Spontaneous Formation of Revival Waves in the 1,4-Cyclohexanedione-Bromate-Ferroin Reaction

Do Sung Huh,* **Young Joon Kim, Hye Sook Kim, Jong Kon Kang, and Sang Joon Choe**

Department of Chemistry, Inje University, Kimhae 621-749, Korea

Received September 4, 2003

The bromate-1,4-cyclohexanedione-ferroin oscillating reactions are uncovered to support two types of wave activities, in which spontaneous formation of circular waves has been achieved after the disappearance of initial waves. The induction period of the revival wave is typically above 10 hours and its dependence on the initial concentrations of reactants is qualitatively different from that of initial waves. In addition to their differences in propagating speed and wavelength, the initial waves and the revival patterns have different colors, suggesting that different reaction mechanisms are involved in the formation of these spatiotemporal behaviors. Our experiments further show that the addition of hydroquinone to the reacting system can significantly shorten the induction time of the revival wave, which implicates that hydroquinone is not only a product in the bromate-1,4-cyclohexanedione-ferroin oscillating reaction but also plays a critical role in the following reactions.

Key Words : Revival wave, Two reaction mechanisms, Hydroquinone effect

Introduction

Pattern formation in reaction diffusion media has been studied extensively in the last three decades by scientists from several disciplines.[1-4] This is partly because reaction diffusion systems constitute the most convenient models for understanding pattern formation in a broad range of media including catalysis, biology, and ecology. A variety of spatiotemporal behavior such as circular waves, spirals, Turing patterns, and scroll waves have been observed in chemical media.[1-11] Among these studies, the Belousov-Zhavotinsky (BZ) reaction has become a prototypical model, which is the oxidation and bromination of an organic substrate by acidic bromate in the presence of metal catalyst.[5] As discussed by Epstein and co-workers,[11,12] an important drawback of the traditional BZ reaction is the production of carbon dioxide gas from malonic acid, which consequently induces hydrodynamic disturbances in the reaction-diffusion media. For that reason, the study of pattern formation has attracted increasing attention in the last decade. Körös' group at Eötvös University and Epstein and co-workers at Brandies University have made significant contributions to the understanding of the reaction mechanism of the bromate-1,4-cyclohexanedione-ferroin oscillating system.[11-15]

Another interesting dynamical property of the bromate-1,4-cyclohexanedione-ferroin oscillating reaction is its response to illumination. Kurin-Csörgei *et al.* reported stronger light sensitivity in such a system,[12] which makes it an attractive model system for studying perturbed spatio-temporal dynamics. Due to the easy implementation of external perturbation, light sensitivity reaction-diffusion media have been investigated intensively in the last two decades in an effort of understanding the interactions between intrinsic dynamics and external perturbations. A number of new dynamical behaviors, which do not exist in unperturbed media, have been reported recently.[16-19] Recent reports by Vang *et al.* showed oscillatory cluster pattern formation in the light-driven BZ medium.[16,17] Tóth and co-workers recently reported light-induced wave initiation in the ferroin-catalyzed BZ reaction, where the excitation was believed to be due to light induced reduction of ferroin.[18] Petrov *et al.* used a video projector to periodically drive a photosensitive BZ system at various frequencies related to the oscillation frequency of the autonomous system. They found a new type of pattern formation involving phase bistability as well as spatiotemporal chaos.[19]

Huh *et al.* recently have introduced an unusual wave propagation in the bromate-1,4-cyclohexanedione-ferroin oscillating reaction system in which two patterns of travelling wave have been induced spontaneously with long time lag.[20,21] By the results, a new wave has been induced as a concentric pattern after an initially induced wave has disappeared. They compared the behavior of the two waves and suggested an appropriate reaction process for the unusual behavior of wave propagation in the system.

In this study, we examine and analyze the spatiotemporal behavior of the bromate-1,4-cyclohexanedione-ferroin reaction in detail by comparing the wave propagation with the wave patterns obtained in the similar traditional BZ reaction to contribute to the understanding of the chemical process of the unusual wave formation in the reaction system. Our investigations draw a conclusion that these two types of waves are induced by different reaction mechanisms, although they occur in the same chemical system and have similar geometric structures.

Experimental Section

Stock solutions were prepared from $NaBrO_3$ (Aldrich, 99%), 0.6 M, dissolved in distilled water, 1,4-cyclohexanedione (Fluka, 98%), 0.2 M, dissolved in distilled water, and sulfuric acid (Aldrich, 98%), 2 M, diluted with distilled water. 0.025 M $Fe(phen)_3SO_4$ was purchased from Sigma (> 99%). All chemicals are used in their commercial grade without further purification.

