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Chemical Oscillations and Waves in the Catalyzed Bromate-Pyrocatechol Reaction

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Long time series of temporal oscillations and wave formation are observed in the catalyzed bromate-pyrocatechol reaction conducted in a batch reactor, in which the induction time is insensitive to the presence of ferroin but is greatly shortened by Ce(III) or Mn(II). On the other hand, the number of oscillations is significantly increased by ferroin, while it is less sensitive to Ce(III) and Mn(II). The ferroin-catalyzed system also exhibits strong photosensitivity, in which illumination could quench the oscillatory behavior. A phase diagram illustrates that the oscillatory behavior of the studied system is more sensitive to the ratio of [pyrocatechol]/[bromate] than their absolute concentrations. Reactions conducted in a spatially extended medium show that the ferroin-catalyzed system supports a two-stage pattern formation with the wave activity surviving for up to 10 h.

1. Introduction

The study of chemical oscillations and wave formation has blossomed in the past three decades, which led to the observation of various nonlinear spatiotemporal behaviors such as both simple and complex oscillations in a stirred system,[1−3] and Turing pattern, target, spiral and scroll waves in reaction-diffusion media.[4−10] Understanding the onset of those exotic phenomena in chemical systems has provided important insight into the formation of similar behaviors in nature.[11−13] One of the most frequently studied and, arguably, best characterized chemical oscillators is the Belousov−Zhabotinsky (BZ) reaction, which is the oxidation and bromination of malonic acid by acidic bromate in the presence of metal catalysts.[14−19] In particular, the photosensitivity of the ruthenium-catalyzed BZ reaction provides a convenient approach for the study of perturbed nonlinear dynamics, which has led to the observation of a number of interesting behaviors which do not exist in a perturbation free environment.[20−24]

The development of nonlinear spatiotemporal structures depends both on the local temporal kinetics and on diffusion transportations.[5] Since most chemical reagents have similar diffuse coefficients in solution, constructing chemical oscillators exhibiting novel nonlinear dynamics has become increasingly desired in the study of nonlinear chemical dynamics. The discovery of the bromate-1,4-cyclohexanedione oscillator in 1982,[25] for example, has eventually led to the recent observation of anomalous dispersion relationships of chemical waves and sequential pattern formation.[26,27] This research aims to build a new chemical reaction system which is capable of showing a long time series of periodic color changes (i.e., temporal oscillations) and thus can later be applied to the investigation of chemical waves. De Kepper et al. have developed a systematic approach of designing chemical oscillators in a continuous flow stirred tank reactor (CSTR).[28] Their method includes four steps: finding an autocatalytic system, running the reaction in a CSTR, finding a bistability region, and then perturbing the system by adding another species to induce oscillations.[28] To facilitate the transformation to the study of chemical waves, this research focuses on nonlinear reactions in a batch reactor. Following the observation of oscillatory behavior in the uncatalyzed pyrocatechol-bromate system, nonlinear kinetics of the Mn^{2+}-, Ce^{3+}-, and ferroin-catalyzed bromate-pyrocatechol reactions were explored. Light influence on the catalyzed bromate-pyrocatechol system was also carried out. Preliminary investigation on the spatially extended system confirms the feasibility of studying wave formation with the ferroin-catalyzed bromate-pyrocatechol medium.

2. Experimental Procedure

All reactions were carried out in a thermal-jacketed 50 mL glass beaker (ChemGlass), in which temperature was kept constant at 25.0 ± 0.1 °C by a circulating water bath (Thermo NesLab RTE 7). A Teflon cap was placed on top of the reactor to hold the electrodes. The solution level was about 1 cm below the Teflon cap. The reaction solution was stirred by a magnetic stirrer (Fisher Isotemp). Reactions were monitored with a platinum electrode coupled with a $Hg|Hg_2SO_4|K_2SO_4$ reference electrode (Radiometer Analytical, XR200 and M231Pt-9). All measurements were recorded through a pH/potential meter (Radiometer PHM220) connected to a personal computer through a PowerLab/4SP data logger. The perturbation of light was implemented with a halogen lamp equipped with dual bifurcated optic fibers and continuous variable light level (Fisher Scientific, model DLS-100HD, 150 W). The illumination was implemented by placing the two fibers either on the opposite or the same sides of the reactor. No difference in the reaction behavior was observed, implying that the mixing was fast enough to generate a situation of homogeneous illumination. The intensity was measured with an optical photometer from Newport (model 1815-C).

