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Subtle Photochemical Behavior in Ferroin−Bromate−Benzoquinone Reaction

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ABSTRACT: This study investigated the photochemical behavior of the ferroin−bromate−benzoquinone reaction in a batch system, in which the reduction of ferriin was dominated by bromide ions rather than by organic substrates as known in most of bromate oscillators. The chemical oscillations exhibited ultrasensitive response to illumination, where both the oscillation frequency and lifetime were significantly increased by ceiling light with an intensity of less than 20 μW/cm^2. As the light intensity was increased, the influence of light evolved from constructive to inhibitory. At a constant illumination, the influence of light also underwent a transition from constructive to inhibitory when the acid concentration was increased from 0.03 to 0.09 M. NMR measurements and absorption spectroscopy indicated photoenhanced bromination of benzoquinone and photoenhanced reduction of ferriin by bromide ions.
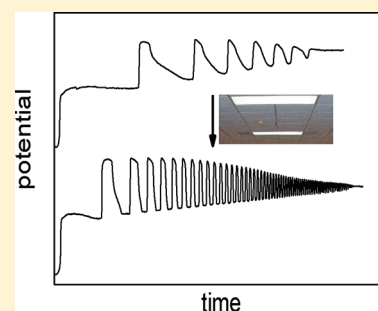
1. INTRODUCTION

The bromate−bromide−metal catalyst reaction has attracted a great deal of attention, as an effort of constructing a chemical oscillators with a minimal number of constituents.[1−4] For example, Geiselar reported that in a continuous flow stirred-tank reactor (CSTR) the bromate−bromide−manganese(II) system could exhibit sustained oscillations and steady state multiplicity.[1] Orban and co-workers obtained a narrow oscillatory region in a flow reactor using cerium or manganous ions as the metal catalyst to react with bromate and have referred those systems as minimal bromate oscillator (MBO).[2] Later Dutt and co-worker investigated stirring and mixing effects in the bromate−bromide−cerium(III) reaction.[4] However, for the lack of necessary sources to modulate the regeneration of bromide ions, which took place through bromination of organic substrates in regular bromate oscillators,[5−12] these minimal bromate oscillators could only function in a CSTR. A very recent study in our group demonstrated the feasibility of introducing an organic substrate into the MBO system to manifest bromide production but does not reduce the oxidized metal catalyst ferriin.[13] This is the distinction from other ferroin−bromate−substrate oscillators, in which one of the main roles of the substrate is to reduce oxidized metal catalysts. The newly developed MBO oscillator (bromate−ferroin−benzoquinone) was able to exhibit spontaneous oscillations in a batch reactor and was referred to as a batch minimal bromate oscillator.[13]

The unique kinetic role of benzoquinone (Q) and its known photochemical property motivated us to explore the importance of photoperturbation in this batch MBO system. Illuminating benzoquinone solution has been known to potentially induce the photoreduction of benzoquinone, leading to the production of hydroquinone,[14] a substance that reacts with bromine dioxide radicals to complete an autocatalytic cycle in bromate oscillators.[15,16] As a result, the illuminated batch-MBO may

become a system consisting of two suboscillators and potentially exhibit novel complex oscillations.[17] So far the bromate−hydroquinone oscillations had only been observed under very intense illumination and required very high acid concentrations in comparison to the acid used in this ferroin−bromate−benzoquinone system.[18,19]

The study of perturbed nonlinear dynamics has attracted increasing attention in the last two decades due to their ubiquitous existence in a variety of systems, and photochemical oscillators provide a convenient way of investigating interactions between intrinsic dynamics and external forcing of various modes.[20−30] The photosensitivity in bromate-based oscillators seems to always involve the production of bromide ions.[31−33] In this batch MBO system, notably, bromide ions have two conflict dynamic roles. One is to reduce ferriin to support the autocatalytic cycle. The second role is to react with HBrO$_2$, which has a negative impact on the autocatalytic feedback. As such, light in this batch-MBO system may potentially modulate a variable that has dual functions and thus inserts intriguing effects. As shown in the following, spontaneous oscillations in the bromate−ferroin−benzoquinone reaction did exhibit subtle response to light, in addition to the extreme photosensitivity.

