Effect of Pulsed Illumination on the Belousov-Zhabotinsky Reaction Catalyzed with Tris(bipyridine) Ruthenium(II) in Continuous Stirred Tank Reactor

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(Received July 23, 1999; CL-990652)

The photochemical response of BZ reaction with photosensitive $Ru(bpy)_3^{2+}$ has been studied under pulsed illumination in a continuous–flow stirred tank reactor, CSTR. Two types of photo-response, the advanced and delayed phase shifts of oscillation, are observed depending on the initial concentrations of malonic acid (MA) or Br^- and the timing of a pulsed illumination.

Currently, the photo-response of the Belousov-Zhabotinsky (BZ) reaction[1,2] has attracted much attention as a possible transducer system of optical information.[3,4] Previously, we found that BZ reaction with $Ru(bpy)_3^{2+}$ catalyst in batch system were perturbed by illumination and the oscillation periods were shortened or elongated.[5] In this paper, the photo-response of BZ reaction with $Ru(bpy)_3^{2+}$ catalyst under pulsed illuminations in a continuous-flow stirred tank reactor, CSTR, is studied with changing the initial concentrations of MA and Br^-, $[MA]_0$ and $[Br^-]_0$, as controlling factors. The experimental system in Figure 1 is composed of reagent tanks (1, 2 and 3), a CSTR, a light source and an ORE, a Horiba type Pt and reference electrodes, connected to a computer. Solutions containing BZ reactants are fed from reagent tanks (1, 2 and 3) to a CSTR by a peristaltic pump with three channel tubes. A 500W high pressure Hg lamp (Ushio) was used as the light source. The reaction system is illuminated by pulse light through quartz windows of the CSTR. The illumination pulse width was fixed at 5 sec by a camera shutter. The temperature was kept at 25℃. The volume of BZ solution in CSTR was 9.6 ml and the total flow rate was 0.005ml/sec, corresponding to the residence time, τ =30.9 min. The oscillation of redox potential is traced with the ORE. The initial concentrations of BZ reactants in the reactor were as follows; 0.2mM-$[Ru(bpy)_3^{2+}]_0$, 53mM-$[BrO_3^-]_0$, 0.8M-$[H_2SO_4]_0$, 0-10 mM -$[Br^-]_0$ and 16-80 mM-$[MA]_0$.

Experiments were carried out with two reaction systems, A and B. In system A, $[MA]_0$ is changed as a control factor and $[Br^-]_0$ =0. MA in tank 1, $Ru(bpy)_3^{2+}$ in tank 2 and BrO_3^- in tank 3 are separately lead through three channel tubes to the CSTR by a peristaltic pump and mixed at the bottom of the reactor. In system B, $[Br^-]_0$ is changed as a control factor, MA, $NaBrO_3$ and NaBr solutions were firstly mixed in a beaker. Immediately, the color of the solution turned to brown due to generation of Br_2. BrMA is produced in the solution according to the following reaction(1)

$$3MA + BrO_3^- + 2\,Br^- + 3\,H^+ \rightarrow 3\,BrMA + 3H_2O \quad (1)$$

After the generation of Br_2 was ceased, the solution is put into tanks 1 and 2, which was mixed with a solution of $Ru(bpy)_3^{2+}$ in tank 3 at the bottom of the CSTR. Under these conditions, sustained oscillations occur as shown in Figure 2. When the reaction system was illuminated by a pulsed light, the next peak came earlier (Figure 2a) or later (Figure 2b) by pulsed illumination than those under non illumination (Figure 2c). These photo responses were analyzed as the phase shift of chemical oscillation.[6,7] In Figure 3, $\Delta\Phi$, the phase shift by illumination, is defined as

$$\Delta\Phi = 2\pi \cdot (T' - T_0)/T_0, \quad (2)$$

Where T_0 and T' are oscillation periods under non-illuminated and illuminated conditions, respectively. In Figure 4 are shown typical

