Control of Oscillation Pattern in the Malonic acid-Bromate-Ruthenium-Hydroquinone Reaction by the Illumination of Visible Light

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Received November 1, 2004

Key Words : Temporal oscillations, Photo-control, Hydroquinone, Visible light

Oscillatory chemical reactions have been in the focus of interest since the early seventies partly due to their uncommon temporal behaviour and partly their connection – at least phenomenologically – to periodic processes occurring at many levels of material organizations. Especially the Belousov-Zhabotinsky type (BZ) reactions which are understood as the catalytic oxidation and bromination of organic reductant compounds by bromate ion in acidic condition have been studied rather thoroughly.[1] The study of photo-controlled chemical reactions is a subject of considerable interest in modern reaction kinetics.[2-5] In addition to the practical applications in such areas as product selections by irradiation, investigations of photosensitive reactions have also provided a unique approach to understand interactions between intrinsic dynamics and external forcing.[6-8]

In this study, we have examined the control of temporal oscillation patterns by the illumination of visible light in the malonic acid/BrO_3^-/Ru^{2+}/H^+ system.[9] The ruthenium catalyzed BZ reaction has been known to be sensitive to the visible light,[10] however, we got more various patterns of temporal oscillation by adding a small amount of hydroquinone to the reaction system. Hydroquinone is a good reagent inducing a characteristic oscillation pattern in the BZ type reaction using 1,4-cyclohexanedione/BrO_3^-/Fe^{2+}/H^+. Such an oscillation system is well-known for being suitable for CO_2 gas-free BZ reactions.[11-14] Recently, many kinds of characteristic temporal and spatio-temporal phenomena have been observed in the reaction system.[15,16] In a very recent investigation, Huh *et al.* have found that hydroquinone could play an important role in characteristic pattern formations in that kind of reaction system.[17]

Figure 1 shows a typical experimental result on the influence of visible light to the oscillation pattern in the malonic acid/BrO_3^-/Ru^{2+}/H^+/hydroquinone system where the hydroquinone compound is added to the reaction solution as an additive. The progressing pattern was changed by the turn-on or turn-off of the light source in a moment. And various pattern changes were obtained by the reaction condition before the illumination. The initial pattern before the illumination was varied by the concentration of hydroquinone and the other reactants in the reaction solution. In this case, two contrastive pattern changes were obtained by the illumination of the visible light in the reaction system. One type of pattern change is from the complex behaviors into simpler behaviors. The other pattern change is simple oscillation behaviors into more complex behaviors. Figure 1(a) and Figure 1(b) show the first type of pattern change. A small and high intensity peak alternate in the periodic oscillations differently from the periodic oscillations patterns. This type of alternating oscillation is called bursting behavior and expressed by the number such as 1^1. The superscript number means the number of small intensity peak.[18] Another type of more complex bursting behaviors are also possible such as 1^2, 1^3 or 2^1, etc. Figure 1(a) shows the pattern change from the bursting behavior of 1^1 to the periodic oscillation. On the other hand, Figure 1(b) shows the pattern change from the bursting behavior of 1^2 to the periodic oscillation. As shown in the figure, the change occurs simultaneously by the turn-on or turn-off of the light source. Reverse type of pattern change was also obtained by adjusting the experimental condition. This type of pattern change is more interesting since more complex behaviors are obtained by the illumination. Figure 1(c) shows a typical pattern change from the periodic oscillation to the bursting behavior of 1^1. We could obtain periodic oscillation before illumination though hydroquinone is added in the reaction solution by adjusting the concentration of the other reactants. This change is a reverse case of the change introduced in Figure 1(a). Another type is given in Figure 1(d) showing a pattern change from the bursting behavior of 1^1 to the bursting behavior of 1^2. In these two cases, more complex behaviors are obtained by the illumination differently from the results shown in Figure 1(a) and Figure 1(b). We could not obtain more complex oscillation such as chaos behavior by the illumination in this experimental condition since all experiments are done in the batch condition.

We assume that the variation of the temporal oscillation pattern of the BZ reaction by addition of a small amount of hydroquinone is induced by an inhibition effect of hydroquinone to the Field-Körös-Noyes (FKN)[18] mechanism of the BZ reaction by the rapid oxidation of hydroquinone (H_2Q) to 1,4-benzoquinone (Q), as shown by the reactions of (R1)-(R3).

$$H_2Q + Br_2 \rightarrow Q + 2\,Br^- + 2\,H^+ \qquad (R1)$$

$$H_2Q + BrO_3^- + H^+ \rightarrow Q + HBrO_2 + H_2O \qquad (R2)$$

$$H_2Q + HOBr \rightarrow Q + Br^- + H^+ + H_2O \qquad (R3)$$

The oxidation processes of (R1)-(R3) could perturb the oscillation condition in the FKN mechanism by changing the