2. EXPERIMENTAL PROCEDURE

All reactions were run in a thermal-jacketed 50 mL glass reactor with the temperature maintained constant at 25.0 ± 0.1 °C by a circulation water bath (ThermoNesLab RTE 7). The reaction was stirred by a magnetic stirrer (Fisher Isotemp) at around 600 rpm for all experiments. A nontransparent Teflon cap was placed on top of the cylindrical reactor to hold electrodes.
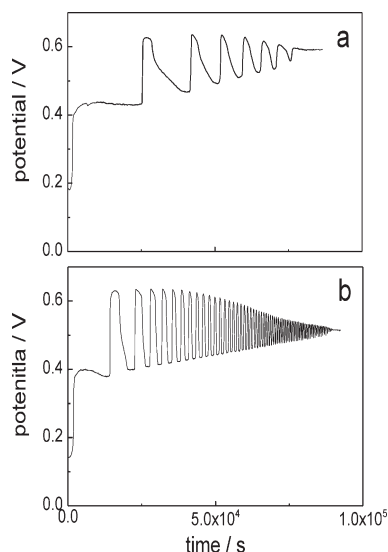
Figure 1. Time series of ferroin—bromate—benzoquinone reaction carried out (a) in a dark room and (b) with the room light on ($I = 20$ $\mu W/cm^2$). Other reaction conditions were [$NaBrO_3$] = 0.05 M, [ferroin] = 1.0×10^{-4} M, [H_2SO_4] = 0.05 M, and [benzoquinone] = 0.035M.

Volume of the reaction solution was fixed at 30.0 mL. Oscillatory profiles were monitored with a platinum or bromide ion selective electrode coupled with a $Hg|Hg_2SO_4|K_2SO_4$ reference electrode (Radiometer Analytical, XR200 and M231Pt-9). All measurements were recorded with a personal computer connected to a pH/potential meter (Radiometer PHM220) through a Power-Lab/4SP data logger. Except otherwise stated, all reactions were conducted under room lighting (i.e., ceiling light from fluorescent lamps) and the controlled light perturbation was implemented with a 150 W halogen light source (Fisher Scientific, Model DLS-100HD). Narrow band filters (Melles Griot) with different wavelength range were placed in front of the light source. Light intensity was measured with an optical photometer from Newport (model 1815-C).

Reaction mixtures were prepared from aqueous stock solutions of analytical-grade sodium bromate ($NaBrO_3$, Aldrich, 99%), 1.0 M, and sulfuric acid (H_2SO_4, Aldrich, 95—98%), 6.0 M. Ferroin stock solution (0.01 M) was prepared from a calculated amount of $FeSO_4 \cdot 7H_2O$ (Aldrich, 99+%) and 1,10-phenanthroline (Aldrich, 99+%). Benzoquinone (Sigma-Aldrich, 98%) was directly dissolved in the reaction mixture. Mass spectrometric measurements were performed on a Varian CP-3800/Varian 1200 L system, using a 15 m Varian CP-Sil 5CB column. All ^1H NMR and ^{13}C NMR studies were performed by Bruker Avance 500 MHz spectrometer and with the same sample that was used for mass spectrometry studies but dissolved in deuterated chloroform (Cambridge Isotope Laboratories, 99.8%). UV/vis spectroscopy was obtained with a spectrophotometer from Ocean Optics (USB 2000).

