Chemistry

COMPLEX OF NICKEL (II) ION WITH TRYPTOPHAN AS A HOMOGENEOUS CATALYST IN THE DECOMPOSITION REACTION OF CUMENE HYDROPEROXIDE IN AQUEOUS SOLUTION

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The formation of Ni^{2+}:Tryptophan (Trp) 1:1 complex, which acts as a model catalyst for decomposition of cumene hydroperoxide (ROOH) in Ni^{2+}+Trp+ROOH+H_2O system, has been confirmed via kinetic study in aqueous solution at pH>7. The kinetic expression of a single catalytic decomposition reaction of ROOH under the influence of $[NiTrp]^+$ complex was brought out. The temperature dependence of the effective rate constant of ROOH decay ($K_{eff} = K_{cat}[Ni^{2+}]_0[Trp]_0$=const) in the temperature range from 323 to 343 K can be expressed by Arrhenius equation (E_{eff} is in *kJ/mol*):

$$K_{eff} = (1.87 \pm 0.02) \cdot 10^6 \exp[-(49.8 \pm 0.3)/RT], \, min^{-1}.$$

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***Keywords*:** nickel (II) ion, amino acid, tryptophan, complex, cumene hydroperoxide, catalytic decay, kinetics.

Introduction. In our studies of the intermolecular interactions between components of complex kinetic systems such as M^{2+}+Ac+ROOH+H_2O the natural α-amino acids (Ac) of different compositions, character and properties were used as ligands [1–9]. These amino acids may form with "vital metals" of the first row transition metals M^{2+} (Cu^{2+}, Co^{2+}, Ni^{2+}, Mo^{2+}, etc.) binary chelate complexes with compositions 1:1 and 1:2 in aqueous solutions at pH 8–12. The complexes with composition 1:1 as model catalysts exhibit an activity in the decomposition reactions of cumene and tert-butyl hydroperoxide by analogy with catalase enzymes.

We have shown that, unlike to alkaline aqueous solutions, the amino acids and metal ions do not form an enzymatically active complexes in acidic media at pH 2–6 and the decomposition of ROOH does not occur [2–5]. It should be noted that separately both metal ions and amino acids (except methionine) do not lead to the decomposition of ROOH in aqueous solutions at pH 2–12 [1–9].

In this work the heterocyclic amino acid tryptophan ((2*S*)-2-amino-3-(1*H*-indol-3-yl)propanoic acid) is used as a ligand:
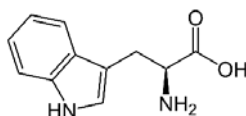
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Trp is one of the essential amino acids and cannot be synthesized in organism [10, 11]. It should be noted that, regardless its low solubility in water (1.14 g/100 g H_2O at 298 K) and low concentration, the complexes of Ni^{2+} with Trp formed in the system M^{2+}+Ac+ROOH+H_2O show significant catalytic activity in the decomposition reaction of ROOH.

The purpose of this work was to study the catalytic activity of the complex formed due to the interaction of Ni(II) ion and Trp in the decomposition reaction of ROOH in an aqueous solution. Moreover, the kinetic regularities of this catalytic reaction under the most optimal conditions for the formation of a complex catalyst (pH 9.6±0.1 and the temperature range from 323 to 343 K) have been studied as well.

Experimental Part. Experiments were carried out in aqueous solutions. Heterocyclic amino acid L-tryptophan was used as a ligand, nickel (II) ion in the form of $NiCl_2·6H_2O$ was used as a complex forming reagent, and cumene hydro-peroxide (99.8% purity) was used as a substrate-reagent. The initial concentrations of the reagents were $[Ni^{2+}]_0$=1.0·10^{-4}, 1.5·10^{-4}, 2.0·10^{-4} M; $[Trp]_0$=0.004, 0.005, 0.006 M; $[ROOH]_0$=0.04 M.

