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Photochemical Behaviour in Macrocyclic Copper Complex-Bromate-Malic Acid System

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The photochemical behaviour in the macrocyclic copper complex-bromate-malic acid system was investigated in this paper. Macrocyclic copper complex $[CuL](ClO_4)_2$, where ligand L is 5,7,7,12,14,14-hexemethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, is an enzyme-like complex. Experimental results indicated that the chemical oscillations exhibited ultrasensitive response to illumination, where the amplitude of oscillation were significantly changed but the frequency remained unaffected by ultraviolet light working at 245 nm with an intensity of more than 450 Lux. Increase in light intensity could enhance inhibition on the oscillations. At a constant illumination, the influences of light were examined with the variation of the concentration of bromate, malic acid, and macrocyclic complex. It was found that the ultraviolet light has affectedly influence on the oscillation trajectories of potentials of platinum electrode vs. those of bromide selective electrode.

Keywords: Belousov-zhabotinsky, Photochemical, Macrocyclic copper complex, Malic acid.

INTRODUCTION

On the condition of far from equilibrium, chemical oscillations may occur as a result of the nonlinear kinetic steps between the reactions which take place in some simple chemical systems[1]. Such chemical systems include Belousov-Zhabotinsky (BZ)[2-4] Bray-Liebhafsky (BL)[5], Bray-Rauscher (BR)[6-9] and chlorine dioxide-iodine-malonic acid system[10]. Because of the simplicity that such chemical systems possess, they could be regarded as ideal model for mimicking some biological oscillations that could be observed, such as Ca^{2+} oscillations in cells.

Photochemical property of some chemical oscillating systems[11-14] has been studied, some of which are mainly bromate-based oscillators where the properties of the reaction kinetics is easier to be controlled. For examples, some catalyzed or uncatalyzed bromate-hydroquinone systems[15-16] show immense photosensitive properties and one of advantages in such systems is that they produce no gas. Such character makes them perfect matrix studying nonlinear dynamics. Besides, ruthenium-catalyzed Belousov-Zhabotinsky photochemical reaction[17-20] has drawn so much attention because it could undergo transitions from photoinhibition to phtoexcitation,yet its mechanism is not easy to be clarified as experiments were done in batch reactor and phenomena were observed at different periods.

In an effort to expand the photochemical oscillators' family, we studied the macrocyclic copper complex-bromate-malic acid system, expecting such system has photosensitive response to illumination. Macrocyclic copper complex $[CuL](ClO_4)_2$ is an enzyme-like complex, where ligand L is 5,7,7,12,14,14-hexemethyl-1,4,8,11-tetraazacyclo tetradeca-4,11-diene. Macrocyclic copper complex-bromate-malic acid system was first reported by our group[21] and many features of such system have been described[22-26]. In this oscillator, there is no ruthenium as catalyst, nor hydroquinone as substrate. However, such a macrocyclic copper complex-catalyzed Belousov-Zhabotinsky system shows ultrasensitive response.

In present studies, we investigated the photochemical behaviour in above-described system. In their ultrasensitive response to illumination, the amplitude of oscillation was significantly changed but the frequency remained unaffected by ultraviolet light working at 245 nm with an intensity of more than 450 Lux. Increase in light intensity could enhance inhibition on the oscillations. At a constant illumination, the influences of light were examined with the variation of the concentration of bromate, malic acid and macrocyclic complex. It was shown that ultraviolet light has affectedly influence on the oscillation trajectories of potentials of platinum electrode *vs*. those of bromide selective electrode.

EXPERIMENTAL

All reactions were run in a 50 mL glass reactor which is thermostated at 25 ± 0.5 °C. Magnetic stirrer was used and the speed was maintained at 540 rpm. Reaction was followed by monitoring the changes of the potentials of platinum and bromide selective electrode; a type 217 saturated calomel electrode connected through a salt bridge containing 1 M Na_2SO_4 as the reference electrode. The potentials of Pt and bromide were connected to an amplifier. This amplifier introduced to a Vernier Go-link which was connected to a computer. Data were recorded through Logger Lite software.

