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Coexistence of Wave Propagation and Oscillation in the Photosensitive Belousov−Zhabotinsky Reaction on a Circular Route

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The photosensitive Belousov−Zhabotinsky (BZ) reaction was investigated on a circular ring, which was drawn using computer software and then projected on a film soaked with BZ solution using a liquid-crystal projector. Under the initial conditions, a chemical wave propagated with a constant velocity on the black ring under a bright background. When the background was rapidly changed to dark, coexistence of the oscillation on part of the ring and propagation of the chemical wave on the other part was observed. These experimental results are discussed in relation to the nature of the photosensitive BZ reaction and theoretically reproduced based on a reaction-diffusion system using the modified Oregonator model.

Introduction

Experimental and theoretical studies on spatiotemporal pattern formation in reaction-diffusion systems may help us not only to understand biological systems[1,2] such as nerve impulses[3] and skin patterns of animals[4,5] but also to create novel methods for artificial processing such as image processing,[6−11] logic operations,[12−17] and the design of nanostructures.[18,19] The Belousov−Zhabotinsky (BZ) reaction has been experimentally and theoretically investigated as an excitable and oscillatory chemical system.[20−22] For the photosensitive BZ reaction, fascinating phenomena have been observed by controlling the intensity of light on the reaction field.[6,7,10,23] For example, Kuhnert and co-workers reported recurrence between negative and positive images as an image-processing system,[6,7] Sakurai et al. investigated on the control of the trajectory of pulse propagation with spatiotemporal feedback,[10] and Muñuzuri et al. investigated on the splitting of a chemical wave by short pulse illumination.[23]

The experimental system of the photosensitive BZ reaction[6] makes it easy to create excitable fields with various geometries, which are drawn by computer software and then projected on a filter membrane soaked with photosensitive BZ solution using a liquid-crystal projector. In this case, light illumination produces bromide ion which inhibits the oscillatory reaction,[24,25] i.e., the degree of excitability can be adjusted by changing the intensity of illumination. Therefore, the number of chemical waves and their locations can be spatiotemporally regulated by the local short-term illumination of unwanted waves.

We recently reported the nature of the collision of two chemical waves in the photosensitive BZ reaction on an excitable field (a figure-eight field composed of two equivalent circular rings) illuminated using a liquid-crystal projector.[26,27] When two chemical waves were generated on the figure-eight field (one chemical wave propagating in the same direction in each circle) as the initial condition, the location of the collision of the waves was either constant or alternated depending on the initial phase difference, thickness of the ring, and the degree of the overlap between the two circular rings.

In the present study, the light intensity of the background brightness was changed and the behavior of chemical wave propagation on a ring-shaped reaction field was investigated. A novel phenomenon was found regarding the coexistence of wave propagation and oscillation on a ring-shaped reaction field using the photosensitive BZ reaction. When the illumination of the reaction field was rapidly decreased, the wave propagation changed to coexistence of two features (wave propagation and oscillation), and the location of the switching between these two features was related to the location of the chemical wave at the time of the light stimuli. The experimental results were theoretically reproduced based on the reaction−diffusion system using the modified Oregonator model.

Experimental Section

$Ru(bpy)_3Cl_2$ (Sigma-Aldrich, St. Louis, MO) was used as a catalyst for the photosensitive BZ reaction. The BZ solution consisted of $[NaBrO_3] = 0.5$ M, $[H_2SO_4] = 0.35$ M, $[CH_2(COOH)_2] = 0.18$ M, $[KBr] = 0.005$ M, and $[Ru(bpy)_3Cl_2] = 1.7$ mM. A cellulose nitrate circular membrane filter (Advantec, A100A025A, membrane diameter: 25 mm) with a pore size of 1 μm was homogeneously soaked in BZ solution (5 mL) for about 1 min. The soaked membrane was gently wiped with another pure filter paper to remove excess solution and placed on a glass plate (77 × 52 × 1.3 mm). The surface of the membrane filter was completely covered with 1 mL silicone oil (Wako, WF-30) to prevent it from drying and to protect it from the influence of oxygen in air. The experiments were carried out in an air-conditioned room at around 298 K. The reaction medium exhibited almost constant behavior for approximately 30 min.

