Chemistry

CATALYTIC ACTIVITY OF THE COBALT(II) ION WITH PHENYLALANINE COMPLEX IN THE DECOMPOSITION REACTION OF CUMENE HYDROPEROXIDE IN AQUEOUS SOLUTION

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The formation of Co^{2+}: phenylalanine (Phe) 1:1 complex has been confirmed via kinetic study in aqueous solution at pH>7, which acts as a model catalyst for the decomposition of cumene hydroperoxide (ROOH) in Co^{2+}+Phe+ROOH+H_2O system. The kinetic expression of a single catalytic decomposition reaction of ROOH under the influence of $[CoPhe]^+$ complex, as well as the Arrhenius equation describing the temperature dependence of the effective constant K_{eff} ($=K_{cat}$ $[Co^{2+}]_0[Phe]_0$) of ROOH decay rate in the temperature range from 323 to 343 K are brought out.

**Introduction.** In our study of the intermolecular interactions between components of complex kinetic systems, such as M^{2+}+Ac+ROOH+H_2O, natural α-amino acids (Ac) with different composition, character and properties were used as ligands [1–9]. These amino acids can form binary chelate complexes with the "vital metals" of the first row transition metals M^{2+} (Cu^{2+}, Co^{2+}, Ni^{2+}, Mo^{2+}, etc.) 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 enzyme.

We have shown that, unlike alkaline aqueous solutions, amino acids and metal ions do not form enzymatically active complexes in acidic media at pH 2–6 and the decomposition of ROOH does not occur [2–4]. 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 aromatic amino acid phenylalanine (2-amino-3-phenylpropanoic acid, Phe) is used as a ligand:

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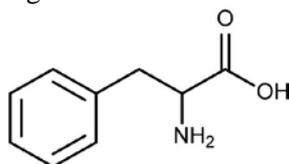
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Phe is one of the essential amino acids and cannot be synthesized in organism [10, 11]. It should be noted that, regardless of its low solubility in water (2.83 $g/100\ g$ H_2O at 298 K) and low concentration, the complexes of Co^{2+} with Phe formed in the system $M^{2+}+Ac+ROOH+H_2O$ show significant catalytic activity in decomposition reactions of ROOH.

The purpose of this work was to study the catalytic activity of the complex formed due to the interaction of Co^{2+} ion and Phe 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, i.e. pH 9.6±0.1 and temperature range from 323 to 343 K, have been studied as well.

Experimental Part. Aromatic amino acid L-phenylalanine was used as a ligand, Co^{2+} ion in the form of $CoCl_2 \cdot 6H_2O$ was used as a complex forming agent, and cumene hydroperoxide (99.8% purity) was used as a substrate-reagent. The initial concentrations of the reagents were $[Co^{2+}]_0=1.0 \cdot 10^{-4}$, $1.5 \cdot 10^{-4}$, $2.0 \cdot 10^{-4}\ M$; $[Phe]_0=0.004$, 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 – cobalt(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 Co^{2+} ion and Phe 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, and in the temperature range from 323 to 343 K. The alkalinity of the medium was regulated by adding an appropriate amount of base (KOH). The pH of the solutions were measured using a JENWAY 4330 pH-meter. The temperature of the system was held constant using a thermostat 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 catalytic decomposition of ROOH in the presence of reactants. Therefore, the order of reaction with respect to each component (Co^{2+}, ROOH and Phe) 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 cobalt(II) ion (i.e., the order of reaction with respect to Co^{2+}) was determined in the concentration range $[Co^{2+}]_0=1.0 \cdot 10^{-4}$–$2.0 \cdot 10^{-4}\ M$, keeping the concentrations of $[ROOH]_0=0.04\ M$ and $[Phe]_0=0.006\ M$ constant (by adding an 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 Co^{2+} 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 the initial rate (W_0) and K_{eff} are shown in Tab. 1. From these data, the orders of reaction with respect to Co^{2+} ion and ROOH were determined. In both cases, the orders of reactions were 1, because $W_0/[Co^{2+}]_0$ = const and $K_{eff}/[Co^{2+}]_0$ = const (Fig. 1, b).

