

Thermodynamic characteristics of L-arginine oscillating system catalyzed by tetraazamacrocyclic nickel(II) complex

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A novel oscillating system with L-arginine (Arg) as organic substrate, catalyzed by a tetraazamacrocyclic nickel(II) complex ($\text{NiL}(\text{ClO}_4)_2$, (L: 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazabutadecacyclo-7,14-diene) is reported for the first time. The system has been quantitatively characterized by kinetic parameters, including the rate constants (k_m , k_p), the apparent activation energies (E_m , E_p), the pre-exponential constants (A_m , A_p), and the thermodynamic functions (ΔH_m , ΔG_m , ΔS_m , ΔH_p , ΔG_p , ΔS_p). The results indicate that the $\text{NiL}(\text{ClO}_4)_2$ can catalyze the Arg oscillating reaction, exhibiting features of irreversible thermodynamics as shown by the negative entropy of the oscillating system. Further, the two active groups of the Arg oscillating system can be activated at higher acidity. A possible mechanism is also proposed for the Arg oscillating system catalyzed by $\text{NiL}(\text{ClO}_4)_2$.

Keywords: Oscillatory systems, Chemical oscillating reactions, Amino acids, Arginine oscillatory system, Induction period, Oscillating period, Irreversible chemical reactions, Kinetic parameters, Thermodynamic parameters, Nickel

Oscillating reactions are complex dynamic systems that involve amplitude or periodic changes with respect to concentration of some component (a reactant, a product or an intermediate) with time¹. After the well-known Belousov-Zhabotinskii (BZ) oscillating reaction with organic acids as the oscillating substance catalyzed by Ce^{3+} , several catalysts including Mn^{2+} , $\text{Fe}(\text{phen})_3^{2+}$, and $\text{Ru}(\text{bipy})_3^{2+}$ have been developed²⁻⁶. In recent years, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclododecane tetradecane has received significant attention as a macrocyclic ligand complex, which has excellent coordination properties and is capable of forming 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}. Recently, nickel(II) complexes have been reported as a new catalyst for the BZ reaction between gallic acid, pyro-gallic acid, pyruvic acid and other organic substrates^{9,10}. However, the oscillating system comprising amino acids as organic substrate catalyzed by the tetraazamacrocyclic nickel(II) complex, ($\text{NiL}(\text{ClO}_4)_2$ (L: 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazabutadecacyclo-7,14-diene), was reported only recently. We reported two new oscillating systems

recently^{11,12}, using alanine and glycine as organic substrates catalyzed by $\text{NiL}(\text{ClO}_4)_2$. Studies on other amino acids participating in oscillating systems have not made any progress in the recent years.

Herein, based on the analysis of amino acids structure, a novel oscillating system consisting of L-arginine (Arg) as organic substrate, catalyzed by $\text{NiL}(\text{ClO}_4)_2$ was successfully constructed. Arg is a semiessential amino acid, which plays an important role in cell division, healing of wounds, removing ammonia from the body, immune function, and release of hormones. Moreover, Arg taken in combination with proanthocyanidins or yohimbine, has been used in treatment of erectile dysfunction¹³⁻¹⁵. Thus, the study of the oscillatory reactions involving Arg participation is of significance. More importantly, the active center and the possible mechanism for Arg catalyzed by $\text{NiL}(\text{ClO}_4)_2$ in the oscillating reaction is also proposed in this study.

Materials and Methods

L-Arginine (Arg, Biochemical Reagent), and other reagents were of analytical grade. $\text{NiL}(\text{ClO}_4)_2$ was synthesized according to the method described in literature^{12,16}, and the results of elemental analysis and

X-ray diffraction characterization are consistent with literature values. A CHI 660D electrochemical workstation (Shanghai Chenhua Instrument), MF-3 elemental analyzer, Enraf-Nonius CAD4SDP44 four-circle diffractometer, CS501 super-heated thermostat (Shanghai Experimental Instrument Factory), and ML2902 magnetic stirrer (Shanghai Pujiang Instrument Factory) were used in the experiment.

