A Novel *Briggs–Rauscher* Oscillation with a Macrocyclic Nickel(II) Complex as Catalyst and Pentane-2,4-dione as the Substrate

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A new *Briggs–Rauscher* oscillating reaction with a tetraazamacrocyclic nickel(II) complex $[NiL](ClO_4)_2$ as catalyst and pentane-2,4-dione (pe) as the substrate is reported. The ligand L is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The experimental results indicate that iodine ion may be an important intermediate, and free radicals can be involved in the reaction. A tentative mechanism based on *Noyes–Furrow* model (*NF* model) is proposed. Moreover, other factors, such as the variation of concentration of the components and temperature on the oscillator, are discussed.

1. Introduction. – An oscillating chemical reaction, a complex process occurring only in being far from equilibrium, involves the change of the parameters such as amplitude or period with time [1]. Because it exhibits several nonlinear behaviors in theoretical and experimental chemical kinetics, it has attracted many chemists' interest since the discovery of the *Belousov–Zhabotinsky* (*B–Z*) oscillator [2][3]. In 1973, another kind of oscillator [4], containing amounts of H_2O_2, acidic iodate, manganous salt, malonic acid, and starch indicator, was discovered by *Briggs* and *Rauscher*. Traditionally, in the so-called *Briggs–Rauscher* (*B–R*) reaction, the process is catalyzed by metal ions (usually Ce^{3+} or Mn^{2+}) [4–7]. In 1994 [8] and 1998 [9], *Rosokha* and *Tikhonova* indicated that a macrocyclic Ni^{II} complex can participate in this kind of oscillation. In their reported system, only malonic acid could be used as organic substrate.

It is known that a tetraazamacrocyclic complex has a structure similar to that of some enzymes, and H_2O_2 plays an important part in the process of metabolism of the animal [10], so this kind of *B–R* system is potentially interesting in the mimic studies of biochemical oscillation processess occurring in cells. To extend the list of tetraazamacrocyclic complex-catalyzed *B–R* reactions, a new oscillating reaction with the tetraazamacrocyclic Ni^{II} complex, $[NiL](ClO_4)_2$, as catalyst and pentane-2,4-dione (pe) as organic substrate is reported. The ligand L is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

2. Experimental. – 2.1. *Apparatus.* The apparatus used to implement the oscillating phenomenon were: a glass container, to which all kinds of the components were injected, and a bright Pt electrode (*Type 213*, *Shanghai Electricity and Light Instrumental Factory*) and a saturated calomel electrode (SCE) *via* a salt bridge containing 1M Na_2SO_4 (*Type 217*, *Shanghai Weiye Instrumental Plant*) as reference electrode to monitor the changes of the potential. Potentials of the electrodes were measured by *Model*

PHS-25B digital voltmeters (*Shanghai Dapu Instrumental Factory*). The kinetic curves of the reaction were recorded with *Model XWT-264 Y-t* recorder (*Shanghai Dahua Instrumental Factory*). All reaction solns. must be homogeneous, so a magnetic stirrer was used.

2.2. *Reagents and Procedure.* All chemicals used were of anal. reagent grade and used as received, except that the catalyst $[NiL](ClO_4)_2$ was synthesized according to [11], and identified by its IR spectra and elemental analyses. Solns. of 0.14M KIO_3, 0.315M pentane-2,4-dione, 0.0173M $[NiL](ClO_4)_2$, and 4M H_2O_2 were prepared in 0.025M H_2SO_4. Twice redistilled H_2O was used in all cases.

During the experiment, the components were injected into the glass container which was kept at 3 ± 0.5°, in the sequence: KIO_3, pe, H_2SO_4, $[NiL](ClO_4)_2$, and H_2O_2. The Pt and the reference electrode were placed into the container before the H_2O_2 addition. After a short induction period, the oscillating phenomenon was observed, and the oscillating curve was recorded by the *Y-t* recorder.