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

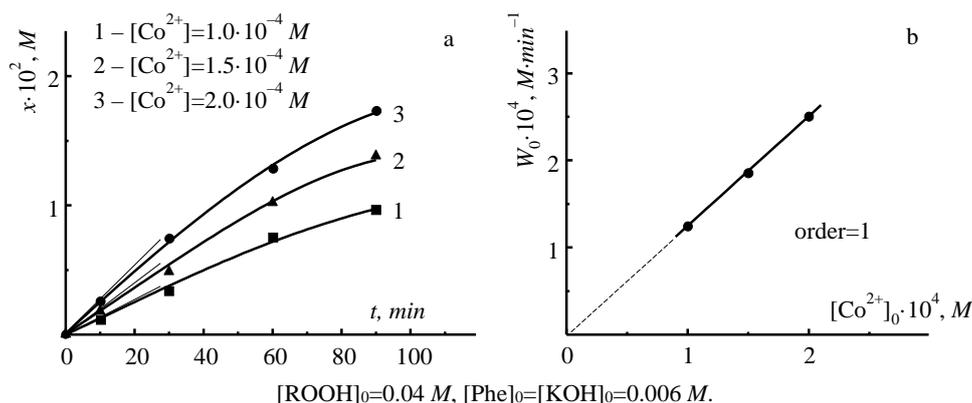$[ROOH]_0=0.04\ M$, $[Phe]_0=[KOH]_0=0.006\ M$.

Fig. 1. a) Kinetic curves of ROOH consumption in the catalytic decomposition reaction at different initial concentrations of Co^{2+};
b) Illustration of the first order of the reaction with respect to Co^{2+} at $T=343\ K$.

Table 1

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

$[Co^{2+}]_0 \cdot 10^4$, M	$W_0 \cdot 10^4$, $M \cdot min^{-1}$	$W_0/[Co^{2+}]_0$	$K_{eff} \cdot 10^3$, min^{-1}	$K_{eff}/[Co^{2+}]_0$
1.0	1.25	1.25	3.13	31.3
1.5	1.86	1.24	4.65	31.0
2.0	2.51	1.26	6.28	31.4

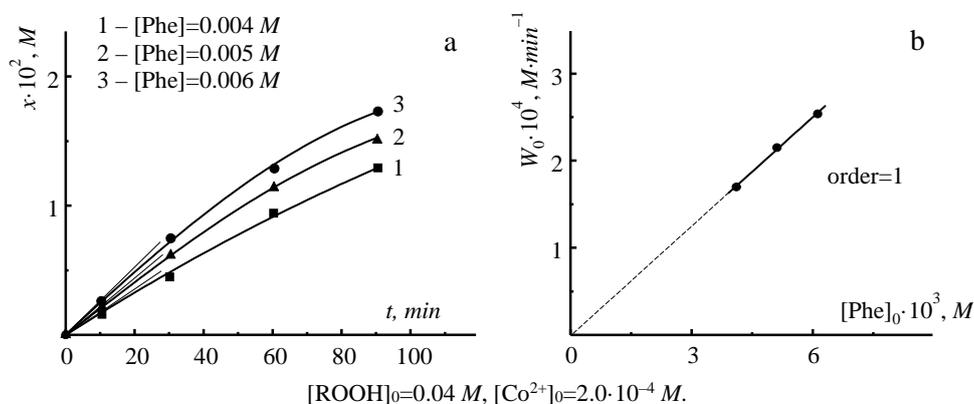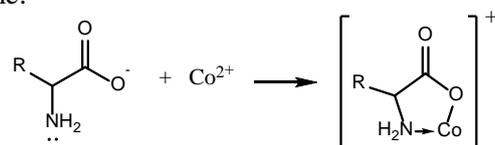$[ROOH]_0=0.04\ M$, $[Co^{2+}]_0=2.0 \cdot 10^{-4}\ M$.

Fig. 2. a) Kinetic curves of ROOH consumption at different initial concentrations of Phe;
b) Illustration of the first order of reaction with respect to Phe at $T=343\ K$.

Thus, as can be seen from the obtained data (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 $Co^{2+}+Phe+ROOH+H_2O$ system only a single ROOH decomposition reaction takes place. This reaction is catalyzed by the complex of cobalt(II) ion with Phe, as in the case with other complexes of M^{2+} and amino acids [1–9]. Moreover, in all our studies and in this system, the individual components (M^{2+} and Ac) do not cause decomposition of ROOH in aqueous solutions.