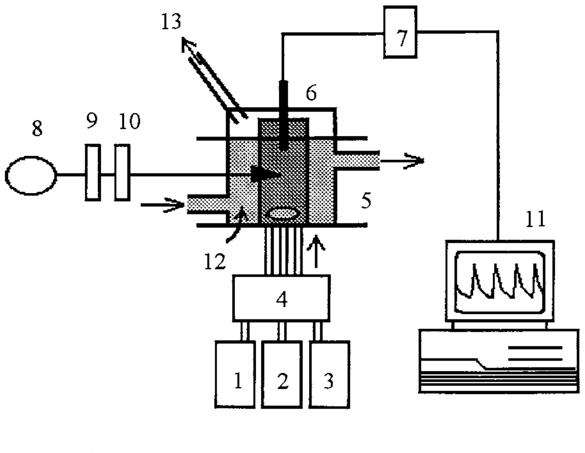

Figure 1. The experimental system of CSTR. 1-3:reagent tank, 4:peristaltic pump, 5:reactor, 6:ORE, 7:volt meter, 8:light source, 9:IR cut filter, 10:shutter, 11:personal computer, 12:water jacket, 13: aspirator.

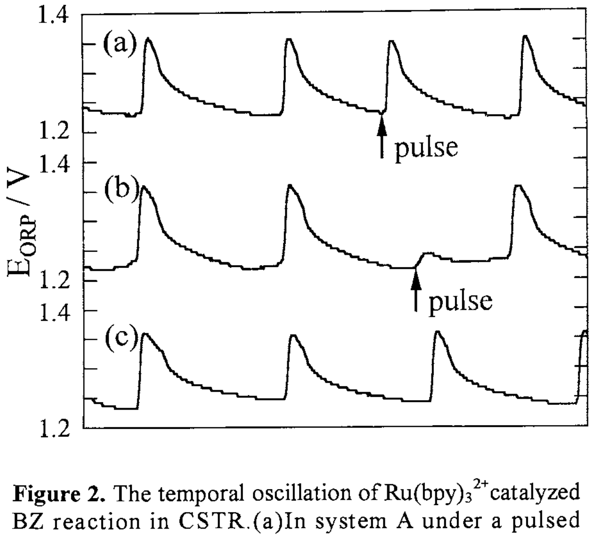

Figure 2. The temporal oscillation of $Ru(bpy)_3^{2+}$catalyzed BZ reaction in CSTR.(a)In system A under a pulsed illumination. (b)In system B under a pulsed illumination. (c) Under non illuminated condition.

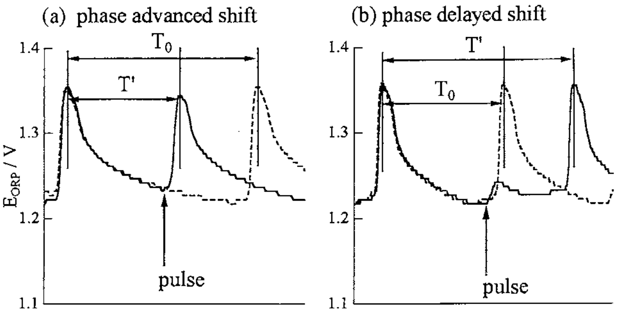

Figure 3. The phase analysis of photochemical response of $\mathrm{Ru(bpy)_3^{2+}}$ catalyzed BZ system under pulsed illumination: (dashed line) non-illuminated, (solid line) illuminated. (a) phase advanced shift.(b) phase delayed shift.

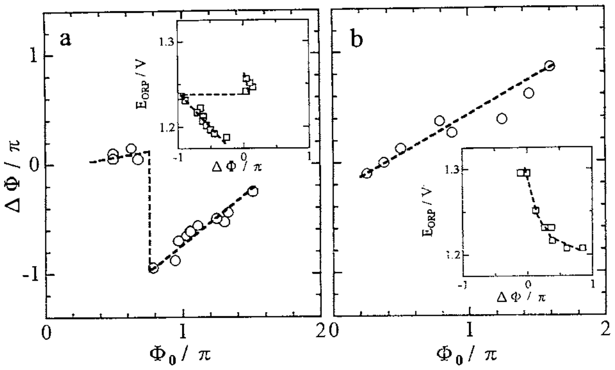

Figure 4. The phase response curves of Φ_0 vs. $\Delta\Phi$ of $\mathrm{Ru(bpy)_3^{2+}}$-catalyzed BZ system under pulsed illumination. Insets: $\Delta\Phi$ vs. E_{ORP}. (a) phase advanced shift. (b) phase delayed shift.

