Asian Journal of Chemistry Vol. 21, No. 1 (2009), 560-566

Effects of the Glucose on Belousov-Zhabotinskii System

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This paper reported the effects of glucose on a novel Belousov-Zhabotinskii (B-Z) system (BrO_3^--[CuL]$(ClO_4)_2$-malic acid-H_2SO_4 system, where L = 5,7,7,12,14,14-hexemethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). Experimental results showed that, by the addition of different amount of glucose to the oscillating system, the change of the oscillation amplitude is linearly proportional to the glucose concentration in the range of 2.5×10^{-3}- 2.5×10^{-2} M (r = -0.99523). The addition of glucose also caused the change of oscillation period in the same concentration range. The influences of the concentration of the components on the change of the oscillation amplitude, as well as their influences on the change of oscillation period, have been studied in detail. A tentative mechanism to explain the effects of glucose on the oscillation was proposed.

Key Words: Belousov-Zhabotinskii (B-Z) oscillating reaction, Glucose, Tetraazamacrocyclic complex.

INTRODUCTION

It is known that certain chemical reactions can oscillate in time or space[1]. An example of such one is the Belousov-Zhabotinskii (B-Z) reaction[2-7], which is thoroughly characterized[8-16]. In these B-Z systems, catalysts are usually Ce(III)-Ce(IV), Ru(II)-Ru(III), $[Fe(II)(phen)]^{2+}$-$[Fe(III)(phen)]^{3+}$ and Mn(IV)-Mn(III) couples *etc*. Recently, oscillating systems with a macrocyclic copper(II) complex as catalyst have been investigated[17]. These kinds of oscillating systems aroused attention in the field of biochemical oscillations, for tetraazamacrocyclic complexes have a similar structure to some enzymes.

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In this paper, we report the effects of glucose on a novel Belousov-Zhabotinskii (B-Z) system (BrO_3^--[CuL]$(ClO_4)_2$-malic acid-H_2SO_4, where L = 5,7,7,12,14,14-hexemethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). Since glucose serves as the chief source of energy in the body and keeping glucose within a normal range is significant to health, the effects of glucose on B-Z reactions are very important for biological studies (malic acid is one of the intermediates existing in cells).

EXPERIMENTAL

All materials were of analytical grade. The catalyst [CuL]$(ClO_4)_2$ was prepared by a known technique[18]. Solutions of 0. 7 M $NaBrO_3$, 2 M malic acid and 1.84×10^{-2} M [CuL]$(ClO_4)_2$ in 1 M H_2SO_4 were prepared separately. Solutions of glucose were freshly made just before the experiments. All solutions were prepared with double distilled water.

Reactions were carried out in a stirred 50 mL reaction glass reactor with a thermostat-magnetic stirrer (Model 85-2 Jintan, China) regulated by a thermostat. Changes of the potential were followed by a bright platinum electrode (Type 213, Shanghai Electricity and Light Instrumental Factory), a saturated calomel electrode connected *via* a salt bridge containing 1 M Na_2SO_4 (Model 217, Shanghai, China) as reference electrode. Potentials of the electrodes *vs.* time were measured with Model PHS-25B digital voltameters (Shanghai, China). The kinetic curves of the reaction were recorded using Model XWT-204 Y-t recorder (Shanghai, China). In the paper, cyclic voltammetry was applied to monitor which species reacted with glucose in the B-Z system. The mechanism was studied by potential sweep voltammetry and the volt-ampere curves were recorded on an electrochemical working station (LK2005, Tianjin, China). A platinum electrode was used as working electrode, SCE as the reference electrode and platinum as counter electrode.

The characteristics of the oscillations (oscillation period, oscillation amplitude, *etc.*) depend greatly on temperature. To obtain stable amplitude (A_0), all of the experiments were performed at 17.5 ± 0.5 ºC. The reactants was filled in this sequence: 1 M, 29 mL sulfuric acid; 0.7 M, 1 mL sodium bromate; 2.0 M, 4 mL malic acid; 1.84×10^{-2} M, 6 mL [CuL]$(ClO_4)_2$ at intervals of 1 min. The volume of the reaction was 40 mL. The mixture was homogenized by continuous magnetic stirring. The oscillating curve was recorded by Y-t recorder. During oscillation, the periodic changes of solution colour (red-orange-red) were observed[17] owing to the oscillations between $[CuL]^{2+}$ and $[CuL]^{3+}$:

$$[CuL]^{2+}\ (red) \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [CuL]^{3+}(orange)$$

After the induction period, the steady state of the oscillating system was obtained and at that time, variable amounts of glucose were added to the reaction system at the bottom of the potentiometric cycle.