The catalyst macrocyclic copper complex $[CuL](ClO_4)_2 \cdot 0.5H_2O$ was prepared by known technique[27] and was identified by its IR spectra and elemental analyses. Sodium bromate (AR), malic acid (AR) and sulfuric acid (AR) were used as received. Twice redistlled water was used in all cases.

To a beaker of 50 mL, 27.80 mL 1.05 M sulfuric acid, 4.20 mL 0.21 M malic acid, 7 mL 0.0039 M $[CuL](ClO_4)_2 \cdot 0.5 H_2O$ and 1 mL 0.015 M sodium bromate were mixed to make a total solution volume of 40 mL. An ultraviolet lamp with continuous variable light intensity was used as the light source (Beijing Cnlight UV lamp Co. Ltd. , Model ZW30S19-Z894 40 W). The distance between the lamp and beaker is 5 cm. The light intensity was measured with an optical photometer from Shenzhen Jin Tatsu Instrument Co., Ltd (model LX1330B).

RESULTS AND DISCUSSION

In the absence of ultraviolet light, typical oscillations of potential of platinum and bromide against time could be obtained in the condition of $[H_2SO_4]_0$ = 1.05 M, [Malic acid]$_0$ = 0.21 M, [Sodium bromate]$_0$ = 0.015 M, $[CuL](ClO_4)_2 \cdot 0.5 H_2O]_0$ = 0.0039 M (Fig. 1). When the oscillations had lasted for 1000 seconds where it is in stable condition, we switched on ultraviolet lamp to study ultraviolet light's effects on the oscillations. We just found that the amplitude of oscillation was significantly decreased but the frequency remained unaffected by ultraviolet light working at 245 nm with an intensity of 1250 Lux. When the light was switched off, the oscillations went back to typical oscillations state (Fig. 2).

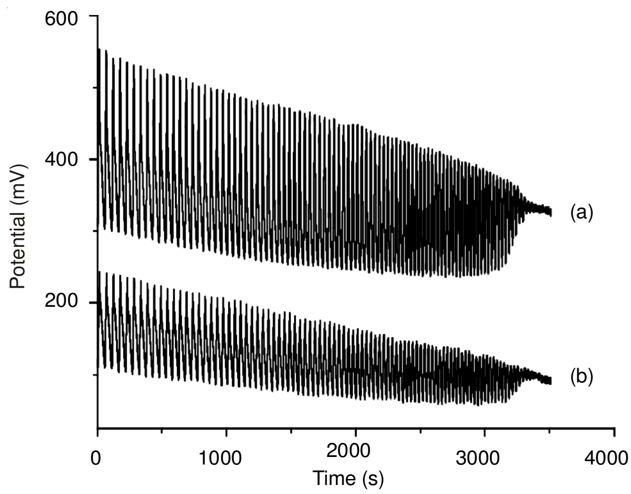

Fig. 1. Curve of potential against time: (a) platinum electrode (b) Bromide ion selective electrode. Common conditions: $[H_2SO_4]_0$ = 1.05 M, [Malic acid]$_0$ = 0.21 M, [Sodium bromate]$_0$ = 0.015 M, $[CuL](ClO_4)_2 \cdot 0.5 H_2O]_0$ = 0.0039 M