Oscillating reaction

The oscillating reaction was conducted in a glass jacketed reactor with a thermostat under magnetic stirring. First, water (H_2O), sulfuric acid (H_2SO_4), Arg, $\text{NiL}(\text{ClO}_4)_2$, and acetone (Act) were added into the above reactor, followed by the addition of KBrO_3 after the temperature of the solution reached 303 K, with the total volume of the solution as 50 mL. The electrochemical workstation was used to determine the change of redox potential ($[\text{Ox}]/[\text{Red}]$) with time by adjusting the concentration of each component in the oscillating system. A 213-platinum electrode and saturated calomel electrode (SCE) were used as the indicator and reference electrodes, respectively. The illustration of experiment setup is shown in Fig. 1.

Results and Discussion

Concentration ranges of the reactants in the oscillating system

By adjusting the concentration of each component in the oscillating reaction, an oscillating system with good reproducibility ($\text{rsd} = 2.7\%$; $n = 10$) and oscillating characteristics was obtained. The initial concentrations of each component in oscillating system were as follows: $[\text{KBrO}_3]_0 = 0.040 \text{ mol dm}^{-3}$, $[\text{Arg}]_0 = 0.040 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4]_0 = 1.766 \text{ mol dm}^{-3}$, $[\text{Act}]_0 = 0.081 \text{ mol dm}^{-3}$, and $[\text{NiL}(\text{ClO}_4)_2]_0 = 0.0118 \text{ mol dm}^{-3}$. A typical oscillating curve is obtained (Fig. 2), showing that this system starts oscillating after a 5 min induction period, while the induction period indicates the accumulation time of Br_2 . The shape of the oscillatory curve has unique features. Although the amplitude in the initial reaction is not uniform, it becomes more stable after several groups of regular oscillations. Sustained oscillations were observed for about 2.5 h, and after that the solution exhibited a change with the color variations between light yellow and dark green. By changing the concentration of only $\text{NiL}(\text{ClO}_4)_2$ and keeping the concentrations of all other reactants constant, the concentration range for $\text{NiL}(\text{ClO}_4)_2$ was obtained. The concentration ranges of other reactants obtained similarly are listed in Table 1.

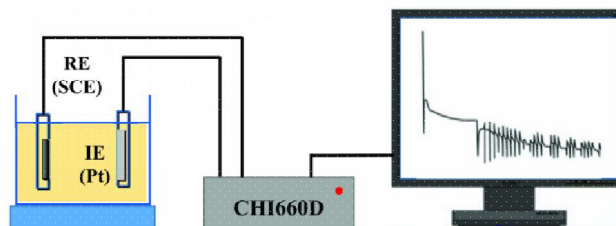


Fig. 1 — The experiment setup of the studied oscillating system.

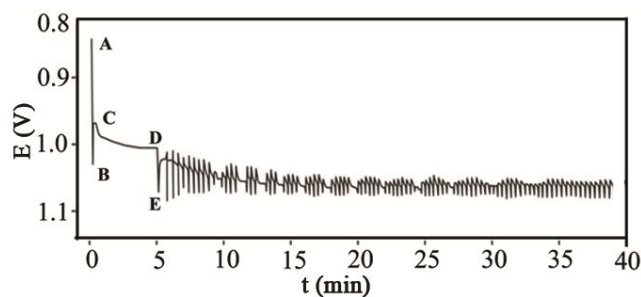


Fig. 2 — Typical oscillating curve of Arg system using $\text{NiL}(\text{ClO}_4)_2$ as catalyst. $[\text{KBrO}_3]_0 = 0.040 \text{ mol dm}^{-3}$, $[\text{Arg}]_0 = 0.040 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4]_0 = 1.766 \text{ mol dm}^{-3}$, $[\text{Act}]_0 = 0.081 \text{ mol dm}^{-3}$, $[\text{NiL}(\text{ClO}_4)_2]_0 = 0.0118 \text{ mol dm}^{-3}$.