The catalytic decomposition reaction rate was determined via iodometric titration according to the method developed for the analysis of ROOH in an aqueous solution and described in [1, 5]. In single experiments, the probability of ROOH decomposition was studied under the influence of system components separately – nickel (II) ion or amino acid. In both cases, the decomposition of ROOH did not occur. The decomposition of ROOH takes place only in the presence of both Ni^{2+} and Trp in the system and in the case of complex formation.

The experiments were carried out in aqueous solutions at pH 9.6±0.1 as optimal for the formation of amino acid anion and complex. The alkalinity of the medium was regulated by adding an appropriate amount of base (KOH). The pH of the solutions were measued using JENWAY 4330 pH-meter. The experiments were carried out in the temperature range from 323 to 343 K. The temperature of the system was held constant using thermostate with an accuracy of ±0.1 K. Processing of the resulting data was performed with "Origin" software.

Results and Discussion. In the first series of experiments, a kinetic equation was derived for the rate of ROOH catalytic decomposition in the presence of reactants. Therefore, the order of reaction with respect to each components (Ni^{2+}, Trp and ROOH) was determined via graphical differentiation and using the dependence of the initial rates (W_0) on the initial concentrations of the reactants.

The dependence of ROOH consumption on the initial concentration of nickel (II) ion (i.e. the order of reaction with respect to Ni^{2+}) was determined in the concentration range $[Ni^{2+}]_0$=1.0·10^{-4}–2.0·10^{-4} M, keeping the concentrations of $[ROOH]_0$=0.04 M and $[Trp]_0$=0.006 M constant (by adding the equivalent amount of KOH to the system to form Ac^- anion). The initial concentrations were calculated via graphical differentiation, drawing tangent to the kinetic plots (Fig. 1, a). The values of the effective rate constant (K_{eff}) for different initial concentrations of Ni^{2+} ion were also obtained graphically from the dependence of the first-order reaction rate with respect to ROOH (ln $a_0/(a_0–x)$ versus t). The calculated values of initial rate (W_0) and K_{eff} parameters are shown in Tab. 1. From these data, the orders of reaction with respect to Ni^{2+} ion and ROOH were determined. In both cases, the order of reaction is 1, because $W_0/[Ni^{2+}]_0$=const and $K_{eff}/[Ni^{2+}]_0$=const (Fig. 1, b and Tab. 1).
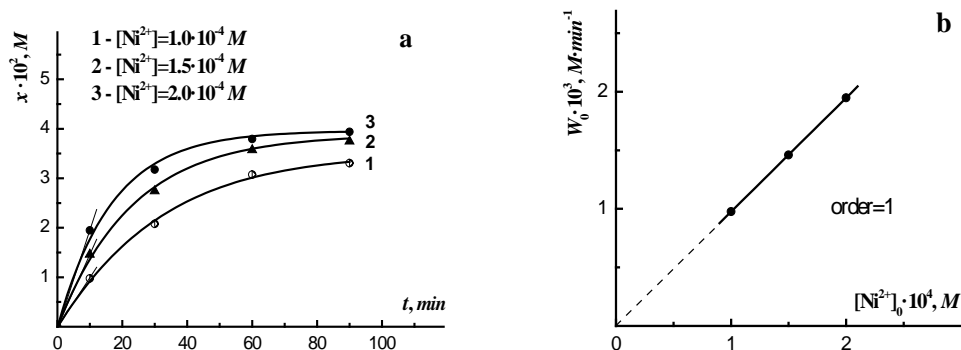
Fig. 1. a) Kinetic curves of ROOH consumption in the catalytic decomposition reaction at different initial concentrations of Ni^{2+} ion; b) Illustration of the first order of the reaction with respect to Ni^{2+} ion at T=343 K; [ROOH]$_0$=0.04 M, [Trp]$_0$=[KOH]$_0$=0.006 M.