Stock solutions of $NaBrO_3$ (Aldrich, 99%), 0.6 M, sulfuric acid (Aldrich, 95−98%), 4.0 M, $Ce_2(SO_4)_3$ (Aldrich, 97%), 0.025 M, and $MnSO_4 \cdot H_2O$ (Aldrich, 98+%), 0.025 M, were prepared with doubly distilled water. Ferroin, 0.025 M, was prepared from a calculated amount of $FeSO_4 \cdot 7H_2O$ (Aldrich, 99+%) and 1,10-phenanthroline (Aldrich, 99+%). Pyrocatechol (Sigma, 99%) was directly dissolved in the reaction mixture.

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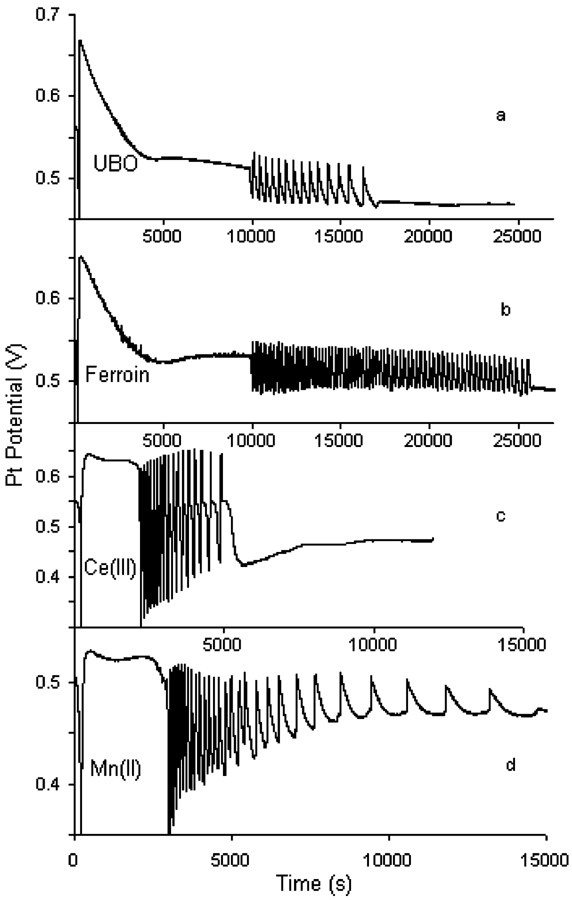

Figure 1. Time series of the (a) uncatalyzed, (b) ferroin-, (c) cerium- and (d) manganese-catalyzed bromate-pyrocatechol reaction. Other reaction conditions are $[H_2SO_4] = 1.30$ M, [pyrocatechol] = 0.043 M, and $[BrO_3^-] = 0.078$ M. The concentration of metal catalysts is equal to 1.0×10^{-4} M in all three cases.

The volume of the reaction mixture was fixed at 30.0 mL in all experiments. Chemical waves were investigated by injecting the reaction solution into a narrow space between two microscope slides, forming a 0.5 mm (or 0.3 mm) thick solution layer without a free surface. The evolution of chemical waves was monitored with a CCD camera equipped with a zoom lens. The CCD camera was connected to a personnel computer running a frame grabber program (Matrox Imaging Library).

3. Results and Discussion

3.1. Transient Temporal Oscillations. Figure 1 presents time series of the (a) uncatalyzed, (b) ferroin-, (c) cerium-, and (d) manganese-catalyzed bromate-pyrocatechol reactions. In all four cases, there is a large excursion in the Pt potential occurring shortly after mixing all reagents together. Throughout this research, bromate is the last reagent added to the reactor. In the uncatalyzed system, the Pt potential decreases gradually after the initial excursion and then reaches a plateau. In general, one may consider that the reaction is over. However, the Pt potential suddenly starts oscillating and the oscillatory process lasts for longer than an hour with about 14 peaks. Similar to existing uncatalyzed bromate oscillators,[25] oscillations here do not commence right after the reaction begins; that is, there is a long induction time. Phenomenologically, the reaction solution turns to dark red from transparent during the initial Pt excursion and then slowly turns into yellow during the long induction period. There is no periodic color change during the oscillations and thus this uncatalyzed system is unsuitable for studying chemical waves, despite its capacity of exhibiting oscillatory dynamics.

