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Photo-induced excitability in the tris-(bipyridyl)ruthenium(II)-catalyzed minimal bromate oscillator

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Abstract

The tris-(bipyridyl)ruthenium(II)-catalyzed minimal bromate oscillator in its reduced state was found to exhibit an excitable pulse response to the pulsed light perturbation in the visible region, while the oxidized steady state did not respond to the light pulse. The oxidized steady state under the continuous illumination was also found to be insensitive to a negative light pulse perturbation. These results are successfully accounted for by the reaction scheme in which the photo-excited metal complex produces additional $HBrO_2$ to enhance the autocatalytic process. No evidence was found to support the photo-production of Br^- in the minimal bromate oscillator. © 1997 Elsevier Science B.V.

1. Introduction

Illumination effects have been studied for several oscillatory chemical reactions in homogeneous [1–7] as well as inhomogeneous systems [8–12]. All these studies have proved that light is an excellent external control parameter for nonlinear chemical events because of its facility in controlling intensity as well as wavelength [13].

The photo-induction of oscillations with visible light is believed to occur through the photo-excitation of one of the component species [5,6]. In the case of steady illumination of the Belousov–Zhabotinsky (BZ) system catalyzed by tris-(bipyridyl)ruthenium(II) (hereafter abbreviated to $Ru(bpy)_3^{2+}$), which exhibits photo-induction and -inhibition of oscillations, the primary light absorber has been confirmed to be $Ru(bpy)_3^{2+}$ [4,5]. The key step is [6,7]

$$Ru(II)^* + Ru(II) + BrO_3^- + 3H^+ \rightarrow 2Ru(III) + HBrO_2 + H_2O, \qquad (1)$$

where Ru(II) and Ru(III) are the catalysts in its reduced and oxidized form, respectively, and $Ru(II)^*$ stands for the photo-excited catalyst.

In the dark reaction, reactions (2) and (3) are known as the key steps to determine the nonlinear behavior of the system [14]:

$$2Ru(II) + HBrO_2 + BrO_3^- + 3H^+ \rightarrow 2Ru(III) + 2HBrO_2 + H_2O, \qquad (2)$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr. \qquad (3)$$

If $[Br^-]$ exceeds a certain threshold ($[Br^-]_{th}$), rapid reaction (3) keeps $[HBrO_2] \approx 0$, where autocatalytic

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reaction (2) never proceeds and the system stays in the reduced steady state (SSI). If $[Br^-]$ decreases below $[Br^-]_{th}$, (2) starts to bring the system to the oscillatory state (OSC). The photo-induction of oscillations should occur if excess $HBrO_2$ produced by (1) reduces $[Br^-]$ below $[Br^-]_{th}$ through (3).

Photo-inhibition of oscillations with the continuous illumination by bringing the system from OSC to the oxidized steady state (SSII) is also understandable on the same basis; namely, intense light produces too much $HBrO_2$ through (1) so that (3) keeps $[Br^-]$ always below $[Br^-]_{th}$. In this case, the autocatalysis (2) operates continuously to keep [Ru(II)] low.

Situation is less clear in the case of another photo-inhibition of oscillations into SSI. In the case of spatial pattern formation, the photo-inhibition of oscillations into SSI is believed to be important and to occur through the reduction of the system by photo-produced Br^- [8–10]. It is well known in the dark reaction that an addition of Br^- to the oscillating BZ system inhibits oscillations through (3). Although the same mechanism would hold in the photo-inhibition of oscillations into SSI, it is not quite clear how the excess Br^- is photo-produced. Kuhnert has proposed the following scheme [8]:

$$6\mathrm{Ru(II)}^* + \mathrm{BrO_3^-} + 6\mathrm{H^+} \rightarrow 6\mathrm{Ru(III)} + 3\mathrm{H_2O} + \mathrm{Br^-}, \qquad (4)$$

while we have proposed [6]

$$\mathrm{Ru(II)}^* + 3\mathrm{Ru(II)} + \mathrm{HBrO_2} + 3\mathrm{H^+} \rightarrow 4\mathrm{Ru(III)} + 2\mathrm{H_2O} + \mathrm{Br^-}. \qquad (5)$$

More recently, Yamaguchi and co-workers [15] have proposed that Br^- is provided by decomposition of bromomalonic acid in the reaction with $Ru(II)^*$. This last scheme seems to be reasonable for the system in which higher concentration of malonic acid and external addition of Br^- are employed. However, it is doubtful if the scheme holds also for the BZ system under 'normal' conditions with much lower concentration of bromomalonic acid.