Table 1 — The concentration ranges of the reactants for obtaining typical oscillating waves in Arg oscillating system

$[\text{Arg}]_0$ (mol dm^{-3})	$[\text{KBrO}_3]_0$ (mol dm^{-3})	$[\text{H}_2\text{SO}_4]_0$ (mol dm^{-3})	$[\text{NiL}(\text{ClO}_4)_2]_0$ (mol dm^{-3})	$[\text{Act}]_0$ (mol dm^{-3})
0.040	0.012–0.060	1.766	0.0118	0.081
0.024–0.144	0.040	1.766	0.0118	0.081
0.040	0.040	1.325–2.061	0.0118	0.081
0.040	0.040	1.766	0.00792–0.0410	0.081
0.040	0.040	1.766	0.0118	0.054–0.135

Dynamics parameters and the thermodynamic functions for the oscillation

The induction period (t_{in} , measured as the time between addition of half volume of KBrO_3 to the time of appearance of first peak of periodic oscillation) and oscillation period (t_p , the average time from the first peak to the third peak after the beginning of oscillation reaction) for the above mentioned system were obtained according to the Arrhenius equation and the method described in literature¹² in the temperature range of 295–313 K. The apparent activation energies of the induction period (E_{in}) and oscillation period (E_p) were obtained from the linear plots of $\ln(1/t_{\text{in}})$ and $\ln(1/t_p)$ versus $1/T$ (Fig. 3) as $34.35 \text{ kJ mol}^{-1}$ and $73.49 \text{ kJ mol}^{-1}$ respectively. The pre-exponential constant A_{in} and A_p , were obtained from the intercept of the corresponding plots.

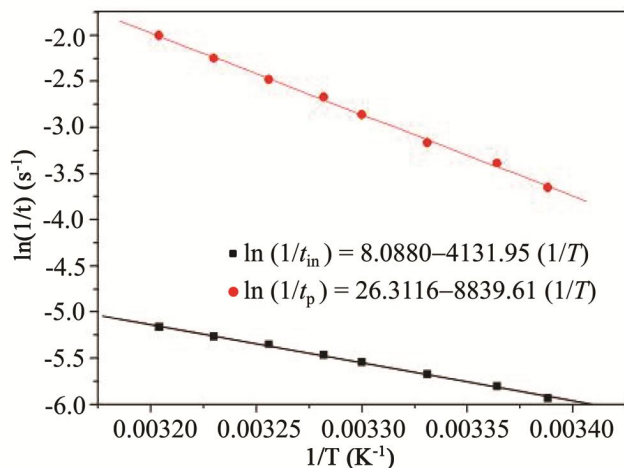


Fig. 3 — The apparent activation energy of the induction period (t_{in}) and oscillating period (t_p) in Arg oscillating system.

Therefore, the Arrhenius logarithm formula can be expressed as follows:

$$\ln t_{in} = -8.09 + 34.35/RT \quad (r_{in} = 0.9988) \quad \dots(1)$$

$$\ln t_p = -26.31 + 73.49/RT \quad (r_p = 0.9991) \quad \dots(2)$$

Based on the Smose method and the method described in literature^{12,17}, a quantitative relationship between concentration and dynamics parameters can be obtained by from the induction and oscillation periods.

$$1/t_{in} = k_{in} c_0(\text{Arg})^a c_0(\text{NiL}(\text{ClO}_4)_2)^b c_0(\text{KBrO}_3)^\gamma \times c_0(\text{H}_2\text{SO}_4)^\delta c_0(\text{Act})^\varepsilon \quad \dots(3)$$

$$1/t_p = k_p c_0(\text{Arg})^a c_0(\text{NiL}(\text{ClO}_4)_2)^b c_0(\text{KBrO}_3)^c \times c_0(\text{H}_2\text{SO}_4)^d c_0(\text{Act})^e \quad \dots(4)$$

