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Photosensitive, Bubble-free, Bromate−1,4-Cyclohexanedione Oscillating Reactions. Illumination Control of Pattern Formation

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We study the effect of visible light on chemical waves in thin layers of solution containing the bromate−1,4-cyclohexanedione bubble-free oscillating reaction with added $Ru(bpy)_3^{2+}$, ferroin, or diphenylamine as the third initial reactant. The light sensitivity was found to be much stronger in the ferroin-catalyzed system than in the $Ru(bpy)_3$-catalyzed one, contrary to observations in the analogous reactions with malonic acid as the reductant. The combination of photosensitivity and absence of bubbles makes these reactions convenient tools for studying waves and patterns in reaction−diffusion systems.

Introduction

Photosensitivity offers a very convenient way to control formation and dynamics of spatiotemporal chemical patterns. So far, the $Ru(bpy)_3$-catalyzed Belousov−Zhabotinsky (BZ) reaction−diffusion system with malonic acid as the initial reductant has been employed almost exclusively for creation of chemical patterns and control of the chemical wave propagation.[1−7] An important drawback of this reaction is the production of carbon dioxide, which results in the formation of bubbles that disturb the reaction−diffusion patterns and makes it difficult to conduct lengthy experiments.

Here we show that the recently developed bromate−1,4-cyclohexanedione (CHD)−ferroin oscillating reaction[8,9] possesses significant photosensitivity. Unexpectedly, the $Ru(bpy)_3^{2+}$-catalyzed $HBrO_3$-CHD system is found to be much less sensitive to illumination with visible light. We also report a new indicator for visualizing the pattern formation. With diphenylamine (DPA) in the $HBrO_3$−CHD system, the patterns are nicely visible and show strong sensitivity to irradiation with visible light.

The combination of photosensitivity and absence of bubbles makes these reactions an attractive tool for experiments on chemical waves and patterns.

Experimental Section

Materials. Stock solutions were prepared from $NaBrO_3$ (Janssen Chimica, 99+%), 1.0 M, dissolved in distilled water; 1,4-cyclohexanedione (Aldrich, 98%), 0.3 M, dissolved in 1.0 M H_2SO_4 by stirring the solution on a hot plate (40−50 °C) for about 30 min; ferroin, 0.025 M, prepared from the calculated amount of $FeSO_4 \cdot 7H_2O$ (Fisher, Certified) and 1,10-phenanthroline (Aldrich, 99+%), dissolved in distilled water; $Ru(bpy)_3Cl_2(H_2O)_6$ (Aldrich), 0.01 M, dissolved in distilled water; diphenylamine (Aldrich), 0.2 M, dissolved in hot 5 M H_2SO_4; and NaBr (Fisher, Certified), 0.2 M, dissolved in distilled water.

Procedures and Apparatus. The working solution was prepared as follows: the $NaBrO_3$, 1,4-cyclohexanedione, H_2SO_4, and NaBr were mixed in a beaker equipped with a Pt vs $Hg/Hg_2SO_4/K_2SO_4$ electrode pair, and the change in the potential of the Pt electrode was monitored under constant stirring. After the induction period of 20−30 min, depending on the initial concentrations, oscillations started. Then the catalyst-indicator, ferroin, $Ru(bpy)_3$, or diphenylamine, was added.

The working solution was spread in a thin layer between a pair of glass plates. The thickness of the layer was either 0.8 or 1.2 mm. The sides of the layers were isolated from the atmosphere by plastic spacers. The reactive layer was illuminated from above by parallel unfiltered light from a 150 W xenon lamp placed in a Universal Lamp Housing (Oriel Co, Model No. 66057) supplemented with a heat-absorbing filter and an additional correction lens to improve uniformity of the illumination field. This configuration reduces the nonuniformity of the light intensity throughout the illumination field to less than 10%, which is adequate for our qualitative study. The intensity at the surface of the reactive layer can be varied from 0 to 40 mW/cm^2. For observation and recording, the layer was illuminated from below by light whose intensity was less than 2% that of the acting light. The light intensity was measured with a Newport 1815 Optical Power Meter. The experiments were performed at $T = 25 \pm 1$ °C. Heating of the working solution by light absorption was measured with a microthermistor probe and found to be negligible.

The effects of the illumination were studied after the entire area of the reactor had been occupied by waves from target or spiral sources.

The evolution of the wave patterns was recorded with a video camera augmented with interference filters with maximum transmission at 450 and 510 nm. The data were processed with an OPTIMAS image-analysis system (BioScan).