The pulse perturbation experiment is expected to provide some additional information for the photoresponse of the system. Effects of addition of a drop of the solution containing Br^- or Ag^+ to the dark BZ system have been examined [16]. However, the effect of light pulse has not yet been examined extensively; a few examples include studies on the photo-induced phase delay of oscillations [6,17], quenching near a bifurcation point [18] and the periodic stimulation of spiral waves [19].

In view of the lack of systematic study on the response of the BZ system to a pulsed light perturbation, we intend, in this and forthcoming papers, to clarify the effect experimentally by applying a pulsed visible light to the minimal bromate oscillator (MBO). This system has an advantage of containing no organic substrate such as malonic acid so that we can discuss the process without being suffered from complicated reactions involving organic species. In this Letter, we shall examine the effect of pulsed illumination on both SSI and SSII of MBO in a CSTR (continuos-flow stirred tank reactor). Effect of the 'negative' light pulse (a pulsed cut-off of light in the steadily illuminated system) will also be examined.

2. Experimental

Reagent grade $NaBrO_3$ and NaBr (Wako Pure Chemical) and H_2SO_4 (Katayama Chemical) were used without further purification. $Ru(bpy)_3SO_4$ was prepared from $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (Aldrich) by reprecipitation in 3 M sulfuric acid in order to make it free from chloride ions [20]. Freshly prepared solutions in distilled water were pumped into a cell through inlet tubes by a peristaltic pump (Eyela, MP-3). Initial concentrations (the concentration which would be realized in the cell if no reaction took place) were fixed at $[Ru(bpy)_3^{2+}]_0 = 0.10$ mM, $[BrO_3^-]_0 = 25$ mM and $[H_2SO_4]_0 = 0.80$ M. A double-jacketed acryl-resin cell was thermostated at 25°C. The cell was equipped with a combined platinum electrode (Metrohm, No. 916-0408-100) and with quartz windows for illumination (optical pathlength = 2 cm). Stirring was carried out with a Teflon-coated magnetic stirrer bar. A 500 W Hg lamp (Ushio, USH-500D) with a L39 filter and a set of neutral density filters (Hoya) was used as a light source, providing major lines ($\lambda = 395$, 405, 436, 545 and 577 nm) in the visible region. The light power was monitored by a photodiode (Hamamatsu, S1723-05). The maximum light power (P_{max}) at the incident cell window was 1.3 W.

3. Results and discussion

The photo-response of MBO with Ru(bpy)$_3^{2+}$ as a catalyst has been examined under the steady illumination, where the state diagrams are given in the $[Br^-]_0$–$[BrO_3^-]_0$ plane and in the P (light power)–$[Br^-]_0$ plane [3]. Here we have tried to characterize the system behavior in terms of the flow rate. The MBO system is known as one of the flow-controlled oscillators, which requires external supply of Br^- to exhibit oscillations. A state diagram in the $[Br^-]_0$–k_0 plane is illustrated in Fig. 1. The flow rate is expressed in the normalized form defined by $k_0 \equiv v/V$, where v is the total flow rate (mL s^{-1}) and V is the cell volume (12 mL). Fig. 1 indicates that, under the dark condition, the system bifurcates from SSI to OSC when k_0 is decreased at a fixed value of $[Br^-]_0$. A further decrease of k_0 induces another bifurcation from OSC to SSII. Fig. 2 is a state diagram in the P–k_0 plane, where P is the incident light power of the steady illumination. The steady illumination of the system in SSI with visible light causes a bifurcation into OSC for P beyond a critical value, while further increase of P in OSC causes a bifurcation into SSII. The threshold values of k_0 for both bifurcations increase with P.