where k_{in} and k_p were the rate constants of induction period and oscillation cycle, respectively. $a, \beta, \gamma, \delta, \varepsilon, a, b, c, d, e$ are empirical constants. In the oscillation system, the variation relationship of t_{in} and t_p with the initial concentration of the one reactant was determined by fixing the concentrations of the other four reactants. The reaction orders, $a, \beta, \gamma, \delta, \varepsilon, a, b, c, d, e$ were derived from the slope of the linear plots of $\ln t_{in}$ or $\ln t_p$ versus $\ln c_A$ ($A = \text{H}_2\text{SO}_4, \text{KBrO}_3, \text{Arg}, \text{NiL}(\text{ClO}_4)_2, \text{Act}$), while the reaction rate constants k_{in} and k_p were obtained from the intercept of the corresponding linear relationship. A representative plot for variation of H^+ is given in Fig. 4 (see also Table 2). The obtained reaction orders (H^+) and rate constants corresponding to the induction and oscillation periods of oscillating system are -1.64 and -2.07 , $10^{-2.61}$ and $10^{-1.81}$, respectively.

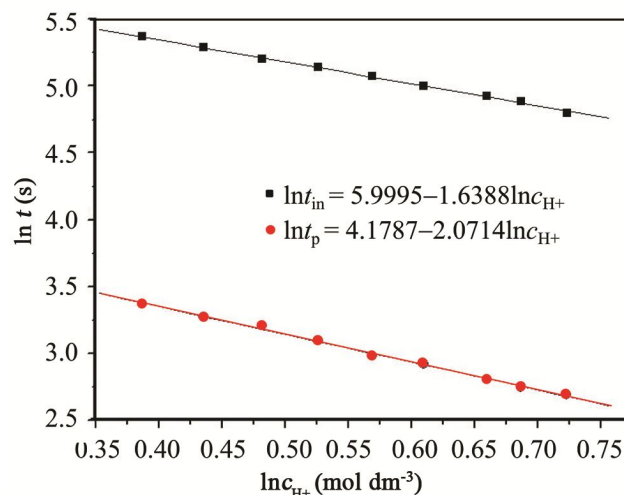


Fig. 4 — The $\ln t_{in}/\ln t_p$ plots as a function of $\ln c_{\text{H}^+}$.

Table 2 — Experimental values of induction period (t_{in}) and oscillating period (t_p) in the Arg oscillating system at varying concentrations of H^+

c_{H^+} ($\text{mol} \cdot \text{dm}^{-3}$)	t_{in} (s)	t_p (s)
1.4720	214.56	29.04
1.5456	197.51	26.34
1.6191	180.96	24.72
1.6928	170.85	22.10
1.7663	159.35	19.68
1.8401	147.81	18.55
1.9344	137.90	16.56
1.9871	132.58	15.57
2.0608	121.32	14.77

According to this method, quantitative relationships between concentration and dynamics parameters of other reactants were obtained as follows:

$$1/t_{in} = k_{in} c_0(\text{Arg})^{0.19} c_0(\text{NiL}(\text{ClO}_4)_2)^{-1.62} c_0(\text{KBrO}_3)^{-0.42} \times c_0(\text{H}_2\text{SO}_4)^{1.64} \exp(-69.53/RT) \quad \dots(5)$$

$$1/t_p = k_p c_0(\text{Arg})^{1.23} c_0(\text{NiL}(\text{ClO}_4)_2)^{-1.05} c_0(\text{KBrO}_3)^{-1.56} \times c_0(\text{H}_2\text{SO}_4)^{2.07} \exp(-37.84/RT) \quad \dots(6)$$

The above discussion reveals the following key points: (1) the induction period and period of the oscillating system decrease with the increase concentration of Arg and H_2SO_4 , and (2) the induction period and period of the oscillating system increase with the increase concentration of KBrO_3 and $\text{NiL}(\text{ClO}_4)_2$. The other kinetic parameters are listed in Table 3.

