Ferroin-Induced Complex Oscillations in the Bromate−Hydroquinone Photochemical Reaction

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This study presents an experimental investigation on the dynamics of the ferroin−bromate−hydroquinone photoreaction, in which two isolated oscillatory regimes emerge due to the presence of ferroin. Oscillations within the two isolated regimes exhibit different dependence on light intensity and initial compositions of the reaction solution. A phase diagram outlining the occurrence of the new oscillatory regime has been established in the bromate−ferroin concentration plane. As opposed to the ferroin-free system, in which there is nearly no difference in the reaction behavior whether benzoquinone or hydroquinone is used as the starting reactant, here the two-staged oscillatory behavior can only be obtained with hydroquinone as the initial reagent. This observation suggests that the reduction of ferriin by hydroquinone and the autocatalytic oxidation of ferroin by acidic bromate may have played a major role in the new oscillation window.

1. Introduction

Since the report of spontaneous oscillations and propagating waves in the Belousov−Zhabotinsky (BZ) reaction,[1,2] there has been a steady effort and increasing interest in expanding the family of bromate-based chemical oscillators.[3−17] In 1979, Orban and Körös explored reactions between acidic bromate and various aromatic compounds with or without the presence of metal catalysts.[5] While chemical oscillations in most of the reported bromate−aromatic compound oscillators are short-lived in a batch system,[5] the bromate−1,4-cyclohexanedione (CHD) system is able to produce well over 200 oscillation peaks under suitable conditions.[6,7] Similar behavior accompanied by visible periodic color changes has been achieved in the ferroin−bromate−CHD reaction system.[17] The absence of gas production and great photosensitivity have made the ferroin−bromate−CHD oscillator an attractive model in recent studies of spatiotemporal nonlinear dynamics.[18,19]

Utilizing the photoreduction of 1,4-benzoquinone (Q) in aqueous solutions,[20] recent studies have successfully constructed photochemical oscillators in which illumination is essential for sustaining chemical reactivity.[14] Similar to other uncatalyzed bromate oscillators, the bromate−Q photochemical oscillator also has an extremely long induction time. Interestingly, under low acidic conditions (<0.2 M) the coexistence of hydroquinone (H_2Q) and Q induces qualitative changes in the reaction behavior, where spontaneous oscillations emerge much earlier and have a quite different concentration profile from those seen in the bromate−Q and bromate−H_2Q oscillators.[15] The formation of quinone complexes has been suggested to be responsible for such dramatic changes.

To gain further insight into the mechanism of bromate−Q/H_2Q photoreactions and potentially expand the research of these photocontrolled nonlinear systems into pattern formation, this report investigated interactions of metal complex ferroin with the bromate−Q and bromate−H_2Q photoreactions. There is a distinct color difference between ferroin and ferriin, which greatly facilitates the observation of spatiotemporal structures. On the other hand, the unique photochemical property of the bromate−Q/H_2Q system offers ways of implementing various spatial and temporal manipulation protocols. Notably, the study of perturbed nonlinear dynamics has attracted increasing attention in the last two decades.[21−30] As presented in the following, the ferroin-added system does produce periodic color changes. However, ferroin also induces dramatic changes in the reaction behavior, in which a new, isolated oscillation window emerges in the bromate−H_2Q system. Chemical oscillations within the new oscillatory window have a short induction time and require less intensive illumination to occur, when compared to oscillations in the ferroin-free systems.

2. Experimental Procedure

All reactions were run in a 50 mL thermal-jacketed glass reactor under isothermal conditions. Reaction temperature was maintained at 25.0 ± 0.1 °C by a circulation water bath (ThermoNesLab RTE 7). The cylindrical reactor was mounted onto a magnetic stirrer, which was operated at approximately 700 rpm for all experiments. Throughout this study, the progress of the reaction was monitored with a platinum electrode coupled with a $Hg|Hg_2SO_4|K_2SO_4$ reference electrode (Radiometer Analytical XR200 and M231 Pt-9). The Pt potential was recorded through an eCorder 201 (eDAQ) data logger connected to a personal computer.

$NaBrO_3$ solution (Aldrich, 99%, 0.6 M) and sulfuric acid (Aldrich, 3 M) were prepared with doubly distilled water. 1,4-Benzoquinone (Aldrich, 98%) and 1,4-hydroquinone (Aldrich, 99%) were directly dissolved in the reaction mixture. A halogen lamp with continuous variable light intensity was used as the light source (Fisher Scientific, Model DLS-100HD, 150 W). A schematic illustration of the equipment can be found in an earlier publication.[14] The light intensity was measured with an optical photometer from Newport (model 1815-C). Despite the strong illumination, there was no temperature increase in the reaction solution.

