B-Z Oscillating Reactions Catalyzed by a Tetraazamacrocyclic Nickel(II) Complex in the Pyruvic Acid-Sulfuric Acid System

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New Belousov-Zhabotinskii (B-Z) oscillating reactions catalyzed by a tetraazamacrocyclic nickel(II) complex in the $NaBrO_3$-pyruvic acid-sulfuric acid system were reported. The complex contains the unsaturated macrocyclic ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The influences of the cocentration of the component in the system and temperature on the oscillations were studied. The oscillation trajectories of the potentials of platinum electrode vs. those of bromide selective electrode are spirals but not limit cycles.

INTRODUCTION

Chemical oscillation phenomenon is an area of current interest. Belousov-Zhabotinskii (B-Z) oscillating reactions catalyzed by tetraazamacrocyclic complexes have been ·observed since 1980's.[1] In these B-Z oscillating reaction systems, both the sorts of macrocyclic complex and organic substrate effect have much marked influence on the oscillations. Our group have reported some new B-Z oscillating reaction systems involving the participation of several tetraazamacrocyclic Ni(II)[2-5] and Cu(II)[6-8] complexes in the presence of various organic substrates. Recently, it was discovered that pyruvic acid, which is an important intermediate in the energy metabolism of animals and the photosynthesis of plants, can act as an alternative organic substrate in B-Z oscillating reactions[9-12].

In this paper we report a new chemical oscillating system: $NaBrO_3$—[NiL] $(ClO)_2$—pyruvic acid—H_2SO_4, where the ligand L in the complex is 5,7,7,12,14, 14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

EXPERIMENTAL

The catalyst $[NiL](ClO_4)_2$ was prepared by known technique[13]. All the reagents were analytical grade and twice redistilled water was used. Oscillating experiments were performed in a closed glass container with a magnetic stirrer (Model 79–1, Hangzhou, China) at $20 \pm 0.5°C$ regulated by a thermostat (Model Jw-0.001, Taixian, China); the volume of the reaction is 40 mL. The reactions were followed by monitoring the changes of the potentials of platinum and bromide selective electrode. Potentials of these two electrodes vs. time were

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measured and recorded by using two ion metres (Model PXD-II, Jiangsu, China) connected to a Y-t recorder (model XWT-464, Shanghai, China); a X-Y recorder (Model LZ-3-204, Shanghai, China) was introduced to investigate the oscillation trajectories of the potentials of platinum electrode vs. those of bromide selective electrode.

RESULTS AND DISCUSSION

When $[NaBrO_3] = 0.175$ mol dm^{-3}, $[Pyr] = 0.5$ mol dm^{-3}, $[H_2SO_4] = 1.00$ mol dm^{-3}, $[NiL](ClO_4)_2 = 0.0013$ mol dm^{-3}, typical potentiometric oscillation of platinum electrode (a) and bromide selective electrode (b) was observed (Fig. 1), and the solution colour changed periodically (yellow-green-yellow). This indicated that the following chemical changes took place:
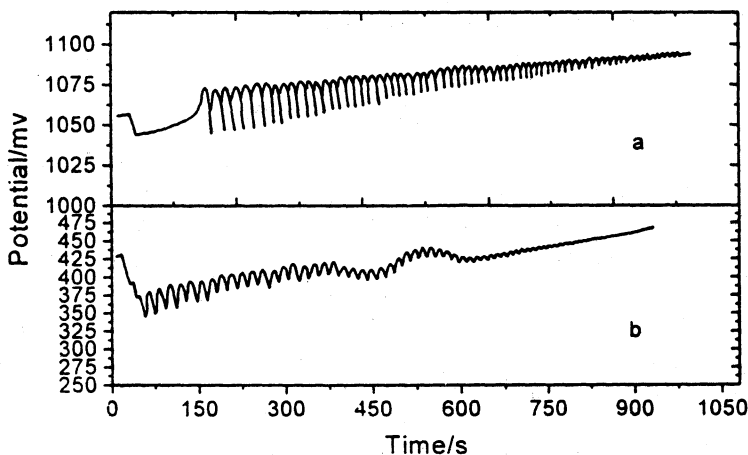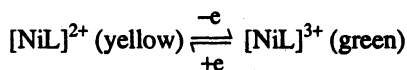
$$[NiL]^{2+} \text{ (yellow)} \underset{+e}{\overset{-e}{\rightleftharpoons}} [NiL]^{3+} \text{ (green)}$$