Table 3 – Kinetic parameters (k_{in} , A_{in} , E_{in} , E_p , A_p , and k_p) of reactants in Arg oscillating system at 303 K

Reactants	Oscillatory induction period				Oscillation cycle			
	k_{in} (s^{-1})	r_{in}	E_{in} ($kJ\ mol^{-1}$)	A_{in} (s^{-1})	k_p (s^{-1})	r_p	E_p ($kJ\ mol^{-1}$)	A_p (s^{-1})
Arg	$10^{-1.87}$	0.9977			$10^{0.52}$	0.9995		
NiL(ClO ₄) ₂	$10^{-5.41}$	0.9989			$10^{-3.46}$	0.9979		
KBrO ₃	$10^{-2.85}$	0.9973	34.35	$10^{3.51}$	$10^{-0.84}$	0.9986	73.49	$10^{11.42}$
H ₂ SO ₄	$10^{-2.61}$	0.9988			$10^{-1.81}$	0.9922		

* k_{in} and k_p , are respectively the reaction rate constants of the oscillatory induction period and the oscillation period at 303 K; E_{in} and E_p , are respectively the apparent activation energies; A_{in} and A_p , are respectively the pre-exponential constants obtained by the $\ln(1/t_{in})$ or $\ln(1/t_p)$ versus $1/T$ plots; and r , is the linear correlation coefficient.

Table 4 — Thermodynamic functions of Arg oscillating system at 303 K

Reactants	Oscillatory induction period			Oscillation cycle		
	ΔH_{in} ($kJ\ mol^{-1}$)	ΔG_{in} ($kJ\ mol^{-1}$)	ΔS_{in} ($J\ mol^{-1}\ K^{-1}$)	ΔH_p ($kJ\ mol^{-1}$)	ΔG_p ($kJ\ mol^{-1}$)	ΔS_p ($J\ mol^{-1}\ K^{-1}$)
Arg		85.12	-175.80		71.27	-0.98
NiL(ClO ₄) ₂		105.66	-243.54		94.35	-77.12
KBrO ₃	31.83	90.80	-194.53	70.97	79.19	-27.11
H ₂ SO ₄		89.40	-189.92		84.82	-45.67

The thermodynamic functions (ΔH_{in} , ΔG_{in} , ΔS_{in} , ΔH_p , ΔG_p , and ΔS_p) obtained according to literature method¹¹ are given in Table 4. The oscillating systems belong to the open system and are accomplished in isothermal-isobaric and isometric conditions, thus the enthalpy is the internal energy. The values of ΔG of oscillating system listed in Table 4 are positive, which indicates that the oscillating reactions are non-spontaneous. However, the values of ΔS of Arg oscillating system are negative, thus indicating that irrespective of the high temperature, the oscillating reaction will not occur, and the oscillating reaction would begin only due to the catalytic or autocatalytic process.

Activation center of the oscillation reaction

In our previous study, we proposed that the oscillating reaction has an active center¹⁸, and each amino acid has the active groups which can react with Br₂. Further, the number and activity of the active groups of each amino acid are different. These active groups form the active center of oscillation reaction, which decides whether the oscillation reaction occurs or not and also the oscillation life.

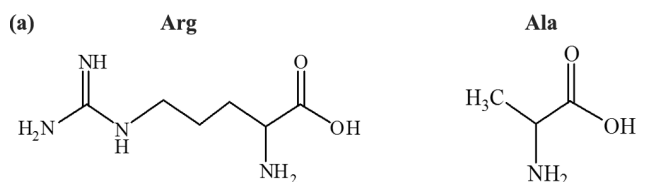
According to literature¹², the typical oscillating curve ($T = 303\ K$) of the alanine (Ala) oscillating system corresponds to the initial concentrations of $[KBrO_3]_0 = 0.040\ mol\ dm^{-3}$, $[Ala]_0 = 0.080\ mol\ dm^{-3}$, $[H_2SO_4]_0 = 1.693\ mol\ dm^{-3}$, $[Act]_0 = 0.081\ mol\ dm^{-3}$, and $[NiL(ClO_4)_2]_0 = 0.0149\ mol\ dm^{-3}$. Compared to

the Ala system, the initial concentrations of KBrO₃, Act and NiL(ClO₄)₂ in Arg oscillating system are basically the same, while the concentrations of Arg and H₂SO₄ vary greatly, i.e., the concentration of Arg is lower ($0.040\ mol\ dm^{-3}$) than the concentration of Ala ($0.080\ mol\ dm^{-3}$), while the concentration of H₂SO₄ is higher ($1.766\ mol\ dm^{-3}$). Based on the analysis of the structure of Arg and experimental data, we proposed the existence of two active groups in the Arg oscillating system, which makes Arg an active organic substrate for oscillating reactions, easily catalyzed by NiL(ClO₄)₂.