Results

Bromate−1,4-Cyclohexanedione−Ferroin Reaction. Previous results on the $Ru(Bpy)_3$−malonic acid BZ reaction suggest that illumination should shift the system to a more reduced state,
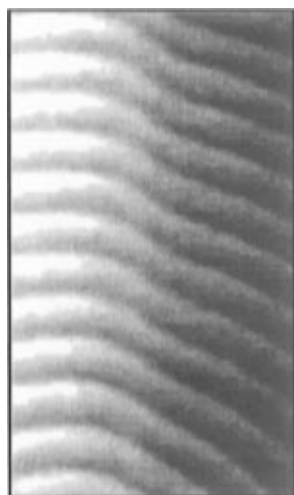
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Figure 1. Refraction of chemical waves resulting from increase of the wave speed in the illuminated area. Intensity of illumination 8.5 mW/cm^2. Initial concentrations (in M): NaBrO$_3$, 0.1; CHD, 0.1; H$_2$SO$_4$, 0.2; KBr, 0.01; Fe(phen)$_3^{2+}$, 0.0005. The wave train is produced by a spiral source with oscillation period 20 s, wavelength 1.3 mm, and wave speed ~4 mm/min. Frame size (mm): 9 × 18.
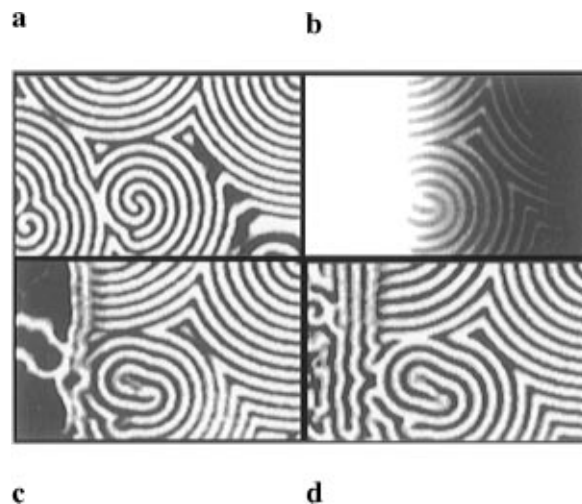

Figure 2. Effect of brief strong illumination: (a) pattern before illumination; (b) the left side of the frame is illuminated with 17 mW/cm^2 for 5 s; (c and d) formation of a wave train perpendicular to the initial one. Initial concentrations (in M): NaBrO$_3$, 0.1; CHD, 0.15; H$_2$SO$_4$, 0.2; KBr, 0.01; Fe(phen)$_3^{2+}$, 0.0005. The wave train is produced by a spiral source with oscillation period 15 s, wavelength ~1 mm, and wave speed ~4 mm/min. Frame size (mm): 25 × 15.4.

resulting in a decrease in wave speed and oscillation frequency and ultimately in suppression of oscillations and wave propagation as the intensity is increased.[10−12] In our case, however, illumination with moderate intensity results in an increase of the frequency of oscillations and the speed of waves. Figure 1 shows a refraction pattern that results from an increase in the wave speed in the illuminated part of the solution layer. The left parts of the frames are illuminated at a constant level of 8.5 mW/cm^2. The resulting angle of refraction is equal to 41 ± 2°, which corresponds to a factor of 1.52 ± 0.06 increase in the wave speed.[13]

We have studied the photosensitivity of this system qualitatively in a narrow range of initial reagent concentrations: [ferroin] = 0.5−2 mM, [CHD] = 0.1−0.15 M, [H$_2$SO$_4$] = 0.2−0.3 M; the initial concentrations of bromate and bromide were kept constant at 0.1 and 0.01 M, respectively. The photosensitivity increases with [H$_2$SO$_4$] and decreases with [Fe(phen)$_3$] and [CHD].

We studied the effect of varying the illumination intensity at [Fe(phen)$_3$] = 0.5 mM. When the intensity of illumination is more than 10 mW/cm^2, the ferroin/ferriin couple shifts to a more oxidized state, and the red parts of the waves become paler. We did not make quantitative amplitude measurements. The shift increases and the time of transition to the new state decreases with increasing intensity.

Figure 2 shows pattern development after a strong local suppression of the excitability. In Figure 2a we display the original pattern of single and double spirals. Figure 2b shows that 5 s illumination at 17 mW/cm^2 results in almost complete suppression of excitation. Because the boundary of the illuminated region is perpendicular to the wave fronts of the preexisting spiral pattern, a perpendicular wave train develops after the illumination ceases (Figure 2c,d).