The medium was illuminated from below as shown schematically in Figure 1. The high-pressure mercury bulb of a liquid-

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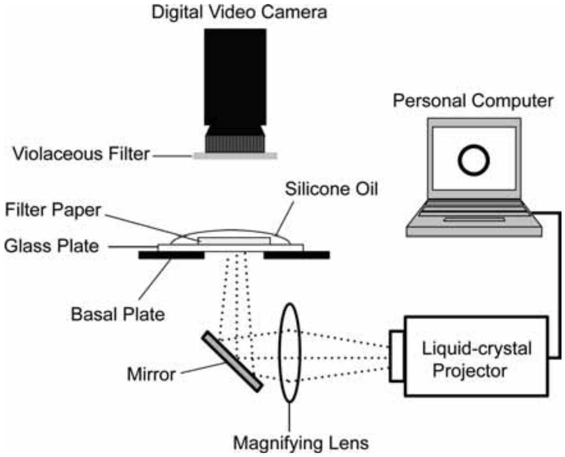

Figure 1. Schematic illustration of the experimental system based on the photosensitive BZ reaction.

crystal projector (Mitsubishi, LVP-XL8) was used as a light source; the spatial distribution of the light intensity was controlled by a personal computer, and a magnifying lens was used to adjust the focus. The black and white picture created by the liquid-crystal projector served as an illumination mask to create the appropriate boundary.

Regarding the number and direction of the chemical waves, one chemical wave was initially generated on a circular ring in the clockwise direction. To prepare a unidirectional chemical wave on the ring, the following processes were performed. (1) Several chemical waves were initially generated on the excitable field under no illumination, i.e., dark condition. (2) When illumination, except for in the dark area of the ring, was started, the chemical waves disappeared in the illuminated area but remained on the ring. (3) Upon local illumination of the unwanted waves for a few seconds, the illuminated waves disappeared, and finally one chemical wave propagating clockwise on the ring was retained.

The experiments were monitored from above with a digital video camera (Sony, DCR-VX700) and recorded on videotape. A violaceous optical filter (Asahi Techno Glass, V-42) with a maximum transparency at 410 nm was used to enhance the image of the green-colored chemical waves, which corresponded to the oxidized state, $[Ru(bpy)_3]^{3+}$. Thus, the white and black parts on the obtained image corresponded to the oxidized ($[Ru(bpy)_3]^{3+}$) and reduced states ($[Ru(bpy)_3]^{2+}$), respectively. The light intensity at the illuminated part was measured with a light intensity meter (Asone, LX-100).

Results

Figure 2 shows snapshots and a spatiotemporal plot of the coexistence of wave propagation and oscillation. Here, the spatiotemporal plot was prepared by aligning the gray-level intensities at $(r_{in} + r_{out})/2$ (r_{in}: inner radius, r_{out}: outer radius) on the ring in the order of events. A chemical wave propagated clockwise with a constant angular velocity ($0.80\pi \times 10^{-2}$ rad s^{-1}) on the circular ring. Here, the light intensities on the gray levels of the ring and the other media were 0.2×10^3 lx and 13.6×10^3 lx. When the gray level of the medium except for the ring was rapidly made darker from 13.6×10^3 lx to 2.1×10^3 lx, the chemical wave continued to propagate with an angular velocity of $0.77\pi \times 10^{-2}$ rad s^{-1} for 7 s, and then the oscillation was simultaneously generated on the ring at around $\theta = 1.2\pi$ to 1.0π rad, where θ is the phase as defined in Figure 2. After oscillation, the chemical wave started to propagate again on the ring from $\theta = 1.0\pi$ rad. When the chemical wave reached $\theta = 1.2\pi$ rad, oscillation was generated again. Thus, wave propagation from $\theta = 1.0\pi$ to 1.2π rad and oscillation at $\theta = 1.2\pi$ to 1.0π rad was alternately repeated for ca. 10 times, although the area of wave propagation slightly increased at 0.02π rad for one cycle. The period of this alternation phenomenon was ca. 20 s.