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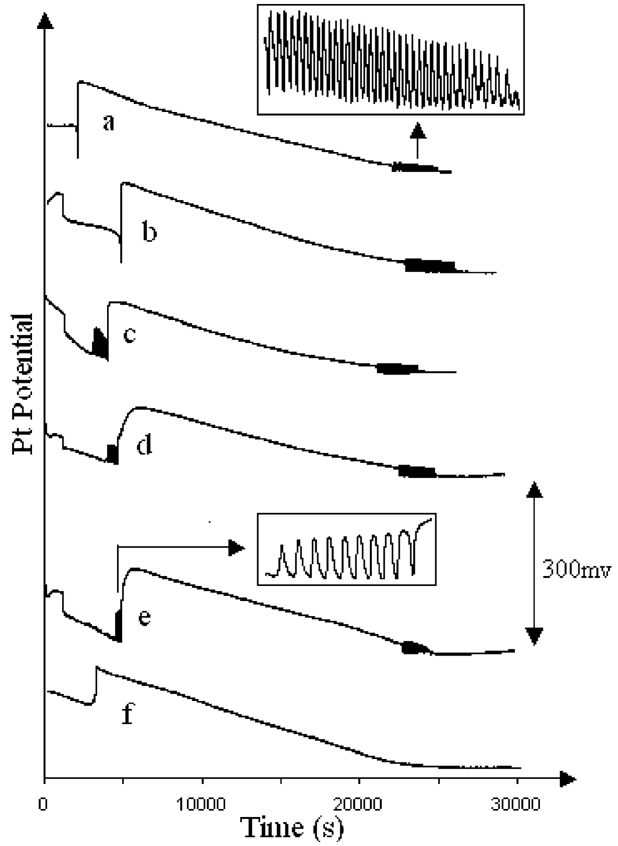

Figure 1. Reaction behavior under different concentrations of ferroin: (a) 0.0, (b) 2.0×10^{-5}, (c) 1.5×10^{-4}, (d) 3.0×10^{-4}, (e) 6.0×10^{-4}, and (f) 3.5×10^{-3} M. Other reaction conditions are $[H_2Q] = 0.02$ M, $[NaBrO_3] = 0.05$ M, $[H_2SO_4] = 1.8$ M, and light intensity = 70 mW/cm^2.

3. Results and Discussion

Figure 1 presents time series of the bromate−H_2Q photoreaction under different concentrations of ferroin: (a) 0.0, (b) 2.0 $\times 10^{-5}$, (c) 1.5×10^{-4}, (d) 3.0×10^{-4}, (e) 6.0×10^{-4}, and (f) 3.5×10^{-3} M. In Figure 1a, at the ferroin free conditions the Pt potential stays flat for about 2000 s and then exhibits a sharp jump. It is followed by a gradual decrease in the Pt potential and subsequent oscillatory evolution. The inset illustrates how the oscillatory waveform looks. Earlier studies suggest that the sharp Pt potential jump seen in Figure 1a signals that most of the H_2Q has been oxidized to Q through an autocatalytic process. In the presence of 2.0×10^{-5} M of ferroin, the Pt potential of the system exhibits a sharp decrease at about 1000 s and then undergoes a sharp increase after remaining steady at the low potential for about 3000 s (see Figure 1b). After the abrupt increase of the Pt potential, the reaction behavior becomes qualitatively the same as the ferroin free system. The delayed occurrence of the sharp Pt potential increase in Figure 1b can be understood based on the fact that ferroin competes with H_2Q for the bromine dioxide radicals and such a competition shall slow down the autocatalytic oxidation of H_2Q by bromine dioxide radicals.[17]

After ferroin concentration was increased to 1.5×10^{-4} M in Figure 1c, several spontaneous oscillations emerged before the abrupt increase in the Pt potential, leading to the coexistence of two isolated oscillation windows. Similar behavior, frequently referred to as sequential oscillations, has been reported in a number of modified BZ reactions and bromate−phenol systems.[31−37] Continuous increase of ferroin concentration greatly increases the total number of oscillation peaks within the first oscillation window until an optimum ferroin concentration is reached. Beyond that, if the concentration of ferroin is increased still further, chemical oscillations cease (see Figure 1f). Since these new chemical oscillations, induced by ferroin, are accompanied by periodic color changes, the following two reaction processes are suggested to take place: (1) the autocatalytic oxidation of ferroin and (2) the reduction of ferriin by H_2Q:

$$\mathrm{Fe(phen)_3}^{2+} + \mathrm{BrO_2}^{\cdot} + \mathrm{H}^+ \rightarrow \mathrm{Fe(phen)_3}^{3+} + \mathrm{HBrO_2} \quad (1)$$

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

As opposed to the phenomenon seen in the first oscillation window, no periodic color was seen within the second oscillation window. Such a difference could be a result of two factors: (1) not enough H_2Q left to reduce ferriin in the late reaction stage, despite the presence of photoreduction of benzoquinone, and (2) the ferroin complex may have been partially decomposed as the red color faded significantly after 3 h.

