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# The Study of Alanine Oscillating Reaction Catalyzed by Tetraazamacrocyclic Nickel(II) Complex[1]

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**Abstract**—A closed oscillation system comprised of alanine, $KBrO_3$, $H_2SO_4$ and acetone catalyzed by tetraazamacrocyclic nickel(II) complex is introduced, and quantitatively characterized with kinetic parameters, namely the rate constant ($k_{in}$, $k_p$), the apparent activation energy ($E_{in}$, $E_p$) and pre-exponential constant ($A_{in}$, $A_p$) and thermodynamic functions ($\Delta H_{in}$, $\Delta G_{in}$, $\Delta S_{in}$ and $\Delta H_p$, $\Delta G_p$, $\Delta S_p$), where indexes "in" and "p" mean "induction period" and "oscillation period," respectively. The results indicate that tetraazamacrocyclic nickel(II) complex can catalyze alanine oscillating reaction and the reaction corresponds exactly to the feature of irreversible thermodynamics as the entropy of system is negative.

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The macrocyclic ligand and its complexes, which have similar structure to some important metal enzymes (vitamin $B_{12}$, chlorophyl, haemachrome and so on) in human body, are important in biomimetic chemistry, biomedical metal enzyme simulation, cell membrane transport and supramolecular assembly [1–3]. For example, 4-aza-14 macrocyclic crown ethers are a class of Curtis macrocycles which received widespread attention [4–6]. Thereinto, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclododecane has excellent coordination properties and can form complexes with most of the metal ions. These compounds with supermolecular recognition features, fluorescence and luminescence properties have a wide range of potential applications in chemistry and biomedical areas [7, 8].

Chemical oscillation is a phenomenon that some state variables (concentration, potential, etc.) in this chemical system change cyclically with time and space. The well-known Belousov–Zhabotinskii (BZ) oscillating reaction is such a system with organic acids as the oscillating substance catalyzed by Ce ion [9–11]. Afterwards, other oscillating systems have been developed with $Mn^{2+}$, $Fe(phen)_3^{2+}$, and tetraazamacrocyclic complex as the catalysts [12–14]. Recently nickel(II) complexes has been found as a new catalyst for the BZ reaction between gallic acid, pyrogallic acid, pyruvic acid and other organic substrates [15–18]. Here, for the first time, we show that amino acids, which are the essential substances in biological body, can be used as the oscillating substrate in a closed oscillation system catalyzed by nickel(II) complex (denoted as $[NiL(ClO_4)_2]$, where L is 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazabutadecacyclo-7,14-diene). The kinetic parameters (the rate constant, the apparent activation energy and pre-exponential constant) of the oscillatory induction period and oscillation period of this oscillation system were determined and the thermodynamic functions were derived, respectively. The results show that the oscillation system is a non-equilibrium system with dissipative structure.

## EXPERIMENTAL SECTION

### *Apparatus and Reagents*

CHI 660D electrochemical analyzer (Shanghai Chen Hua Instrument), MF-3 elemental analyzer, Enraf-Nonius CAD4SDP44 four-circle diffractometer, CS501 superheated thermostat (Shanghai Experimental Instrument Factory), ML2902 magnetic stirrer (Shanghai Pujiang Instrument Factory), 213-type platinum electrode, and 217-type saturated calomel electrode (SCE) were used.

The reaction was conducted in glass reactor with a thermostat jacket (50 ml). Alanine (Ala) was biochemical reagent, other reagents were of analytical grade. $NiL(ClO_4)_2$ was synthesized according to the method described in literature [19]. All stock solutions were prepared separately in doubly distilled water.