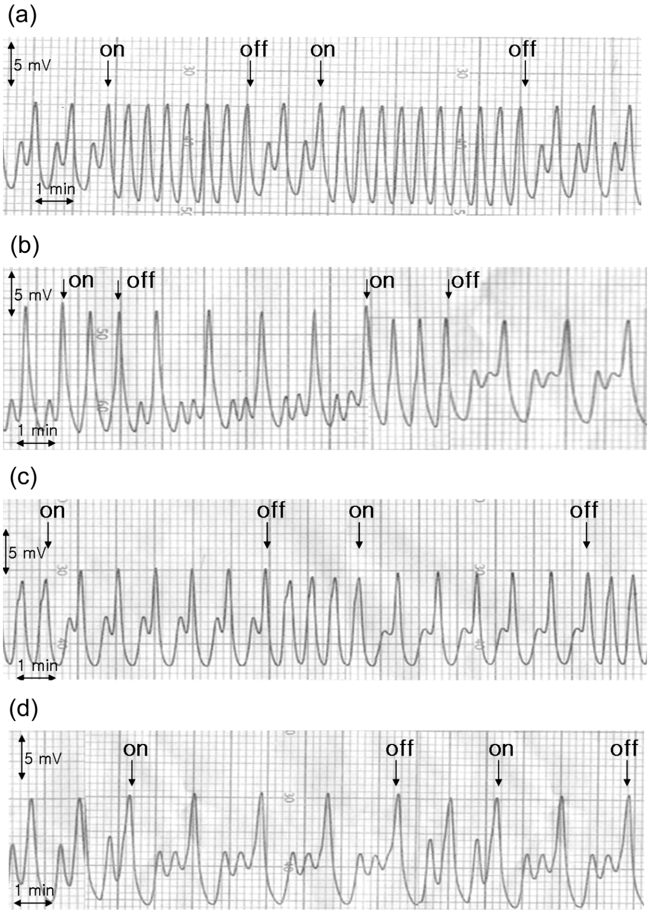

Figure 1. The pattern change induced by the illumination of visible light on the reaction system where hydroquinone is added. Initial compositions of the reaction mixture are : (a) [MA] = 0.05 M, $[BrO_3^-]$ = 0.125 M, $[H^+]$ = 0.375 M, $[Ru^{2+}]$ = 7.5×10^{-5} M, $[H_2Q]$ = 0.020 M; (b) [MA] = 0.05 M, $[BrO_3^-]$ = 0.12 M, $[H^+]$ = 0.375 M, $[Ru^{2+}]$ = 8.4×10^{-5}, $[H_2Q]$ = 0.018 M; (c) [MA] = 0.05 M, $[BrO_3^-]$ = 0.125 M, $[Ru^{2+}]$ = 6.0×10^{-5} M, $[H^+]$ = 0.375 M, $[H_2Q]$ = 0.020 M; (d) [MA] = 0.05 M, $[BrO_3^-]$ = 0.125 M, $[Ru^{2+}]$ = 1.00×10^{-4} M, $[H^+]$ = 0.375 M, $[H_2Q]$ = 0.010 M.

steady state concentration of reaction intermediates for the oscillation reaction. By the mechanism, the illumination of visible light would help the perturbation of the FKN mechanism by the acceleration of the oxidation reaction of hydroquinone in the system. Therefore, those pattern changes shown in Figure 1(c) and Figure 1(d) are obtained such as from the simple oscillation behaviors to the more complex behaviors. However, those pattern changes shown in Figure 1(a) and Figure 1(b) can be interpreted by the result of hydroquinone addition effect. In the case when we added the hydroquinone above a limit concentration, a periodic oscillation pattern was rather obtained. This means that the rapid oxidation of hydroquinone does not always induce complex bursting behaviors. However, it is difficult to interpret exactly for the obtained pattern variations only by this experimental result since the pattern in this BZ system is dependent on the concentration of the other reactants by the FKN mechanism. The effect of the illumination of the visible light on the malonic acid/BrO_3^-/Ru^{2+}/H^+/hydroquinone system will be studied continuously in our future research.

Acknowledgement. This work was supported by a Grant (R01-2002-000-00030-0) from the Korea Science and Engineering Foundation.

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9. Typical experimental condition is as follows: Stock solutions of 0.6 M $NaBrO_3$, 0.2 M of malonic acid, 0.2 M hydroquinone, 1.0×10^{-3} M $Ru(bpy)_3^{2+}$, and 2.0 M nitric acid are prepared with double distilled water. Reactions are carried out in a thermostated 50 mL vessel, where the temperature is controlled at room temperature at 25 ± 0.1 °C. The oscillating reactions were monitored by a platinum redox electrode. The potential was recorded with a multi-channel recorder (Cole-Parmer, G08373-20) through a pH/ISE meter (Orion, 940). A 100 W halogen lamp (Microtech, Model No. DLS-100HD) with continuous variable light level is used as a light source. The illumination has been done by optical fiber on both side of the reaction beaker.
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