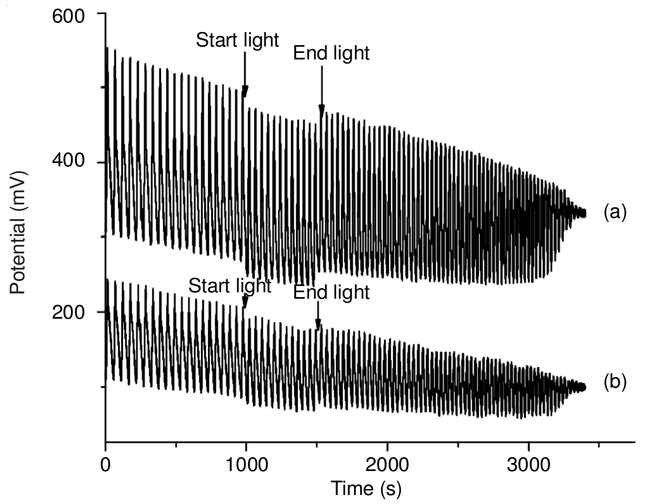

Fig. 2. Typical potential oscillation profiles in the presence of light; (a) platinum electrode (b) Bromide ion selective electrode. Common conditions: $[H_2SO_4]_0$ = 1.05 M, [Malic acid]$_0$ = 0.21 M, [Sodium bromate]$_0$ = 0.015 M, $[CuL](ClO_4)_2 \cdot 0.5H_2O]_0$ = 0.0039 M. Ultraviolet light working at 245 nm with an intensity of 1250 Lux

At the fixed concentration of reactants: $[H_2SO_4]_0$ = 1.05 M, [Malic acid]$_0$ = 0.21 M, [Sodium bromate]$_0$ = 0.015 M, $[CuL](ClO_4)_2 \cdot 0.5 H_2O]_0$ = 0.0039 M, we studied the different light intensity' effect on the B-Z oscillation system. We set A as the actual amplitude of oscillation in the presence of light illumination and A_0 as the actual amplitude of oscillation during that period there is an absence of light. ΔA is the changed of amplitude of oscillation which can be expressed as $\Delta A = (A_0\text{-}A)$. And the ratio of ΔA to A_0 can be expressed as $\Delta A/A_0$. If the value of ΔA or $\Delta A/A_0$ is positive, it indicates that the oscillations were inhibited.

The light intensity's effects on the oscillations were studied. As the light intensity was increased from 450 to 1250 Lux, the change of amplitude of oscillation (ΔA) and $\Delta A/A_0$ increased (Fig. 3), indicating increase in light intensity could enhance inhibition on the oscillations. Following linear expression was obtained:

$$\Delta A/A_0 = 0.0000397\ [\text{light intensity}]/\text{Lux} + 0.03135$$

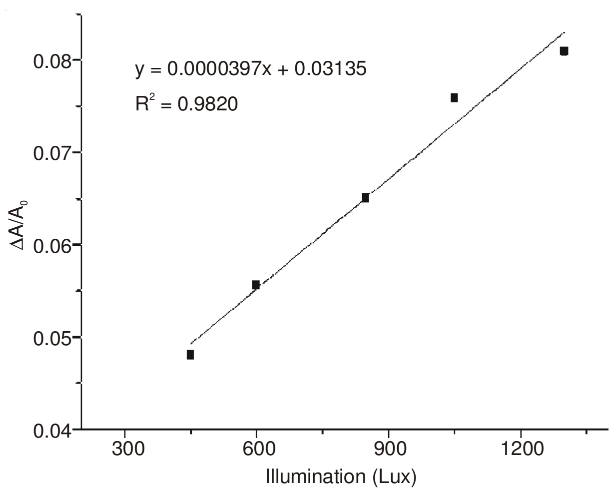

Fig. 3. $\Delta A/A_0$ *vs.* light intensity. Common conditions: $[H_2SO_4]_0$ = 1.05 M, [Malic acid]$_0$ = 0.21 M, [Sodium bromate]$_0$ = 0.015M, $[CuL](ClO_4)_2 \cdot 0.5 H_2O]_0$ = 0.0039 M. Ultraviolet light working at 245 nm

At a constant illumination, the influences of light were examined with the variation of the concentration of bromate, malic acid and macrocyclic complex.

