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A New Chemical Oscillator: Belousov-Zhabotinskii-Type Reaction Catalyzed by a Macrocyclic Nickel(II) Complex

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A new B-Z oscillator, the $NaBrO_3$-malic acid-H_2SO_4-$[NiL](ClO_4)_2$ system (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), is reported. The oscill- ating reactions are measured by monitoring the changes of the potentials of platinum and bromide selective electrode. The experimental results indicate that the concentration of bromide ion (Br^-) can act as an on-off switch in oscillating reaction while free radicals and $HBrO_2$ may be involved in the reaction process. The influences of the concentration of the component in the system and temperature on the oscillations are studied. It is found that oscillation period (T_p) is dependent on the initial concentrations of malic acid or H_2SO_4 but independent of the initial concentrations of $NaBrO_3$.

Key Words: Belousov-Zhabotinskii reaction, Ni(II) macrocyclic complex, Oscillator.

INTRODUCTION

The so-called Belousov-Zhabotinskii (BZ) reaction, the oscillatory oxidation of several organic compounds by acid bromate media in the presence of a catalyst (Ce^{3+}, Mn^{2+}, $Fe(phen)_3^{2+}$ or $Ru(bipy)_3^{2+}$), is the most studied classical oscillator[1–4].

Recently, BZ reaction catalyzed by tetraazamacrocyclic Ni(II) (or Cu(II)) complexes[5, 6] has attracted attention since they bring about new types of oscillators that are different from the classical one. However, only limited examples have been reported so far, such as the oscillators involving malonic acid[7], gallic acid[8] or pyruvic acid[9, 10] as the organic substrates. A continuous desire to look for more oscillators of these kinds was motivated by the fact that tetraazamacrocyclic complexes are of considerable importance in catalytic properties as well as in biochemical processes.

The BZ oscillators based on malic acid have been investigated and, in these oscillators, the catalysts[11–14] were Ce^{3+}, Mn^{2+}, $Fe(phen)_3^{2+}$, $Ru(bipy)_3^{2+}$ or Cu(II) tetraazamacrocyclic complexes. In order to search for the possibilities that Ni(II) macrocyclic complex may participate in oscillating reactions, a nickel complex

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$[NiL](ClO_4)_2$, L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, is investigated. As a result, a new oscillator, $NaBrO_3$-$[NiL](ClO_4)_2$-malic acid-H_2SO_4, is here reported.

EXPERIMENTAL

The perchlorate salt of $[NiL](ClO_4)_2$ was synthesized as per reported procedure[15] identified by its IR elemental analyses. Sulfuric acid (AR) and malic acid (AR) were used as such without purification. Sodium bromate (AR) was recrystallized in hot water twice to remove Br^- and other impurities, double-distilled water was used in all case.

A glass container, thermostated at 22 ± 0.2°C, was filled, in this sequence: an aqueous of sodium bromate, an aqueous of sulfuric acid, an aqueous of malic acid and an aqueous of $[NiL](ClO_4)_2$, at intervals of 1 min. The mixture was homogenized by magnetic stirring. Changes of the potential of the sample were followed by a platinum electrode and a bromide selective electrode. The reference electrode was a saturated calomel electrode connected *via* a salt bridge containing 10% KNO_3. Potentials of these two electrodes were measured with two digital voltmeters (DVM) and recorded by using a y-t recorder. The volume of the reaction is 40 mL.

RESULTS AND DISCUSSION

Fig. 1 shows a typical oscillation trace of bromide selective electrode (a) and platinum electrode (b). This typical oscillation under standard conditions ($[NaBrO_3] = 0.0175$ M, [malic acid] = 0.1 M, $[H_2SO_4] = 0.75$ M, $[[NiL](ClO_4)_2] = 0.0030$ M), had an oscillation amplitude of 50 mv (Br) or 12 mv (Pt), a total of 43 oscillations, a total duration of 187 min, an oscillation period of 3.4 min. During oscillations, the solution colour changed periodically between yellow and green, showing the oscillations between $[NiL]^{2+}$ and $[NiL]^{3+}$