Fig. 1   Typical potentiometric oscillation trace of platinum electrode (a) and bromide selective electrode (b) vs. time for the system at 20°C: $[NaBrO_3] = 0.175$ mol dm^{-3}, $[Pyr] = 0.5$ mol dm^{-3}, $[H_2SO_4] = 1.00$ mol dm^{-3}, $[[NiL][(ClO_4)_2] = 0.0013$ mol dm^{-3}.

By varying concentration of one component and fixing that of the other, a series of data of critical concentrations were gotten. The range of existent oscillation of the system is shown in Table-1.

TABLE-1
THE RANGE OF EXISTENT OSCILLATION OF THE SYSTEM

NaBrO$_3$ (mol dm^{-3})	H$_2$SO$_4$ (mol dm^{-3})	Pyruvic acid (mol dm^{-3})	[NiL](ClO$_4$)$_2$ (mol dm^{-3})
0.175	1.000	0.075–1.36	1.3×10^{-3}
0.044–0.228	1.000	0.500	1.3×10^{-3}
0.175	0.300–1.050	0.500	1.3×10^{-3}
0.175	1.000	0.500	8.0×10^{-4}–4.6×10^{-3}

Variations in initial concentration of reactants resulted in obvious variation of four capital potentiometric oscillation parameters. They are inducing period (t_{in}), the amplitude of oscillation (A), the oscillation times (I) and the oscillation period (t_p, the average of first ten steps of the oscillation). The dependence of potentiometric oscillation parameters of platinum electrode on initial concentration of pyruvic acid and $NaBrO_3$ is shown in Figs. 2 and 3.
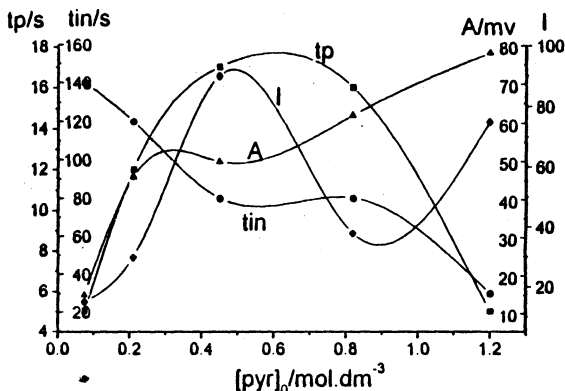

Fig. 2.   The effects of $[pyr]_0$ on the oscillation periods (t_p), inducing periods (t_{in}), the amplitude of oscillation (A) and the oscillation times (I) of platinum electrode at 20°C: $[NaBrO_3]_0 = 0.175$ mol dm^{-3}, $[H_2SO_4]_0 = 1.00$ mol dm^{-3}, $[NiL^{2+}]_0 = 1.3 \times 10^{-3}$ mol dm^{-3}
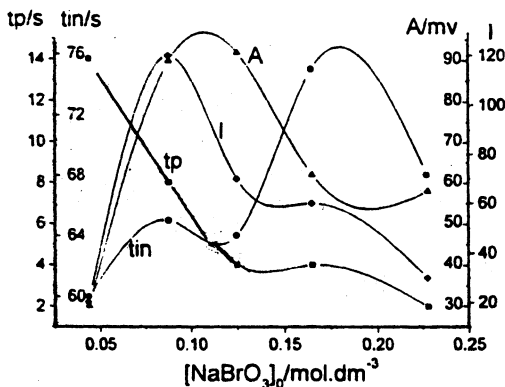