3. Results and Discussion. – 3.1. *$[NiL]^{2+}$-Catalyzed Oscillating Reaction.* The experiments were performed according to the procedure and fixing the amounts of all components: 6 ml of 0.14M KIO_3, 3.6 ml of 0.315M pe, 19.4 ml of 0.025M H_2SO_4, 8 ml of 0.0173M $[NiL](ClO_4)_2$, and 3 ml of 4M aq. H_2O_2. A typical oscillating curve is shown in *Fig. 1*. During the oscillation, the periodic change of solution color (yellow–brown–yellow) was observed. We had expected that yellow and green (NiL^{2+} and NiL^{3+}) alternated during oscillating [12]. However, we observed brown instead of green, because I_2 was produced and dissolved periodically during oscillation in the solution, and we will discuss this in detail in *Sect. 3.5*.

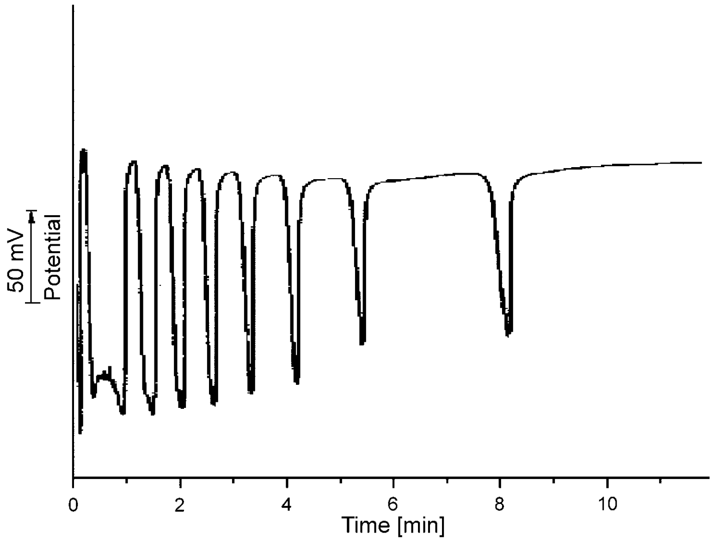

Fig. 1. *Typical potentiometric oscillation trace of Pt* vs. *time of the oscillator at 3 ± 0.5°*. Conditions: $[KIO_3] = 0.021M$, $[pe] = 0.02835M$, $[NiL] = 3.46 \times 10^{-3}$ M, $[H_2SO_4] = 0.025M$, $[H_2O_2] = 0.3M$.

The typical oscillation lasted for *ca.* 502 s with seven cycles. When the oscillator had ceased, several aliquots of solution of KIO_3 were successively added to the container. To some extent, the oscillation could be revived. But addition of $[NiL](ClO_4)_2$, H_2O_2, or pe could not revive the oscillation. These phenomena show that the damping of oscillations is neither due to the depletion of pe or H_2O_2 nor due to $[NiL](ClO_4)_2$, but is dependent on the consumption of KIO_3.

3.2. *Critical Concentration for the Oscillation System.* By varying the concentration of one reactant and fixing those of the other four reactants, a series of concentration ranges for oscillations were obtained. For the KIO_3–pe–H_2SO_4–$[NiL](ClO_4)_2$–H_2O_2 system, the ranges of the concentration for visible oscillations are compiled in the *Table.*

Table. *The Range of the Main Component Oscillations Observed*

KIO_3 [mol/l]	Pentane-2,4-dione [mol/l]	$[NiL](ClO_4)_2$ [mol/l]	H_2SO_4 [mol/l]	H_2O_2 [mol/l]
≥ 0.014	0.02835	3.46×10^{-3}	0.025	0.3
0.021	0.00315 – 0.0441	3.46×10^{-3}	0.025	0.3
0.021	0.02835	$\geq 3.03 \times 10^{-4}$	0.025	0.3
0.021	0.02835	3.46×10^{-3}	0.012 – 0.15	0.3
0.021	0.02835	3.46×10^{-3}	0.025	0.04 – 2.19

3.3. *Variation of the Oscillating Parameters with the Concentration of One Component.* In *Fig. 1*, it is shown that this oscillator exhibits damped oscillating behavior. The oscillating parameters, including the induction period (t_{in}), oscillation period (t_p; the mean value of the first three oscillating cycles), amplitude (A; the mean value of the first three oscillating cycles), and number of oscillations (n), are discussed. For this oscillator, varying the initial concentration of one component, while fixing concentrations of the other four, resulted in obvious variation of induction period, oscillation period, amplitude, and number of oscillations.