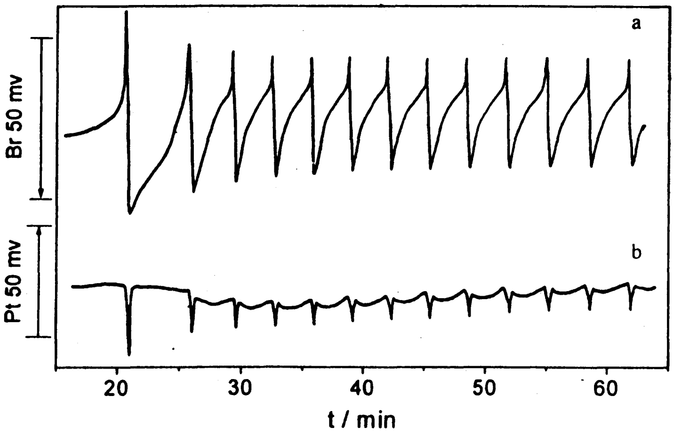

Fig. 1. Typical potentiometric oscillation trance of bromide selective electrode (a) and platinum electrode (b) *vs.* time for the system at 22°C: $[NaBrO_3] = 0.0175$ M, [malic acid] = 0.1 M, $[H_2SO_4] = 0.75$ M, $[[NiL](ClO_4)_2] = 0.003$ M

When several aliquots of solution of $[NiL](ClO)_2$ or $NaBrO_3$ were successively added to the system in which the oscillations have ceased, the oscillations could be revived to some extent, but addition of malic acid cannot revive oscillation at all. These phenomena show that the damping of oscillations is neither due to the depletion of malic acid nor due to the accumulation of products that inhibit oscillations, but owing to the consumption of the catalyst and $NaBrO_3$.

In order to understand the role of each consitituent in the oscillatory reaction, the effect of varying the concentration of constituents, taken one at a time, was considered.

Bromate variation: The sodium bromate concentration was varied in the range of 0.0044–0.0525 M. The oscillation period remained constant with the increasing concentration of bromate.

Sulfuric acid variation: The concentration of sulfuric acid was varied in the range of 0.287–1.73 M. When the other reactant concentrations were kept constant at standard conditions, the oscillation period (t_p) decreased with the increasing acid concentration. Concentrations larger than 1 M lead to a decrease in the number of oscillations.

Malic acid variation: Oscillations were observed in the wide concentration range of 0.000025–0.8 M. The oscillation period (t_p) decreases when the concentration of malic acid increases in the range of 0.005–0.4 M (Fig. 2).

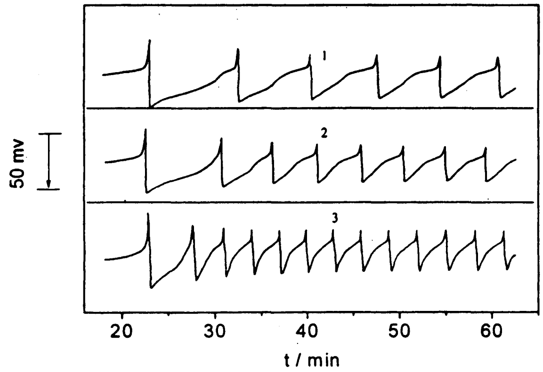

Fig. 2. The effects of [malic acid] on potential traces of bromide selective electrode *vs.* time for the system at 22°C: (1) [malic acid] = 0.005 M, (2) [malic acid] = 0.025 M, (3) [malic acid] = 0.1 M. Concentrations: $[NaBrO_3] = 0.0175$ M, $[H_2SO_4] = 0.75$ M, $[[NiL](ClO_4)_2] = 0.003$ M

Oscillations were observed, when the concentrations of $[NiL](ClO_4)_2$ exceeded 4.65×10^{-4} M. The oscillation periods of the system were proportional to the initial concentrations of $[NiL](ClO_4)_2$, while the initial concentrations of $NaBrO_3$, malic acid and H_2SO_4 were fixed.

The oscillation period (t_p) as a function of the initial concentration of malic acid and H_2SO_4 is given in Figs. 3 and 4.