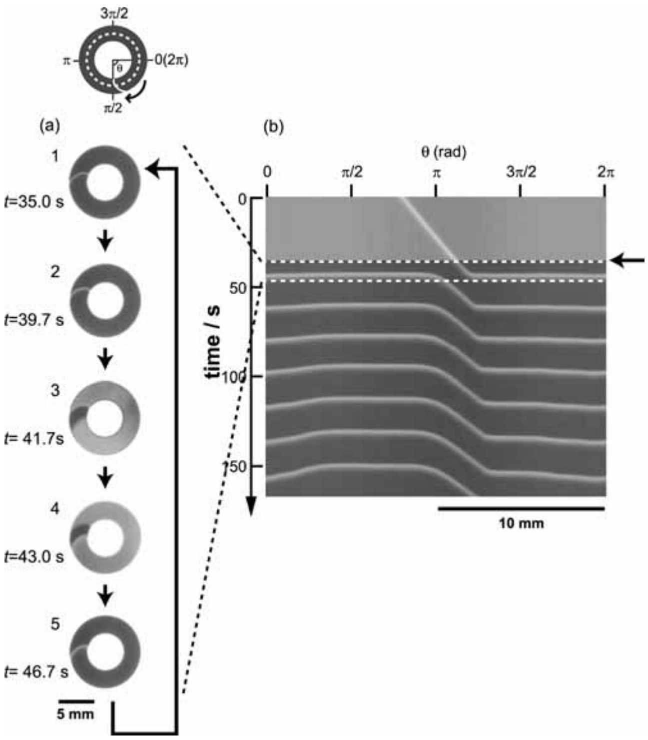

Figure 2. (a) Snapshots of the top view of the coexistence of wave propagation (1, 2, 5) and oscillation (3, 4) on the ring, and (b) a spatiotemporal plot of chemical wave propagation on the ring. The left-facing arrow denotes the time when the illumination of the background was rapidly changed from 13.6×10^3 to 2.1×10^3 lx.

Discussion

We performed numerical calculations based on the modified Oregonator[17,28,29] to theoretically discuss the mechanism of this phenomenon:

$$\frac{\partial u}{\partial t} = f(u,v) + D_u\nabla^2 u = \frac{1}{\epsilon}\left\{u(1-u) - (\beta v + A)\frac{u-q}{u+q}\right\} + D_u\nabla^2 u \quad (1)$$

$$\frac{\partial v}{\partial t} = g(u,v) + D_v\nabla^2 v = u - v + D_v\nabla^2 v \quad (2)$$

where u and v are dimensionless variables that correspond to the concentrations of the activator ($HBrO_2$) and the oxidized catalyst ($[Ru(bpy)_3]^{3+}$), respectively. $f(u, v)$ and $g(u, v)$ denote the local dynamics on u and v. β, ϵ, and q are the positive parameters that determine the nature of the BZ reaction, D_u and D_v are the diffusion constants for the activator and the oxidized catalyst, and A is an increasing function of the light intensity. The inner and outer radii of the ring-shaped reaction field, or the darker area, are 60 and 90, respectively. A numerical calculation is performed on the ring-shaped area with two-dimensional polar coordinates ($r = 40$ to 110, $\Delta r = 1$, number of meshes in the θ direction: 400) using the Euler method ($\Delta t = 10^{-4}$). As the initial condition, we set $A = 0.03$ in the brighter area and 0.005 in the darker area. The parameters used in the calculations are $\beta = 1$, $\epsilon = 0.05$, $q = 0.00015$, and $D_u = D_v =$

1. The chemical wave is initiated by setting $u = 0.5$ at a certain point ($r = (r_{\mathrm{in}} + r_{\mathrm{out}})/2$, $\theta = \pi$) at $t = 0$. Some time later the two chemical waves propagate in opposite directions. By increasing the variable for light intensity, A, over $\theta = \pi/2$ to π, from $t = 1$ to 5, we can make one wave disappear, and a chemical wave propagating clockwise is achieved. In this condition, the variable that corresponds to the light intensity is changed from $A = 0.005$ to 0 at $t = 10$.

In the actual experiments, coexistence of wave propagation and oscillation was also observed by changing the brightness only on the ring. However, the reproducibility of the phenomenon under this condition was not very good since the experimental regulation was very severe. Here, we noticed that the brightness on the ring was also changed by the brightness of the background (the medium except for the ring) because of the scattering of light. Actually, the velocity and persistence of the wave propagation on such a narrow ring were influenced by the brightness of the background. Thus, we assume that the change in the brightness of the background in the experiment corresponds to that of the ring in the numerical calculation and may increase the stability of the oscillatory state.

Figure 3 shows spatiotemporal plots at $r = (r_{\mathrm{in}} + r_{\mathrm{out}})/2$ and snapshots of the ring based on the numerical results on chemical wave propagation on a ring-shaped reaction field. After A is changed to 0, coexistence of oscillation and wave propagation can be observed. Thus, the numerical calculations qualitatively reproduce the experimental observation (Figure 2a) and the profile of the velocity (Figure 2b) on the chemical wave.