### *Experimental Methods*

**Synthesis and characterization of $NiL(ClO_4)_2$.** According to literature [19], $NiL(ClO_4)_2$ was synthesized and characterized by elemental analysis and X-ray diffraction method (see Fig. 1). It is a bright yellow crystal with the formula $C_{16}H_{32}N_4Cl_2O_8Ni$ (calcu-

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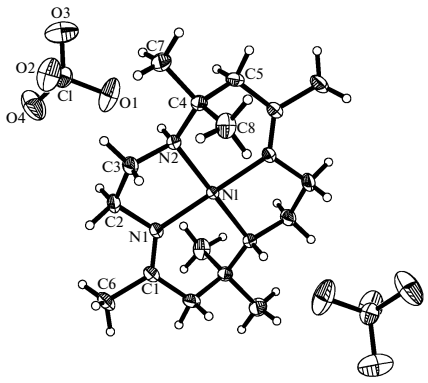


**Fig. 1.** Structure unit of $C_{16}H_{32}N_4Cl_2O_8Ni$.

lated composition, %: C 35.80, H 6.01, N 10.51; found, %: C 35.71, H 5.95, N 10.41). These were consistent with literature values.

Crystal structure: molecular formula $C_{16}H_{32}N_4Cl_2O_8N_i$, M = 538.07, monoclinic, space group *P*2(1)/c. Crystal size: 0.48 mm × 0.38 mm × 0.24 mm. Cell parameters: $a = 10.268(2)$ Å, $b = 10.756(1)$ Å, $c = 10.893(2)$ Å, $\alpha = 90.00°$, $\beta = 111.40(1)°$, $\gamma = 90.00°$, $V = 1120.1(3)$ Å$^3$, $Z = 2$, $Dx = 1.595$ mg/m$^3$, $\mu = 1.155$ mm$^{-1}$, $F(000) = 564$, $R = 0.0422$, $Rw = 0.0847$.

**Oscillating reaction.** Oscillating reaction was conducted in a glass jacketed reactor with a thermostat and under magnetic stirring. The reactor temperature was controlled at 303 ± 0.2 K. The total solution volume was 50 ml. $H_2O$, $H_2SO_4$, alanine, $NiL(ClO_4)_2$, and acetone (**Act**) were sequentially added into the above mentioned glassware. Finally, $KBrO_3$ was added after the solution reached a constant temperature at 303 ± 0.2 K. CHI 660D electrochemical analyzer was used to determine change of the redox potential ([Ox]/[Red]) with time by adjusting the concentration of each component of oscillating system with 213-type platinum electrode as the indicator electrode and 217-type SCE as the reference electrode.

## RESULTS AND DISCUSSION

### *Oscillation Occurrences*

The oscillation system was optimized with good reproducibility by adjusting the concentration of each component. Low concentration of catalyst and high concentration of acid were found to be the key factors for the oscillation. A typical oscillating curve ($T = 303$ K) is shown in Fig. 2, while the initial concentrations in oscillating system were (in mol/dm$^3$): $[KBrO_3]_0 = 0.040$, $[Ala]_0 = 0.080$, $[H_2SO_4]_0 = 1.693$, $[Act]_0 = 0.081$, $[NiL(ClO_4)_2]_0 = 0.0149$.

As seen in Fig. 2, the system started oscillating after about 5 min of the induction period. The amplitude early in the oscillatory curve was not uniform, but after several groups of the regular oscillation, the amplitude of the unique oscillation curve became stable. A typical duration of these oscillations is only about 1.5 h because of degradation of the closed system followed by a color change of the solution from light yellow to dark green.

### *The Concentration Ranges of Reactants*

In the oscillation system, the concentration ranges of one reagent can be obtained by fixing the concentration of all other reagents (cf. Table 1).

### *Dynamics Parameters of the Oscillation*

**The activation energy during induction and oscillation periods [20].** During the induction period, the reaction rate markedly increased with increasing temperature of the solution, resulting in reduced oscillation period and the oscillation duration. In our system, the temperature was controlled below 40°C to maximize the activity of amino acids.

By plotting $\ln(1/t_{in})$ or $\ln(1/t_p)$ vs. $1/T$ (Fig. 3) the apparent activation energy during the induction period ($E_{in} = 69.53$ kJ/mol) and the oscillation period ($E_p = 37.84$ kJ/mol) were obtained. The pre-exponential constants, $A_{in}$ and $A_p$, can be obtained from the

