CHEMISTRY LETTERS, pp. 1309-1312, 1993.

Photo-response of the $[Ru(bpy)_3]^{2+}$ / BrO_3^- / H^+ System in a Continuous-Flow Stirred Tank Reactor

Tetsuo SEKIGUCHI,† Yoshihito MORI,†,†† and Ichiro HANAZAKI†,††*
†The Graduate University for Advanced Studies, Myodaiji, Okazaki 444
††Institute for Molecular Science, Myodaiji, Okazaki 444

Effect of photo-irradiation on the autocatalytic oxidation of $[Ru(bpy)_3]Cl_2$ by acidic bromate has been investigated in a continuous-flow stirred tank reactor. The photo-induced bifurcation structure and phase diagram have been determined. It is shown that, for a certain range of the bromate concentration, the photo-irradiation can either promote or inhibit the autocatalytic oxidation of $[Ru(bpy)_3]^{2+}$ depending on the irradiation light power.

Photo-irradiation is a useful tool to extract latent informations about the nature of nonlinear chemical systems. The effect of photo-irradiation on various types of chemical oscillators has been investigated with considerable interest in recent years. Among them, the ruthenium-catalyzed B-Z(Belousov-Zhabotinsky) system1-5) exhibits peculiar phenomena such as the photo-induced spatial pattern formation in the inhomogeneous system,2,3) and the inhibition of oscillation in the homogeneous system under the batch1,3) and flow conditions.4) Although the primary photochemical processes in the photo-inhibition of the B-Z oscillator has recently been clarified,3,4) the full mechanism has not yet been elucidated. In this letter, we report a study on the photo-response of a simpler system, $[Ru(bpy)_3]^{2+}$ and BrO_3^- in acidic solution in CSTR(Continuous-flow Stirred Tank Reactor). This is a subsystem of the B-Z system without substrate such as malonic acid, which is suitable for elucidating the nature of the photo-response of nonlinear oscillations in more detail. It shows no oscillatory behavior without external supply of Br^- but exhibits an autocatalytic oxidation of $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_3]^{3+}$ (hereafter, $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$ are abbreviated to Ru(II) and Ru(III), respectively). When $[Ru(bpy)_3]Cl_2$ is used as a source of Ru(II), the system exhibits a bistable nature with hysteresis in a certain range of external parameters. Here we have determined the bifurcation structure and phase diagram of this system taking $[BrO_3^-]_0$ and the incident light power (P_0) as external parameters. Throughout this paper, the suffix "0" on the concentration stands for the concentration which would be attained in the reactor if no chemical reaction takes place.

Tris(2,2'-bipyridyl)Ru(II) chloride hexahydrate (Aldrich), $KBrO_3$, H_2SO_4 (Katayama) of analytical grade were used without further purification. Three stock solutions, the first containing 0.256 mM (1 M = 1 mol dm^{-3}) $[Ru(bpy)_3]Cl_2$ and 0.375 M H_2SO_4, the second containing $KBrO_3$ and 0.375 M H_2SO_4 and the third containing 0.375 M H_2SO_4 were prepared prior to use and independently fed into the CSTR by a peristaltic pump (Eyela MP-32) with a fixed flow rate. An aspirator was used to drain the excess solution at the top of a quartz reactor, in which the solution was stirred by a magnetic stirrer. Its temperature was regulated by circulating water thermostated at 25 ± 0.1 °C. Time profiles of the system were monitored by either measuring the optical absorbance due to [Ru(III)] at 675.2 nm with a spectrophotometer (Hitachi U-3200) or the redox potential with a Pt-electrode. [Br^-] was also monitored with a bromide-ion selective electrode (Horiba 8005-06T) combined with a Ag | AgCl reference electrode through a salt bridge (K_2SO_4). Irradiation light was obtained either from a 500 W Hg lamp (Ushio UI-501C) through band-pass filters (425-473 nm) or from Okazaki Large Spectrograph (452 nm, with a spectral half width: 12 nm).[5)] The light power was varied by a series of ND filters(Hoya). The volumes of solution were 5.6 ml for the former light source and 8.0 ml for the latter. The corresponding residence times were $\tau = 1.9 \times 10^2$ s and 1.8×10^2 s, respectively. The irradiation effect depends on the reactor volume. Assuming an ideally rapid stirring, the effective incident power P_0 is proportional to the reciprocal of the solution volume, V.[6)] In the following, we take the V = 8.0 ml case as a standard and normalized P_0 for the 5.6 ml case by multiplying a factor 8.0 / 5.6 to the measured P_0.