phase-response curves, plots of $\Delta\Phi$ against various phase(timing) of pulsed illumination, where Φ_0 changes from 0 to 2 π. The phase advanced shift, $\Delta\Phi<0$, corresponds to such a photo-response as the next peak comes earlier by illumination. While the phase delayed shift, $\Delta\Phi>0$, to that it comes later by illumination. The detailed phase analysis for system A shows both $\Delta\Phi>0$ and $\Delta\Phi<0$, however, $\Delta\Phi<0$ is more predominant as shown in Figure 4a. It is noticed that, switching of the phase shift from $\Delta\Phi>0$ to $\Delta\Phi<0$, occurs at a particular Φ_0. On the other hand, in system B, $\Delta\Phi>0$ over wide range of Φ_0 as shown in Figure 4b.

Based on the FKN mechanism of BZ reaction,[8] these phase shifts are interpreted with the inhibition and promotion of the autocatalytic formation process, AC, of an unstable intermediate $\mathrm{HBrO_2}$.

$2\,\mathrm{Ru(bpy)_3^{2+}} + \mathrm{HBrO_2} + \mathrm{BrO_3^-} + 3\mathrm{H^+}$
$\rightarrow 2\mathrm{Ru(bpy)_3^{3+}} + 2\mathrm{HBrO_2} + \mathrm{H_2O}$ (AC)(3)

$^*\mathrm{Ru(bpy)_3^{2+}}$ produced by pulsed illumination might cause the photochemical effect on the AC process. The photoinduced abrupt increase of redox potential in the oscillation of system A corresponds to autocatalytic production of $\mathrm{HBrO_2}$ and oxidation of $\mathrm{Ru(bpy)_3^{2+}}$. The photochemical promotion of AC by $^*\mathrm{Ru(bpy)_3^{2+}}$ might be as follows;

$^*\mathrm{Ru(bpy)_3^{2+}} + \mathrm{Ru(bpy)_3^{2+}} + \mathrm{HBrO_2} + \mathrm{BrO_3^-} + 3\mathrm{H^+}$
$\rightarrow 2\,\mathrm{Ru(bpy)_3^{3+}} + 2\mathrm{HBrO_2} + \mathrm{H_2O}$ (4)

The reaction (4) is a candidate, which causes the advanced phase shift. When these phase shifts are plotted vs. the change of oxidation-reduction potential, the ORP, at Pt electrode, it is noticed that the switching of $\Delta\Phi$ occurs at 1.24V vs. NHE. as shown in the insets of Figure 4. This potential is nearly equal to the reduction potential of $\mathrm{BrO_3^-}$ to $\mathrm{HBrO_2}$.[8,9] This result is a new finding, the chemical condition of system A, with higher $[\mathrm{MA}]_0$ and $[\mathrm{Br^-}]_0 = 0$, seems to influence this advanced phase shift. It is suggested that there is a threshold point at which the reaction process of $\mathrm{HBrO_2}$ production and consumption is switched. On the other hand, in system B, $^*\mathrm{Ru(bpy)_3^{2+}}$ reacts with BrMA, generated at initial stage through reaction(1), and considerable amounts of $\mathrm{Br^-}$ is formed as follows (5).[10]

$\mathrm{BrMA} + {}^*\mathrm{Ru(bpy)_3^{2+}} + 3\mathrm{H^+}$
$\rightarrow \mathrm{Ru(bpy)_3^{3+}} + \mathrm{Br^-}$ + organic product (5)

The AC process is inhibited by $\mathrm{Br^-}$ as follows;

$\mathrm{HBrO_2} + \mathrm{Br^-} + \mathrm{H^+} \rightarrow 2\mathrm{HOBr}$ (6)

The faster the rate of $\mathrm{Br^-}$ formation under illumination, the higher the rate of the consumption of $\mathrm{HBrO_2}$, which results in the delayed phase shift. MA seems to promote the AC process under illumination, while $\mathrm{Br^-}$ inhibit it. Further study is underway to specify the more detail photochemical reaction mechanism.

We gratefully acknowledge support for this work from Hayashi Memorial Foundation For Female Natural Scientists and The Grant in Aid(10554046) for Scientific Research from Ministry of Education, Science, Sport and Culture of Japan.

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