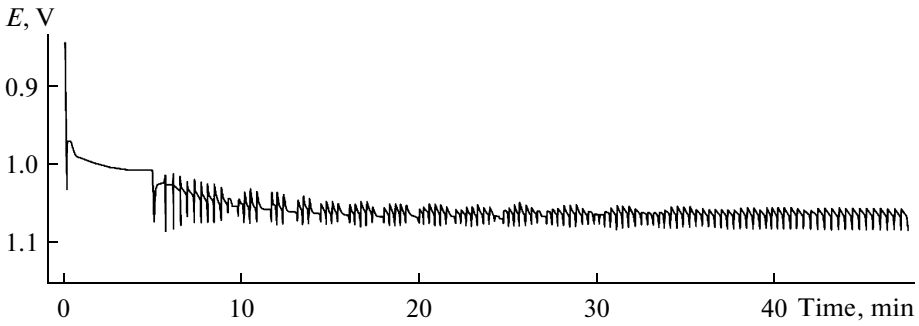


**Fig. 2.** Typical oscillating curve of Ala system using $NiL(ClO_4)_2$ as the catalyst.

**Table 1.** Concentration of the reactants in Ala oscillating system (mol/dm$^3$)

| Entry | $[Ala]_0$ | $[KBrO_3]_0$ | $[H_2SO_4]_0$ | $[NiL(ClO_4)_2]_0$ | $[Act]_0$ |
|---|---|---|---|---|---|
| 1 | 0.080 | 0.012–0.058 | 1.693 | 0.0149 | 0.081 |
| 2 | 0.032–0.169 | 0.040 | 1.693 | 0.0149 | 0.081 |
| 3 | 0.080 | 0.040 | 0.812–2.429 | 0.0149 | 0.081 |
| 4 | 0.080 | 0.040 | 1.693 | 0.0112–0.0398 | 0.081 |
| 5 | 0.080 | 0.040 | 1.693 | 0.0149 | 0.027–0.162 |

intercept of the corresponding lines. Therefore, the Arrhenius logarithm formula can be expressed as

$$\ln t_{in} = -19.79 + 69.53/RT \ (r_{in} = 0.9993), \quad (1)$$

$$\ln t_p = -9.67 + 37.84/RT \ (r_p = 0.9963). \quad (2)$$

**The effect of the initial concentration of reactants on $t_{in}$ and $t_p$.** Based on the Smose method [21] to process the data during the induction and the oscillation periods of oscillation system, one can assume that the induction and the oscillation periods are power functions relative to the initial substrate concentrations, namely,

$$1/t_{in} = k_{in} C_{0,Ala}^{\alpha} C_{0,Nil(ClO_4)_2}^{\beta} C_{0,KBrO_3}^{\gamma} C_{0,H_2SO_4}^{\delta} C_{0,Act}^{\varepsilon}, \quad (3)$$

$$1/t_p = k_p C_{0,Ala}^{a} C_{0,NiL(ClO_4)_2}^{b} C_{0,KBrO_3}^{c} C_{0,H_2SO_4}^{d} C_{0,Act}^{e}, \quad (4)$$

where $k_{in}$ and $k_p$ are the rate constants during the induction and the oscillation periods, respectively, $\alpha$, $\beta$, $\gamma$, $\delta$, $\varepsilon$, $a$, $b$, $c$, $d$, $e$ are empirical constants. In the oscillation system, the $t_{in}$ and $t_p$ of the fifth reactant can be determined by fixing the initial concentration of all the other reagents. The $\alpha$, $\beta$, $\gamma$, $\delta$, $\varepsilon$, $a$, $b$, $c$, $d$, $e$ values can be derived from the slope of the linear plot of $\ln t_{in}$ or $\ln t_p$ vs. $\ln c_A$ (A = $H_2SO_4$, $KBrO_3$, Ala, $NiL(ClO_4)_2$, Act), respectively. The reaction rate constants $k_{in}$ and $k_p$ can be obtained from the intercept of the corresponding lines. With these parameters determined, a typical curve of $KBrO_3$ is shown in Fig. 4 ($\gamma$ and $c$ are –0.13 and 1.95, and $k_{in}$, $k_p$ are $10^{-3.37}$ and $10^{0.59}$, respectively).