Fig. 3.   The effects of $[NaBrO_3]_0$ on the oscillation periods (t_p), inducing periods (t_{in}), the amplitude of oscillation (A) and the oscillation times (I) of platinum electrode at 20°C: $[Pyr]_0 = 0.5$ mol dm^{-3}, $[H_2SO_4]_0 = 1.00$ mol dm^{-3}, $[NiL^{2+}]_0 = 1.3 \times 10^{-3}$ mol dm^{-3}

Temperature also affected the oscillation system. Fixing the concentration of the reactants in the system as $[(NiL)^{2+}]_0 = 2.2 \times 10^{-3}$ mol dm^3, $[pyr]_0 = 0.5$ mol dm^{-3}, $[NaBrO_3]_0 = 0.175$ mol dm^{-3}, $[H_2SO_4]_0 = 0.9$ mol dm^{-3}, and investigating six potentiometric oscillation traces of platinum electrode over the temperature range of 293 ~ 318 K, both the inducing period (t_{in}) and oscillation periods (tp) were found decreased with increase in temperature (Table 2).

TABLE-2

INFLUENCE OF THE TEMPERATURE ON THE INDUCING PERIODS (t_{in}) AND THE OSCILLATION PERIODS (t_p)

t_{in}/s	54.6	33.1	20.08	13.10	7.76	4.85
t_p/s	36.6	23.3	16.4	11.02	6.70	4.17
T/K	293	298	303	308	313	318

Plotting ln ($1/t_{in}$) and ln ($1/t_p$) against $1/T$, respectively, two straight lines are obtained (Fig. 4), and the following two equations are established:

$$\ln (1/t_{in}) = -9.69 \ 1/T + 28.9 \qquad \text{(the correlation coefficient } R_1 \text{ is 0.9977)}$$

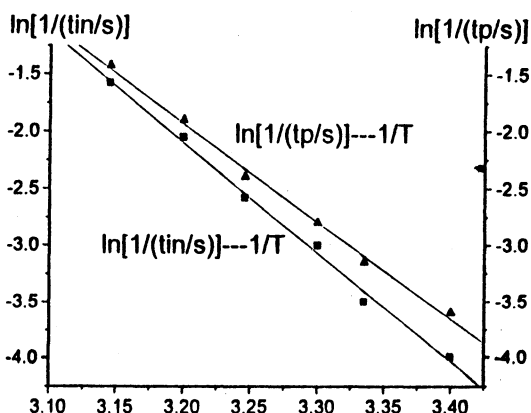$$\ln (1/t_p) = -8.63 \ 1/T + 25.68 \qquad \text{(the correlation coefficient } R_2 \text{ is 0.9979)}$$

Fig. 4.   The plot of ln ($1/t_{in}$) against $1/T$ and ln ($1/t_p$) against $1/T$: $[NiL^{2+}]_0 = 2.2 \times 10^{-3}$ mol dm^{-3}, $[Pyr]_0 = 0.5$ mol dm^{-3}, $[NaBrO_3]_0 = 1.175$ mol dm^{-3}, $[H_2SO_4]_0 = 0.9$ mol dm^{-3}

From these equations, the apparent activation energy of inducing periods and the apparent activation energy of oscillation periods are calculated to be 8.06×10^4 J mol^{-1} and 7.17×10^4 J mol^{-1}, respectively.

A X-Y recorder showed that the oscillation trajectories of potentials of platinum electrode vs. those of bromide selective electrode are spirals instead of limit cycles[14], (Fig. 5). This indicated that the mechanism of this system might be different from that of B-Z oscillation system catalyzed by Ce(III).

On addition of acetonitrile to reaction mixture at a concentration of 3.75×10^{-3} mol dm^{-3}, the duration and amplitude of the oscillations were decreased. 1.9×10^{-3} mol dm^{-3} H_2O_2 in the system inhibits oscillation temporarily. This indicates that free radical steps are involved in the mechanism of the oscillation.