3. RESULTS AND DISCUSSION

Figure 1 presents two time series of the ferroin—bromate—Q reaction performed (a) in a dark room and (b) under room light. The intensity of the room light was about 20 $\mu W/cm^2$ before passing through two glass walls of the reactor and a layer of circulating water. Other reaction conditions were [$NaBrO_3$] = 0.05 M,
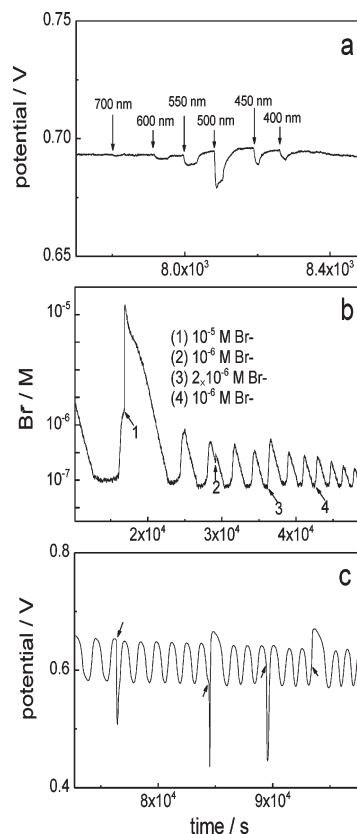

Figure 2. Response of ferroin—bromate—benzoquinone reaction to perturbation of (a) 5 s light pulse of different wavelengths, (b) bromide ions, and (c) 5 s light pulse of $\lambda = 500 \pm 40$ nm and $I = 20$ mW/cm^2. Other reaction conditions were the same as those used in Figure 1b.

[ferroin] = 1.0×10^{-4} M, [Q] = 0.035 M, and [H_2SO_4] = 0.05 M. The reactor was sealed with parafilm to prevent the loss of volatile species such as bromine. As shown in Figure 1a, in the absence of light spontaneous oscillations appeared after an extremely long induction time (2.5×10^4 s). There were 6 oscillation peaks in total. The spontaneous oscillation stopped at a high Pt potential, which corresponded to an oxidation steady state with a low bromide concentration and high concentration of ferriin. Under the room light illumination in Figure 1b, the oscillatory behavior emerged much earlier, in less than 15 000 s from the beginning of the reaction. Notably, the total number of oscillations as well as oscillation frequency was significantly increased. Because the unilluminated system eventually evolved to an oxidized state, whether the autocatalytic feedbacks dominate, the observed constructive influence is more likely arising from the improved suppression on the autocatalytic cycle, e.g., the production of inhibitor.[34,35]

Figure 2a examines the dependence of photosensitivity on wavelength of the incident light. This experiment was performed by placing a narrow band filter between the reactor and a 150 W halogen light source. Each illumination lasted for 5 s. Other reaction conditions were the same as those in Figure 1b. This result demonstrates that illumination with 700 $\pm$ 40 nm light did not cause any change, whereas the strongest response was seen with the incident light of 500 $\pm$ 40 nm. A similar trend was seen when the illumination was applied throughout the reaction process, where the oscillatory behavior including the induction time remained the same when the system was illuminated with
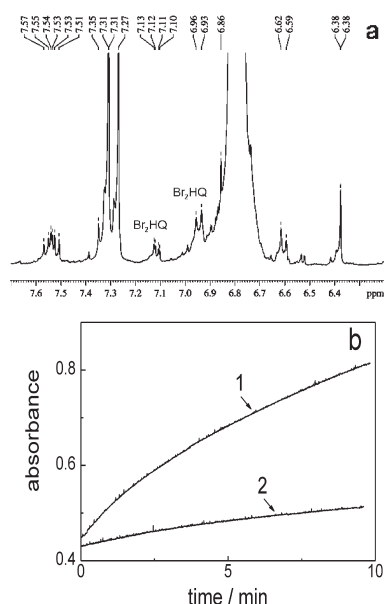
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Figure 3. (a) ^{1}H NMR spectrum of an illuminated MBO reaction. (b) Time series of ferriin and bromide reaction collected at 510 nm, where reaction 1 was illuminated with 30 mW/cm^2 light and reaction 2 was unilluminated.

Figure 4. Time series of ferroin−bromate−benzoquinone reaction illuminated with light of different intensities: (a) 4 μW/cm^2, (b) 15 μW/cm^2, and (c) 46 μW/cm^2. Other reaction conditions were the same as those used in Figure 1a.

700 ± 40 nm light. No influence was observed either, when a narrow band filter of 260 ± 20 nm was used. It is likely because the halogen light source does not emit much light within UV range. Nevertheless, the result suggests that photoreduction of benzoquinone does not play a role in the ultra photosensitivity reported here. On the other hand, spontaneous oscillations were quenched when the system was illuminated with light of 500 ± 40 or 400 ± 10 nm.