The same methods have been applied to other reactants to obtain a quantitative relationship between concentration and dynamics parameters:

$$1/t_{in} = k_{in} C_{0,Ala}^{-0.67} C_{0,NiL(ClO_4)_2}^{-1.29} C_{0,KBrO_3}^{-0.13} C_{0,H_2SO_4}^{-0.30} \times \exp(-69.53/RT), \quad (5)$$

$$1/t_p = k_p C_{0,Ala}^{-0.26} C_{0,NiL(ClO_4)_2}^{-1.54} C_{0,KBrO_3}^{1.95} C_{0,H_2SO_4}^{1.57} \times \exp(-37.84/RT). \quad (6)$$

The above data show that: 1) the induction period and period of the oscillating system increase with increasing concentration of Ala and/or $NiL(ClO_4)_2$; 2) the induction period increases also with increasing $KBrO_3$ and/or $H_2SO_4$ concentrations, while the period of the oscillation system decreases. The kinetic parameters are shown in Table 2 [20].

**Nonlinear thermodynamic parameters of the oscillation system [22–24].** Under constant temperature

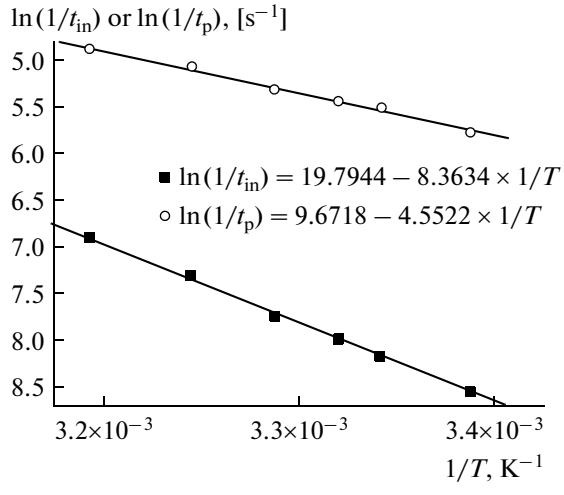


**Fig. 3.** Apparent activation energy of the induction period ($t_{in}$) and oscillation period ($t_p$) in Ala oscillating system.

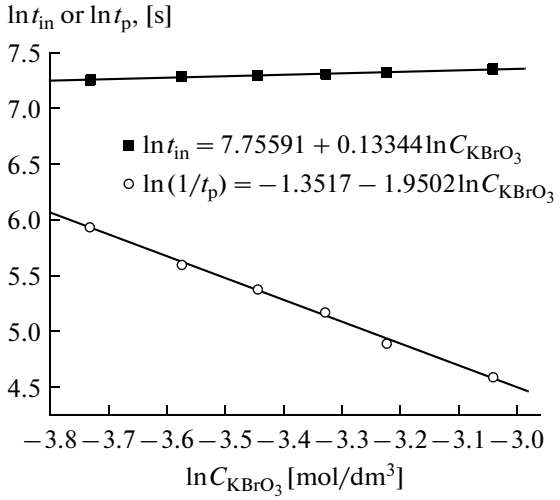


**Fig. 4.** Plots of $\ln t_{in}$ and $\ln t_p$ as a function of $\ln C_{KBrO_3}$.

**Table 2.** Kinetic parameters of the reactants in Ala oscillating system at 30°C

| Reactant | The oscillatory induction period | | | | The oscillation cycle | | | |
|---|---|---|---|---|---|---|---|---|
| | $k_{in}$, $s^{-1}$ | $r_{in}$ | $E_{in}$, kJ/mol | $A_{in}$, $s^{-1}$ | $k_p$, $s^{-1}$ | $r_p$ | $E_p$, kJ/mol | $A_p$, $s^{-1}$ |
| Ala | $10^{-3.93}$ | 0.9971 | 69.53 | $10^{8.60}$ | $10^{-2.55}$ | 0.9990 | 37.84 | $10^{4.20}$ |
| $NiL(ClO_4)_2$ | $10^{-5.53}$ | 0.9988 | | | $10^{-5.14}$ | 0.9974 | | |
| $KBrO_3$ | $10^{-3.37}$ | 0.9989 | | | $10^{0.59}$ | 0.9985 | | |
| $H_2SO_4$ | $10^{-3.34}$ | 0.9976 | | | $10^{-2.76}$ | 0.9992 | | |

Note: $r$ is the linear correlation coefficient.

