior became qualitatively the same as the uncatalyzed bromate- $\text{H}_2\text{Q}$  photoreaction. The delayed occurrence of the sharp Pt potential increase in Fig. 6b is presumably due to that ferroin competed with  $\text{H}_2\text{Q}$  for the bromine dioxide radicals and such competition consequently slowed down the autocatalytic oxidation of  $\text{H}_2\text{Q}$ .



**Fig.6 Reaction behavior under different concentrations of ferroin**

[ferroin]/( $\text{mol}\cdot\text{L}^{-1}$ )(a) 0.0, (b)  $2.0\times 10^{-5}$ , (c)  $1.5\times 10^{-4}$ , (d)  $6.0\times 10^{-4}$ . Other reaction conditions:  $[\text{H}_2\text{Q}]=0.02 \text{ mol}\cdot\text{L}^{-1}$ ,  $[\text{NaBrO}_3]=0.05 \text{ mol}\cdot\text{L}^{-1}$ ,  $[\text{H}_2\text{SO}_4]=1.8 \text{ mol}\cdot\text{L}^{-1}$ , and  $I=75 \text{ mW}\cdot\text{cm}^{-2}$ .

After ferroin was increased to  $1.5\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  in Fig.6c, notably, several spontaneous oscillations emerged before the abrupt increase in the Pt potential, leading to the co-existence of two isolated oscillation windows. Similar behavior, called sequential oscillations, has been reported in a number of modified BZ reactions and bromate-phenol systems<sup>[74–79,93,94]</sup>. Continuous increase of ferroin concentration greatly increased the number of chemical oscillations within the first oscillation window until an optimum ferroin concentration was reached. These new chemical oscillations, induced by ferroin, may be understood based on the autocatalytic oxidation of ferroin coupled with the reduction of ferriin by  $\text{H}_2\text{Q}$  as listed in the following:



Periodic color changes have been indeed observed in the first, but not within the second oscillation window. The result that no periodic color was seen within the second oscillation window could result from two factors: (1) not enough  $\text{H}_2\text{Q}$  exists in the late reaction stage, despite the presence of photoreduction of BQ; (2) ferroin complex may have partially decomposed as the red color faded significantly after 3 h.

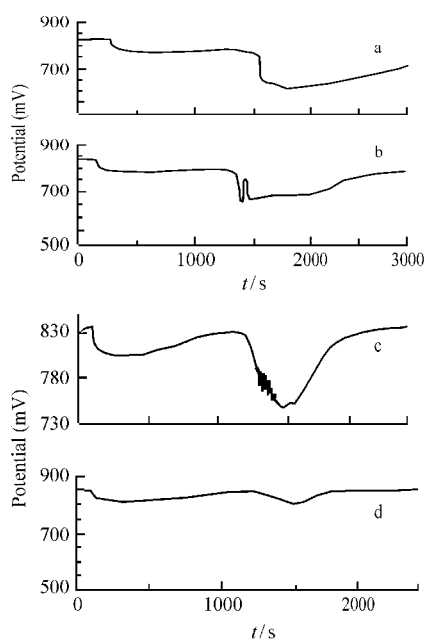
In addition to yielding visible periodic color changes, ferroin leads to the emergence of complicated oscillatory behavior in the bromate- $\text{H}_2\text{Q}$  photochemical reaction. However, no similar effect has been achieved in the bromate-BQ photochemical system, suggesting that the reduction of ferriin by  $\text{H}_2\text{Q}$  is essential for the emergence of those initial oscillations, i.e.,  $\text{H}_2\text{Q}$  acts like an ordinary organic substrate in a classic BZ reaction. Therefore, the new oscillatory window is mostly a result of the coupling of the autocatalytic oxidation of ferroin by acidic bromate and the reduction of ferriin by  $\text{H}_2\text{Q}$ .

## 2 Bromate-mBQ photoreaction

The photoreduction product  $\text{H}_2\text{Q}$  is involved in the autocatalytic feedback in the bromate-BQ oscillator. Any change in the reactivity of  $\text{H}_2\text{Q}$  is expected to have great impacts on the photoreaction behavior. To examine the above speculation, a derivative of 1,4-benzoquinone, namely, 2-methyl-1,4-benzoquinone (mBQ), is investigated here in this section. The presence of a methyl function group does not only alternate the reactivity of  $\text{H}_2\text{Q}$ , but also affect the bromination process, which is predicted to be important in all bromate-based chemical oscillators. Similar to the photolysis of BQ, studies have illustrated that the photolysis of mBQ in aqueous solution leads to the production of 2-methyl-1,4-hydroquinone (m $\text{H}_2\text{Q}$ ).