Figure 2b presents time series of the reaction subjected to bromide perturbations, where all conditions were the same as those in Figure 1b. The reaction was followed by a bromide ion selective electrode. A rapid color change from red to blue took place when the bromide concentration decreased close to the bottom of the peak, which was around $[Br^-] = 10^{-7}$ M. After evolving at the low concentration range for a while, the bromide concentration underwent a phase of rapid increase. During such a process, the color of the solution changed from blue to red. After a large bromide perturbation at the top of the peak, the oscillation required a very long time to recover. When the perturbation was applied at a phase where the bromide concentration decreased in time, the bromide concentration continued its decrease after a brief increase due to the addition of bromide. When the same amount of bromide was added at the bottom of the peak, however, the system moved right away into the phase where bromide concentration increased rapidly in time. Perturbations 3 and 4 further illustrate that the amplitude of the first oscillation after the perturbation depends on the amount of bromide added.

Figure 2c shows how spontaneous oscillations responded to a pulse light perturbation ($\lambda = 500 \pm 40$ nm, $\Delta t = 5$ s, intensity = 20 mW/cm^2). The Pt potential shifted immediately to a low value when the perturbation was applied at the top, bottom, or a declining phase of the Pt potential peak. In contrast, there was barely any change when the same light pulse was applied at a phase where the Pt potential increased in time. However, an oscillation with larger amplitude and lower frequency was
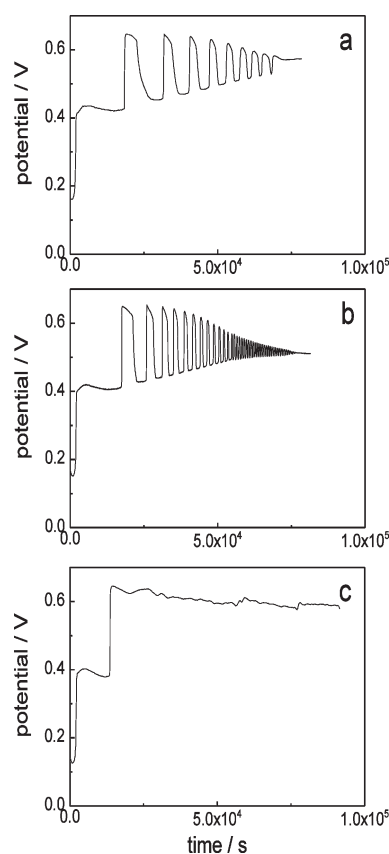
developed after the perturbation. Detailed examination indicates that there was indeed a tiny drop in the Pt potential when the light perturbation was applied. Characterization with a bromide selective electrode indicates that a low Pt potential corresponds to a high bromide concentration. The phenomenon that Pt potential always shifted toward a lower value following a pulse illumination suggests the occurrence of light-induced bromide production.