Table 1

The values of W_0 and K_{eff} at different initial concentrations of the nickel (II) ion.
[ROOH]$_0$=0.04 M, [Trp]$_0$=[KOH]$_0$=0.006 M, T=343 K

[Ni^{2+}]$_0$·10^4, M	W_0·10^3, $M \cdot min^{-1}$	W_0/[Ni^{2+}]$_0$	K_{eff}·10^2, min^{-1}	K_{eff}/[Ni^{2+}]$_0$
1.0	0.976	9.76	2.44	244.0
1.5	1.461	9.73	3.65	243.3
2.0	1.948	9.74	4.87	243.5

The initial rates of ROOH decay at different initial concentrations of Trp were also determined using graphical differentiation of ROOH consumption plots over time (Fig. 2, a). For that reason, the tangents of the plots were depicted, and the slope gave W_0. From the data obtained, the plot of dependence of W_0 on [Trp]$_0$ was depicted (Fig. 2, b). These data show that the reaction is also the first-order with respect to amino acid (W_0/[Trp]$_0$=const).
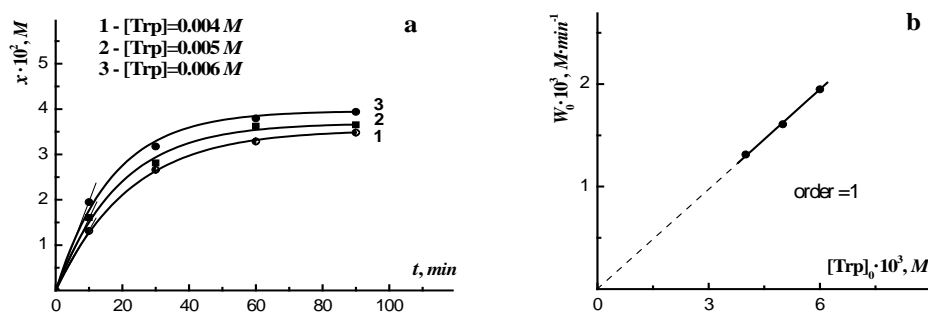

Fig. 2. a) Kinetic curves of ROOH consumption at different initial concentrations of Trp; b) Illustration of the first order of the reaction with respect to Trp at T=343 K; [ROOH]$_0$=0.04 M, [Ni^{2+}]$_0$= 2.0·10^{-4} M.
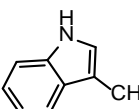
Thus, as can be seen from the data obtained (Figs. 1, 2 and Tab. 1), the reaction order with respect to components is equal to unity. The straight line dependencies passing through the origin (Figs. 1, 2) mean not only the first order with respect to components, but also the fact that in Ni^{2+}+Trp+ROOH+H_2O system only a single ROOH decomposition reaction takes place. This reaction is catalyzed by the

complex of Ni^{2+} ion with Trp, as in the case with other complexes of M^{2+} and Ac [1–9]. Moreover, in all our studies and in this system, the individual components (M^{2+} and Ac) do not cause the decomposition of ROOH in aqueous solutions.

The established first order of the ROOH catalytic decomposition reaction with respect to Ni^{2+} and Trp confirms that the complex catalyst formed in the system actually has a 1:1 composition ($[NiTrp]^+$), as in the case of other M^{2+} of first row transition metals and α-amino acids [1–9]. It should be noted that although the initial concentration of Ac is one order of magnitude greater than the initial concentration of the nickel (II) ion, the concentration of the complex with compositions 1:1 cannot be greater than the initial concentration of the metal(II) ion, that is, the maximum concentration of the $[NiTrp]^+_0$ complex will be equal to the $[Ni^{2+}]_0$.