The influence of changing of the concentration of KIO_3 on the oscillating parameters is shown in *Fig. 2*. In *Fig. 2*, over the range of concentration from 0.015 to 0.045 mol/l, induction period (t_{in}) and oscillation period (t_p) decreased with the increase of KIO_3, but, after falling to a minimum at a concentration of 0.028 mol/l, they increased. The amplitude (A) increased first and then sharply went down at the concentration of 0.035 mol/l. Number of oscillations (n) rose with the increase of the concentration of KIO_3.

Increase of the concentration of pe from 0.02 to 0.034 mol/l resulted in a marked alteration of the four parameters. The induction period (t_{in}) first dropped to a minimum and then increased. The oscillation period (t_p) showed a similar tendency as the induction period. In contrast, the amplitude (A) and number of oscillations (n) rose to a maximum at a concentration of 0.26 mol/l. When the concentration was lower, the amplitude (A) and the number of oscillations (n) increased with the increase of concentration. But, above the concentration of 0.26 mol/l, A and n decreased, when the concentration increased. The change in curves of the four parameters are shown in *Fig. 3*.

The influence of H_2O_2 was investigated over the range of concentration from 0.1 to 1.5 mol/l. It could be easily noted that the induction period (t_{in}) and the oscillation period (t_p) decreased gradually, while $[H_2O_2]$ increased. This tendency is illustrated in *Fig. 4,a*. In *Fig. 4,b*, the change in the curve of amplitude (A) was similar to those of the oscillation period and the induction period. The number of oscillations (n) reached a

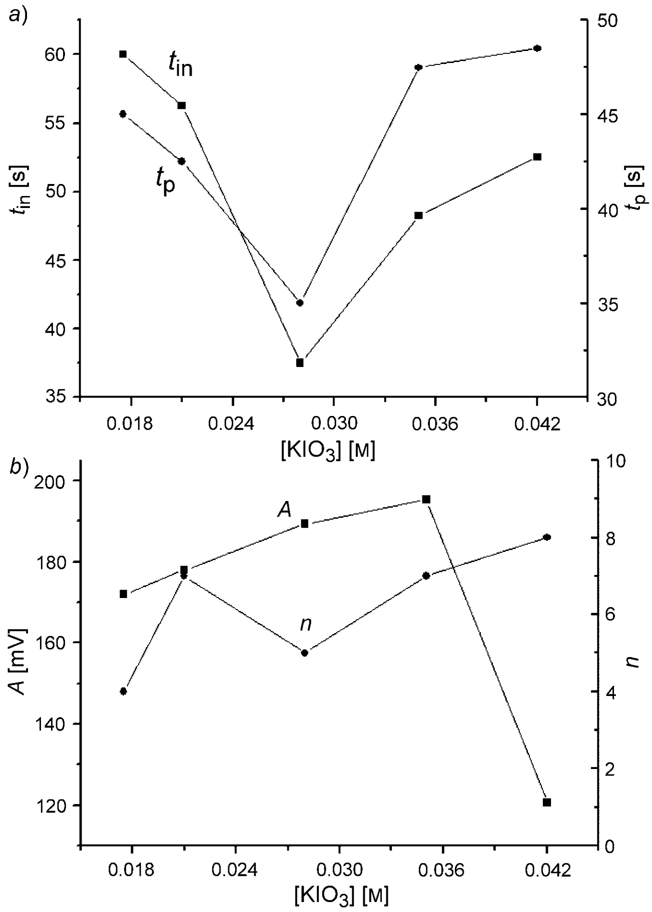

Fig. 2. *The influence of* $[KIO_3]_0$ a) *on induction period* (t_{in}) *and oscillation period* (t_p), *and* b) *on amplitude* (A) *and number of oscillations* (n) *at* $3 \pm 0.5°$. Conditions: [pe] = 0.02835M, $[H_2SO_4]$ = 0.025M, $[H_2O_2]$ = 0.3M, $[NiL^{2+}]$ = 0.00346M.

maximum at $[H_2O_2]$ of 0.6 mol/l and then decreased slowly with further increasing of $[H_2O_2]$.