Figure 3a shows a ^{1}H NMR spectrum recorded in the CDCl$_3$ solution obtained from the reaction carried out at $[NaBrO_3]$ = 0.05 M, $[ferroin] = 1.0 \times 10^{-4}$ M, $[H_2SO_4]$ = 0.05 M, and $[Q]$ = 0.035 M with the illumination of 15 μW/cm^2 (500 ± 40 nm). The selection of the 500 ± 40 nm wavelength range was based on the result listed in Figure 2a. The reaction solution was extracted shortly after the disappearance of those spontaneous oscillations. The ^{1}H NMR spectral resonance appearing at δ = 6.96 and 7.13 indicates that 2,3-dibromohydroquinone and 2,5-dibromohydroquinone (Br$_2$HQ) are produced in the illuminated system.[36] The production of dibromohydroquinones was further confirmed by mass spectrometry. The spectrum in Figure 3a suggests that the bromination of benzoquinone was enhanced by the incident light. Because benzoquinones do not have strong absorption within 500 ± 40 nm, but bromine does, the photochemical process is likely through the reaction between photoexcited bromine and benzoquinone/monobromobenzoquinone and could be qualitatively accounted for by the reactions: Q + Br$_2$* → BrQ + Br$^-$ or BrQ + Br$_2$* → Br$_2$HQ + Br$^-$, where Br$_2$* denotes
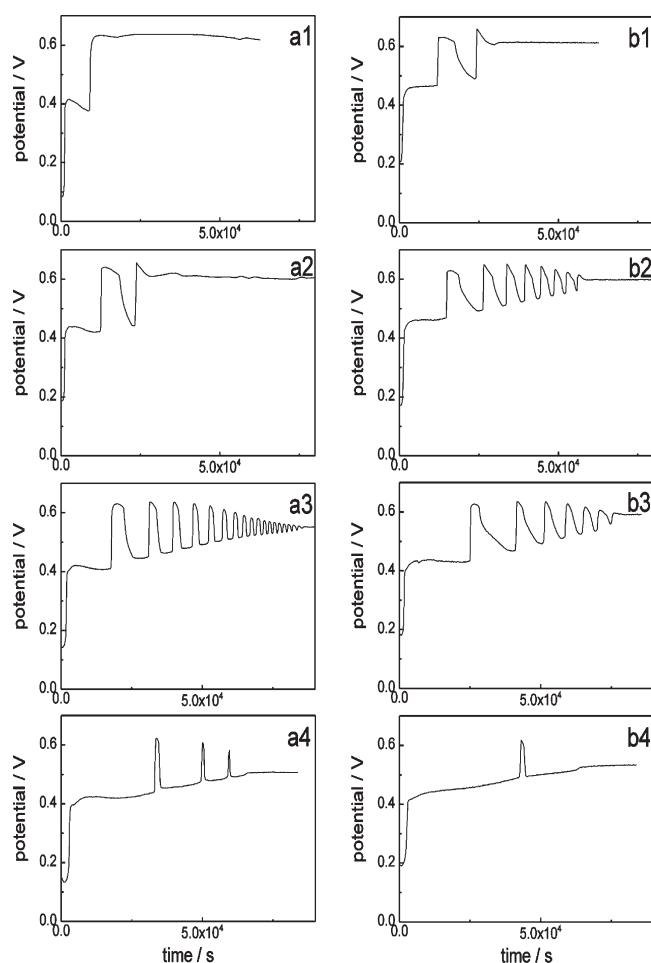
Figure 5. Time series of the ferroin—bromate—benzoquinone reaction at different sulfuric acid concentrations: (a1, b1) 0.08 M, (a2, b2) 0.07 M, (a3, b3) 0.05 M, and (a4, b4) 0.03 M. Reactions (a1)—(a4) were illuminated with 500 ± 40 nm light of $15 \ \mu W/cm^2$. Reactions (b1)—(b4) were carried out in a dark room. Other conditions were $[NaBrO_3] = 0.05$ M, $[ferroin] = 1.0 \times 10^{-4}$ M, and $[Q] = 0.035$ M.

photoexcited bromine molecules, and BrQ represents monobrominated benzoquinones.

Figure 3b shows two time series of ferriin and bromide reaction measured with the UV/vis spectrophotometer at 510 nm. Reaction 1 was conducted under the illumination of 30 mW/cm² light from a halogen light source, whereas reaction 2 was in the absence of illumination except the light from the spectrophotometer. Ferriin was obtained by mixing 3.0×10^{-4} M ferroin with 3.0×10^{-4} M Ce⁴⁺ in 0.05 M sulfuric acid solution. After 60 min, 0.05 M sodium bromide was added into the cuvette. The two time series illustrate that the reduction of ferriin by bromide was accelerated by light. The increased supply of ferroin, which reacts with bromine dioxide radicals, shall have constructive influence on the autocatalytic cycle. However, if the nonlinear dynamics is already dominated by autocatalytic feedback, such as the case in Figure 1a, enhancement of the autocatalytic cycle would insert negative impact on the emergence of spontaneous oscillations.

Figure 4 presents three time series of the ferroin—bromate—Q reaction illuminated with 500 ± 40 nm light of different intensities: (a) $4 \ \mu W/cm^2$, (b) $15 \ \mu W/cm^2$, and (c) $46 \ \mu W/cm^2$.