**Table 3.** Thermodynamic parameters of Ala oscillating system at 30°C

| Reactant | The oscillatory induction period | | | The oscillation cycle | | |
|---|---|---|---|---|---|---|
| | $\Delta H_{in}$, kJ/mol | $\Delta G_{in}$, kJ/mol | $\Delta S_{in}$, J $mol^{-1}$ $K^{-1}$ | $\Delta H_p$, kJ/mol | $\Delta G_p$, kJ/mol | $\Delta S_p$, J $mol^{-1}$ $K^{-1}$ |
| Ala | 67.10 | 97.10 | −99.26 | 35.32 | 90.73 | −182.77 |
| $NiL(ClO_4)$ | | 106.38 | −129.87 | | 99.90 | −213.04 |
| $KBrO_3$ | | 93.83 | −88.47 | | 70.88 | −117.30 |
| $H_2SO_4$ | | 93.68 | −87.98 | | 90.31 | −181.41 |

and pressure, the rate constant $k$ in non-reversible process can be expressed as

$$k = \frac{RT}{Nh} K^{\neq}, \quad (7)$$

where $N$ is the Avogadro constant, $h$ is the Plank constant, $K^{\neq}$ is the equilibrium constant in non-reversible process:

$$\Delta G_{\neq} = -RT \ln K^{\neq}, \quad (8)$$

$$\Delta G_{\neq}^{\varphi} = \Delta H_{\neq}^{\varphi} - T\Delta S_{\neq}^{\varphi}. \quad (9)$$

Substitution (7) into (8) gives

$$\Delta G_{\neq}^{\varphi} = RT \ln \frac{RT}{Nhk}. \quad (10)$$

From Eqs. (7)–(10), the reaction rate $k$ can be expressed in the following form:

$$k = \frac{RT}{Nh} e^{\frac{-\Delta G_{\neq}^{\varphi}}{RT}} = \frac{RT}{Nh} e^{\frac{T\Delta S_{\neq}^{\varphi} - \Delta H_{\neq}^{\varphi}}{RT}} = \frac{RT}{Nh} e^{\frac{\Delta S_{\neq}^{\varphi}}{R}} e^{\frac{\Delta H_{\neq}^{\varphi}}{RT}}. \quad (11)$$

Then

$$\ln \frac{k}{T} = \ln \frac{k^{\neq}}{h} + \frac{\Delta S_{\neq}^{\varphi}}{R} + \frac{\Delta H_{\neq}^{\varphi}}{RT}. \quad (12)$$

Thus, $\Delta H_{\neq}^{\varphi}$ can be derived from the slope of the linear plot of $\ln k/T$ vs. $1/T$. Other thermodynamic parameters of the oscillatory induction period and the oscillation period ($\Delta H_{in}$, $\Delta G_{in}$, $\Delta S_{in}$ and $\Delta H_p$, $\Delta G_p$, $\Delta S_p$) can be obtained in a similar fashion (see Table 3).

The oscillating reactions were carried out under isothermal, isobaric and isometric conditions, and therefore, $H = U$, namely the value of the enthalpy equals to that of the internal energy of this system.

The $\Delta G$ values of all reactants of the oscillating system listed in Table 3 are positive, indicating that the oscillating reactions are non-spontaneous processes.

From Table 3, one can see that the entropy $\Delta S$ of Ala oscillating system is negative, i.e. the internal energy and the entropy flow are provided by the environment. In the open system, one may expect a continuous oscillation. On the contrary, in the closed system one may expect an attenuating oscillation. Typical duration of this oscillation for the closed system is only about 1.5 h.

So, chemical oscillating reactions exist in the open system with a dissipative structure in the presence of negative entropy flow, and in the closed system at lower temperature. The non-equilibrium thermodynamics are their thermodynamic basis and their kinetic rate equations are nonlinear differential equations. Our research shows that tetraazamacrocyclic nickel(II) complex is a catalyst for the BZ oscillating reaction using alanine as substrate. The entropy $\Delta S$ of the induction period and period in alanine oscillation system are shown to be negative, and thus they become further evidence for the chemical oscillation in non-equilibrium systems with dissipative structure.

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