In Fig. 1(A) plotted is the oxidation ratio, $\eta \equiv [Ru(III)] / [Ru(II)]_0$, against $[BrO_3^-]_0$ under some typical irradiation conditions. Figure 1(B) shows a plot of the redox potential against P_0 at various $[BrO_3^-]_0$. The other external constraints are fixed at $[Ru(II)]_0 = 0.256$ mM, and $[H_2SO_4]_0 = 0.375$ M. In Fig. 1(A), the system exhibits a bistability with hysteresis under the dark: it stays in SSI, the "reduced" steady state, at lower values of $[BrO_3^-]_0$ and, upon increasing $[BrO_3^-]_0$, undergoes a transition to SSII, the "oxidized" steady state, at a critical concentration, γ_O, of $[BrO_3^-]_0$. On the other hand, when $[BrO_3^-]_0$ is decreased, the system undergoes a transition from SSII to SSI at γ_R ($< \gamma_O$). It is known that similar systems containing Ce^{3+} or Mn^{2+} with the feed-in of Br^- show hysteresis.[7,8)] Although Br^- is not supplied externally in this system, the chloride ion supplied as a counter anion of Ru(II) would play the same role as Br^- does. In fact, when we used ruthenium sulfate instead of the chloride, only oxidized stationary state was observed under the same condition. These results are summarized in Fig. 2 as a state diagram in the $[BrO_3^-]_0$-P_0 plane, where the data for $P_0 < 40$ mW, are taken from Fig. 1(A), and those for $P_0 > 40$ mW are taken from Fig. 1(B). Curves γ_R and γ_O are the traces of the transition points SSII → SSI and SSI → SSII, respectively. The region of bistability between γ_R and γ_O disappears for $P_0 > 230$ mW. In order to determine the boundary between SSI and SSII in this region, we have measured the redox potential as a function of $[BrO_3^-]_0$ as illustrated in Fig. 3 for $P_0 = 360$ mW. We assume the

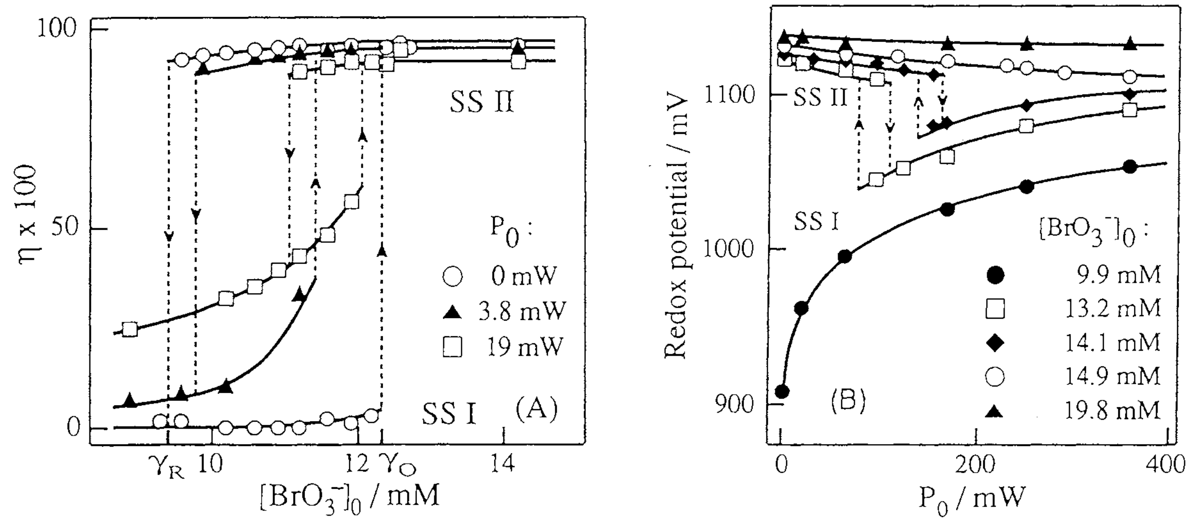

Fig. 1. Bifurcation structure of the Ru(II) / BrO_3^- / H^+ system under irradiation. $[Ru(II)]_0 = 0.256$ mM, $[H_2SO_4]_0 = 0.375$ M. (A) Oxidation ratio, η , vs. $[BrO_3^-]_0$; $\tau = 1.9 \times 10^2$ s. (B) The redox potential vs. P_0; $\tau = 1.8 \times 10^2$ s.