### 2.1 Spontaneous oscillations

Fig.7 presents time series of the bromate-mBQ reaction at different concentrations of bromate: (a) 0.03, (b) 0.04, (c) 0.07 and (d)  $0.08 \text{ mol}\cdot\text{L}^{-1}$ . The equipment used in the bromate-mBQ experiments is different from the one used in bromate-BQ/ $\text{H}_2\text{Q}$  reactions. Details of the setup can be found in our earlier publication<sup>[48]</sup>. Here, upon turning on the illumination, Pt potential exhibited a sharp drop, which was followed by a gradual increase over the next 1300 s until another large magnitude sharp drop



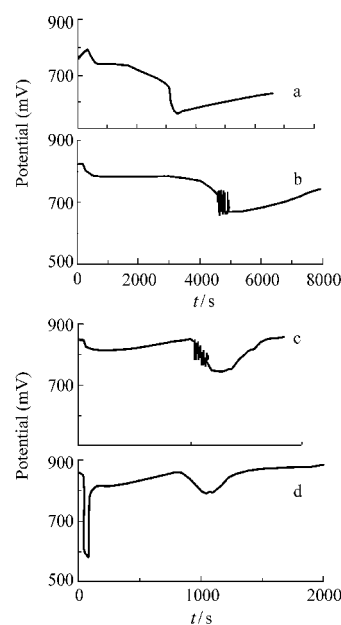
**Fig.7 Time series of the bromate-mBQ photoreaction at different concentrations of NaBrO<sub>3</sub>**

[NaBrO<sub>3</sub>]/(mol·L<sup>-1</sup>): (a) 0.03, (b) 0.04, (c) 0.07, (d) 0.08. Other reaction conditions: [mBQ]=0.011 mol·L<sup>-1</sup>, [H<sub>2</sub>SO<sub>4</sub>]=1.6 mol·L<sup>-1</sup>, *I*=0.52 W·cm<sup>-2</sup>

took place. At the low bromate concentration, such as presented in Fig.7a, the Pt potential eventually returned to the level before reaction took place. As bromate concentration was increased to 0.04 mol·L<sup>-1</sup> in Fig.7b, there was a large amplitude oscillation after the abrupt decrease of the Pt potential. The number of oscillations increased with respect to the increase of bromate, but the oscillation amplitude decreased. When bromate concentration became too high, no spontaneous oscillations could be achieved. Notably, the reaction time before the occurrence of oscillatory phenomenon (i.e., induction time) was nearly unchanged when bromate concentration was adjusted. Such a response is different from that in the bromate-BQ photoreaction, in which the reduction was prolonged by increasing bromate concentration. The way how oscillatory behavior emerged in the bromate-mBQ system as bromate concentration was adjusted is the same as that in the bromate-BQ system: large amplitude oscillations were developed at low bromate concentration and oscillations with diminishing amplitude took place at high bromate concentration.

## 2.2 Dependence on other reaction conditions

Fig.8 presents time series of the bromate-mBQ photoreaction under different initial concentrations of mBQ: (a) 0.075, (b) 0.055, (c) 0.016 and (d) 0.011 mol·L<sup>-1</sup>. Please note that the time scale in (a) and (b) are larger than that used in (c) and (d). Fig.8a illustrates that no oscillations could be obtained under high mBQ concentration, where the evolution of the reaction was qualitatively the same as seen at the conditions of low bromate concentration. As mBQ concentration decreased, large amplitude oscillations emerged in the system and the number of oscillations increased. The oscillation amplitude decreased with mBQ concen-