RESULTS AND DISCUSSION

Fig. 1 shows a typical oscillation profile for the B-Z oscillation chemical system in the absence (Fig. 1a) and in the presence (Fig. 1b) of glucose perturbation. When the glucose is introduced to the B-Z medium, the amplitude of oscillation decreases (Fig. 1b).

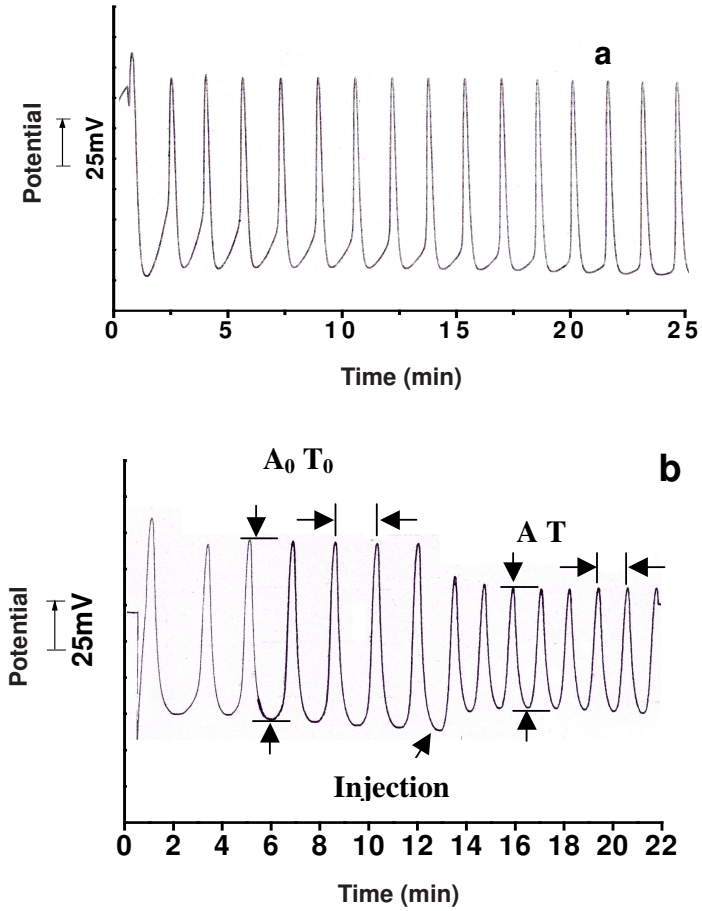


Fig. 1. Typical oscillation profiles for the proposed oscillating system obtained in the absence and in the presence of variable amounts of glucose perturbation using platinum electrode and SCE: (a) [glucose] = 0; (b) [glucose] = 1.05×10^{-2} M. Common conditions (at 17.5 ºC): H_2SO_4, 1 M; $NaBrO_3$, 0.0175 M; malic acid, 0.2 M; $[CuL]^{2+}$, 2.76×10^{-3} M. Temperature, 17.5 ºC

In present survey of effects of glucose on the B-Z oscillation, it is found that introduction of glucose causes changes in both oscillation amplitude and oscillation period. The changes of oscillation amplitude is noted as ΔA ($\Delta A = A\text{-}A_0$, where A_0 and A are the oscillation amplitude before and after

the injection respectively). The changes of oscillation period as is also noted ΔT ($\Delta T = T\text{-}T_0$, where T_0 and T are the oscillation period before and after the injection, respectively). When the concentration of glucose is in the range 2.5×10^{-3} M-2.5×10^{-2} M, changes of oscillation amplitude (ΔA), as well as changes of oscillation period (ΔT), is linearly proportional to the concentration of glucose, respectively.

Plotting the changes of oscillation amplitude (ΔA) *vs.* the concentration of glucose, a straight line is obtained (Fig. 2a) and the following equation is established:

$$\Delta A/mV = 4.549 + (-2964.033) \times [\text{glucose}] \quad (r = -0.99523)$$

Plotting the changes of oscillation period (ΔT) *vs.* the concentration of glucose, a straight line is obtained (Fig. 2b) and the following equation is established:

$$\Delta T/\text{min} = (-0.086) + (-36.714) \times [\text{glucose}] \quad (r = -0.99239)$$

In order to understand the role of each constituent in the oscillation reaction. The influences of the concentration of the components on the change of the oscillation amplitude (ΔA), as well as their influence on the change of the oscillation amplitude (ΔT) have been studied.