Pattern formation occurs in a thin layer of cation-exchange beads loaded with the metal catalyst ferroin. The analytical grade cation-exchange resin (Dowex 50W-X4) of mesh 400 (bead diameter 40-70 μm) was purchased from Sigma company. The cation resin was first washed several times by distilled water to modify its acidity. To load the metal catalyst ferroin into the resin, the resin was mixed with a predetermined amount of ferroin solution. The mixture was stirred for one hour. To begin our experiments, 50.0 mL BZ solution containing 5.0 g of beads loaded with ferroin was poured into a Petri-dish (10 cm in diameter), which formed a uniform thin film of resin on the bottom of the Petri dish. The thickness of the bead film was calculated from the volume of the resin divided by the area of the bottom of the Petri-dish, which gave us a magnitude of 1 ± 0.3 mm. The Petri-dish was maintained at room temperature of 20.0 ± 0.5 ^{o}C. All experiments were monitored with a CCD camera (Sony, SSC-370) equipped with a zoom lens (Niko, 1.4X). The CCD camera is connected to a personal computer running a frame grabber (Flash Point, Optimus 6.1).

Results and Discussion

Figure 1 presents a series of snapshots of wave patterns in the bromate-1,4-cyclohexanedione-ferroin system. The initial color of the resin film is green, suggesting that the chemical system is at an oxidized state. After an induction period, which is influenced by the initial compositions of the solution, reddish spots (*e.g.* reduction wave) appear spontaneously on the resin film. These reduction waves are similar to the oxidation waves studied earlier by Showalter and co-workers in the ferroin-malonic acid BZ reactions.[22,23] In consistent to earlier studies of waves in the bromate-1,4-cyclohexanedione-ferroin system, we observed that these waves normally lasted for a couple of hours (Figure 1b). However, after these initial wave disappear from the medium, new patterns, which is called revival waves in this study, occur spontaneously after long quiescent period (>10 hours) (see Figure 1c). No such behavior has been reported in the classical BZ reactions and in the uncatalyzed bromate oscillators. These revival waves have different wavelengths from the initial reduction waves. During the quiescent period, the medium has thick red color, suggesting that the system is at reduced stable steady states. Right before the occurrence of revival waves, the color of the medium turns to green and then yellow colored revival waves appear. The propagation speed of the revival wave is within the range between 0.5 and 0.8 mm per minute, which is about three times slower than the initial waves. The quantitative comparison of their speeds is not feasible because the propagation speed of the initial wave cannot be measured accurately due to the presence of too many wave activities in the medium.

Revival waves typically appear as a target pattern as shown in Figure 1d and survive for several hours, which is significantly longer than the life period of the initial waves. The fact that the revival wave also has different wavelengths from the initial wave suggests that the appearance of the above unusual behavior is likely governed by a different

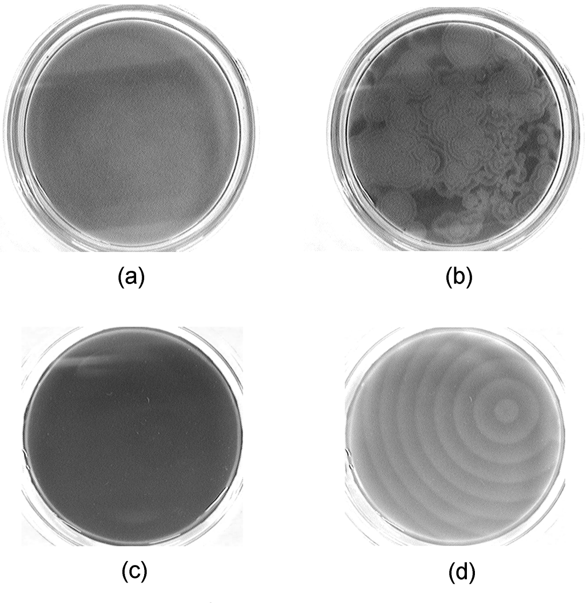


Figure 1. Snapshots of waves in the bromate-1,4-cyclohexanedione-ferroin reactions; (a) 60 min, (b) 200 min, (c) 600 min, and (d) 1200 min after starting the reaction. The green color represents a high concentration of ferroin, while red color represents the low concenreation of ferroin. The initial compositions of the solution are: [1,4-CHD] = 0.05 M, $[BrO_3^-]$ = 0.15 M, $[H_2SO_4]$ = 1.0 M, and $[Fe(phen)_3^{2+}] = 1.5 \times 10^{-3}$ M.