On the basis of the experimental and numerical results, we now discuss the coexistence of wave propagation and oscillation. Since the light illumination produces Br^-, the concentration of Br^- on the reaction field under a bright background was higher than that under a dark background, and thus light illumination inhibits the BZ reaction.[6,28] Under the bright condition, the state of the reaction field on the ring is excitable, and a wave in the excitable medium generates the initial condition for the evolution. The existence of an induction time until the coexisting phenomenon suggests that the concentration of Br^- gradually decreases and the system reaches an oscillatory state after the background becomes darker. Thus, the coexisting phenomenon can be regarded as the time evolution of the oscillatory medium, which starts from a heterogeneous initial condition. The period of the coexisting phenomenon was determined from the elapsed time of pulse propagation from $\theta = 1.0\pi$ to 1.2π rad, as shown in Figure 2.

Figure 4 shows a schematic illustration of the mechanism of the coexistence of wave propagation and oscillation. During the induction period, the reaction field on the ring reaches an oscillatory state. In Area I, the chemical wave propagates during the induction period, which increases the concentration of Br^- in Area I (Figure 4b). In Area II, oscillation is generated because of the lower concentration of Br^- when the chemical wave reaches the boundary line B (top of Figure 4c). After oscillation, a chemical wave is newly generated by the excitation at the boundary between Areas I and II (Line A in the top of Figure 4c) and begins to propagate again (Figure 4d). The concentration of Br^- in Area II decreases during propagation in Area I, and therefore oscillation is generated again in Area II (Figure 4c). Thus, the coexistence of oscillation in Area II and wave propagation in Area I continues repeatedly (Figures 4c and 4d).

Next, we discuss the relationship between the status of the reaction field and nullcline.[21,22] Here, the function $f(u, v)$ is changed by illumination, and the intersection between $g(u, v) = 0$ and $f(u, v) = 0$ is also changed; i.e. the system exhibits an excitable state for $f_{\mathrm{a}}(u, v)$ under the bright condition and the oscillatory state for $f_{\mathrm{b}}(u, v)$ under the dark condition. At the moment the background becomes darker, the BZ medium is in the steady state in Area II (Point S in Figure 4a). On the other hand, the medium in Area I is in the refractory state due to the higher concentration of Br^- which is produced by hysteresis in chemical wave propagation. After the decrease in brightness, the steady state no longer exists, and thus the BZ medium is in the oscillatory state. In Area II, the medium is initially in the same state (Point S), which leads to uniform oscillation (every point over Area II oscillates simultaneously) after a certain time, during which time the medium changes from S to T. In Area I, a gradient of the concentration exists due to the previous wave propagation, and uniform oscillation is not observed. When the uniform oscillation in Area II is complete, the concentration of Br^- decreases at one of the boundaries (Line A in the top of Figure 4c) between Areas I and II, and the chemical wave begins to propagate in Area I. The boundaries between Areas I and II seem to be determined by the location of the chemical wave when the brightness is changed, and by the degree of the change in brightness.