In 1:1 chelate complexes of M^{2+} with α-amino acids at pH=8–12, metal (II) ions are linked to the oxygen atom of the carboxyl group of the amino acid by electrostatic interaction, and to the amine functional group by the coordination bond through free electron pairs of the nitrogen atom, which we have shown by spectroscopic methods in our previous studies [3–6], as well as by the authors of similar works [12–18]. According to the kinetic data obtained and by analogy with our early spectroscopic studies of the complex formation of Ni^{2+} ion with other amino acids, the structure of the chelate, catalytically active complex of nickel (II) ion with anion of Trp can be represented by the following scheme:
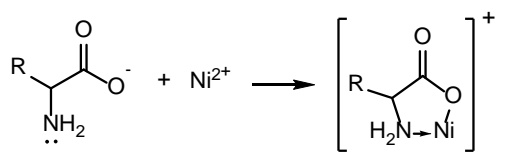
where R is a CH_2- group .

In the second part of the experiments, the temperature dependence of the ROOH decomposition reaction rate under the influence of the $[NiTrp]^+$ complex catalyst was determined. The kinetic curves of the ROOH catalytic decomposition reaction at temperatures of 323, 328, 333 and 343 K are presented in Fig. 3, a.
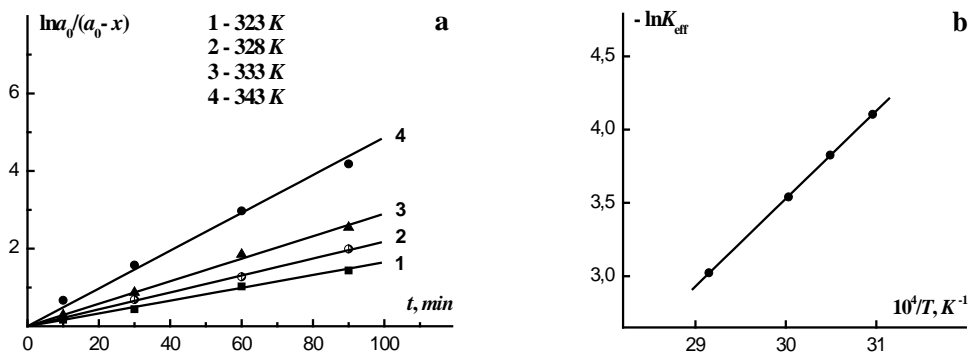

Fig. 3. a) The kinetic curves of ROOH catalytic decomposition reaction at different temperatures; $[ROOH]_0=0.04\ M$, $[Ni^{2+}]_0=2.0\cdot10^{-4}\ M$, $[Trp]_0=[KOH]_0=0.006\ M$; b) The dependence of lnK_{eff} versus $1/T$.

From Fig. 3, a, the values of the effective rate constant (K_{eff}) were graphically calculated at the indicated temperatures. And from the graphical dependence of $\ln K_{eff}$ versus $1/T$ (Fig. 3, b), the effective activation energy (E_{eff}) and the value of the pre-exponential factor (PZ) were calculated. The correlation coefficients obtained via regression analysis using the least square procedure are 0.99995. The calculated values of K_{eff}, E_{eff} and PZ are given in Tab. 2.

Table 2

The values of K_{eff}, E_{eff} and PZ in the temperature range from 323 to 343 K.
$[ROOH]_0=0.04$ M, $[Ni^{2+}]_0=2.0 \cdot 10^{-4}$ M, $[Trp]_0=[KOH]_0=0.006$ M

T, K	$10^4/T$, K^{-1}	$K_{eff} \cdot 10^2$, min^{-1}	E_{eff}, kJ/mol	PZ
323	30.96	1.65		
328	30.49	2.18	49.8 ± 0.3	$(1.87 \pm 0.02) \cdot 10^6$
333	30.03	2.90		
343	29.15	4.87		