Changes in the $[NiL](ClO_4)_2$ concentration over the range from 3.46×10^{-4} to 1.18×10^{-2} mol/l had a significant effect on the four parameters (*Fig. 5*). The tendency of changes in induction period (t_{in}), oscillation period (t_p), and number of oscillations (n) for varying $[NiL](ClO_4)_2$ concentration is similar to those with varying $[H_2O_2]$, though in a different concentration range. The variation of A is shown in *Fig. 5,b*.

Unlike all of the oscillating parameters varying with the change of concentration of the reactants KIO_3, H_2O_2, pe, or $[NiL](ClO_4)_2$, only the induction period (t_{in}) and the number of oscillations (n) vary with the acidity, *i.e.*, $[H_2SO_4]$ increasing from 0.015 to 0.044 mol/l. The oscillation period (t_p) and A remained almost unchanged when varying the acidity in the same range (in *Fig. 6*).

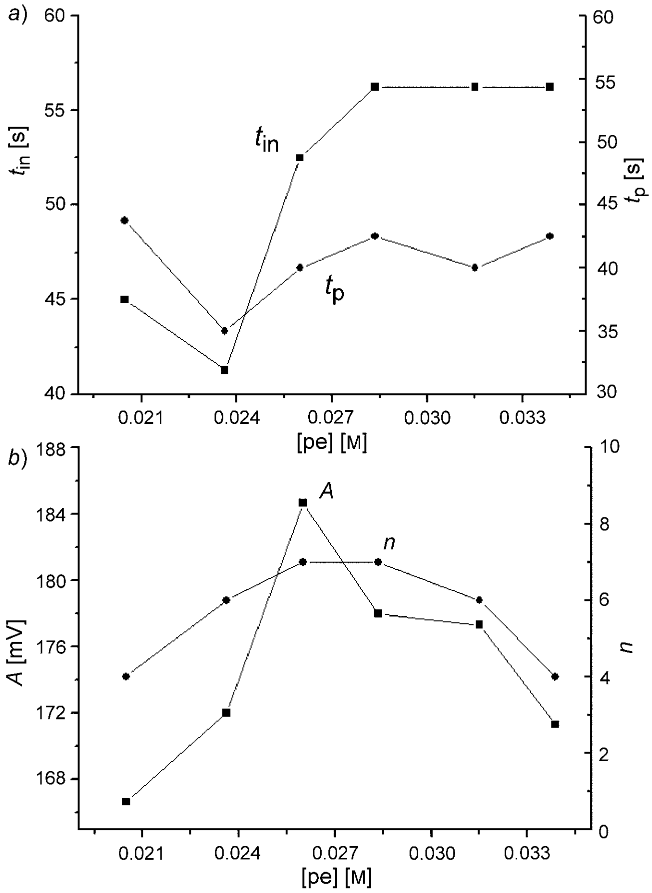

Fig. 3. *The influence of* $[pe]_0$ a) *on induction period* (t_{in}) *and oscillation period* (t_p), *and* b) *on amplitude* (A) *and number of oscillations* (n) *at 3 ± 0.5°*. Conditions: $[KIO_3] = 0.021$M, $[H_2SO_4] = 0.025$M, $[H_2O_2] = 0.3$M, $[NiL^{2+}] = 0.00346$M.