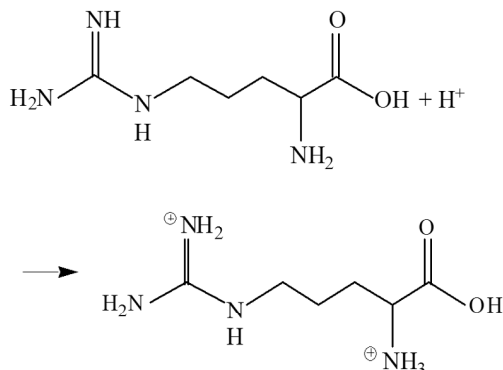
The structures of Arg and Ala are shown in Scheme 1. Under acidic condition, the 2-amino group of the two amino acids can become a positive ion due to acid hydrolysis. However, 5-guanidino of Arg can be a positive ion only at higher acidity (Scheme 1). These are the active groups which subsequently react with Br₂ by bromide reaction (Scheme 1). Thus, Arg has two active groups while Ala only has one active group. This is why the initial concentrations of KBrO₃, Act and NiL(ClO₄)₂ in the two oscillating systems are basically the same, while the concentrations of Arg and H₂SO₄ vary significantly.

Proposed mechanism for Arg oscillating system

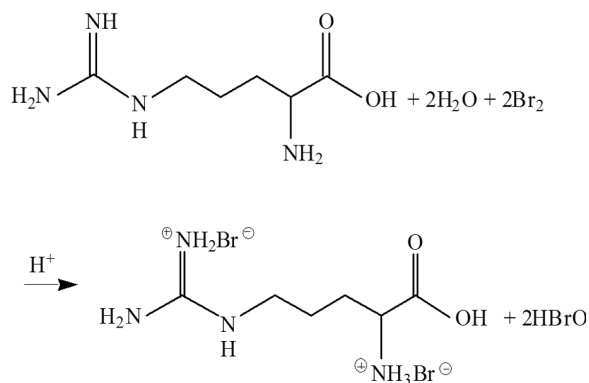
An oscillating system usually consists of many kinetic steps and involves several independent variables, thus the mechanism of oscillating reactions



(b) Acid hydrolysis of Arg



(c) The two active groups of Arg reacting with Br₂ by bromide reaction



Scheme 1

is usually rather complex. The Arg oscillating system catalyzed by NiL(ClO₄)₂ exhibits a feature of periodic changes in color between light yellow and dark green. In the oscillating system, the solution is colorless before the addition of NiL(ClO₄)₂; the electric potential of the system is at point A (Fig. 5a). However, with the addition of NiL(ClO₄)₂ (light yellow), the electric potential rapidly reaches point B, and the color of the solution becomes dark green. Further, with the change in the electric potential from B to C, the color of the solution changes from dark green to yellow. After 5 min induction period (line CD), the system starts oscillating and is accompanied with the cyclic changes in the color of the solution. The color deepens from D to E, and becomes lighter from E to F. The above mentioned phenomenon indicates that the category of this NiL₂²⁺ catalyzed oscillator belongs to oxidation because of a rapid excursion of the oxidized form. Therefore, it exhibits a periodic change in the concentration of the reduced and oxidized forms of NiL₂²⁺ and NiL₃³⁺. Furthermore, the influence of the catalyst NiL(ClO₄)₂ on the oscillating system was investigated in the concentration range of 0.00792 mol dm⁻³ to 0.041 mol dm⁻³. However, when the concentration of NiL(ClO₄)₂ was ≤ 0.00792 mol dm⁻³ (Fig. 5b) or higher than 0.041 mol dm⁻³, no oscillating reaction occurred. This shows that the accumulation of Br₂ required a specific minimum concentration of the catalyst.