Conclusion. Thus, on the basis of the obtained experimental and calculated results, in the $Ni^{2+}+Trp+ROOH+H_2O$ system, the initial rate of the ROOH catalytic decomposition under the influence of the $[NiTrp]^+$ complex catalyst is expressed by the following kinetic equation:

$$W_0 = -d[ROOH]_0/dt = K_{cat}[Ni^{2+}]_0[Trp]_0[ROOH]_0 = K_{eff}[ROOH]_0,$$

where $K_{eff}=K_{cat}[Ni^{2+}]_0[Trp]_0$=const at a given temperature and initial constant concentrations of Ni^{2+} ion and Trp. The temperature dependence of the effective rate constant of the ROOH catalytic decomposition reaction under the influence of the $[NiTrp]^+$ complex in aqueous alkaline solutions is expressed by the following Arrhenius equation:

$$K_{eff} = (1.87 \pm 0.02) \cdot 10^6 \exp[-(49.8 \pm 0.3)/RT], \, min^{-1}:$$

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Գ. Ս. ԳՐԻԳՈՐՅԱՆ

ՏՐԻՊՏՈՖԱՆԻ ՀԵՏ ՆԻԿԵԼԻ (II) ԻՈՆԻ ԿՈՄՊԼԵՔՍԸ ՈՐՊԵՍ ՀՈՄՈԳԵՆ ԿԱՏԱԼԻԶԱՏՈՐ ՋՐԱՅԻՆ ԼՈՒԾՈՒՅԹՈՒՄ ԿՈՒՄՈԼԻ ՀԻԴՐՈՊԵՐՕՔՍԻԴԻ ՔԱՅՔԱՅՄԱՆ ՌԵԱԿՑԻԱՅՈՒՄ

Կինետիկական հետազոտությամբ հաստատվել է նիկելի (II) իոնի և տրիպտոֆանի (Trp) միջև 1:1 բաղադրության [NiTrp]⁺ կոմպլեքսի առաջացումը ջրային միջավայրում (pH>7), որը ցուցաբերում է հոմոգեն կատալիզատորի հատկություն՝ կումոլի հիդրոպերօքսիդը (ROOH)

Ni^{2+}+Trp+ROOH+H_2O համակարգում բայքայելիս: Դուրս է բերվել [NiTrp]$^+$ կոմպլեքսի ազդեցությամբ ROOH-ի կատալիտիկ բայքայման ռեակցիայի կինետիկական հավասարումը: Հաստատվել է այդ ռեակցիայի արագության էֆեկտիվ հաստատունի ($K_{Է.ֆ}$=$K_{կատ}$[Ni^{2+}]$_0$[Trp]$_0$) ջերմաստիճանային կախվածությունը 323–343 Կ միջակայքում, որն արտահայտվում է հետևյալ արենիուսական հավասարումով ($E_{Է.ֆ}$՝ կՋ/մոլ).

$$K_{Է.ֆ} = (1.87 \pm 0.02) \cdot 10^6 \exp[-(49.8 \pm 0.3)/RT], \text{րոպե}^{-1}:$$

Г. С. ГРИГОРЯН

КОМПЛЕКС ИОНА НИКЕЛЯ(II) С ТРИПТОФАНОМ КАК ГОМОГЕННЫЙ КАТАЛИЗАТОР В РЕАКЦИИ РАСПАДА ГИДРОПЕРОКСИДА КУМОЛА В ВОДНОЙ СРЕДЕ

Кинетическим исследованием установлено образование комплекса между ионом никеля(II) и триптофаном (Trp) состава 1:1 – [NiTrp]$^+$, проявляющего себя как гомогенный катализатор при распаде гидропероксида кумола (ROOH) в водной среде (pH>7). Выведено кинетическое уравнение скорости каталитической реакции, протекающей в системе Ni^{2+}+Trp+ROOH+H_2O под действием комплексного катализатора [NiTrp]$^+$. Установлена температурная зависимость эффективной константы скорости ($K_{эфф}$=$K_{кат}$[Ni^{2+}]$_0$[Trp]$_0$) каталитического распада ROOH в интервале 323–343 K, которая выражается следующим аррениусовским уравнением ($E_{эфф}$ в $кДж/моль$):

$$K_{эфф} = (1.87 \pm 0.02) \cdot 10^6 \exp[-(49.8 \pm 0.3)/RT], \text{мин}^{-1}.$$