

New B-Z Oscillating Reactions Involving a Tetraazamacrocyclic Nickel(II) Complex

GANG HU*, ZHI-QIANG XU, FU-XING XIE, LIN HU† and SHI-SHENG NI
Department of Chemistry, Anhui University, Hefei, 230 039, P.R. China

New Belousov-Zhabotinskii reactions using a tetraazamacrocyclic nickel complex as catalyst in NaBrO₃-pyruvic acid-H₂SO₄ system have been investigated. This complex contains unsaturated macrocyclic ligand 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-1,10,12-triene. The concentration oscillations of this system are damped rapidly due to the consumption of the catalyst. Acrylonitrile, H₂O₂, vitamin C, glucose or CCl₄ present in the system can inhibit the oscillations. Unlike the classical B-Z oscillating system, variations in the initial concentrations of the components markedly affect the potentiometric oscillation parameters and the shapes of the oscillations.

INTRODUCTION

Oscillating chemical reactions are of considerable interest due to their unusual kinetic behaviour and the possibility of their use as chemical models for oscillating biosystem. Study of tetraazamacrocyclic complexes catalyzed Belousov-Zhabotinskii (B-Z) oscillating reactions have been reported in literature¹. Recently, we have described a number of new B-Z oscillating reaction systems catalyzed by transition metal complexes with tetraazamacrocyclic ligands²⁻¹³. These tetraazamacrocyclic ligands, the carbon member of the ring from 13 to 15, contain two or four double bonds. Until now, the oscillating reactions involving tetraazamacrocyclic ligands that contain three double bonds have not yet been reported. In continuation with our work in this field, we investigated oscillating reactions catalyzed by a tetraazamacrocyclic nickel(II) complex, [NiL](ClO₄)₂, where ligand L is 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-1,10,12-triene.

EXPERIMENTAL

Oscillating experiments were performed in a closed glass container with a magnetic stirrer (Model 79-1, Hangzhou, China) at 20 ± 0.5°C regulated by a thermostat (Model JW-0.001, Taixian, China). The volume of the reaction is 40 mL. The redox potential and instantaneous bromide concentration were monitored by a platinum electrode and bromide selective electrode, respectively. The reference electrode was a saturated calomel electrode connected *via* a salt bridge containing 10% KNO₃. Potentials of these two electrodes *vs.* time were measured by using two ion meters (Model PXD-II, Jiangsu, China) connected to a Y-t recorder (model XWT-464, Shanghai, China) to display the potentiometric trace. From potentiometric oscillation trace, capital potentiometric oscillation parameters such as inducing period (*t*_{in}), the amplitude of oscillation (A), the

†East China Jiaotong University, Nanchang 330013, P.R. China.

oscillation time (I) and the oscillation period (t_p , the average of first five steps of the oscillation) were recorded.

The catalyst $[\text{NiL}](\text{ClO}_4)_2$ was prepared by the method of Cummings¹⁴ and Hipp¹⁵ and identified by IR spectra and elemental analysis. All the reagents were analytical grade and double distilled water was used.

RESULTS AND DISCUSSION

$[\text{NiL}]^{2+}$ -Catalyzed oscillating reactions: After catalytic quantities of $[\text{NiL}](\text{ClO}_4)_2$ solution were added to the solution containing NaBrO_3 , H_2SO_4 and pyruvic acid, damped potentiometric oscillations of platinum electrode (a) and bromide selective electrode (b) were observed (Fig. 1). The solution colour changed

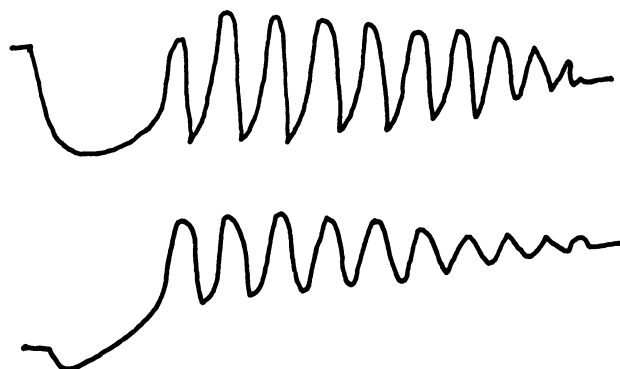
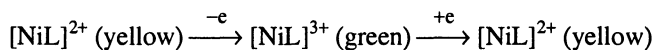