Fig. 3 represents the plot of Ln t_p against Ln [malic acid]$_0$. A linear graph is obtained according to the following equation:

$$\text{Ln } t_p(s) = 4.55 + (-0.293) \text{ Ln [malic acid]}_0 \qquad (1)$$

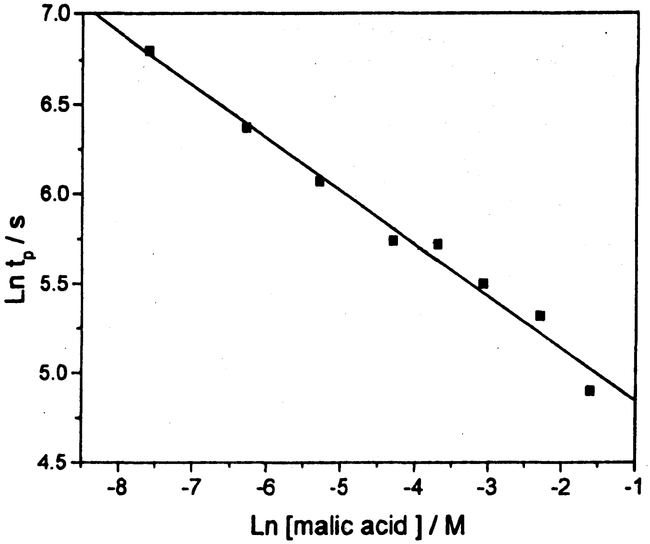

Fig. 3. The plot of Ln t_p against Ln [malic acid]: $[NaBrO_3] = 0.0175$ M; $[H_2SO_4] = 0.75$ M; $[NiL](ClO_4)_2] = 0.003$ M; 0.0005 M ≤ [malic acid] ≤ 0.4 M, R = –0.9917.

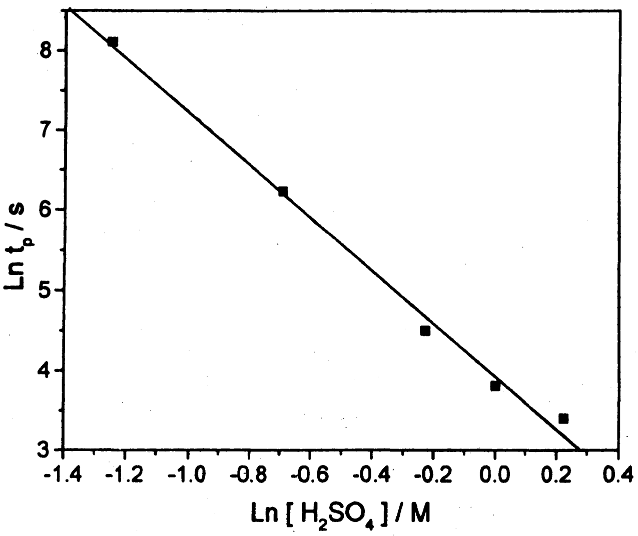

Fig. 4. The plot of Ln t_p against Ln $[H_2SO_4]$: $[NaBrO_3] = 0.0175$ M; [malic acid] = 0.1 M; $[NiL](ClO_4)_2] = 0.003$ M, R = –0.9969

So t_p(s) can also be expressed as:

$$t_p(s) = 94.6[\text{malic acid}]_0^{-0.293} \tag{2}$$

As shown in Fig. 4, a straight line is obtained by plotting Ln t_p against Ln $[H_2SO_4]_0$. From this straight line, following equation is established:

$$\text{Ln } t_p(s) = 3.92 + (-3.31) \text{ Ln } [H_2SO_4]_0 \tag{3}$$

So t_p can be expressed as:

$$t_p(s) = 50.4[H_2SO_4]_0^{-3.31} \tag{4}$$

The above results can be summarized in the general expression (5),

$$t_p(s) = 0.25[\text{malic acid}]_0^{-0.293}[H_2SO_4]_0^{-3.31} \tag{5}$$

with $[[NiL](ClO_4)_2] = 3.0 \times 10^{-3}$ M, $[NaBrO_3] = 0.0175$ M and temperature = 22 ± 0.2°C.