On addition of Ag^+ to the oscillation system at a concentration of 6.25×10^{-5} mol dm^{-3} or Hg^{2+} at a concentration of 9.2×10^{-5} mol dm^{-3}, the potential of bromide selective electrode decreased temporarily because of the formation of

AgBr or $[HgBr_4]^{2-}$. Apparently the concentration of Br^- also acts as an on-off switch in $NaBrO_3$—pyruvic acid—H_2SO_4—[NiL]$(ClO_4)_2$ oscillation system.

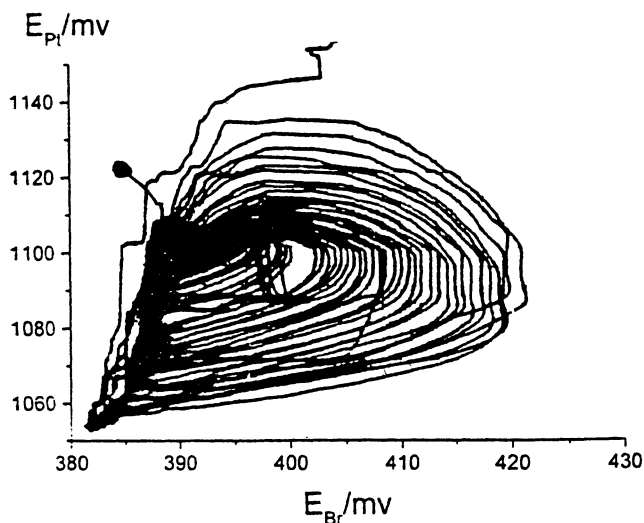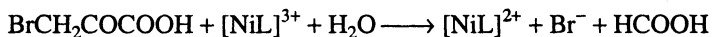If the concentration of vitamin C in the oscillation system reaches 5×10^{-3}

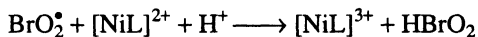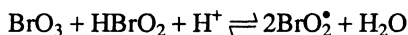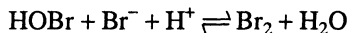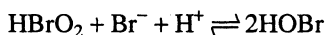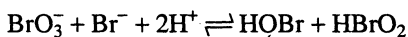Fig. 5   The oscillation trajectories of potentials of platinum electrode vs. those of bromide selective electrode at 20°C: $[NaBrO_3]_0 = 1.175$ mol dm^{-3}, $[Pyr] = 0.5$ mol dm^{-3}, $[H_2SO_4]_0 = 0.925$ mol dm^{-3}, $[NiL^{2+}]_0 = 2.2 \times 10^{-3}$ mol dm^{-3}

mol dm^{-3} or that of glucose reaches 1×10^{-2} mol dm^{-3}, the chemical oscillations were inhibited temporarily, similar to the effect of vitamin C in Ce(III) catalyzing B-Z ocillation system[15]. This shows that the $HBrO_2$ is still a very important intermediate in the system.

According to experimental results and literature[16], the mechanism for the oscillation reactions of the system is proposed tentatively as follows:

$$BrO_3^- + Br^- + 2H^+ \rightleftharpoons HOBr + HBrO_2$$

$$HBrO_2 + Br^- + H^+ \rightleftharpoons 2HOBr$$

$$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O$$

$$BrO_3 + HBrO_2 + H^+ \rightleftharpoons 2BrO_2^{\bullet} + H_2O$$

$$Br_2 + CH_3COCOOH \longrightarrow Br^- + H^+ + BrCH_2COCOOH$$

$$BrO_2^{\bullet} + [NiL]^{2+} + H^+ \longrightarrow [NiL]^{3+} + HBrO_2$$

$$BrCH_2COCOOH + [NiL]^{3+} + H_2O \longrightarrow [NiL]^{2+} + Br^- + HCOOH$$

$$+ CH_3COOH + H^+$$

ACKNOWLEDGEMENT

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