Our experiments show that if the H_2Q concentration is low, only the first oscillation window can be achieved. The number of oscillation peaks within the first window increases as the H_2Q concentration is increased until an optimum condition is reached. Both oscillation windows disappear when the H_2Q concentration becomes too high. When the sulfuric acid concentration is adjusted as the sole variable, our study indicates that at a low acid concentration, behavior of the ferroin−bromate−H_2Q system is qualitatively the same as that of the ferroin free system. There was an abrupt Pt potential increase at about 5000 s and spontaneous oscillations emerged a few hours later. Importantly, there was only one oscillatory regime. When the acid concentration was increased to 1.2 M, several oscillations took place ahead of the sharp Pt potential jump, resulting in two isolated oscillation windows. Oscillations within the first window increased greatly with the further increase of acid concentration. When the H_2SO_4 concentration became too high, both oscillation windows disappeared. As opposed to the scene seen at the low acid condition, the second oscillation window disappeared first.

When bromate concentration was adjusted as the sole variable, while other conditions were fixed at $[H_2Q] = 0.02$ M, [ferroin] $= 2.0 \times 10^{-4}$ M, $[H_2SO_4] = 1.8$ M, and light intensity = 75 mW/cm^2, our experiments showed that no oscillatory phenomenon could be observed for bromate concentration above 0.065 M or below 0.02 M. As bromate concentration was increased above the low threshold value, the first oscillation window appeared. Further increasing bromate concentration allowed the development of the second group of oscillations a few hours later. Still the increase of bromate concentration eliminated the second oscillation window first, while the number of oscillation peaks within the first oscillation window was increased. The first oscillation window also disappeared when bromate concentration became too high (>0.07 M). This illustrates that the second oscillation window exists within a narrower bromate concentration range than the first one.

The dependence of these initial oscillations on ferroin and bromate concentrations is summarized in Figure 2. There are three dynamic regimes in this bromate−ferroin phase diagram. Within region I, the ferroin system exhibits sequential oscillations as seen in Figure 1d, whereas only these initial oscillations can be achieved in region II. In region III, the system is unable to exhibit spontaneous oscillations. This phase diagram shows that regardless of the concentration of ferroin, bromate concentration must be within a suitable range for the system to

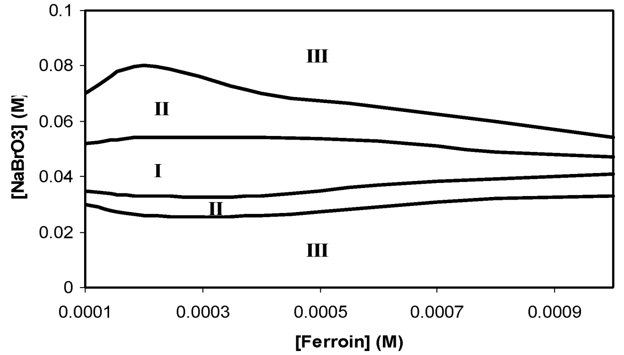

Figure 2. Phase diagram in the hydroquinone and benzoquinone concentration space. Other reaction conditions are $[H_2Q] = 0.02$ M, $[H_2SO_4] = 1.8$ M, and light intensity = 75 mW/cm^2.

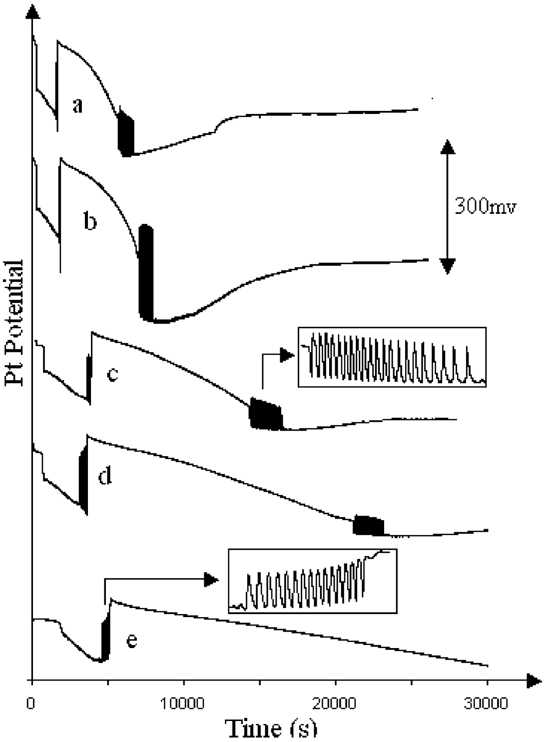

Figure 3. Behavior of the ferroin−bromate−H_2Q reaction under different illumination intensities: (a) 150, (b) 120, (c) 90, (d) 75, and (e) 60 mW/cm^2. Other reaction conditions are $[H_2Q] = 0.02$ M, $[H_2SO_4] = 1.8$ M, $[NaBrO_3] = 0.05$ M, and [ferroin] = 2.0×10^{-4} M.

exhibit spontaneous oscillations and such a range decreases as ferroin concentration increases. As expected, when ferroin concentration is low, the system evolves in the same way as the uncatalyzed bromate−H_2Q or bromate−Q system.[14] At the opposite end, when the concentration of ferroin is too high the studied system does not produce spontaneous oscillations.