It was found that H₂SO₄ and KBrO₃ play the same role as NiL(ClO₄)₂ in the oscillatory reaction, and the electric potential changes from A to B after their addition. H₂SO₄ and KBrO₃ were found to be required in the concentration range of 1.325–2.061 mol dm⁻³ and 0.011–0.072 mol dm⁻³, respectively. However, when the concentration of H₂SO₄ was lower than

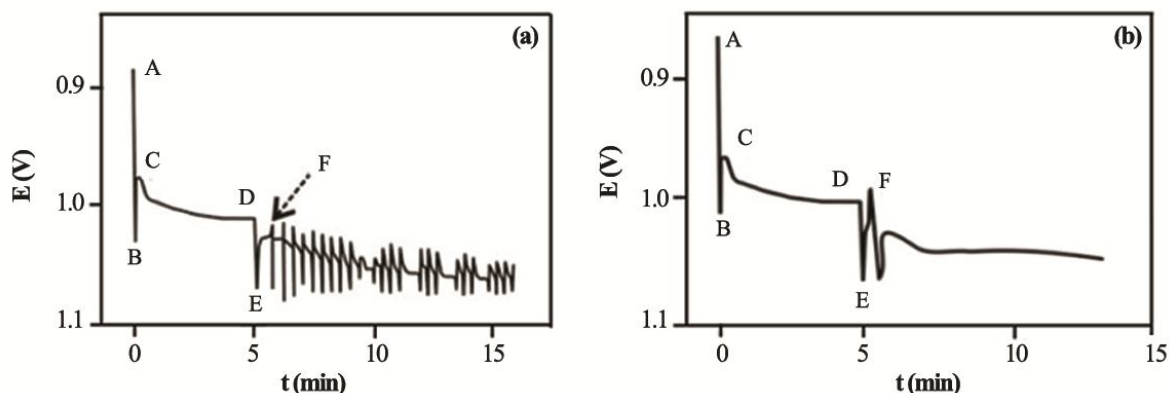
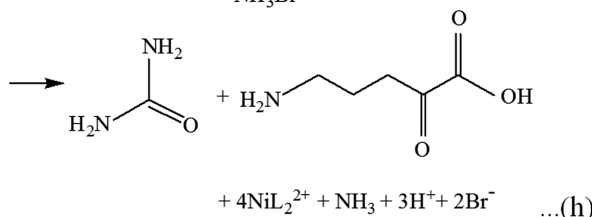
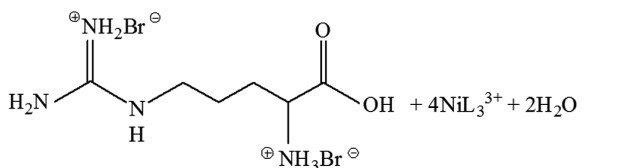
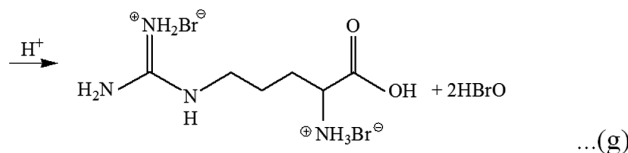
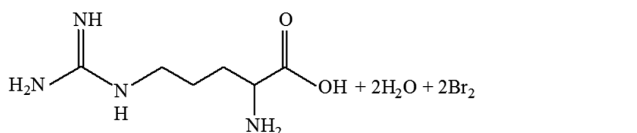
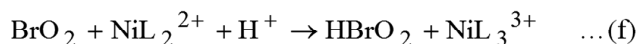
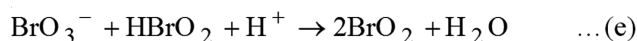
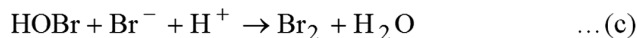
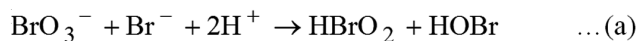


Fig. 5 — The effect of NiL(ClO₄)₂ on the Arg oscillating system. [Concentrations of all other reactants as in Fig. 2, with (a) [NiL(ClO₄)₂]₀ = 0.0118 mol dm⁻³, and, (b) [NiL(ClO₄)₂]₀ = 0.00792 mol dm⁻³].