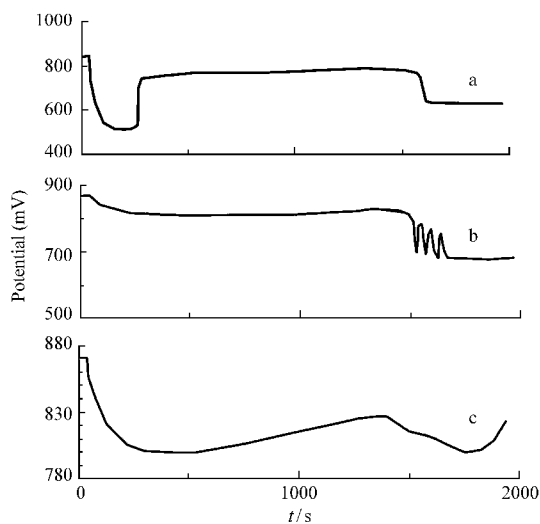


**Fig.8 Time series of the bromate-mBQ photoreaction at different concentrations of mBQ**

[mBQ]/(mol·L<sup>-1</sup>): (a) 0.075, (b) 0.055, (c) 0.016, (d) 0.011. Other reaction conditions: [BrO<sub>3</sub>]=0.06 mol·L<sup>-1</sup>, [H<sub>2</sub>SO<sub>4</sub>]=1.6 mol·L<sup>-1</sup>, *I*=0.52 W·cm<sup>-2</sup>

tration and eventually became too small to be seen (see Fig.8d) at very low mBQ concentration. The largest number of oscillations was obtained at a moderate, but close to the low critical concentration of mBQ. Another significant change in the reaction behavior was the variation of induction time, which was greatly reduced by decreasing mBQ concentration.

Fig.9 presents time series at different concentrations of H<sub>2</sub>SO<sub>4</sub>. At a high acid concentration, such as the case presented in Fig.9a, there was a rapid decrease in the Pt potential right after turn-



**Fig.9 Time series of the bromate-mBQ photoreaction at different concentrations of H<sub>2</sub>SO<sub>4</sub>**

[H<sub>2</sub>SO<sub>4</sub>]/(mol·L<sup>-1</sup>): (a) 2.7, (b) 2.9, (c) 3.5. Other reaction conditions: [NaBrO<sub>3</sub>]=0.02 mol·L<sup>-1</sup>, [mBQ]=0.011 mol·L<sup>-1</sup>, *I*=0.52 W·cm<sup>-2</sup>.

ing on the illumination, followed by a rapid recovery. Then, Pt potential of the studied system stayed nearly flat for the next 1300 s until another sharp drop in the potential took place. No chemical oscillation was achieved during the above process. In Fig.9b, acid concentration was increased to  $2.9 \text{ mol} \cdot \text{L}^{-1}$ , spontaneous oscillations took place at about 1500 s after the reaction began. Such an induction time coincides with the sharp drop in the redox potential recorded in Fig.9a. With the further increase of acid concentration, the number of oscillations increased, but the amplitude decreased at the same time. As shown in Fig.9c, these spontaneous oscillations became barely visible at the acid concentration of  $3.5 \text{ mol} \cdot \text{L}^{-1}$ . Note that in order to show the occurrence of these small amplitude oscillations the scale used for the y-axis in Fig.9c is smaller than that used in Figs.9a and 9b. Another change in the oscillatory behavior as a result of increasing acid concentration is that these oscillations emerged during the course of a gradual decrease of the Pt potential, as opposed to the more abrupt occurrence such as seen in Fig.9a at the low acid concentration. Similar to bromate, the concentration of acid almost has no effect on the induction time.

### 3 Modeling

#### 3.1 A generic model for the reaction of bromate and hydroquinones

Considering the similarity in their molecular structures, the oxidation and bromination of 1,4-hydroquinone ( $\text{H}_2\text{Q}$ ) and 2-methyl-1,4-hydroquinone ( $\text{mH}_2\text{Q}$ ) by acidic bromate are anticipated to follow the same processes, which shall also be qualitatively the same as the reactions between acidic bromate and oth-

er aromatic compounds such as CHD. In 1979 Orbán, Körös and Noyes developed a general model for the uncatalyzed bromate-aromatic compounds reactions<sup>[86]</sup>. The original mechanism, which is referred as OKN model in the following, is composed of sixteen reaction steps, i.e., ten steps K1–K10 in Scheme I and six steps K11–K16 in Scheme II. The ten reaction steps K1–K10 in Scheme I and the first four reaction steps K11–K14 in Scheme II can be applied for reactions of acidic bromate with  $\text{H}_2\text{Q}$  or with  $\text{mH}_2\text{Q}$ . Steps K15 and K16 suggest how phenol and its derivatives could be involved in the reactions with acidic bromate and are not applicable here since the two substances  $\text{H}_2\text{Q}$  and  $\text{mH}_2\text{Q}$  have two phenolic groups.