When 1.0×10^{-4} M ferroin is added to the bromate-pyracatechol reaction, spontaneous oscillations commence at about the same time as the uncatalyzed system. However, there are significant increases in the frequency of oscillation as well as the total number of oscillations. Notably, oscillations last for longer than 4 h in this catalyzed system during which the system exhibits periodic color changes from yellowish green to faint pink. A higher concentration of ferroin results in a better contrast but reduces the lifetime of the oscillatory window. When the ferroin concentration is higher than 1.0×10^{-3} M, the blue colored reaction solution does not yield periodic color changes in the stirred system, although, as shown in the following, traveling waves could be obtained under those conditions.

For the cerium-catalyzed reaction in Figure 1c, the Pt potential stays flat after the initial excursion. Spontaneous oscillations occur at about 2000 s after mixing all reactants together, which is a significant reduction in the induction time. Note that time scales used in c and d are different from that used in a and b. The amplitude of oscillation also becomes larger than that of the uncatalyzed or the ferroin-catalyzed system, but there is no significant increase in the total number of oscillations. Unlike the ferroin-catalyzed system, here, no periodic color change is achieved, and thus the system is unfit for studying waves. A short induction time and large oscillation amplitude (>300 mV), however, make the cerium-catalyzed system suitable for exploring temporal nonlinear dynamics in a CSTR; in particular, these oscillations have a broad shoulder which may potentially develop into complex oscillations.

The time series of the Mn^{2+}-catalyzed reaction (see Figure 1d) is very similar to that of the cerium-catalyzed one, in which the Pt potential stays flat after the initial excursion and the oscillations commence much earlier. Figure 1 demonstrates that the three metal catalysts investigated have different effects on the dynamics of the bromate-pyrocatechol reaction. It is known that redox potentials of cerium and manganese are both above the redox potential of $BrO_2\bullet/HBrO_2$.[1] The observation that manganese and cerium exhibit nearly the same influence on the reaction behavior implies that the oxidation of metal catalyst by bromine dioxide radicals may be the major reactions participated by those catalysts. Certainly, the ability of the three catalysts reacting with the intermediate products of pyrocatechol may also contribute to their different impacts on the dynamics of the studied system, in a way similar to what was discussed in an earlier research on the source of the carbon monoxide in the BZ reaction.[18]

Figure 2 summarizes the dependence of the number of oscillations (*N*) and the induction time (IP) on the concentrations of ferroin, Mn^{2+}, and Ce^{3+}. Other reaction conditions were kept constant at $[H_2SO_4] = 1.30$ M, [pyrocatechol] = 0.043 M, and $[BrO_3^-] = 0.078$ M. The sharp increase in the number of oscillations at the low concentration of metal catalysts illustrates that the presence of metal catalysts favors the oscillatory behavior. As the concentration of catalysts continues to increase, however, the number of oscillations decreases, which may be attributed to the increased consumption of the reactants. Figure 2a illustrates that Mn^{2+} and Ce^{3+} do not affect the number of peaks as significantly as ferroin, although they could still double the number of peaks at an optimized condition. On the other hand, ferroin shows little effect on the induction time. As shown in Figure 2b, increasing ferroin concentration to 0.002 M only reduces the IP by about 10%. In contrast, cerium and