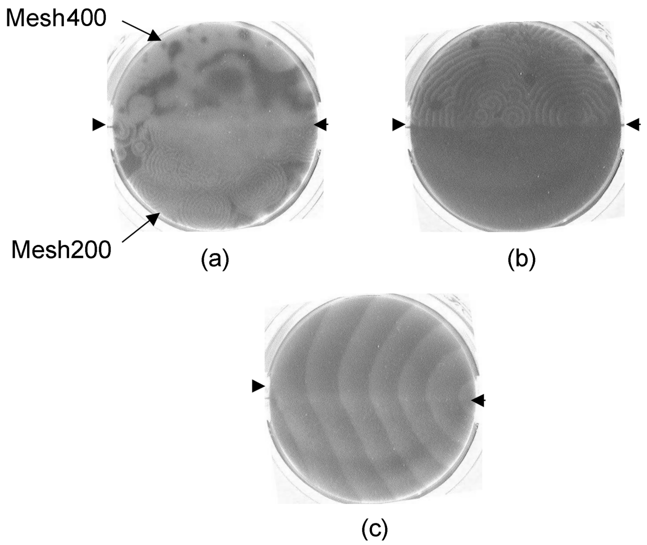


Figure 2. Wave sequences obtained in the bromate-1,4-cyclohexanedione-ferroin reactions, where resin beads of different mesh size were used. The beads on the top half of the Petri-dish has the mesh size of 400, whereas beads of size 200 are precipitated in the bottom half of the Petri-dish. Other initial conditions are: [1,4-CHD] = 0.05 M, $[BrO_3^-]$ = 0.15 M, $[H_2SO_4]$ = 1.0 M, and $[Fe(phen)_3^{2+}] = 1.4 \times 10^{-3}$ M. Images are collected at: (a) 100 min, (b) 2000 min, (c) 12000 min.

reaction mechanism in comparison to the formation of the initial waves. However, we cannot preclude that the large wavelength is not due to the decrease of the concentrations of chemicals, in particular these revival waves normally appear after 12 hours of the start of the reaction. To shed light on this issue, we investigated the dependence of wave behavior on the size of resin beads. These experiments were performed in a Petri-dish loaded with beads of different sizes (400 and 200 mesh, respectively) in each half. As shown in Figure 2a, initial waves appeared spontaneously on both parts of the reactor. However, waves survived a much shorter period in the area loaded with beads of larger sizes, (see the image shown in Figure 2b). In contrast, the revival waves (see the image in Figure 2c) had the same life time in both areas of the medium. Careful comparisons of their propagation speed and wavelength also revealed that the initial wave and the revival wave exibited different dependences on the size of resins, although these differences were too small to draw a conclusive conclusion.

Earlier studies conducted in both stirred and reaction-diffusion systems have shown that the induction period of the oscillating reaction of bromate-1,4-cyclohexanedione-ferroin depends on the initial compositions of this system. In this investigation, we found that the induction period of the initial waves is also susceptible to the variation of the initial compositions. Same as reported earlier,[20] the increase of the sulfuric acid concentration will reduce the induction period of the initial waves. Meanwhile, the induction period of the revival wave, which is defined as the time duration after the disappearance of the last initial wave and before the appearance of the first revival wave, also decreases with increasing sulfuric acid concentration. However, the induction period of the revival wave is less sensitive and remains above 10 hours throughout this study. The variation of sodium bromate concentration exhibits opposite impacts on the induction periods of initial waves and revival waves. Such a result is plotted in Figure 3, where the increase of bromate concentration prolongs the induction period of the initial waves. Such a negative impact may be understood based on the classical BZ reaction-mechanism: the initial green color indicates that the initial dynamical state of the system is in an oxidized state; FKN mechanism suggests that the increase of bromate concentration will drive the BZ system further to the oxidized state, and consequently the system requires longer time to evolve back to oscillatory states or excitable states with a smaller excitation threshold.[24] On the other hand, increasing bromate concentration accelerates the production rates of other reactants, which may be important in the formation of revival waves. If it is the case, one can expect to see the decrease of the induction period of the revival wave with respect to the increase of bromate concentration. This is indeed the result presented in Figure 3. As shown in the figure, the decrease of the induction period for the revival wave and the increase of the induction period for the initial wave become flat when BrO_3^- concentration is increased further.