Our previous investigation on the bromate-1,2-hydroquinone oscillator has illustrated that eliminating step K11 from the OKN model does not influence the oscillatory behavior qualitatively<sup>[95]</sup>. Therefore, the model employed in the following calculations also excluded the step K11 from the OKN overall reaction steps. More specifically, the present model, as listed in Table 1, consists of thirteen reaction steps K1–K10, and K12–K14, and eleven variables,  $\text{BrO}_3^-$ ,  $\text{Br}^-$ ,  $\text{BrO}_2^*$ ,  $\text{HBrO}_2$ ,  $\text{HOBr}$ ,  $\text{Br}^*$ ,  $\text{Br}_2$ ,  $\text{HAr}(\text{OH})_2$ ,  $\text{HAr}(\text{OH})\text{O}^*$ ,  $\text{HArO}_2$ , and  $\text{BrHQ}$ , where  $\text{HAr}(\text{OH})_2$  is hydroquinone ( $\text{H}_2\text{Q}$ ),  $\text{HAr}(\text{OH})\text{O}^*$  is hydroquinone radical,  $\text{HArO}_2$  is benzoquinone (BQ) and  $\text{BrAr}(\text{OH})_2$  is brominated hydroquinone.

#### 3.2 The photochemical process

As discussed earlier, the chemical principle behind the two photo-controlled chemical oscillators is the photoreduction of BQ (or mBQ), which is otherwise a final product in the bromate- $\text{H}_2\text{Q}$  (or bromate- $\text{mH}_2\text{Q}$ ) reaction. The photochemistry of light-induced reduction of BQ to  $\text{H}_2\text{Q}$  (or mBQ to  $\text{mH}_2\text{Q}$ ) in aqueous solution is a rather complicated process involving multiple reac-

**Table 1 Reaction mechanism for photo-controlled bromate-benzoquinone systems**

No.	Reaction	Rate constant ( $\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ )		Ref.
		forward	reverse	
Scheme I				
(K1)	$\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \rightleftharpoons \text{HBrO}_2 + \text{HOBr}$	$k_1 = 2.1[\text{H}^+]^2$	$k_{-1} = 1 \times 10^4$	a
(K2)	$\text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightleftharpoons 2\text{HOBr}$	$k_2 = 2 \times 10^9[\text{H}^+]$		a
(K3)	$\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightleftharpoons 2\text{BrO}_2^* + \text{H}_2\text{O}$	$k_3 = 1 \times 10^7[\text{H}^+]$	$k_{-3} = 2 \times 10^7$	a
(K4)	$\text{BrO}_2^* + \text{HAr}(\text{OH})_2 \rightleftharpoons \text{HBrO}_2 + \text{HAr}(\text{OH})\text{O}^*$	$k_4 = 2.5 \times 10^2$		a, b
(K5)	$2\text{HBrO}_2 \rightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+$	$k_5 = 4 \times 10^7$		a
(K6)	$\text{HOBr} + \text{HAr}(\text{OH})\text{O}^* \rightleftharpoons \text{Br}^* + \text{HArO}_2 + \text{H}_2\text{O}$	$k_6 = 2 \times 10^5$	$k_{-6} = 2 \times 10^3$	a, b
(K7)	$\text{Br}^* + \text{HAr}(\text{OH})\text{O}^* \rightarrow \text{Br}^- + \text{HArO}_2 + \text{H}^+$	$k_7 = 4 \times 10^4$		a, b
(K8)	$\text{HOBr} + \text{Br}^- + \text{H}^+ \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O}$	$k_8 = 8 \times 10^9[\text{H}^+]$	$k_{-8} = 1.1 \times 10^{23}$	a
(K9)	$\text{Br}_2 + \text{HAr}(\text{OH})_2 \rightarrow \text{BrAr}(\text{OH})_2 + \text{Br}^- + \text{H}^+$	$k_9 = 7 \times 10^2$		a, b
(K10)	$\text{HOBr} + \text{HAr}(\text{OH})_2 \rightarrow \text{BrAr}(\text{OH})_2 + \text{H}_2\text{O}$	$k_{10} = 1$		a, b
Scheme II				
(K12)	$\text{Br}^* + \text{HAr}(\text{OH})_2 \rightarrow \text{Br}^- + \text{HAr}(\text{OH})\text{O}^* + \text{H}^+$	$k_{12} = 1 \times 10^3$		a, b
(K13)	$\text{HAr}(\text{OH})_2 + \text{HArO}_2 \rightleftharpoons 2\text{HAr}(\text{OH})\text{O}^*$	$k_{13} = 1 \times 10^{-2}$	$k_{-13} = 1 \times 10^4$	a, b
(K14)	$2\text{HAr}(\text{OH})\text{O}^* \rightarrow \text{Ar}_2(\text{OH})_2$	$k_{14} = 1 \times 10^5$		a, b
Photochemical reaction step				
P(1)	$2\text{HArO}_2 + \text{H}_2\text{O} + h\nu \rightarrow \text{HAr}(\text{OH})_2$	$k_{\text{PI}}$		c