To shed light on the role of illumination within each of the two oscillation windows, Figure 3 presents a time series of the ferroin−bromate−H_2Q reaction at different light intensities. This figure illustrates that the first oscillation window requires less intense illumination to develop. As shown in Figure 3e, it emerges for light intensity as low as 60 mW/cm^2. The total number of oscillation peaks within the first window decreases as the light intensity is increased from (e) to (a). The first oscillation window appears to disappear first at the elevated light intensity. The above result shows that these ferroin-induced oscillations are also photocontrolled. Since there is still a large amount of H_2Q during the initial reaction stage, the influence of light is least likely through the photoreduction of Q. Our earlier investigation has shown that illumination affects the reaction between H_2Q and bromine: In the presence of illumination, the reaction products are brominated hydroquinones and brominated benzoquinones rather than benzoquinone and bromide ions.[13,38] The reduced production of bromide shall favor the autocatalytic processes. More investigations are needed to develop a conclusive explanation.

In our earlier investigation on chemical oscillations in the bromate−Q system,[14] the behavior was nearly identical when Q was replaced by H_2Q as the starting material. Such an observation has been interpreted based on the assumption that H_2Q was quickly and extensively oxidized to Q by acidic bromate. Therefore, after a brief reaction period the bromate−H_2Q reaction was essentially transformed into the bromate−Q system. In this study, however, after ferroin was introduced to the bromate−Q system no initial oscillations such as those occuring at around 5000 s in Figure 1c could be achieved. This supports our earlier suggestion that a major role of H_2Q during these initial oscillations is to reduce ferriin, and the autocatalytic oxidation of ferroin by bromine dioxide radicals is the dominant nonlinear feedback.[3,4] Those initial oscillations are therefore expected to be governed by the same mechanism as the classic BZ oscillations. A perturbation experiment with bromide ions, an inhibitor of the autocatalysis in the BZ oscillator, shows that those new oscillations could be indeed quenched temporally by the addition of 5.0×10^{-4} M bromide ion, consistent with the quenching experiments in the BZ oscillator (see the Supporting Information).

4. Summary

In addition to leading visible periodic color changes, ferroin also causes the emergence of sequential oscillations in the bromate−H_2Q photochemical system, but not in the bromate−Q reaction. Such a contrasting influence of ferroin implicates that the reduction of ferriin by H_2Q is essential for the emergence of those initial oscillations. In other words, during the initial stage of the ferroin−bromate−H_2Q reaction, H_2Q acts like an ordinary organic substrate in the classic BZ reaction. The new oscillatory window is a result of the coupling of two processes: (1) the autocatalytic oxidation of ferroin by acidic bromate and (2) the reduction of ferriin by H_2Q. This explains why periodic color change can be achieved within the first oscillation window. It is important to point out that H_2Q can also be oxidized by bromine dioxide radicals through reaction 3,[13]

$$H_2Q + 2BrO_2^{\cdot} \rightarrow Q + 2HBrO_2 \qquad (3)$$

Therefore, reaction 1 must be greatly faster than reaction 3 in order to achieve these initial oscillations. Such a conclusion will be useful in developing a simple mechanism for the ferroin−bromate−CHD reaction, in which both reactions 1 and 3 exist.

In the ferroin free system, a major role of light is the photoreduction of benzoquinone to hydroquinone.[14,20] The inclusion of such a step has successfully reproduced most of the photochemical reaction behaviors reported in the bromate−CHD system.[39] However, as discussed above, the photoreduction of Q to H_2Q is unlikely to play an important role in these initial oscillations, despite that both oscillatory regimes require the presence of strong illumination to emerge. It is interesting to point out that there are a number of aromatic compounds having similar chemical reactivity, like 1,4-H_2Q, which are capable of reducing ferriin and being oxidized by bromine dioxide radicals. Yet, no spontaneous oscillations have been observed when they react with acidic bromate.[5] This study suggests that illumination may be employed as a viable means to achieve spontaneous oscillations in those systems.

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Supporting Information Available: Time series of the ferroin−bromate−H_2Q reaction at different initial concentrations of bromate, H_2SO_4, or H_2Q and quenching experiments with bromide ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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