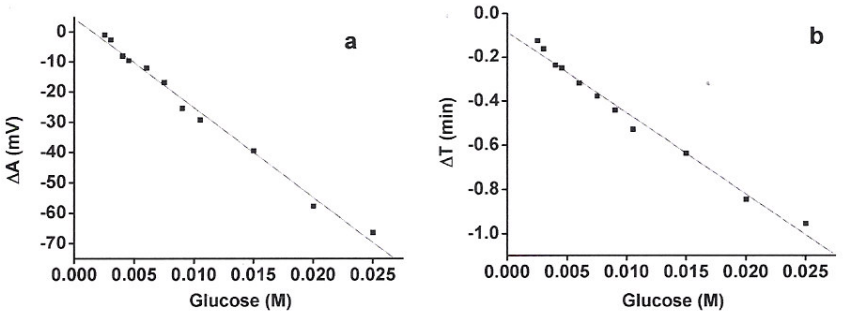


Fig. 2. Curve of the decrease in oscillation amplitude (a) and oscillation period (b) *vs.* the [glucose] in the range 2.5×10^{-3}-2.5×10^{-2} M (other conditions are the same as those in Fig. 1

Variation of sulfuric acid concentration: The effect of the sulfuric acid concentration was studied over the range of 0.7825 to 1.3625 M. The change of the oscillation amplitude (ΔA), as well as changes of the oscillation period (ΔT), increased with increasing sulfuric acid concentration (Fig. 3a).

Variation of $[CuL]^{2+}$ concentration: The concentration of $[CuL]^{2+}$ was changed between 1.84×10^{-3} M and 3.22×10^{-3} M (Fig. 3b). As it can be seen, with the increase of $[CuL]^{2+}$ concentration, the change of the oscillation amplitude (ΔA) decreased. Similar results were found while investigating the effects of $[CuL]^{2+}$ concentration on the change of the oscillation period (ΔT).

Variation of the malic acid concentration: The influence of the malic acid concentration was investigated over the range of 0.15-0.25 M (Fig. 3c). Similar to the effect of the sulfuric acid concentration, the change of the oscillation amplitude (ΔA), as well as changes of the oscillation period (ΔT), increased with increasing malic acid concentration.

Variation of the sodium bromate concentration: Changes in the sodium bromate concentration is in the range from 8.75×10^{-3} M to 2.28×10^{-2} M (Fig. 3d). The change of the oscillation amplitude (ΔA) was found to linearly increase with increasing sodium bromate concentration. Increasing sodium bromate concentration from 8.75×10^{-3} to 1.75×10^{-2} M resulted in the decrease of the change of the oscillation period (ΔT), but further increase of sodium bromate concentration resulted in the increase of the change of the oscillation period (ΔT). When the sodium bromate concentration is to *ca.* 0.0175 M, the change of the oscillation period (ΔT) reached the minimum.

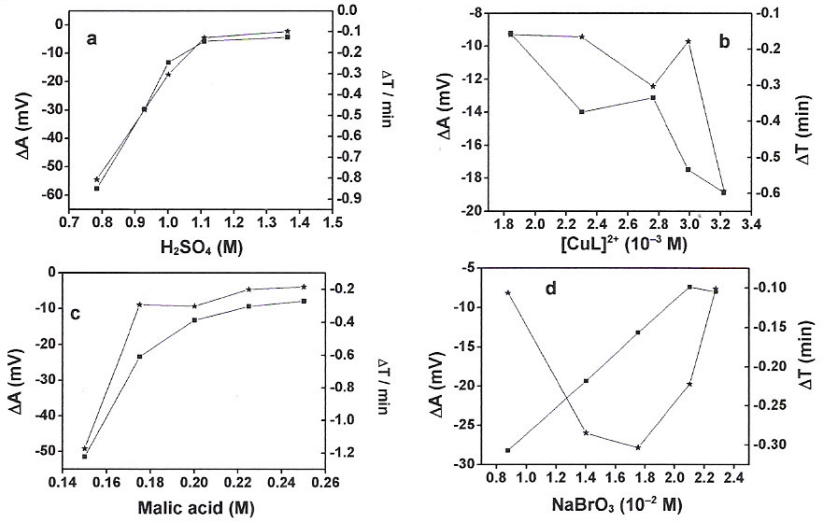


Fig.3. Influence of the concentration: (a) sulfuric acid; (b) $[CuL](ClO_4)_2$; (c) malic acid and (d) sodium bromate on oscillating reaction (■ refer to ΔA; ★ refer to ΔT). Conditions: (a) 2.76×10^{-3} M $[CuL](ClO_4)_2$ + 0.2 M malic acid + 1.75×10^{-2} M $NaBrO_3$ + 5.0×10^{-3} M Glu; (b) 0.2 M malic acid + 1.75×10^{-2} M $NaBrO_3$ + 1 M H_2SO_4 + 5.0×10^{-3} M Glu; (c) 2.76×10^{-3} M $[CuL](ClO_4)_2$ + 1.75×10^{-2} M $NaBrO_3$ + 1 M H_2SO_4 + 5.0×10^{-3} M Glu; (d) 2.76×10^{-3} M $[CuL](ClO_4)_2$ + 0.2 M malic acid + 1 M H_2SO_4 + 5.0×10^{-3} M Glu

According to literatures[17,19,20], the mechanism for the oscillation reaction of the system {malic acid-$NaBrO_3$-H_2SO_4-$[CuL](ClO_4)_2$} is known as the reactions (1-7).