Fig. 1. Typical potentiometric oscillation trace of platinum electrode (a) and bromide selective electrode (b) vs. time for the system at 20°C: $[\text{NaBrO}_3] = 0.28 \text{ mol dm}^{-3}$, $[\text{Pyr}] = 0.4 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.80 \text{ mol dm}^{-3}$, $[[\text{NiL}](\text{ClO}_4)_2] = 0.003 \text{ mol dm}^{-3}$

periodically (yellow-green-yellow) due to the following one reduction-oxidation cycle of the catalyst:



When several aliquots of solution of $[\text{NiL}](\text{ClO}_4)_2$ were successively added to the system in which the oscillations have ceased, the oscillations could be revived to some extent, but addition of solution of NaBrO_3 or pyruvic acid cannot revive oscillation at all. These phenomena show that the damping of oscillations is neither due to the depletion of pyruvic acid and bromate nor due to the accumulation of products that inhibit oscillations, but owing to the consumption of the catalyst.

Reactant concentration for the oscillation system: Extensive studies have revealed sequential concentration oscillations in NaBrO_3 -pyruvic acid- H_2SO_4

-[NiL](ClO₄)₂ system. The main component oscillations observed are shown in Table-1.

TABLE-1
THE MAIN COMPONENT OSCILLATIONS OBSERVED

NaBrO ₃ (mol dm ⁻³)	H ₂ SO ₄ (mol dm ⁻³)	Pyruvic acid (mol dm ⁻³)	[NiL](ClO ₄) ₂ (mol dm ⁻³)
0.21	0.80	0.35–0.56	3.0 × 10 ⁻³
0.13–0.38	0.80	0.50	3.0 × 10 ⁻³
0.21	0.5–0.9	0.50	3.0 × 10 ⁻³
0.21	0.5	0.50	(2.4–6.2) × 10 ⁻³

Effect of radical scavengers: Varadi and Beck¹⁶ have reported that homogeneous periodic reactions of a B–Z system were inhibited by radical scavengers (for example, acrylonitrile and H₂O₂), and hence have a free radical mechanism. For the NaBrO₃-pyruvic acid-H₂SO₄ -[NiL](ClO₄)₂ system, the duration and amplitude of the oscillations were decreased on adding 5 × 10⁻³ mol dm⁻³ solution of acrylonitrile and 3.1 × 10⁻³ mol dm⁻³ solution of H₂O₂ present in the system inhibited oscillation temporarily. This indicates that there are free radical steps involved in the mechanism of the oscillation.

Effect of Ag⁺ or Hg²⁺: When 5 × 10⁻⁵ mol dm⁻³ solution of Ag⁺ or 7.1 × 10⁻⁵ mol dm⁻³ solution of Hg²⁺ was added to the oscillation system, the potential of bromide selective electrode decreased temporarily due to the formation of AgBr or [HgBr₄]²⁻. Apparently Br⁻ is a control intermediate, the variation of concentration of Br⁻ can “turn on” and “turn off” certain chemical processes in the oscillatory reactions¹⁷.

Effect of vitamin C or glucose: When the concentration of Vitamin C present in the oscillation system exceeds 5.5 × 10⁻³ mol dm⁻³ or that of glucose exceeds 1.5 × 10⁻² mol dm⁻³, the chemical oscillations were inhibited temporarily, similar to the effect of vitamin C in a Ce(III) catalyzing B-Z oscillation system¹⁸. This shows that the HBrO₂ is still a very important intermediate in the system.

Effect of CCl₄: Addition of small quantity (0.5 mL) of CCl₄ did not stop the oscillations whereas addition of sufficient amount of CCl₄ (1.5 mL) during oscillations immediately stopped the oscillations. Similar results were reported by Rastogi *et al.*¹⁹ while investigating a Ce(III) catalyzing B-Z oscillation system. The phenomenon implies that free Br₂ is also an important intermediate in the oscillating reactions.