We studied the influences of light with the variation of the concentration of bromate at a constant intensity (1250 Lux) and fixed concentration of other reactants: $[H_2SO_4]_0$ = 1.05 M, [Malic acid]$_0$ = 0.21 M, $[CuL](ClO_4)_2{\cdot}0.5\ H_2O]_0$ = 0.0039 M. When the concentration of bromate increases from 0.005 to 0.025 M, there is a decrease in change in the amplitude of oscillation (Fig. 4 a).

Influences of light with the variation of the concentration of malic acid were examined. When the concentration of malic acid increases form 0.11 to 0.31 M, the influence of light underwent a transition from increase in amplitude of oscillation to decrease in amplitude of oscillation ($\Delta A\%$ underwent a transition from negative to positive) (Fig. 4b).

Influences of light with the variation of the concentration of macrocyclic complex were studied. When the concentration of macrocyclic complex increases from 0.0019 to 0.0059 M, the change in the amplitude of oscillation increases to the maximum at macrocyclic complex concentration of 0.0039 M and then it decrease with further increase in macrocyclic complex concentration (Fig. 4c).

The ultraviolet light has affectedly influence on the oscillation trajectories of potentials of platinum electrode *vs.* those of bromide selective electrode. Some cycles appeared to be lost in the trajectories when the ultraviolet light switched on (Fig. 5).

In the absence of light, the mechanism for the macrocyclic copper complex-bromate-malic acid system has been proposed[21], as it is shown in reactions (1) to (7).

$$BrO_3^- + Br^- + 2H^+ \rightleftharpoons HOBr + HBrO_2 \qquad (1)$$

$$HBrO_2 + Br^- + H^+ \rightleftharpoons 2HOBr \qquad (2)$$

$$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O \qquad (3)$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2{\cdot} + H_2O \qquad (4)$$

$$Br_2 + HOOCCHOHCH_2COOH \longrightarrow Br^- + H^+ + HOOCCHOHBrCHCOOH \qquad (5)$$

$$BrO_2{\cdot} + [CuL]^{2+} + H^+ \longrightarrow [CuL]^{3+} + HBrO_2 \qquad (6)$$

$$HOOCCHOHBrCHCOOH + 4\,[CuL]^{3+} + 3H_2O \longrightarrow 4[CuL]^{2+} + Br^- + 2HCOOH + 2CO_2 + 7H^+ \qquad (7)$$