(a) from Ref.[8]; (b) adjustable parameter chosen to give a good fit to data; (c) Adjusted in the present study. In this scheme,  $\text{HAr}(\text{OH})_2$  is an aromatic compound containing two phenolic groups such as 1,4-hydroquinone or 2-methyl-1,4-hydroquinone,  $\text{HAr}(\text{OH})\text{O}^*$  is the radical obtained by hydrogen atom abstraction,  $\text{HArO}_2$  is the related benzoquinone,  $\text{BrAr}(\text{OH})_2$  is the brominated derivative, and  $\text{Ar}_2(\text{OH})_2$  is the coupling product,  $\text{HAr}(\text{OH})$  is phenol,  $\text{HArO}^*$  is the hydrogen-atom abstracted radical, and  $\text{Ar}(\text{OH})_2$  is the product; (d) unit in  $\text{s}^{-1}$

tion steps. For simplicity, the following schematic step is employed to represent the complicated photoreduction of BQ (or mBQ):



where for the photoreduction of 2-methyl-1,4-benzoquinone, BQ and  $\text{H}_2\text{Q}$  would be replaced by mBQ and m $\text{H}_2\text{Q}$ , respectively. The stoichiometric coefficient 2 was determined in earlier photolysis experiments of BQ and mBQ in aqueous solution<sup>[56,57]</sup>. We would like to point out that the coefficient 2 in the reaction step P1 is not essential for the achievement of spontaneous oscillations; it just reflects the correct yield of  $\text{H}_2\text{Q}$  (m $\text{H}_2\text{Q}$ ) in the above photochemical process.

Reaction rate of the above schematic step is represented by a second-order with respect to BQ (or mBQ) with a rate constant  $k_{\text{P1}}$  that was adjusted arbitrarily to reflect the variation of illumination intensity. The complete model for the bromate-BQ (or mBQ) photoreaction consists of 14 steps as listed in Table 1.