3.4. *Influence of Temperature.* Changes of the temperature had a strong influence on the oscillating system, especially on the induction time (t_{in}) and the average oscillation period (t_p). A series of oscillating traces were measured at different temperatures (from 275 to 298 K), when the concentration of the components were fixed, following the concentration of typical oscillation. No oscillations were observed when the temperatures were higher than 300 K. We found that the induction period (t_{in}) and oscillation period (t_p) decreased with increasing temperature. It may be due to the increasing rates of the reactions.

Fig. 7,a, represents $\ln(1/t_{in})$ *vs.* $1/T$, and $\ln(1/t_p)$ *vs.* $1/T$ is shown in *Fig. 7,b*. Two satisfactory linear results have been obtained according to the following equation:

$$\ln(1/t_{in}) = -2992.5/T + 6.73 \ (r = -0.99244)$$

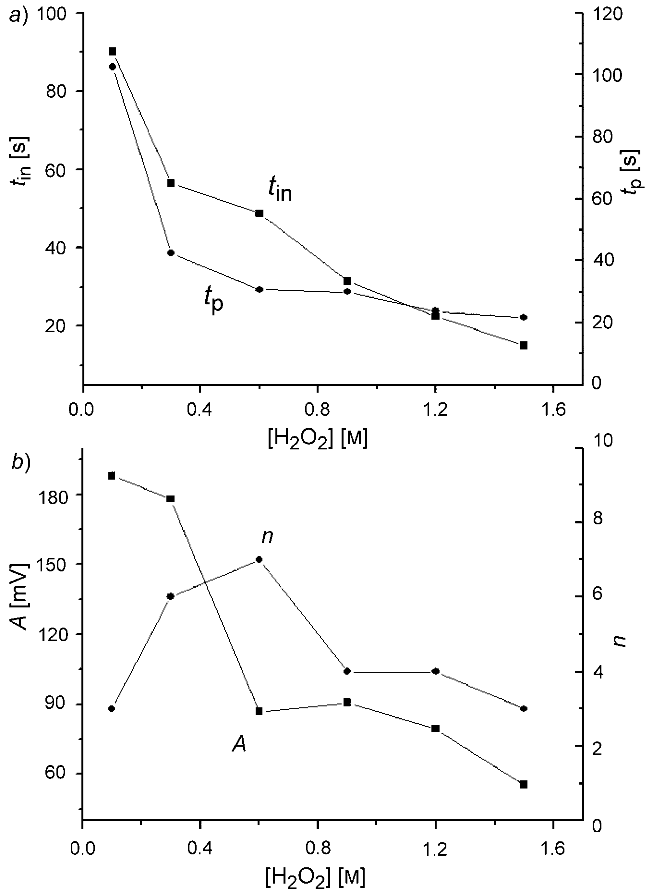

Fig. 4. *The influence of* $[H_2O_2]_0$ a) *on induction period* (t_{in}) *and oscillation period* (t_p), *and* b) *on amplitude* (A) *and number of oscillations* (n) *at* $3 \pm 0.5°$. Conditions: $[KIO_3] = 0.021$M, [pe] = 0.02835M, $[H_2SO_4] = 0.025$M, $[NiL^{2+}] = 0.00346$M.

$$\ln(1/t_p) = -4981.7/T + 13.75 \ (r = -0.99074)$$

From these equations, the apparent activation energy $E_1 = 24.88 \pm 1.78$ kJ/mol (for induction period) was calculated, and an apparent activation energy $E_2 = 41.42 \pm 3.28$ kJ/mol (for oscillation period) were determined.