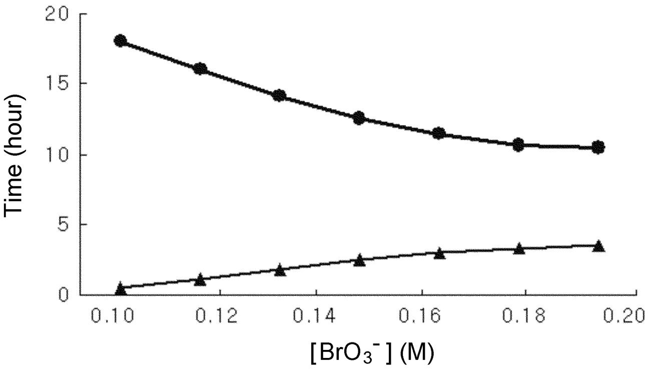
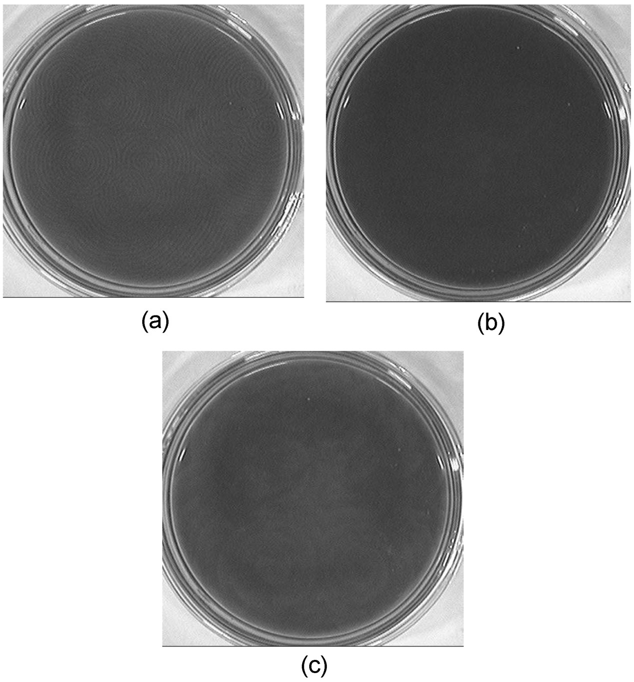


Figure 3. The induction period of wave formation as a function of the initial concentration of BrO_3^-. The induction period of the initial wave is represented by ▲, whereas ● indicates the induction period of the revival waves. The initial concentrations of other reactants are: [1,4-CHD] = 0.05 M, [H_2SO_4] = 1.0 M, and [$Fe(phen)_3^{2+}$] = 1.5 × 10^{-3} M.

The concentration of ferroin in our experiments equals 1.5 × 10^{-3} M. As discussed by Epstein and co-workers, when the concentration of ferroin s above 1 × 10^{-5} M in the bromate-ferroin-1,4-cyclohexanedione reaction, ferroin will play more than the role of an indicator.[11] Instead, ferroin complexes participate in the autocatalytic reactions to lead the system reacting as a classical BZ reaction system. Therefore, the formation of these initial waves in the above experiments could be understood bases on the BZ reaction mechanism.[24] During the course of the initial waves, new reactants such as hydroquinone are formed from 1,4-cyclo-


(a) (b)

(c)

Figure 4. Spontaneous formation of revival waves after the addition of hydroquinone to the medium. Hydroquinone is added after the disappearance of initial waves and the concentration of added hydroquinone is about 1.5 × 10^{-3} M. The initial compositions of the reaction solution are: [1,4-CHD] = 0.05 M, [H_2SO_4] = 1.0 M, and [$Fe(phen)_3^{2+}$] = 1.5 × 10^{-3} M. Images are collected at: (a) 250 min, (b) 450 min, (c) 650 min.

hexanedione. To understand the possible dynamical roles played by these intermediate products, in the following we conducted a series of experiments in which hydroquinone was added to the medium after the disappearance of initial waves. Shown in Figure 4a is a snapshot of initial waves taken 4 hours after the start of the reactions. Figure 4b is taken after the addition of hydroquinone, which was implemented by adding hydroquinone solution to the mixture right after the disappearance of initial waves. This thus represents a global perturbation. Shown in Figure 4c is a result of 3 hours after the addition of hydroquinone, where revival waves with similar features of concentric wave patterns with large wave length as shown in Figure 1c are achieved. Experiment under different initial conditions show the same result that the addition of hydroquinone significantly shortens the induction period of revival waves. These experiments further implicate that the formation of revival waves is governed by a different reaction mechanism which involves the products from the initial stage of the reactions such as hydroquinone and its derivatives.