reflection point in this curve (indicated by an arrow) to be the boundary, which is shown by a broken curve in Fig. 2. In Fig. 2, γ_R increases monotonously with increasing P_0, whereas γ_O decreases with P_0 for lower P_0, and turns to increase for higher P_0. Significance of this behavior may be understood more clearly in Fig. 4, where the effect of light irradiation is shown for the fixed value of $[BrO_3^-]_0$ = 11.6 mM corresponding to the dotted line in Fig. 2. When the system is in SSI under the dark, increase of the light power causes a transition from SSI to SSII at $P_0 \cong$ 2mW corresponding to point L (Figs. 2 and 4). It stays in SSII for $P_0 \cong 2-30$ mW, and turns back to SSI at M. With decreasing P_0, the system undergoes a transition from SSI to SSII at $P_0 \cong$ 18 mW (point N), below which the system stays in SSII down to $P_0 = 0$. This means that two bistable regions exist when P_0 is taken as a control parameter. The autocatalytic oxidation is promoted by the irradiation with lower P_0, but inhibited by the irradiation with higher P_0. The behavior of $[Br^-]$ is consistent with this view as shown in Fig. 5; namely, $[Br^-]$ in SSI takes a higher value and decreases with increasing P_0. In contrast, $[Br^-]$ in SSII has a lower value and increases with increasing P_0. For an intermediate $[BrO_3^-]_0$, $[Br^-]$ shows a bistability with hysteresis.

Under the dark condition, oxidation occurs through the autocatalytic process (1) and the switching reaction (2):9)

$$2\,Ru(II) + HBrO_2 + BrO_3^- + 3\,H^+ \rightarrow 2\,Ru(III) + 2\,HBrO_2 + H_2O \tag{1}$$

$$Br^- + HBrO_2 + H^+ = 2\,HOBr \tag{2}$$

In the case of the irradiation of the Ru(II)-catalyzed B-Z system, it has been suggested that processes (3), (4) and (5) would be responsible for the photo-response of the B-Z and related systems.4)

$$^*Ru(II) + Ru(II) + BrO_3^- + 3H^+ = 2\,Ru(III) + HBrO_2 + H_2O \tag{3}$$

$$^*Ru(II) + 3\,Ru(II) + HBrO_2 + 3\,H^+ = 4\,Ru(III) + Br^- + 2\,H_2O \tag{4}$$

$$^*Ru(III) + Ru(III) + HBrO_2 + H_2O = 2\,Ru(II) + BrO_3^- + 3H^+ \tag{5}$$

where *Ru(II) is Ru(II) in its electronically excited state. The same primary photochemical processes should apply to the present system without substrate. The monotonous increase of γ_R in Fig. 2 with increasing P_0 is considered as due to the consumption of $HBrO_2$ by (4) or (5). This tends to bring the system to the reduced state as $[^*Ru(II)]$ increases with P_0. More BrO_3^- is required to keep the system in SSII. Therefore, the γ_R boundary moves to the right in Fig. 2 as P_0 increases. The peculiar variation of γ_O with P_0 may also be

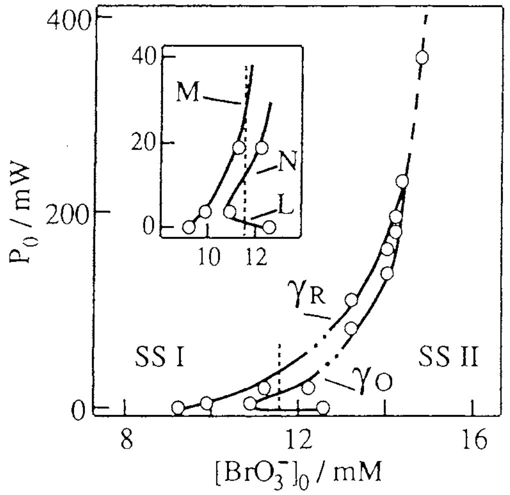

Fig. 2. Phase diagram in the $[BrO_3^-]_0$-P_0 plane. External constraints are the same as those in Fig. 1.