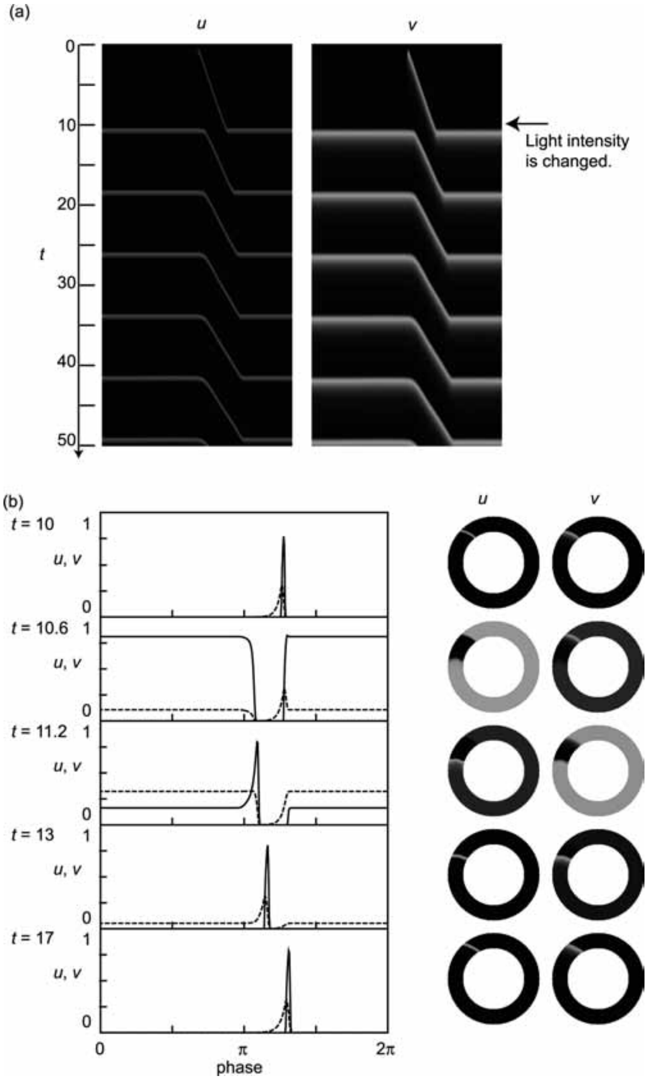

Figure 3. Results of the numerical simulation for a reaction field in the shape of a circular ring based on the modified Oregonator model shown in eqs 1 and 2. (a) Spatiotemporal diagrams for u and v. At $t = 10$, the light intensity is changed from $A = 0.005$ to 0. (b) Profiles of u (continuous line) and v (dotted line) depending on the phase θ (Left) and snapshots of u and v (Right). The time t corresponds to that in part (a), and θ is defined as shown in Figure 2.

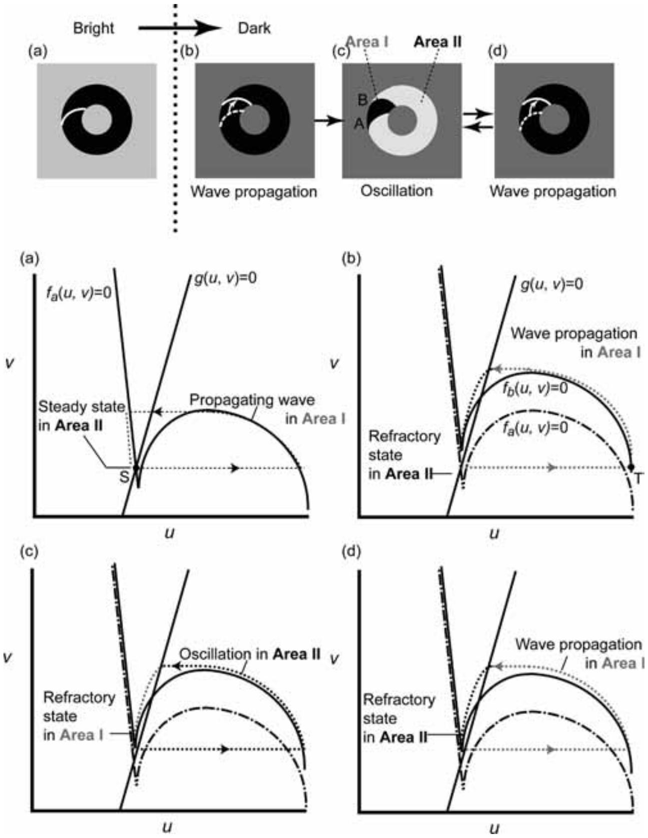

Figure 4. Schematic illustration of the phenomenon (top) and nullcline (bottom) under the bright (a) and dark conditions (b−d) to explain the mechanism of the coexistence of oscillation and wave propagation. $f(u,v) = 0$ and $g(u,v) = 0$ are the nullclines of the dynamical systems described by eqs 1 and 2. $f_a(u,v) = 0$ and $f_b(u,v) = 0$ correspond to the cases before and after the background was changed to dark, respectively.

Conclusion

The coexistence of wave propagation and oscillation was observed in the photosensitive BZ reaction on a circular ring field illuminated with a liquid-crystal projector. The period of this alternation and the individual regions on the ring were determined by the time and trajectory of wave propagation, respectively. The coexistence phenomenon was well reproduced by a numerical simulation based on the modified Oregonator model for the photosensitive BZ reaction. Although we have not yet discussed it clearly in this paper, the slight increase in the area of wave propagation in Figure 2 may correspond to the relaxation of the phenomenon for the light stimuli. The relationship between the increase in the area and relaxation will be clarified by changing the feature of light stimuli in the future work. These results suggest that various features of spatiotemporal phenomena in the photosensitive BZ reaction can be created by controlling the shapes of the reaction fields, which are drawn using computer software, and by changing the nature of the reaction fields, such as excitable and oscillatory fields, by modifying the degree of light illumination.

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