Conclusion

In this study we observed in detail abnormal spatiotemporal behavior in the bromate-1,4-cyclohexanedione-ferroin gas free reaction system, in which spontaneous wave formation appears after more than 10 hours of the disappearance of initial waves. The revival wave has different wavelengths and propagation speeds from the initial waves. Its induction period also exhibits qualitatively to the variation of the initial concentration of bromate. Our preliminary results suggest that these two types of waves are induced by different reaction mechanisms, although they occur in the same chemical system and have similar geometric structures. Their response to external light perturbations is under investigation and will be reported in our future report.

Our experiments show that hydroquinone, which is known as a product in the bromate-1,4-cyclohexanedione-ferroin BZ reaction, plays an important role in the appearance of revival patterns. Such a result is in accord with earlier mechanistic studies of this oscillatory chemical system, which suggest that hydroquinone is involved in several reaction steps including the autocatalytic process of reacting with bromous acid radicals to from bromous acid. However, the result that the revival wave does not occur immediately after the addition of hydroquinone suggest that hydroquinone is more likely functioning as a precursor of other chemicals which are directly involved in the formation of these revival waves. Experiments with derivatives of hydroquinone will be pursued in our future research to provide in-depth understanding of the mechanism of this reaction system.

Acknowledgement. This work was supported by the 2002 Inje University research grant. And partially supported by grant No. R01-2002-000-00030-0 from the Korea Science and Engineering Foundation, and by a grant No. 02-PJ3-PG3-31402-0004 from the Korean Health 21 R&D Project, Minstry of Health and Welfare of Korea.

References

1. *Chemical Waves and Patterns*; Kapral, R.; Showalther, K., Eds.; Kluwer Academic Publishers: Netherland, 1995.
2. Cross, M. C.; Hohenberg, P. C. *Rev. Mod. Phys*. **1993**, *65*, 851.
3. Swinney, H. L.; Krinsky, V. I. *Physica D* **1991**, *49*, 7.
4. Winfree, A. T. *The Geometry of Biological Time*; Springer: Heidelbers, 2000.
5. *Oscillations and Traveling Waves in Chemical System*; Field, R. J.; Burger, M., Eds.; Wiley-Interscience: New York, 1985.
6. Winfree, A. T. *Science* **1972**, *175*, 634.
7. Winfree, A. T. *Chaos* **1998**, *8*, 1.
8. Winfree, A. T. *Chaos* **1998**, *8*, 57.
9. Agladze, K.; Thouvenel-Romans, S.; Steinbock, O. *J. Phys. Chem. A* **2001**, *105*, 7356.
10. Bertram, M.; Masere, J.; Pojman, J. A.; volke, F. *J. Polymer Science A* **2001**, *39*, 1075.
11. Kurin-Csörgei, K.; Zhabothinsky, A. M.; Orban, M.; Epstein, I. R. *J. Phys. Chem*. **1996**, *100*, 5393.
12. Kurin-Csörgei, K.; Zhabothinsky, A. M.; Orban, M.; Epstein, I. R. *J. Phys. Chem*. **1997**, *101*, 6827.
13. Kurin-Csörgei, K.; Szalai, I.; Molnár-Perl, I.; Körös, E. *React. Kinet. Catal. Lett.* **1994**, *53*, 115.
14. Kurin-Csörgei, K.; Szalai, I.; Körös, E. *React. Kinet. Catal. Lett*. **1995**, *54*, 217.
15. Szalai, I.; Körös, E. *J. Phys. Chem. A* **1998**, *102*, 6892.
16. Vanag, V. K.; Yang, L.; Dolnik, M.; Zhabothinsky, A. M.; Epstein, I. R. *Nature* **2000**, *406*, 389.
17. Vanag, V. K.; Zhabothinsky, A. M.; Epstein, I. R. *Phys. Rev. Lett*. **2001**, *86*, 552.
18. Tóth, R.; Gaspar, V.; Belmoute, A.; O'Connell, M. C.; Taylor, A.; Scott, S. K. *Phys. Chem. Chem. Phys*. **2000**, *2*, 413.
19. Kuhnert, L.; Agladze, K. I.; Krinsky, V. I. *Nature* **1989**, *337*, 224.
20. Huh, D. S.; Choe, S. J.; Kim, M. S. *React. Kinet. Catal. Lett.* **2001**, *74*, 11.
21. Huh, D. S.; Kim, M. S.; Choe, S. J. *Bull. Korean Chem. Soc*. **2001**, *22*, 867.
22. Maselko, J.; Reckley, J. S.; Showalter, K. *J. Phys. Chem*. **1989**, *93*, 2774.
23. Maselko, J.; Showalter, K. *Physica D* **1991**, *49*, 21.
24. Field, R. J.; Körös, E.; Noyes, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8649.