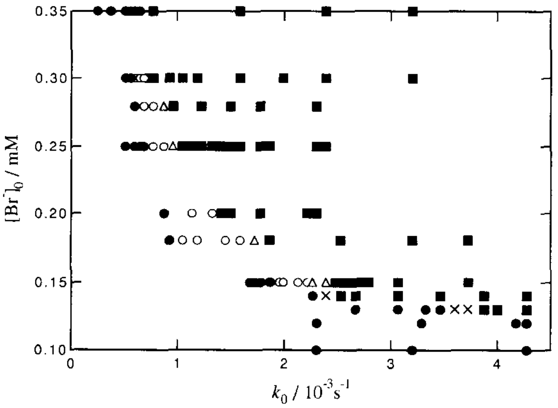

Fig. 1. State diagram in the k_0–$[Br^-]_0$ plane for the MBO system in the dark, with $[Ru(bpy)_3^{2+}]_0 = 0.10$ mM, $[BrO_3^-]_0 = 25$ mM and $[H_2SO_4]_0 = 0.80$ M. (○) OSC; (△) irregular oscillatory; (■) SSI; (●) SSII; (×) bistable.

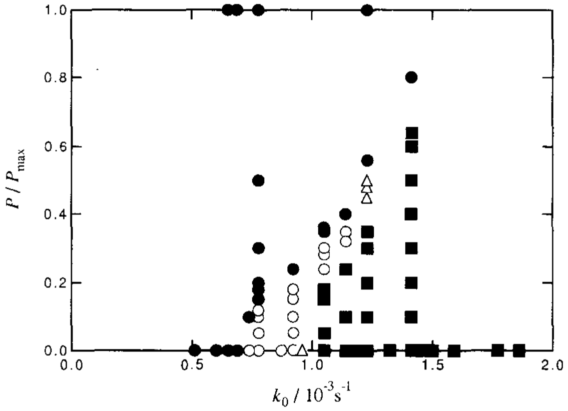

Fig. 2. State diagram in the $k_0 - P$ plane for the MBO system under steady illumination. P is the light power incident to the cell window and $P_{max} = 1.3$ W. Concentrations are the same as those in Fig. 1 except for $[Br^-]_0 = 0.25$ mM. (○) OSC; (△) irregular oscillatory; (■) SSI and (●) SSII.

Fig. 3 illustrates some typical responses of MBO in SSI for a single light pulse of duration $\tau = 1.0$ s. The system exhibits a pulse response only for $P > P_c$, where P_c is a certain critical value of P, and its amplitude is independent of P, suggesting that the system exhibits an excitable character. Fig. 4 shows a map spanned by P/P_c and τ, where the responding and non-responding regions are divided approximately by the solid curve corresponding to $P_c \times \tau = 0.65$ J. This implies that the threshold is not determined by the peak power but determined by the total pulse energy.

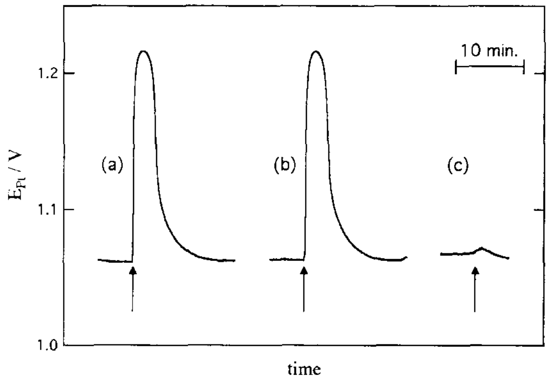

Fig. 3. Time profile of the redox potential for the MBO system in SSI after a single pulse light irradiation. The arrows indicate the time of pulse illumination with duration $\tau = 1.0$ s. $P/P_{max} = 1.0$ (a), 0.5 (b) and 0.25 (c), where $P_{max} = 1.3$ W. Initial concentrations are the same as those in Fig. 2. $k_0 = 1.05 \times 10^{-3}$ s^{-1}.

The excitable behavior is reasonably understood on the basis of reactions (2) and (3) combined with (1). If excess $HBrO_2$ photo-produced by (1) reduces $[Br^-]$ below $[Br^-]_{th}$, the autocatalysis (2) starts to give a sharp rise in the redox potential. After the light pulse is terminated, the system returns slowly back to SSI with a rate corresponding to k_0; namely, a 'wash-off' of the cell content is required for the system to return to SSI, since MBO has no internal source of Br^-. The threshold in the light energy corresponds to the number of photons required to produce a sufficient amount of $HBrO_2$ to reduce $[Br^-]$ below $[Br^-]_{th}$. The independence of peak height of the response on the light energy is also understandable since, once the autocatalysis starts, the system would experience a single turn along the limit cycle for the dark oscillations.