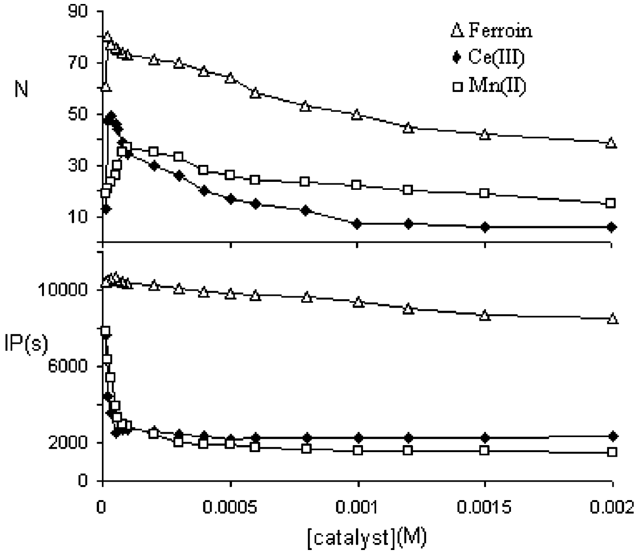

Figure 2. Dependence of the number of oscillations (*N*) and induction period (IP) on the concentration of metal catalysts. Other reaction conditions are $[H_2SO_4] = 1.30$ M, $[BrO_3^-] = 0.078$ M, and [pyrocatechol] = 0.043 M.

manganese dramatically reduce the induction time. Specifically, when the concentration of manganese is increased from 0 to 2.0×10^{-4} M, the induction time decreases from 3 to 0.5 h. A similar result is achieved when the concentration of cerium is increased from 0 to 5.0×10^{-5} M.

We also examined the response of the catalyzed systems to the addition of the same catalyst at different reaction stages. It has been reported earlier that the effect of one-electron redox couple in the uncatalyzed oxidation of aromatic compounds by acidic bromate strongly depends on the reaction stage.[29] Here, experiments were carried out at the conditions employed in Figure 1. For the cerium- and manganese-catalyzed system, the addition of 2.5×10^{-4} M of the same catalyst quenches the spontaneous oscillations immediately, but for the ferroin-catalyzed system, oscillations continue after the addition of 2.5×10^{-4} M ferroin. The amplitude of oscillation in the ferroin system is amplified upon the addition of the extra amount of ferroin, yet there is no obvious change in the total number of peaks. The quenching effect of Ce^{3+} and Mn^{2+} may arise from their reactions with bromate producing bromine, a well-known inhibitor of the autocatalysis in the bromate-based oscillators.[29] Interestingly, when the catalyst was added after oscillations have terminated, the addition of 6.0×10^{-4} M ferroin was able to revive the oscillation, whereas adding the same amount of cerium or magnesium ions did not show any influence on the reaction behavior.

Since the ferroin-catalyzed bromate-pyrocatechol reaction is the only system exhibiting periodic color changes, which is desired for the study of chemical waves, the influence of bromate and sulfuric acid on the number of peaks (*N*) and induction period (IP) in the ferroin system was also explored in this report. The results (see Supporting Information Figure 1s) show that increasing bromate concentration prolongs the induction period, while the number of peaks ascends first and then declines slightly with respect to increasing bromate concentration. On the other hand, both *N* and IP increase monotonically with the increase of the acid concentration, and the system exhibits spontaneous oscillations only when the concentration of sulfuric acid is between 1.0 and 1.4 M.

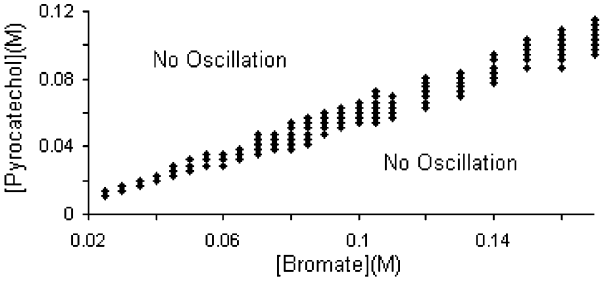

Figure 3. Phase diagram of the ferroin-catalyzed reaction in the bromate-pyrocatechol concentration plane. (◆) Denotes where the system exhibits simple periodic oscillations. The concentration of ferroin is 1.0×10^{-4} M.