Effect of initial concentration: Somes²⁰ reported a ferroin-catalyzed oscillating system in which oscillation period is dependent on initial concentration. To

NaBrO₃-pyruvic acid-H₂SO₄-[NiL](ClO₄)₂ system, variations in initial concentration of reactants markedly affected capital potentiometric oscillation parameters such as inducing period (*t*_{in}), the amplitude of oscillation (*A*), the oscillation time (*I*) and the oscillation period (*t*_p), and hence changed the shape of oscillations. Marked changes in potentiometric oscillation parameters of platinum electrode

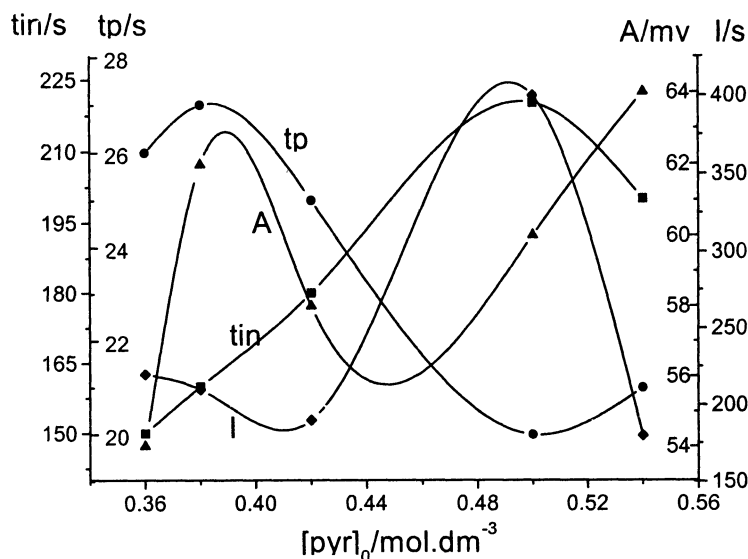


Fig. 2. The effects of [pyr]₀ on the oscillation period (*t*_p), inducing period (*t*_{in}), the amplitude of oscillation (*A*) and the oscillation time (*I*) of platinum electrode at 20°C: [NaBrO₃]₀ = 0.21 mol dm⁻³, [H₂SO₄]₀ = 0.8 mol dm⁻³, [NiL²⁺]₀ = 3 × 10⁻³ mol dm⁻³.

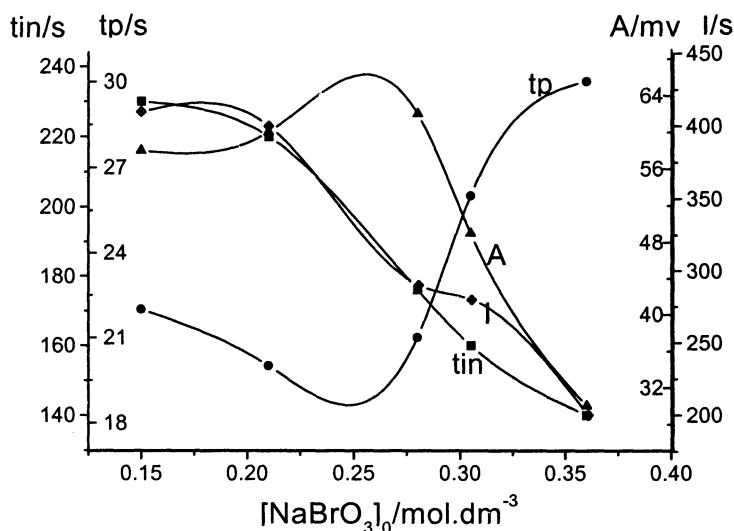


Fig. 3. The effects of [NaBrO₃]₀ on the oscillation period (*t*_p), inducing period (*t*_{in}), the amplitude of oscillation (*A*) and the oscillation time (*I*) of platinum electrode at 20°C: [pyr]₀ = 0.5 mol dm⁻³, [H₂SO₄]₀ = 0.8 mol dm⁻³, [NiL²⁺]₀ = 3 × 10⁻³ mol dm⁻³.

as a function of initial concentration of pyruvic acid and NaBrO_3 are shown in Fig. 2 and 3, respectively.