No response of MBO to a pulsed illumination in SSII (Fig. 5(a)) should be due to the extremely low [Ru(II)] for this condition. There is no indication of effective photo-production of Br^-, which could induce a bifurcation into OSC or SSI. This is consistent with our results for the steady illumination; namely, the slopes of the SSI/OSC and OSC/SSII bifurcation lines are positive for P (Fig. 2), which indicates the opposite effect of illumination to the increase of $[Br^-]$, which has negative-slope bifurcation lines (Fig. 1).

It is then interesting to see what would happen if the illumination light is cut off for a short period (the 'negative' light pulse) when the system stays in SSII under steady illumination (Fig. 5(b) and (c); $k_0 = 1.05 \times 10^{-3}$ s^{-1} and $P = 0.47$ W). A negative pulse with duration $\tau = 1.0$ s (the same duration as the positive pulse in Fig. 3) gives no response (Fig. 5(b)). For much longer τ of 30 s, the redox potential shows a dull response (Fig. 5(c)), which is, however, not of excitable nature. The potential decreases slowly with a rate corresponding to k_0 during the pulse duration. When the light is applied again, it returns back rather quickly (the last stage in the autocatalytic response).

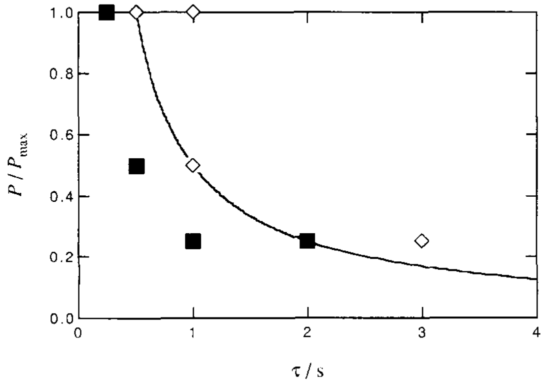

Fig. 4. Effect of pulse duration τ in the pulse illumination of MBO, indicated by ◇ (pulse response) and ■ (no response). Initial concentrations are the same as those in Fig. 1 except for $[Br^-]_0 = 0.18$ mM. $k_0 = 1.86 \times 10^{-3}$ s^{-1}. The curve represents the dependence of P_c/P_{max} on τ as $P_c \times \tau = 0.65$ J, where P_c is the critical power for the pulse response and $P_{max} = 1.3$ W.

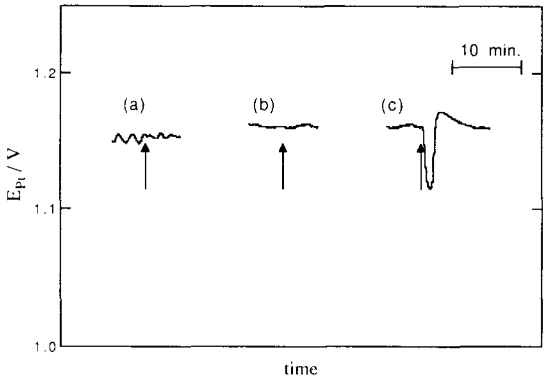

Fig. 5. Response of MBO in SSII. Arrows indicate the time of application of pulsed-light perturbation. Initial concentrations are the same as those in Fig. 1 except for $[Br^-]_0 = 0.25$ mM. (a) Response of the system in SSII in the dark at $k_0 = 0.69 \times 10^{-3}$ s^{-1} to a pulsed light ($P = 1.3$ W and $\tau = 1.0$ s). (b) Response to a pulsed cut-off of the steady illumination. The system is initially in SSII at $k_0 = 1.05 \times 10^{-3}$ s^{-1} and $P = 0.47$ W. P is instantaneously decreased to 0 for an interval of $\tau = 1.0$ s. (c) Same as (b) except for $\tau = 30$ s.

4. Conclusions

Response of the $Ru(bpy)_3^{2+}$-catalyzed minimal bromate oscillator in a CSTR to the pulsed light perturbation has been examined to confirm the previous suggestion [6,7] that the direct effect of pulse illumination is to produce additional $HBrO_2$ through (1). This induces autocatalytic reaction (2), resulting in a sharp excitable response when the light pulse is applied to the system in SSI. On the other hand, the system in SSII does not respond. Application of a 'negative' light pulse to the system in SSII is also ineffective. It is essential for the system to be excitable that the external light pulse triggers the autocatalytic step directly. In this sense, the MBO system in SSI is excitable, whereas the system in SSII is not excitable since it is insensitive to both positive and negative light pulses.

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