Bromate−1,4-Cyclohexanedione−Ru(bpy)$_3$ Reaction. Qualitatively similar results were obtained with the following initial concentrations (M): [NaBrO$_3$] = 0.1, [CHD] = 0.1, [H$_2$SO$_4$] = 2.0, [KBr] = 0.02, [Ru(bpy)$_3^{2+}$] = 0.0002. However, the photosensitivity is lower than in the ferroin-catalyzed system. A 40 s illumination at 20 mW/cm^2 produces only minor effects with initial reagent concentrations in the range [Ru(bpy)$_3$] = 0.5−2.0 mM, [CHD] = 0.1−0.15 M, [H$_2$SO$_4$] = 0.3−2.0 M, [NaBrO$_3$] = 0.1−0.2 M, and [KBr] = 0.01−0.02 M. Decreas-

ing [Ru(bpy)$_3$] to 0.2 mM increases the photosensitivity, but even at this level 5 s illumination at 20 mW/cm^2 cannot produce complete oxidation and total elimination of the preexisting patterns.

Bromate−1,4-Cyclohexanedione−Diphenylamine Reaction. The photosensitivity of this system is approximately the same as for the ferroin-catalyzed system. Effects similar to those shown in Figures 1 and 2 were obtained with the following initial concentrations (in M): [NaBrO$_3$] = 0.2, [CHD] = 0.15, [H$_2$SO$_4$] = 0.5, [KBr] = 0.02, [DPA] = 0.001.

Discussion

The response of the CHD systems to illumination is more complex than that of the frequently employed Ru(bpy)$_3$−malonic acid system. In the latter case the speed of waves usually decreases with the intensity of illumination.[9] This observation is in accord with the main effect of illumination on the Ru(bpy)$_3$−malonic acid system, which is production of Br$^−$ by direct oxidation of the excited Ru(bpy)$_3^{2+}$ by bromate.[10,11] In the CHD systems moderately intense illumination excites the system, i.e., shifts it to a more oxidized state, rather than inhibiting (reducing) it. This phenomenon probably arises from the photochemistry of products of CHD oxidation, since the ferroin−malonic acid system has very low sensitivity to visible light. Only at rather high levels of illumination, 20 mW/cm^2 and higher, do the CHD systems and the Ru(bpy)$_3$−malonic acid system show the same response, i.e., total suppression of excitability. Analyzing the mechanism of photosensitivity in the CHD oscillating reactions requires knowledge of the mechanism of the oscillations. At present, only very limited knowledge about the chemistry of the CHD portion of the mechanism is available.[14]

A direct, quantitative comparison of photosensitivity of the three systems is not possible, because their kinetics differs considerably. The Ru(bpy)$_3$ couple has significantly higher redox potential than the ferroin−ferriin couple. As a result, higher acidity is needed to obtain approximately the same dynamic regimes. The reaction with DPA also needs a higher acidity than the ferroin-catalyzed system to produce oscillations. The concentrations of initial reagents that give rise to maximum photosensitivity are quite different for the three systems.

Bromate−1,4-Cyclohexanedione Oscillating Reactions

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We can compare the CHD systems with respect to ease of controlling pattern formation, i.e., obtaining similar results at the lowest possible intensity of illumination. We find that the ferroin-catalyzed system is the most convenient for illumination control of pattern formation. The phosensitivity of this system and the possibility of using it for control of pattern formation have been pointed out by Winfree.[15]

As an illustration, we consider two modes of control. Constant illumination at moderate intensity increases the oscillation frequency and the wave speed. A good demonstration of this effect is refraction, which results from the entrainment of wave trains at the boundary between the illuminated and dark parts of the medium (Figure 1). On the other hand, brief, strong illumination suppresses oscillation, eliminating preexisting patterns and putting the illuminated region in a uniform state. Such illumination of a wave train with the dark−light boundary parallel to the wave vector results in formation of a wave train transverse to the original one (Figure 2).

The absence of CO_2 production is a great advantage of the CHD systems. Without CO_2 bubbles it is easy to prevent mechanical perturbation of the solution, thereby facilitating operation of both batch systems and continuously fed unstirred reactors. For these reasons, photosensitive BZ reactions with 1,4-cyclohexanedione as the reductant should be a valuable tool for the study of chemical waves and patterns in experiments of long duration.

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