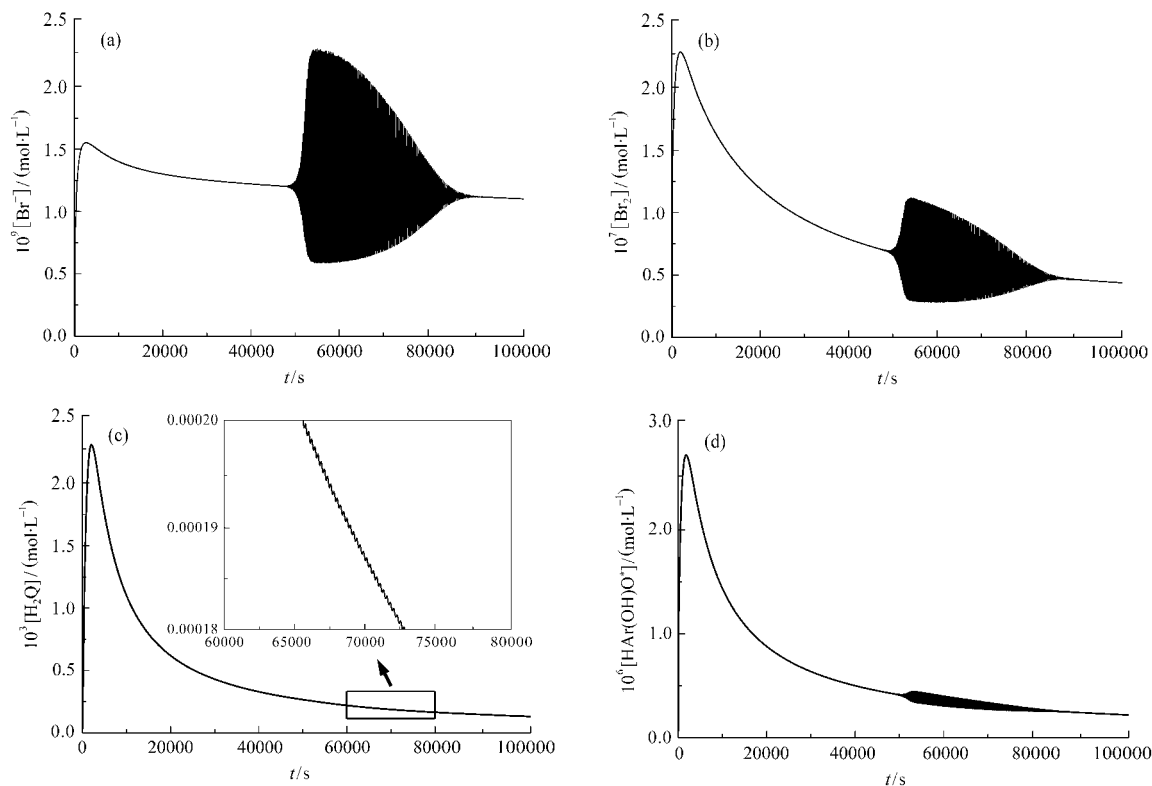
### 3.3 Numerical results

The calculation was carried out by integrating a set of differential equations resulting from the application of the law of mass action to the reactions with the rate constants listed in Table 1. Values of these rate constants for reactions K1–K3, K5, K8 have been determined in the studies of the Belousov-Zhabotinsky reaction<sup>[96–100]</sup>. Rate constants of all other reactions were either chosen from a related work by Herbine and Field<sup>[87]</sup> on the modified OKN mechanism or were adjusted here to give good agreement

between experimental results and simulations.

Fig.10 shows oscillatory behaviors of four variables ( $\text{Br}^-$ ,  $\text{Br}_2$ ,  $\text{H}_2\text{Q}$ , and  $\text{HAr}(\text{OH})\text{O}^*$ ) obtained with the model listed in Table 1. Same as measured with a bromide selective electrode in experiments, the above calculation illustrates that bromide concentration decreased during the induction time and spontaneous oscillations emerged after bromide concentration became low enough. As shown in the inset of Fig.10(c) with a blowup of between 60000–9000 s, the concentration of  $\text{H}_2\text{Q}$  oscillates with very tiny amplitudes and this small amplitude oscillations in  $\text{H}_2\text{Q}$  became more pronounced (not shown) when a simulation was carried out with a different set of rate constants. The periodic variation in  $\text{H}_2\text{Q}$  (or m $\text{H}_2\text{Q}$ ) concentration arises from the competition of two processes: (1) its autocatalytic oxidation by bromine dioxide radicals (see step K4 in the model) and (2) the photoreduction of BQ (or mBQ) through step P1. The calculation shows that variables  $\text{HBrO}_2$ ,  $\text{BrO}_2^*$ ,  $\text{HOBr}$ , and  $\text{Br}^*$  also exhibited periodic oscillations, whereas the rest variables, namely  $\text{BrO}_3^-$ , BQ, and  $\text{BrAr}(\text{OH})_2$ , did not oscillate in the present configuration.