The temperature was varied in the range of 295–313 K and the oscillations were provoked. It was found that oscillation periods (t_p) decreased with an increase in temperature (T) (Table-1).

TABLE-1
INFLUENCE OF TEMPERATURE ON THE OSCILLATION PERIODS (t_p)

T (K)	t_p (s)
295	162
297	151
299	126
301	105
305	84
307	70
309	60

Plotting Ln ($1/t_p$) against 1/T, a straight line is obtained (Fig. 5) and the following equation is established:

Ln ($1/t_p$) = –6.55 (1/T) + 17.09 (the correlation coefficient R is 0.9963)

From this equation, the apparent activation energy is calculated to be 54.4 kJ mol^{-1}

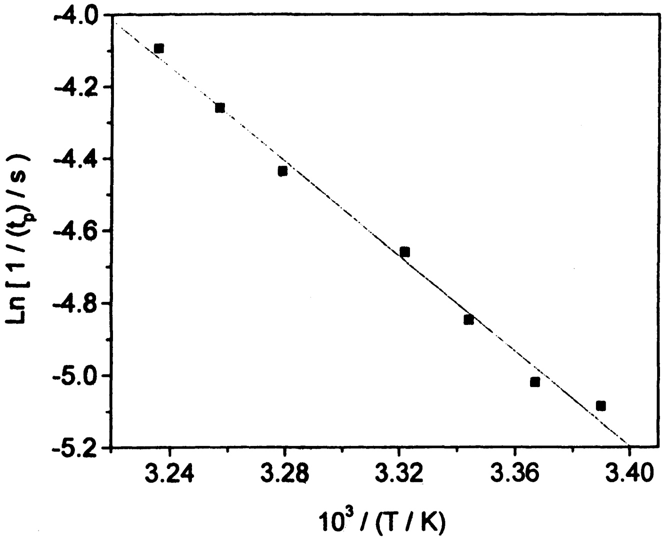

Fig. 5. The plot of Ln ($1/t_p$) against 1/T: $[(NiL)^{2+}]_0 = 3 \times 10^{-3}$ M; $[\text{malic acid}]_0 = 0.1$ M; $[NaBrO_3]_0 = 0.0175$ M; $[H_2SO_4]_0 = 0.75$ M, R = 0.9963

Addition of radical scavengers: Varadi and Beck[16] have reported that the periodic reactions of the BZ system were inhibited by radical scavengers like acrylonitrile or H_2O_2 and they occurred by a free-radical mechanism. In the present case, the duration and amplitude of the oscillations were decreased on adding 6×10^{-3} M solution of acrylonitrile. And 9.9×10^{-3} M solution of H_2O_2 present in the system inhibits oscillation temporarily. This indicates that free radical steps are involved in the mechanism of the oscillating reaction.

Addition of vitamin C or glucose: Zhao[17] reported that the chemical oscillations were inhibited temporarily by addition of vitamin C. For $NaBrO_3$-$[NiL](ClO_4)_2$-malic Acid -H_2SO_4 system, the chemical oscillations were inhibited temporarily when the concentration of vitamin C present in the oscillation system reaches 1.2×10^{-3} M or that of glucose reaches 1.0×10^{-2} M. This shows that $HBrO_2$ is still a very important intermediate in the system.

Addition of Ag$^+$: It is found that when 2.5×10^{-5} M $AgNO_3$ is present in the oscillation system, oscillations of the potential of bromide selective electrode can be temporarily suppressed due to the formation of AgBr. Apparently, the concentration of bromide ion (Br^-) can act as an on-off switch in oscillating reaction[18].

According to experimental results and literature[18], the mechanism for the oscillation reactions of the system is proposed tentatively as follows:

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

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

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

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

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

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

$$HOOCCHOHBrCHCOOH + 4[NiL]^{3+} + 3H_2O \longrightarrow 4[NiL]^{2+} + Br + 2HCOOH + 2CO_2 + 7H^+ \quad (7)$$

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