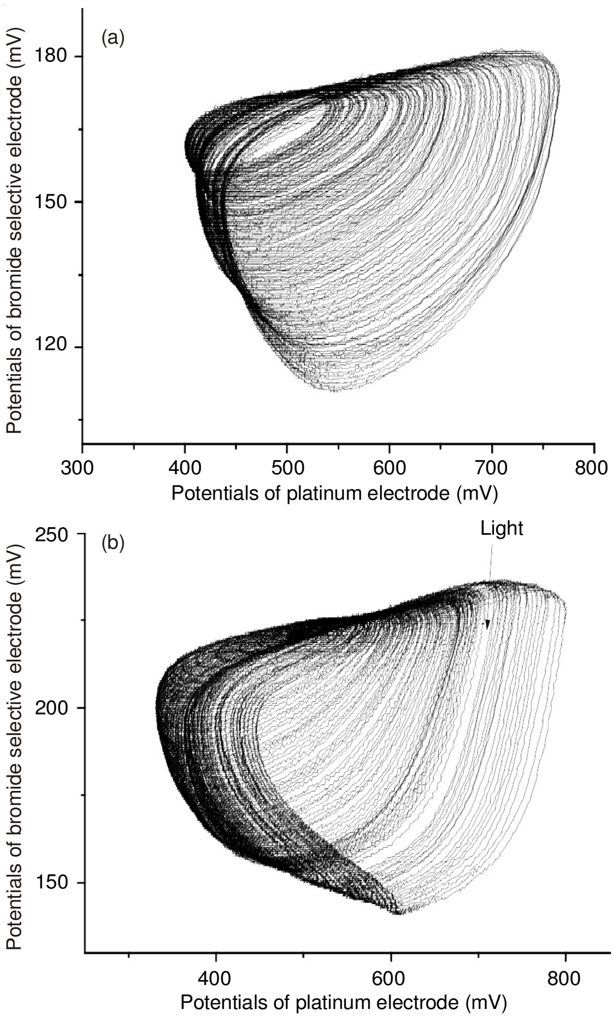

Fig. 5. (a) Trajectories of potentials of platinum electrode vs. those of bromide selective electrode (b) The influence of light on the trajectories of potentials of platinum electrode vs. those of bromide selective electrode on the oscillation: Ultraviolet light working at 245 nm with an intensity of 1250 Lux. Common conditions: $[H_2SO_4]_0$ = 1.05 M, [Malic acid]$_0$ = 0.21 M, [Sodium bromate]$_0$ = 0.015M, $[CuL](ClO_4)_2{\cdot}0.5\ H_2O]_0$ = 0.0039 M

When the light was utilized to the oscillations, the probable mechanism for the effects of light on the oscillations may be contributed to followings:

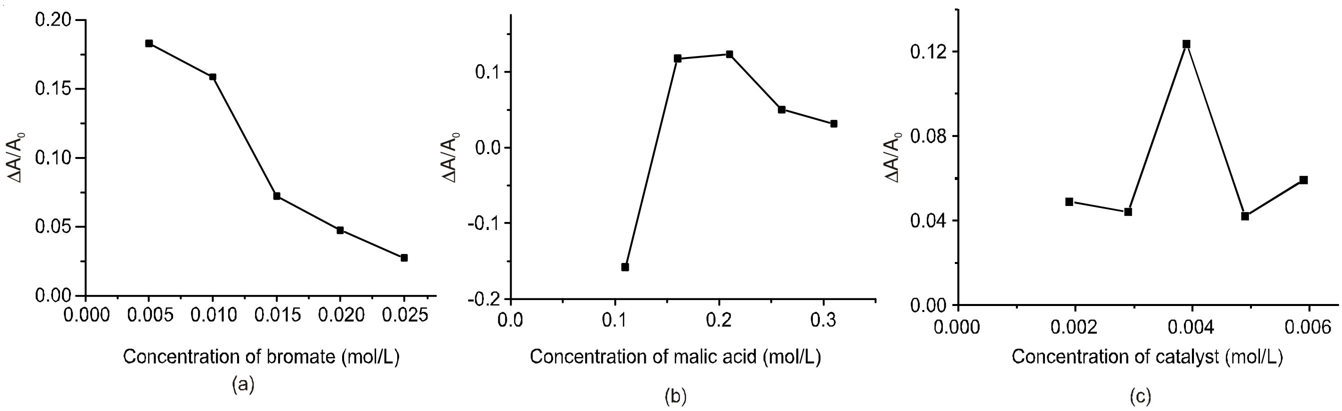

Fig. 4. (a) Influences of light with the variation of the concentration of bromate; (b) The influences of light with the variation of the concentration of malic acid; (c) The influences of light with the variation of the concentration of macrocyclic complex. Common conditions: $[H_2SO_4]_0$ = 1.05 M, [Malic acid]$_0$ = 0.21 M, $[CuL](ClO_4)_2{\cdot}0.5\ H_2O]_0$ = 0.0039 M. Ultraviolet light working at 245 nm with an intensity of 1250 Lux

$$BrO_3^- + Br^- + 2H^+ \underset{\text{light}}{\rightleftharpoons} HOBr + HBrO_2 \qquad (1a)$$

In the presence of light, there would be more $HBrO_2$ that could be produced according reaction (1a). As the concentration of $HBrO_2$ increase, the equilibrium of reaction (6) will shift to the left, resulting the increase in the concentration of $[CuL]^{2+}$. Because of the increase in the concentration of $[CuL]^{2+}$, there is a decrease in the ln ($[CuL]^{3+}/[CuL]^{2+}$), resulting the decrease in the amplitude of oscillation.

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