Other reaction conditions were the same as those used in Figure 1a. This series of experiments illustrate that low intensity light, e.g., $4 \ \mu W/cm^2$, shortened the induction time and increased the number of oscillation peak, exhibiting constructive influence on the oscillatory behavior. When the light intensity was increased to $46 \ \mu W/cm^2$, however, spontaneous oscillations were quenched. Note that the attained nonoscillatory state has a high Pt potential value, which corresponds to a state of low Br⁻ concentration and high ferriin concentration (i.e., an oxidation state), implicating that the autocatalytic feedback overwhelms the production of inhibitor.

Figure 5 presents time series of the ferroin—bromate—Q reaction at different concentrations of H_2SO_4: (a1, b1) 0.08 M, (a2, b2) 0.07 M, (a3, b3) 0.05 M, and (a4, b4) 0.03 M. The (a) series of reactions were carried out under the illumination of 500 ± 40 nm light with an intensity of $15 \ \mu W/cm^2$. Reactions in the (b) series illustrate that for the unilluminated system spontaneous oscillations could only be observed for the H_2SO_4 concentration within 0.09 and 0.03 M. This acid condition is significantly lower than the concentration commonly used in the BZ oscillators or in the bromate—hydroquinone photochemical oscillator.[18,19] Spontaneous oscillations were quenched in (a1), indicating that light has negative impact on the nonlinear behavior. As the acid concentration was decreased, which consequently weakened the autocatalytic feedback via $BrO_3^- + HBrO_2 + H^+ \longleftrightarrow 2BrO_2 + H_2O$ and ferroin + $BrO_2 + H^+ \longrightarrow$ ferriin + $HBrO_2$, the same light illumination only partially quenched the oscillatory behavior (comparing (a2) and (b2)). As the acid concentration was decreased gradually, the influence of light became negligible. Later, constructive influences took place in (a3) and (a4) as a result of further decrease of H_2SO_4 concentration.

4. CONCLUSIONS

The ferroin—bromate—benzoquinone reaction was found to have great photosensitivity, in which light was capable of enhancing or quenching the chemical oscillations. The required light intensity was significantly lower than that reported earlier in a similar chemical system, in which photoreduction of benzoquinone was responsible for the overall oscillatory phenomenon.[19] Characterization with NMR and mass spectrometry suggests light-enhanced bromination of benzoquinone, which is accompanied by bromide production. Meanwhile, UV/vis spectroscopy indicates that light accelerates the reduction of ferriin by bromide, which consumes bromide ions and supplies ferroin for the autocatalytic process. The above preliminary mechanistic study highlights that light could simultaneously implement two opposite effects. Which path plays a dominant role depends on the dynamics of the system. This could be the reason that a transition from constructive to inhibitory effect took place as merely the acid concentration was adjusted. In addition, as illustrated in Figure 4, the influence of light also underwent a transition from constructive to inhibitory when light intensity was increased monotonically. These results clearly demonstrate that illumination is an effective means to implement subtle manipulation of the nonlinear dynamics of the ferroin—bromate—benzoquinone reaction. This low cost, easy to prepare chemical reaction provides a good model system for exploring novel complex nonlinear behavior via subjecting it to light with an intensity being modulated in time.

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■ REFERENCES

(1) Geiselar, W. *J. Phys. Chem.* **1982**, *86*, 4394–4399.

(2) Orban, M.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 2657–2658.

(3) Bar-Eli, K. *J. Phys. Chem.* **1985**, *89*, 2855–2860.

(4) Dutt, A. K.; Menzinger, M. *J. Chem. Phys.* **1999**, *110*, 7591–7593.

(5) Field, R. J.; Boyd, P. M. *J. Phys. Chem.* **1985**, *89*, 3707–3714.

(6) Srivastava, P. K.; Mori, Y.; Hanazaki, I. *J. Phys. Chem.* **1991**, *95*, 1636–1639.