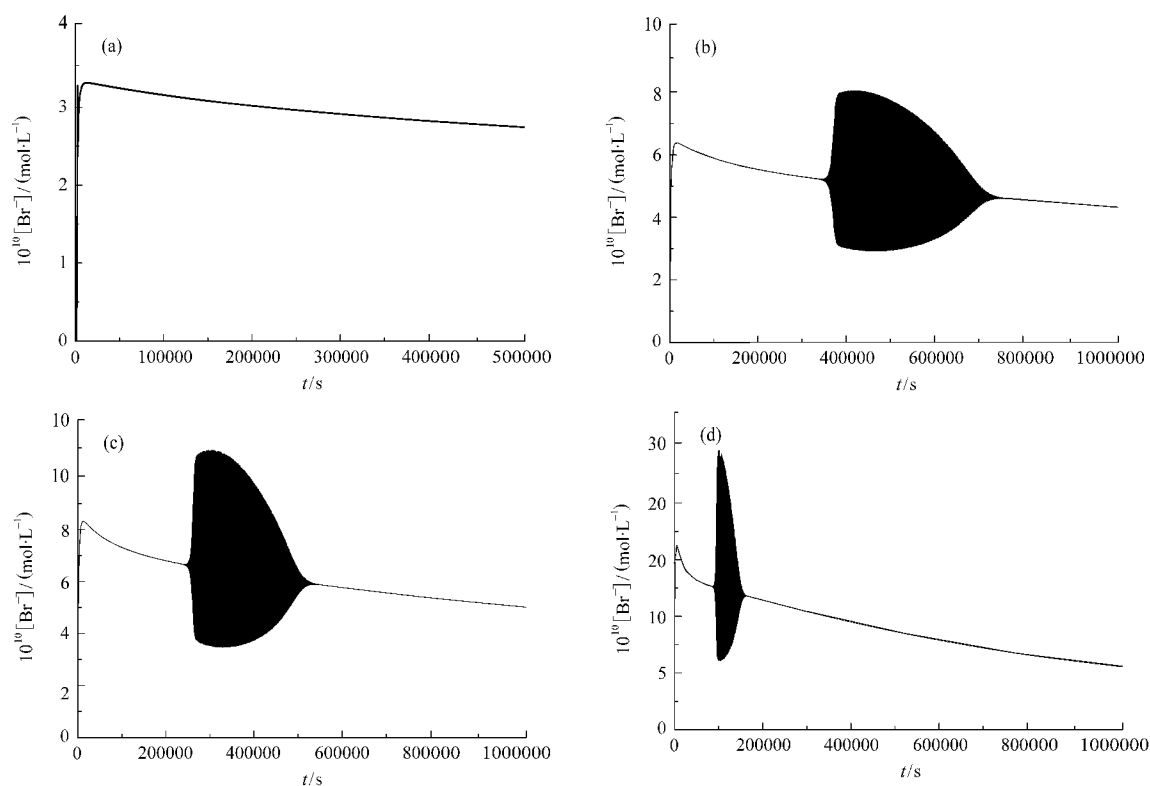
The above model did not only reproduce the spontaneous oscillations but also reproduced the presence of a long induction time seen in experiments. The induction behavior in the simulation was, however, about several times larger than that achieved in the experiments (Figs.1–3 and 7–9). Such a quantitative difference in the time scale may simply arise from the selection



**Fig.10 Simulated results for (a)  $[\text{Br}^-]$ , (b)  $[\text{Br}_2]$ , (c)  $[\text{H}_2\text{Q}]$ , and (d)  $[\text{HAr}(\text{OH})\text{O}^*]$  obtained from numerical integration of the set of differential equations resulting from the reaction steps K1–K10, K12–K14, and P1 with rate constants as listed in Table 1**

The rate constant  $k_{\text{P1}}$  was  $8.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ , and the initial concentrations were  $[\text{BrO}_3^-] = 0.06 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{H}_2\text{SO}_4] = 1.8 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{BQ}] = 0.02 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{Br}^-] = 1.0 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$ , and the other initial concentrations were zero.





**Fig.11 Simulated results of dependence of oscillatory behavior on the illumination intensity**

The values of rate constant  $k_{pi}$  were (a)  $1 \times 10^{-4}$ , (b)  $5 \times 10^{-4}$ , (c)  $1 \times 10^{-3}$ , and (d)  $1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ . The other simulated conditions were the same as those used in Fig.10.

of rate constants. Notably, due to the lack of experimental values rate constants involving BQ and mBQ were adjusted here based on the data from pyrocatechol system. Overall, the above calculation offers strong supports that the photochemical reaction of bromate-BQ (and bromate-mBQ) could be qualitatively accounted for by the model of uncatalyzed bromate- $\text{H}_2\text{Q}$  reactions plus the photolysis of BQ (or mBQ). Further improvement of the agreement between experiment and simulation could be achieved in the future by tuning the rate constants involving the reagent of  $\text{H}_2\text{Q}$  and  $\text{mH}_2\text{Q}$ .

### 3.4 Effects of illumination intensity

Experiments have illustrated that in both systems light intensity has significant effects on the reaction behavior. Fig.11 presents time series calculated under different light intensities, which was implemented *via* adjusting rate constant  $k_{pi}$  with a higher  $k_{pi}$  value corresponding to a more intensive illumination. All other conditions were kept the same as employed in Fig.10. This result illustrates that, same as seen in experiments, the induction period is shortened as a result of increasing the rate constants  $k_{pi}$  (i.e. increasing the light intensity). From Fig.11b to 11c, as the light intensity was increased the number of oscillations decreased. Such a qualitatively agreement between experiment and simulation further supports that the above proposed model in Table 1 has capture the core of the two photo-controlled chemical oscillators.