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

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

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

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2^\bullet + H_2O \quad (4)$$

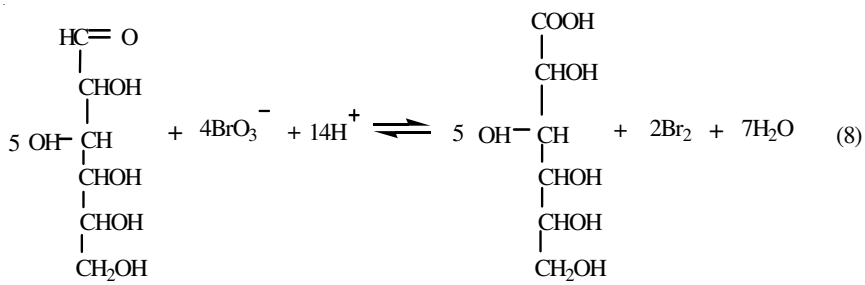
$$Br_2 + HOOCCHOHCH_2COOH \longrightarrow Br^- + H^+ + HOOCCHOHBrCHCOOH \quad (5)$$

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

$$HOOCCHOHBrCHCOOH + 6[CuL]^{3+} + 3H_2O \longrightarrow 6[CuL]^{2+} + Br^- + 2HCOOH + 2CO_2 + 7H^+ \quad (7)$$

Reactions from eqns. 1-4 are all reversible. They include some bromine species with various oxidation states as reactants or products. Reaction 5 and 6 are irreversible reactions. Reaction 5 represents the bromination of the malic acid in present system. Reaction 6 represents the oxidation of $[CuL]^{2+}$ into $[CuL]^{3+}$ in acidic condition. The colour of solution changes from red to orange periodically. The $[CuL]^{3+}$, which generated from reaction 6, is reduced to $[CuL]^{2+}$ by the HOOCCHOHBrCHCOOH, as is shown in reaction 7. The orange colour of solution again turns into red.

From the results of cyclic voltammograms (Fig. 4) and literature[21], a possible mechanism to explain the effects of glucose is proposed.



(8)

When glucose is added into the system, it can immediately be oxidized to gluconic acid by BrO_3^- in the system (reaction 8). In reaction 8, when large amounts of Br_2 generated, the accumulation of Br_2 makes up for its consumption in the reaction 5. Besides, it also makes reaction 3 turn to the negative direction, thus the concentration of HOBr and Br^- increase accordingly. Then, reaction 2 also turns to the negative direction. The accumulation of HOBr and $HBrO_2$ led to the rate of reaction 5 slower and then, the concentration of $[CuL]^{2+}$ increases to some extent in reaction 6. So it results in a decline in the potential, which in turn causes the oscillation amplitude to decrease to a minimum. When the concentration of glucose is lower than 2.5×10^{-3} M, it virtually has no effect on the oscillation system.

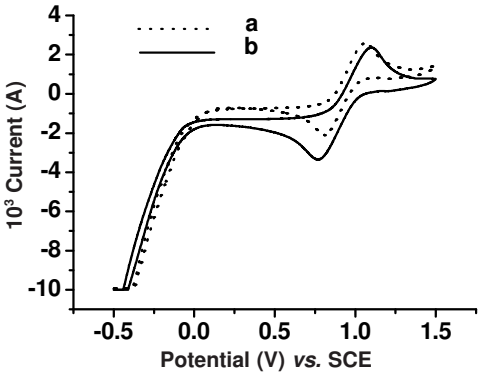


Fig. 4. Cyclic voltammograms of the reactions between glucose and $NaBrO_3$ obtain in the absence and in the presence of variable amounts of glucose at 0.5 v/s: (a) [glucose] = 0, (b) [glucose] = 0.0185 M. Common conditions: $[NaBrO_3]$ = 0.0175 M, $[H_2SO_4]$ = 1 M

ACKNOWLEDGEMENTS

This work is sponsored by the National Science Foundation of China (20501001, 30760137), the Foundation of Education Committee of Anhui Province (KJ2008A118) and Rencai Foundation of Anhui University (02203105), China.

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(*Received*: 16 January 2008; *Accepted*: 30 August 2008) AJC-6801