3.5. *A Tentative Mechanism.* It is known that the behavior of the oscillator is prone to be disturbed by extraneous species in its oscillating period. In our experiment, the effects of Ag^+, I^-, and acrylonitrile were considered in order to study the mechanism. When 0.2×10^{-3} mol of Ag^+ was added to the oscillating system, the system stopped oscillating immediately due to precipitation of AgI. On the other hand, when 0.2×10^{-3} mol of I^- was added, the oscillation ceased right away too. Besides, when the concentration of acrylonitrile in the oscillation system reached 1.29×10^{-3} mol/l, the

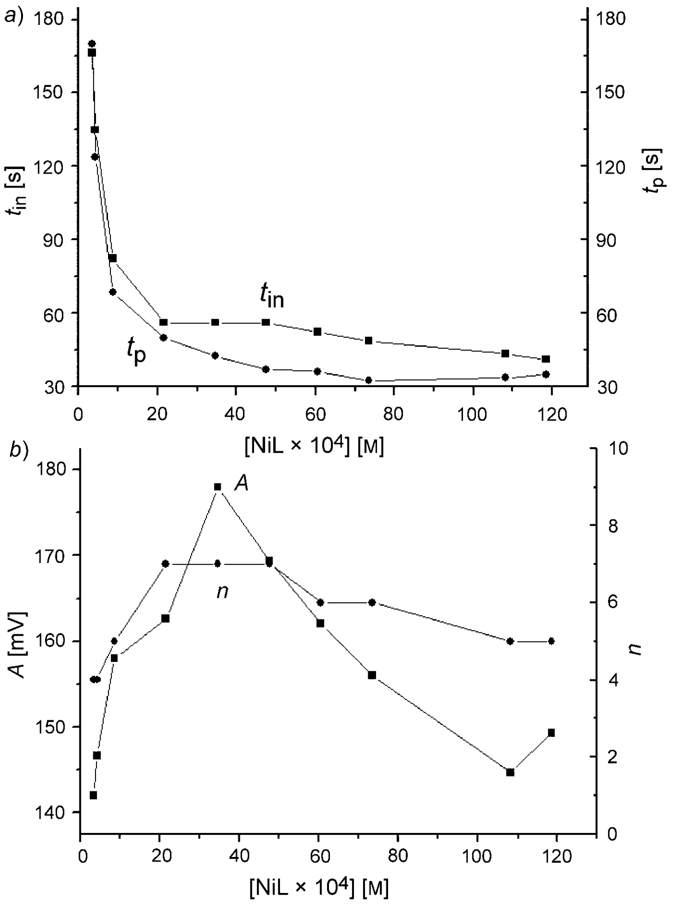

Fig. 5. *The influence of* $[NiL^{2+}]_0$ a) *on induction period* (t_{in}) *and oscillation period* (t_p), *and* b) *on amplitude* (*A*) *and number of oscillations* (*n*) *at* $3 \pm 0.5°$. Conditions: $[KIO_3] = 0.021$M, [pe] = 0.02835M, $[H_2SO_4] = 0.025$M, $[H_2O_2] = 0.3$M.

oscillations were inhibited temporarily. It is reasonable to argue that the concentration of I^- exerts a key control to oscillations, and radical steps may be involved in the mechanism.

It is an arduous work to separate and identify the products by traditional chemical methods. So, we employed GC/MS analyses. Only one product, namely 3-iodopentane-2,4-dione (peI), was identified by GC/MS. Pentane-2,4-dione has an reactive CH_2 group. So it can react with I_2 to produce peI.

Although some oscillating systems are very complex, and it is not easy to explain how the oscillation occurs, several reaction mechanisms were proposed [13–17]. *Noyes* and *Furrow* [15], and *Kepper* and *Epstein* [17] proposed some skeleton processes that account for oscillation catalyzed by Mn^{2+}. Based on the *N–F* model and the experimental observations, we suggest a tentative mechanism for the oscillator.