### 3.5 Dependence on the reactivity of BQ and mBQ

Experiments have shown that the nonlinear photoreaction be-

haviors in the bromate-BQ and bromate-mBQ oscillators are not quite the same, in particular in their responses to the variation of reaction conditions. Such difference may arise from the changes in the reactivity of the photo reagents, i.e. BQ and mBQ. To shed light on the above issue, in the simulation we have examined how the reaction rate constant involving the organic substrate (i.e.  $\text{H}_2\text{Q}$  and its derivative or  $\text{mH}_2\text{Q}$  and its derivatives) affects the photochemical behavior. In the model listed in Table 1, step K4 is crucial as it forms a positive feed back loop. In the present simulation, the value of rate constant  $k_4$  used is nearly the same as that ( $7.0 \times 10^2 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ ) of the oxidation of phenol in the modified OKN mechanism<sup>[86]</sup>. Oscillations have been achieved in the range of  $2.2 \times 10^2 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} < k_4 < 2.9 \times 10^3 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ , when all other parameters were kept the same as used in Fig. 11d. Increasing the value of  $k_4$  from  $2.2 \times 10^2$  to  $1.0 \times 10^3 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$  shortened the induction period, but later prolonged the induction periods when its value was further increased such as to  $2.9 \times 10^3 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ .

In an earlier study, the equilibrium step K13 was a key reference to reduce the reaction steps from the uncatalyzed bromate-aromatic compounds reaction model. In the present model, increasing the value of  $k_{13}$  ( $5.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} < k_{13} < 2.0 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ ) monotonically shortened the induction period, whereas increasing the value of the reverse reaction  $k_{r13}$  affected the induction period differently: it did not change the induction period in the range of  $0 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} < k_{r13} < 1.0 \times 10^3 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ , then monotonically lengthened the induction period in the range of

$1.0 \times 10^3 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} < k_{r13} < 5.5 \times 10^4 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ . However, when considering that the equilibrium should lie well to the left, the value of the rate constant  $k_{r13}$  shall be much larger than that of  $k_{13}$ , thus the above behavior of the induction period obtained in the range of small value of  $kr_{13}$  may be ignored.

#### 4 Summary

This report reviewed nonlinear behavior in two photo-controlled chemical oscillators, in which the presence of illumination is essential in initiating and sustaining the reaction process. Such a critical role played by light ensures that the two systems can be employed to explore perturbed nonlinear dynamics that could not be achieved with existing photosensitive media. More specifically, the new systems now allow one to switch the dynamics periodically/aperiodically between a reactive and non-reactive state where the relaxation time toward the non-reactive state is normally significantly slow. We anticipate that novel nonlinear behavior could be uncovered there.

Both systems are based on the photo-reduction of benzoquinone in acidic bromate solution, in which the photoreaction product (i.e.,  $\text{H}_2\text{Q}$  or  $\text{mH}_2\text{Q}$ ) can be autocatalytically oxidized by bromate. Such a principle may be applied to other photosensitive reagents to develop new photo-controlled chemical oscillators. The success of obtaining chemical oscillation with the methyl substituted benzoquinone strongly suggests that aromatic compounds with a similar structure shall also be able to form photochemical oscillator with acidic bromate. From the results discussed in this review, however, it is critical to have proper initial reaction conditions, which represents a big obstacle in the discovery of any new chemical oscillator. The exploration presented in this review suggests that in general a strong light favors the occurrence of oscillatory phenomena. In general, an illumination from a single 150 W halogen light source or from a 150 W Xe lamp shall lie in the oscillatory window if the system is capable of oscillating. Regarding the selection of the initial concentration of bromate and acid, the nonlinear photoreaction behavior appears to be more sensitive to the ratio of bromate and acid than their absolute concentrations. The suitable range of acid concentration is broader at a low initial concentration of bromate. For example, in the bromate-mBQ system, chemical oscillations have been obtained for the acid concentration between 2.8 and  $3.5 \text{ mol} \cdot \text{L}^{-1}$  at  $[\text{BrO}_3^-] = 0.02 \text{ mol} \cdot \text{L}^{-1}$ , as opposed to be between 0.9 and  $1.2 \text{ mol} \cdot \text{L}^{-1}$  at  $[\text{BrO}_3^-] = 0.1 \text{ mol} \cdot \text{L}^{-1}$ . Despite that the underlying reaction mechanism remains to be understood, the model presented in Table 1 was able to qualitatively reproduce the chemical oscillations and shall serve as a template for future study of the photochemistry of related chemical oscillators.

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