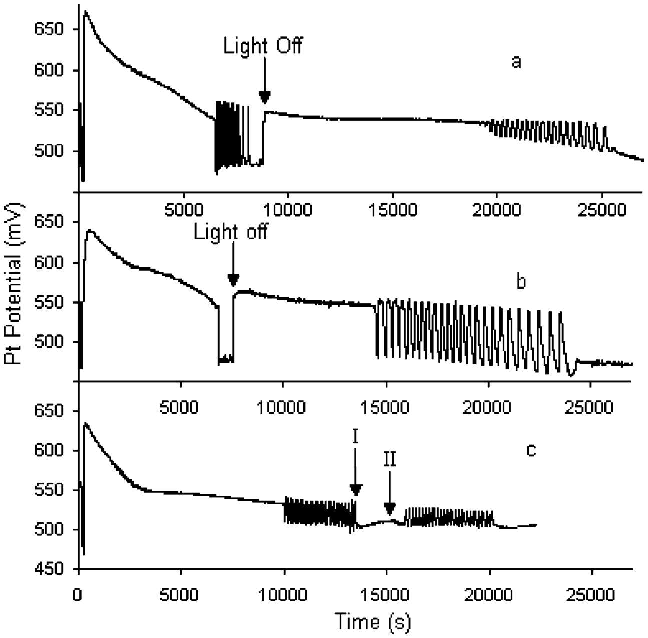

Figure 4. Light effects on the ferroin-bromate-pyrocatechol reaction: In a and b, 70 mW/cm^2 light was turned on from the beginning, and the reaction conditions are $[BrO_3^-] = 0.10$ M, $[H_2SO_4] = 1.40$ M, [pyrocatechol] = 0.057 M, and [ferroin] = (a) 5.0×10^{-4} M and (b) 1.0×10^{-3} M. In c, 100 mW/cm^2 light was switched on as indicated by the arrow I and was reduced to 30 W/cm^2 at arrow II. All other reaction conditions are the same as those used in (a) except here [ferroin] = 1.0×10^{-4} M.

Figure 3 is a phase diagram of the ferroin-catalyzed system in the pyrocatechol and bromate concentration plane, where ◆ indicates the conditions under which the system exhibits spontaneous oscillations. A first glance of this figure indicates that the system is able to exhibit oscillatory dynamics over a broad range of bromate and pyrocatechol concentrations. However, at each given concentration of pyrocatechol (or bromate), the proper concentration range of bromate (or pyrocatechol) within which the system oscillates is quite narrow. This phase diagram suggests that nonlinear behavior of the studied system is more sensitive to the ratio of [pyrocatechol]/[bromate] than their absolute concentrations. In comparison to the uncatalyzed bromate-pyrocatechol system, the presence of ferroin does not change the shape of the phase diagram but does make the area of the oscillation window slightly bigger, implying that ferroin favors the oscillatory behavior.

3.2. Photosensitivity. The photosensitivity of the ferroin-catalyzed bromate-pyrocatechol reaction is examined in Figure 4, in which the concentration of ferroin was adjusted. As shown in Figure 4a, when the system was exposed to light from the beginning of the reaction, spontaneous oscillations appeared earlier, where the induction time was about 6000 s. However, the oscillatory process lasted for a shorter period of