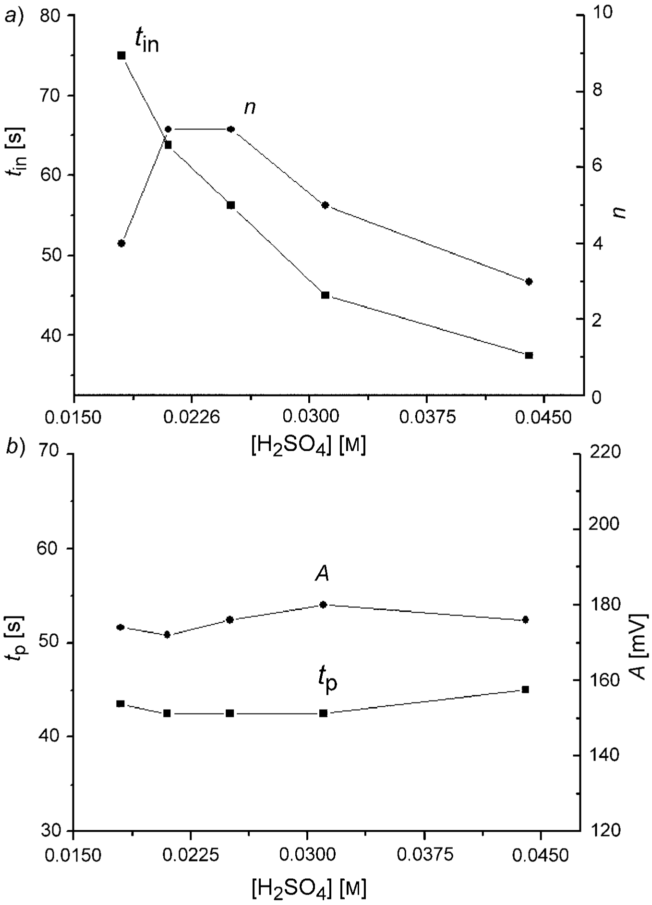

Fig. 6. *The influence of* $[H_2SO_4]_0$ a) *on induction period* (t_{in}) *and number of oscillations* (n), *and* b) *on oscillation period* (t_p) *and amplitude* (A) *at* $3 \pm 0.5°$. Conditions: $[KIO_3] = 0.021$M, [pe] = 0.02835M, $[NiL^{2+}] = 0.00346$M, $[H_2O_2] = 0.3$M.

The mechanism involves twelve reaction steps. When the concentration of I^- reaches a certain level, IO_3^- is reduced to I_2 *via Reactions 1–5.*