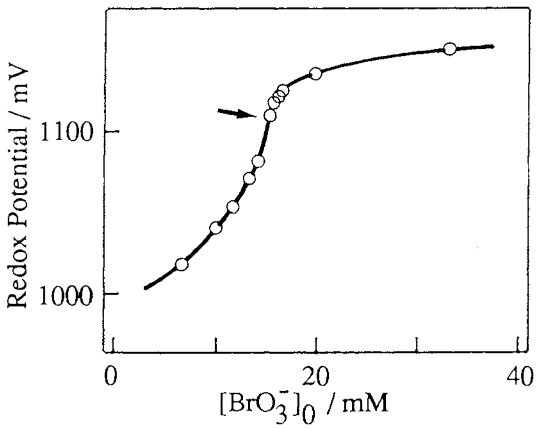

Fig. 3. Dependence of the redox potential on $[BrO_3^-]_0$ at P_0 = 360 mW. Other external constraints are the same as those in Fig. 1(B).

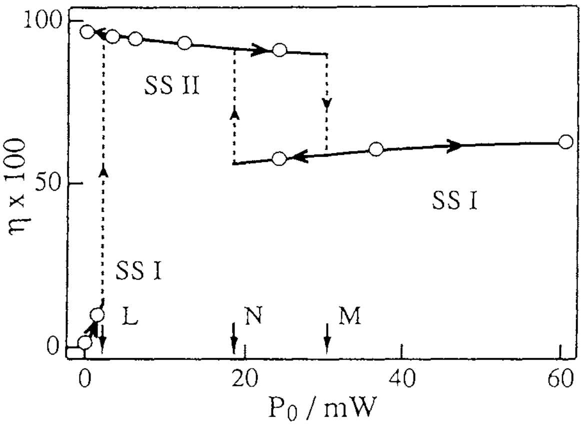

Fig. 4. Photo-response of η at $[BrO_3^-]_0$ = 11.6 mM. Other external constraints are the same as those in Fig. 1(A).

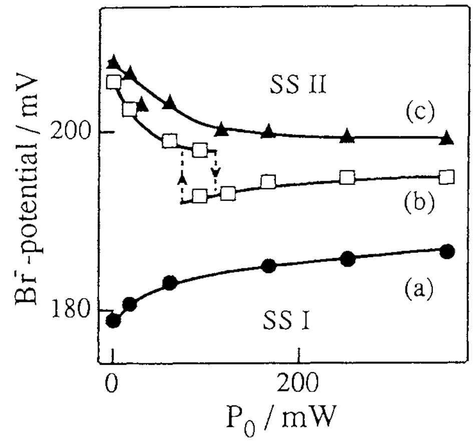

Fig. 5. The Br^--selective electrode potential vs. P_0; $[BrO_3^-]_0$ = 9.9 mM (a), 13.2 mM (b), 16.5 mM (c). Other external constraints are the same as those in Fig. 1(B).

understood as follows: At lower P_0 ($P_0 < 10$ mW), γ_0 decreases with increasing P_0. This is presumably due to (3), which enhances the autocatalytic oxidation by producing $HBrO_2$. Less amount of BrO_3^- is required for higher P_0 to bring the system into SSII. Upon increasing P_0 further, γ_0 turns to increase with P_0. This is presumably due to the incorporation of (4), which consumes $HBrO_2$ and increases $[Br^-]$. More BrO_3^- is required to start the autocatalytic oxidation (1) as P_0 increases. The change of the primary step from (3) to (4) seems to be reasonable, since (4) requires an encounter of *Ru(II) and $HBrO_2$, both of which are in very low concentrations at lower P_0.

We have determined the photo-response of the bistable system, $[Ru(bpy)_3]Cl_2$ / $KBrO_3$ / H_2SO_4 to show the light irradiation can either promote or inhibit the autocatalytic oxidation depending on the experimental conditions. A similar study is under way in our laboratory for the "minimal" oscillator configuration,[8] in which Br^- is supplied externally to the system containing the Ru(II) sulfate complex in stead of the chloride. This will clarify the role of the inhibitor Br^- in more detail and will be published in a forthcoming paper. This study was carried out partly under the NIBB Cooperative Research Program for Okazaki Large Spectrograph(92-507).

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(Received May 6, 1993)