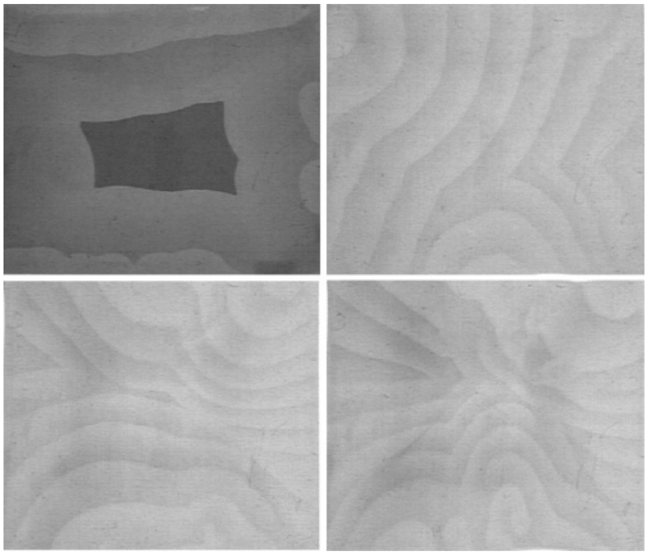

Figure 5. Snapshots of wave in the second stage of wave activity in ferroin-pyrocatechol-bromate system: (a) 17, (b) 133, (c) 238, and (d) 345 min after setting up the reaction-diffusion medium. The initial concentrations are [pyrocatechol] = 0.091 M, [BrO_3^-] = 0.13 M, [H_2SO_4] = 1.40 M, and [ferroin] = 3.0×10^{-3} M.

time. After the system evolved into the non-oscillatory stage, turning off the illumination caused a Pt potential jump to a higher value immediately. More significantly, oscillations revived after a long induction time. The above result indicates that the influence of light in the ferroin-catalyzed system is quite subtle: on one hand, it seems to favor the oscillation by shortening the induction time, but later quenches the oscillations.

The system in Figure 4b was also illuminated from the beginning, but no oscillation was achieved there; except, a sharp drop in the Pt potential occurred at about the same time as that in Figure 4a. Again, upon turning off the light, the non-illuminated system exhibited oscillatory behavior after a long induction time. In Figure 4c, light was applied during the oscillatory process, in which the 100 mW/cm^2 light immediately quenched the oscillatory behavior. Oscillations revived shortly after reducing the light intensity to 30 mW/cm^2. The cerium- and manganese-catalyzed systems performed under the same reaction conditions exhibited less photosensitivity, in which light only slightly reduced the amplitude of oscillation and no quenching behavior was obtained.

3.3. Chemical Waves. Preliminary exploration on pattern formation in the ferroin system has been performed in the following. To be observable with bare eyes, the concentration of ferroin used in the reaction-diffusion medium was increased to 3.0×10^{-3} M. As discussed earlier, the stirred system has a large excursion in the Pt potential shortly after mixing all reagents together. Such an initial reactivity leads to the formation of propagating fronts and target patterns (see snapshots in Supporting Information Figure S2), which could survive for up to 150 s. The disappearance of these chemical waves is due to the spontaneous occurrence of a large number of new wave centers, which collide with each other quickly, leading the whole medium to a homogeneous state with a red color. In general, increasing ferroin concentration shortens the life time of these initial waves.

As expected, chemical waves are also obtained when the system evolves into the oscillatory window, which commences typically at 3 h after the reaction has begun. Under the conditions explored, these chemical wave activities could last for up to 10 h. Figure 5 presents several snapshots of the waves collected at (a) 17, (b) 133, (c) 238, and (d) 345 min after setting up the reaction-diffusion medium. The above reaction-diffusion solution layer was prepared by allowing the reaction to evolve first in a stirred batch reactor for 2.5 h, which is about half an hour before spontaneous oscillations would commence. As shown in this figure, waves emerged from the edges shortly after the system was set up, that is, before the system evolved into the oscillation window. Such a result indicates that before entering the oscillatory evolution the ferroin-bromate-pyrocatechol medium is excitable.

4. Summary

This research illustrates that the catalyzed bromate-pyrocatechol reaction is capable of producing long time series of temporal oscillations and wave formations in a closed system, making it an appropriate model for exploring nonlinear dynamics. In particular, the new system exhibits subtle photosensitivity and does not produce gases, which are important advantages in exploring novel spatiotemporal behavior. In addition, the system reported here exhibits a unique dynamic feature that the reaction dynamics is more sensitive to the ratio of [substrate]/[oxidant] than their absolute concentrations. Such a dependence on the organic substrate may result in a new wave formation in a reaction-diffusion medium. However, a major drawback is that the mechanism remains largely unknown. The similarity between this and existing bromate-aromatic compound oscillators leads us to speculate that nonlinear feedbacks in the studied systems are also through the autocatalytic production of $HBrO_2$. Such a conclusion is consistent with our quenching experiments which show that the bromate-pyrocatechol oscillator is bromide-controlled. Systematic mechanistic study is required and will be pursued in future work.