$$IO_3^- + I^- + 2\,H^+ \rightleftharpoons HIO_2 + HOI \tag{1}$$

$$HOI + I^- + H^+ \rightleftharpoons I_2 + H_2O \tag{2}$$

$$HIO_2 + I^- + H^+ \rightarrow 2\,HOI \tag{3}$$

$$2\,HIO_2 \rightarrow IO_3^- + HOI + H^+ \tag{4}$$

$$HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O \tag{5}$$

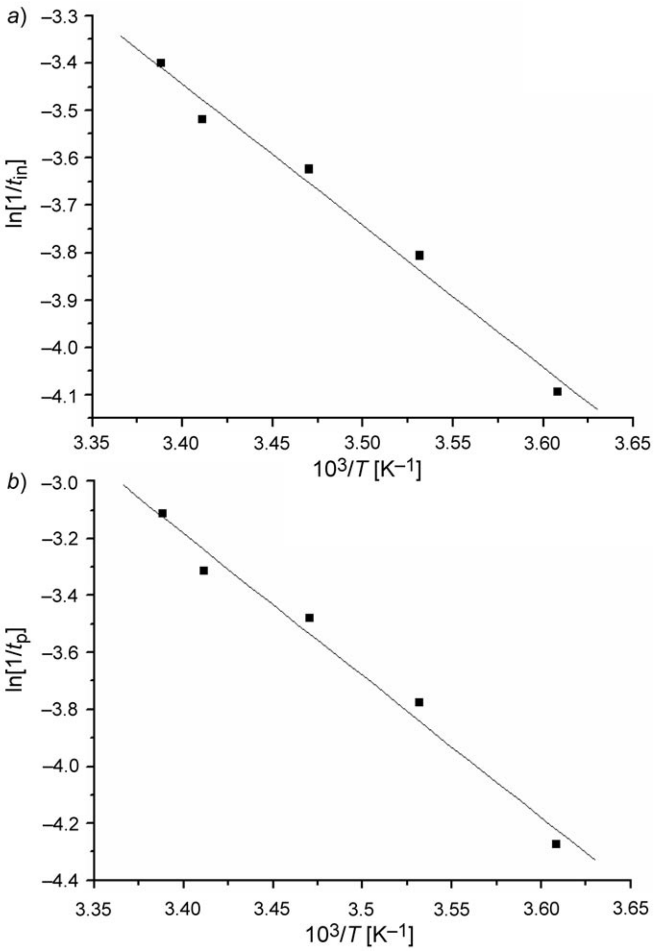

Fig. 7. a) *Plot of* $\ln(1/t_{in})$ vs. $1/T$, b) *plot of* $\ln(1/t_p)$ vs. $1/T$. Conditions: $[KIO_3] = 0.021$ M, $[H_2SO_4] = 0.025$ M, $[pe] = 0.02835$ M, $[NiL^{2+}] = 0.00346$ M, $[H_2O_2] = 0.3$ M.

When the concentration of I^- is too small to remove HIO_2 according to *Reaction 3*, *Reaction 6* takes place and produces $IO_2^{\bullet}$, which will oxidize NiL^{2+} to NiL^{3+}. At the same time, HIO_2 accumulates according to *Reaction 7*.

$$IO_3^- + HIO_2 + H^+ \rightleftharpoons 2\,IO_2^{\bullet} + H_2O \tag{6}$$

$$IO_2^{\bullet} + NiL^{2+} + H^+ \rightleftharpoons HIO_2 + NiL^{3+} \tag{7}$$

Reactions 8 and *9* represent the iodation of pentane-2,4-dione *via* its enol structure, and release a mass of I^-.

$$\mathrm{MeC(O)CH_2C(O)Me} \rightleftharpoons \mathrm{MeC(OH){=}CHC(O)Me} \qquad (8)$$

$$\mathrm{I_2 + MeC(OH){=}CHC(O)Me} \rightleftharpoons \mathrm{MeC(O)CH(I)C(O)Me + I^- + H^+} \qquad (9)$$

When NiL^{3+} reaches a critical concentration in *Reaction 7*, NiL^{3+} is reduced to NiL^{2+} according to *Reaction 10*, and *Reactions 11* and *12* show the cycle of H_2O_2.

$$\mathrm{NiL^{3+} + H_2O_2 \rightarrow NiL^{2+} + 2\ HO^\bullet} \qquad (10)$$

$$\mathrm{HO^\bullet + H_2O_2 \rightarrow H_2O + HOO^\bullet} \qquad (11)$$

$$\mathrm{2\ HOO^\bullet \rightarrow H_2O_2 + O_2} \qquad (12)$$

When the accumulation of HIO_2, I^-, and NiL^{2+} reached a certain concentration in *Reactions 7*, *9*, and *10*, respectively, the *Reactions 1–7* will take place again on the condition that there is a suitable concentration of IO_3^- in the system. In this way, the system exhibits the oscillating behavior. To a certain extent (in *Reactions 1–4*), this mechanism is similar to that of the *B–Z* oscillator [18].

In brief, this series of reactions involves the consumption of IO_3^-. When the concentration of IO_3^- is too low to sustain the reaction, the oscillation ceases. This hypothesis is also supported by the phenomenon that addition of some KIO_3 reveived the oscillation, while addition of the other substrates do not exert any effect.

4. Conclusions. – Iodation of pentane-2,4-dione in the presence of H_2O_2 and a tetraazamacrocylic Ni^{II} complex exhibits oscillating behavior. The oscillating parameters, such as the induction period, oscillation period, and amplitude and number of oscillations, are prone to be influenced by the variation of any kind of the concentration of the reactants. The apparent activation energy E_1 (for induction period) and the apparent activation energy E_2 (for oscillation period) were calculated to amount to 24.88 ± 1.78 kJ/mol and 41.42 ± 3.28 kJ/mol, respectively. The oscillation mechanism can be rationalized on the basis of a simplified *N–F* mechanism. To some extent, the discussed oscillator is similar to the *B–Z* oscillator.

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