Scheme 2

1.325 mol dm⁻³, oscillating reaction did not occur. The induction period and oscillating period of the system increased with the increase of the concentrations of H₂SO₄, KBrO₃ and NiL(ClO₄)₂. Such a mechanism involves six main kinetically distinct reactions and is described in terms of Eqs (a)–(f) (Scheme 2).

The influence of Arg and Act on oscillating system is presented in Fig. 6. The study shows that the potential of the system is constant without Arg

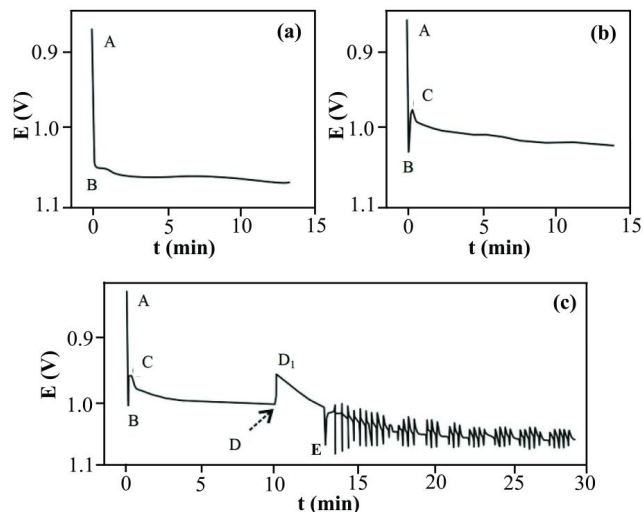


Fig. 6 — The effect of Arg and Act on oscillating system. [Concentrations of all other reactants as in Fig. 2, with (a) absence of Arg and Act, (b) only Arg added, and, (c) Act added to the Arg system].

(Fig. 6a), indicating that Br₂ produced according to Eqs (a)–(f) has not been consumed. After the addition of Arg (0.040 mol dm⁻³), the potential drops to point C, and a certain amount of Br₂ is consumed, however, there is still no oscillatory behavior (Fig. 6b). When Act is added (at point D), the electric potential continues to decrease to point D₁, and the oscillation begins through an induction period (Fig. 6c). Figure 6 shows that both Act and Arg act as double oscillating substrates to consume Br₂ as described by Eqs. (g)–(i) (Scheme 2).

The above discussion shows that Scheme 2 correctly describes the NiL(ClO₄)₂ catalyzed oscillating system in terms of the experimental observations and the well known FKN mechanism.

Conclusions

The oscillating system comprising Arg as organic substrate and catalyzed by NiL(ClO₄)₂ is a new oscillating system proposed in this study. The concentration of Arg required in oscillating reaction was found to be very low due to the existence of the two active groups which could react with Br₂ in Arg {[Arg]₀ = 0.040 mol dm⁻³; [KBrO₃]₀ = 0.040 mol dm⁻³; [H₂SO₄]₀ = 1.766 mol dm⁻³; [Act]₀ = 0.081 mol dm⁻³; [NiL(ClO₄)₂]₀ = 0.0118 mol dm⁻³} oscillating system, and these two groups could become active groups only at higher acidity. The kinetic parameters and thermodynamic functions of the oscillating system at 303 K were systematically studied and calculated.

Furthermore, the entropy of the induction period and the oscillating period in the Arg oscillating system were negative, which is further evidence that the Arg oscillating system is a non-equilibrium system with dissipative structure.

Acknowledgement

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