Effect of the temperature: A series of potentiometric oscillation traces of platinum electrode were measured at different temperatures but at constant $[\text{NaBrO}_3]_0$, $[\text{pyr}]_0$, $[\text{H}_2\text{SO}_4]_0$ and $[\text{NiL}^{2+}]_0$. It was found that both the inducing period (t_{in}) and oscillation period (t_p) decrease with increasing temperature which may be due to the increase in rates of reactions with rise in temperature (Table-2).

TABLE-2
INFLUENCE OF THE TEMPERATURE ON THE INDUCING PERIODS (t_{in})
AND THE OSCILLATION PERIODS (t_p)

T/K	t_{in}/s	t_p/s
298	175.90	24.50
303	104.70	17.50
308	53.50	11.94
313	27.11	7.77
318	14.87	4.90
323	7.77	3.30

Fig. 4. represents the plot of $\ln(1/t_{in})$ and $\ln(1/t_p)$ against $1/T$, respectively. A satisfactory linearity has been obtained according to the following two equations:

$$\ln(1/t_{in}) = -12.87 \quad 1/T + 37.8 \quad (\text{the correlation coefficient } R_1 \text{ is } 0.9977)$$

$$\ln(1/t_p) = -8.25 \quad 1/T + 24.33 \quad (\text{the correlation coefficient } R_2 \text{ is } 0.9983)$$

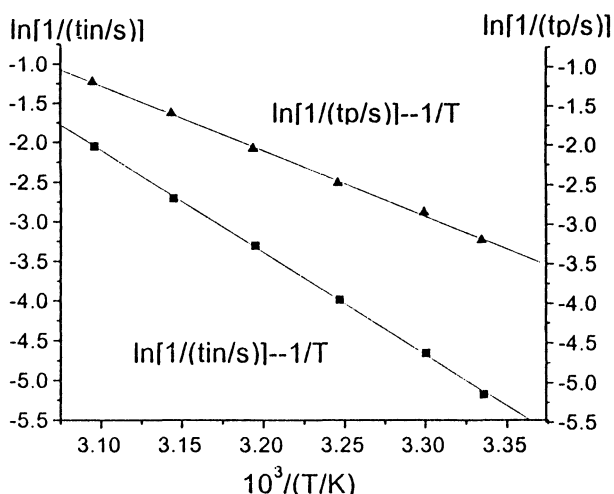
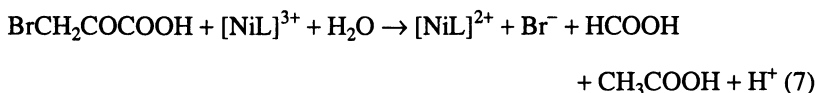
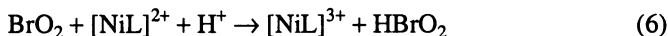
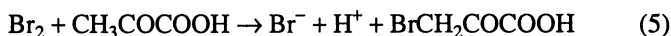
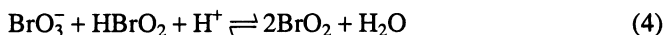
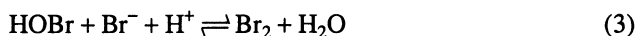
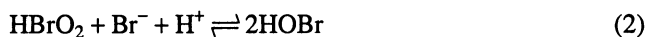
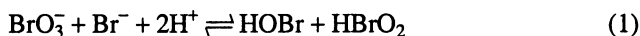


Fig. 4. The plot of $\ln(1/t_{in})$ and $\ln(1/t_p)$ against $1/T$: $[\text{NiL}^{2+}]_0 = 3 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{pyr}]_0 = 0.4 \text{ mol dm}^{-3}$, $[\text{NaBrO}_3]_0 = 0.28 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4]_0 = 0.8 \text{ mol dm}^{-3}$,

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

Probable mechanism: Different oscillation mechanisms were proposed to elucidate the general regularities of oscillating systems. FKN mechanism¹⁷ has been the most effective one and was strongly supported by modeling computations^{21,22}. Here, on the basis of above experimental results, a simplified FKN mechanism is tentatively used for the oscillating reactions. This mechanism involves seven main kinetically distinct reactions and is described by eqns. (1)–(7).



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