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Supporting Information Available: Additional results on pattern formation and the dependence of the number of oscillation and induction time on the reaction conditions. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Field, R. J.; Burger, M., Eds.; *Oscillations and Traveling Waves in Chemical Systems*; Wiley-Interscience: New York, 1985.

(2) Scott, S. K. *Chemical Chaos*; Oxford University Press: New York, 1994.

(3) Epstein, I. R.; Pojman, J. A. *An introduction to nonlinear chemical dynamics;* Oxford University Press: New York, 1998.

(4) Castets, V.; Dulos, E.; Boissonade, J.; De Kepper, P. *Phys. Rev. Lett.* **1990**, *64*, 2953−2956.

(5) Kapral, R.; Showalter, K., Eds.; *Chemical Waves and Patterns*; Kluwer Academic Publishers: Netherlands, 1995.

(6) Berenstein, I.; Yang, L.; Dolnik, M.; Zhabotinsky, A. M.; Epstein, I. R. *J. Phys. Chem. A* **2005**, *109*, 5382−5387.

(7) Sevcikova, H.; Schreiber, I.; Marek, M. *J. Phys. Chem.* **1996**, *100*, 19153−19164.

(8) Horvath, D.; Petrov. V.; Scott, S. K.; Showalter, K. *J. Chem. Phys.* **1993**, *98*, 6332−6343.

(9) Vanag, V. K.; Epstein, I. R. *Proc. Natl. Acad. Sci.* **2003**, *100*, 14635−14638.

(10) Bansagi, T., Jr.; Palczewski, C.; Steinbock, O. *J. Phys. Chem. A* **2007**, *111*, 2492−2497.

(11) Winfree, A. T. *The Geometry of Biological Time;* Springer: Heidelberg, 2000.

(12) Kadar, S.; Wang, J.; Showalter, K. *Nature* **1998**, *391*, 700−702.

(13) Danø, S.; Sørensen, P. G.; Hynne, F. *Nature* **1999**, *402*, 320−322.

(14) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649−8664.

(15) Kurin-Csörgei, K.; Zhabotinsky, A. M.; Orbán, M.; Epstein, I. R. *J. Phys. Chem.*, **1996**, *100*, 5393−5397.
(16) Hamik, C. T.; Manz, N.; Steinbock, O. *J. Phys. Chem. A* **2001**, *105*, 6144−6153.
(17) Huh, D. S.; Kim, Y. J.; Kim, H. S.; Kang, J. K.; Wang, J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3188−3192.
(18) Onel, L.; Wittmann, M.; Pelle, K.; Noszticzius, Z.; Sciascia, L. *J. Phys. Chem. A* **2007**, *111*, 7805−7812.
(19) Szalai, I.; Kurin-Csörgei, K.; Horváth, V.; Orbán, M. *J. Phys. Chem. A* **2006**, *110*, 6067−6072.
(20) Kuhnert, L.; Agladze, K. I.; Krinsky, V. I. *Nature* **1989**, *337*, 244−247.
(21) Wang, J.; Kádár, S.; Jung, P.; Showalter, K. *Phys. Rev. Lett.* **1999**, *82*, 855−858.
(22) Volkov, E.; Ullner, I. E.; Zaikin, A. A.; Kurths, J. *Phys. Rev. E* **2003**, *68*, 026214.
(23) Yang, L.; Epstein, I. R. *J. Phys. Chem. A* **2002**, *106*, 11676−11682.
(24) Petrov, V.; Ouyang, Q.; Swinney, H. L. *Nature* **1997**, *388*, 655−657.
(25) Farage, V. J.; Janjic, D. *Chem. Phys. Lett.* **1982**, *93*, 621−624.
(26) Manz, N.; Müller, S. C.; Steinbock, O. *J. Phys. Chem. A* **2000**, *104*, 5895−5897.
(27) Huh, D. S.; Choe, S. J.; Kim, M. S. *React. Kinet. Catal. Lett.* **2001**, *74*, 11−22.
(28) De Kepper, P.; Epstein, I. R.; Kustin, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 2133−2134.
(29) Körös, E.; Orbán, M.; Habon, I. *J. Phys. Chem*. **1980**, *84*, 559−560.