(7) Pelle, K.; Wittmann, M.; Noszticzius, Z.; Lombardo, R; Sbriziolo, C.; Turco Liveri, M. L. *J. Phys. Chem. A* **2003**, *107*, 2039–2047.

(8) Rastogi, R. P.; Chand, P.; Pandey, M. K.; Das, M. *J. Phys. Chem. A* **2005**, *109*, 4562–4567.

(9) Adamčiková, L.; Farbulová, Z.; Ševčík, P. *New J. Chem.* **2001**, *25*, 487–490.

(10) Szalai, I.; Kurin-Csörgei, K.; Epstein, I. R.; Orbán, M. *J. Phys. Chem. A* **2003**, *107*, 10074–10081.

(11) Harati, M.; Wang, J. *J. Phys. Chem. A* **2008**, *112*, 4241–4245.

(12) Kumli, P. I.; Burger, M.; Hauser, M. J. B.; Müller, S. C.; Nagy-Ungvárai, Zs. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5454–5458.

(13) Li, J.; Wang, J. *Chem. Phys. Lett.* **2011**, *508*, 320–323.

(14) Görner, H. *J. Phys. Chem. A* **2003**, *107*, 11587–11595.

(15) Farage, V. J.; Janjic, D. *Chem. Phys. Lett.* **1982**, *88*, 301–304.

(16) Szalai, I.; Körös, E. *J. Phys. Chem. A* **1998**, *102*, 6892–6897.

(17) Chen, Y.; Wang, J. *J. Phys. Chem. A* **2005**, *109*, 3950–3956.

(18) Zhao, B.; Wang, J. *J. Photochem. Photobiol. A: Chem.* **2007**, *192*, 204–210.

(19) Li, N.; Wang, J. *J. Phys. Chem. A* **2009**, *113*, 6297–6300.

(20) Kuhnert, L.; Agladze, K. I.; Krinsky, V. I. *Nature* **1989**, *337*, 244–247.

(21) Steinbock, O.; Zykov, V.; Müller, S. C. *Nature* **1993**, *366*, 322–324.

(22) Petrov, V.; Ouyang, Q.; Swinney, H. *Nature* **1997**, *388*, 655–657.

(23) Kádár, S.; Wang, J.; Showalter, K. *Nature* **1998**, *391*, 770–772.

(24) Wang, J.; Kádár, S.; Jung, P.; Showalter, K. *Phys. Rev. Lett.* **1999**, *82*, 855–858.

(25) Ruoff, P. *J. Phys. Chem.* **1984**, *88*, 2851–2857.

(26) Kaminaga, A.; Mori, Y.; Hanazaki, I. *Chem. Phys. Lett.* **1997**, *279*, 339–343.

(27) Martinez, K.; Lin, A. L.; Kharrazian, R.; Sailer, X.; Swinney, H. L. *Physica D* **2002**, *1*, 168–169.

(28) Cassidy, I.; Müller, S. C. *Phys. Rev. E* **2006**, *74*, 026206:1–9.

(29) Treindl, L.; Knudsen, D.; Nakamura, T.; Matsumura-Inoue, T.; Jørgensen, K.; Ruoff, P. *J. Phys. Chem. A* **2000**, *104*, 10783–10788.

(30) Huh, D. S.; Kim, Y. J.; Kim, H. S.; Kang, J. K.; Wang, J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3188–3192.

(31) Sorensen, P. G.; Lorenzen, T.; Hynne, F. *J. Phys. Chem.* **1996**, *100*, 19192–19196.

(32) Kaminaga, A.; Hanazaki, I. *J. Phys. Chem. A* **1998**, *102*, 3307–3314.

(33) Kadar, S.; Amemiya, T.; Showalter, K. *J. Phys. Chem. A* **1997**, *101*, 8200–8206.

(34) Scott, S. K. *Chemical Chaos*; Oxford University Press: Oxford, U.K., 1991.

(35) Field, R. J., Burger, M., Eds. *Oscillations and Travelling Waves in Chemical Systems*; John Wiley & Sons: New York, 1985.

(36) Li, N.; Green, J. R.; Wang, J. *Chem. Phys. Lett.* **2007**, *447*, 241–246.

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