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

In 1:1 chelate complexes 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 coordination bond through free electron pairs of the nitrogen atom, which was shown by us by spectroscopic methods in previous studies [1–8], as well as by the authors of similar works [12–17]. According to the obtained kinetic data and by analogy with our early spectroscopic studies of the complex formation of cobalt(II) ion with other amino acids, the structure of the chelate, catalytically active complex of Co^{2+} with phenylalanine anion can be represented by the following scheme:

where R is a $C_6H_5–CH_2$ group.
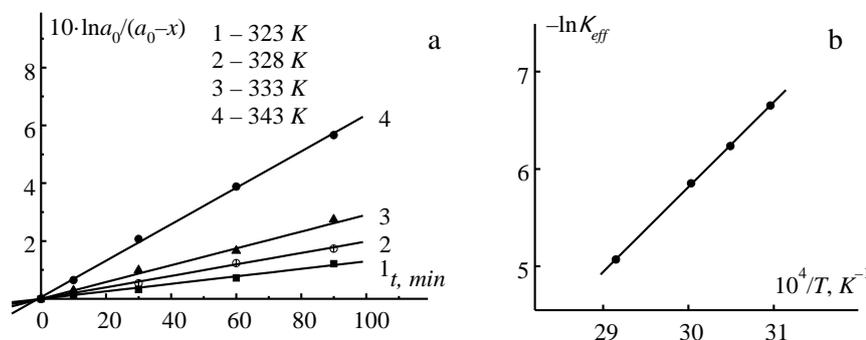
$[ROOH]_0=0.04\ M$, $[Co^{2+}]_0=[CoPhe]^+_0=2.0\cdot10^{-4}\ M$, $[Phe]_0=[KOH]_0=0.006\ M$.

Fig. 2. a) The kinetic curves of ROOH catalytic decomposition reaction at different temperatures;
b) The dependence of $\ln K_{eff}$ versus $1/T$.

In the second part of the experiments, the temperature dependence of the ROOH decomposition reaction rate under the influence of the $[CoPhe]^+$ 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.

The values of K_{eff}, E_{eff} and PZ at different temperatures.
($[ROOH]_0=0.04$ M, $[Co^{2+}]_0=[CoPhe]^+{}_0=2.0 \cdot 10^{-4}$ M, $[Phe]_0=[KOH]_0=0.006$ M)

T, K	$10^4/T$, K^{-1}	$K_{eff} \cdot 10^3$, min^{-1}	E_{eff}, kJ/mol	PZ
323	30.96	1.29		
328	30.49	1.96		
333	30.03	2.87	72.5 ± 0.7	$(6.87 \pm 0.07) \cdot 10^8$
343	29.15	6.28		

From Fig. 3, a, the values of the K_{eff} were graphically calculated at the indicated temperatures. And from the graphical dependence $\ln K_{eff}$ 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 were 0.99992. The calculated values of K_{eff}, E_{eff} and PZ are given in Tab. 2.

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

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

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

$$K_{eff} = (6.87 \pm 0.07) \cdot 10^8 \exp[-(72.5 \pm 0.7)/RT], \ min^{-1}.$$

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Գ. Ս. ԳՐԻԳՈՐՅԱՆ

ՖԵՆԻԼԱԼԱՆԻՆԻ ՀԵՏ ԿՈԲԱԼՏԻ(II) ԻՈՆԻ ԿՈՄՊԼԵՔՍԻ ԿԱՏԱԼԻՏԻԿ ԱԿՏԻՎՈՒԹՅՈՒՆԸ ՋՐԱՅԻՆ ԼՈՒԾՈՒՅԹՈՒՄ ԿՈՒՄՈԼԻ ՀԻԴՐՈՊԵՐՕՔՍԻԴԻ ՔԱՅՔԱՅՄԱՆ ՌԵԱԿՑԻԱՅՈՒՄ

Կինետիկական ուսումնասիրությամբ հաստատվել է կոբալտի(II) իոնի և ֆենիլալանինի (Phe) միջև 1:1 բաղադրության [CoPhe]$^+$ կոմպլեքսի առաջացումը ջրային միջավայրում (pH>7), որը ցուցաբերում է հոմոգեն կատալիզատորի հատկություն` կումոլի հիդրոպերօքսիդը (ROOH) Co^{2+}+Phe+ROOH+H$_2$O համակարգում քայքայելիս: Դուրս են բերվել [CoPhe]$^+$ կոմպլեքսի ազդեցությամբ Co^{2+}+Phe+ROOH+H$_2$O համակարգում ընթացող ROOH-ի կատալիտիկ քայքայման ռեակցիայի կինետիկական հավասարումը, ինչպես նաև 323–343 Կ միջակայքում այդ ռեակցիայի արագության էֆեկտիվ հաստատունի $K_{էֆ.}$ ($=K_{կատ.}$[Co^{2+}]$_0$[Phe]$_0$) ջերմաստիճանային կախվածության արենիուսական հավասարումը:

Г. С. ГРИГОРЯН

КАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ КОМПЛЕКСА ИОНА КОБАЛЬТА(II) С ФЕНИЛАЛАНИНОМ В РЕАКЦИИ РАСПАДА ГИДРОПЕРОКСИДА КУМОЛА В ВОДНОЙ СРЕДЕ

Кинетическим исследованием установлено образование комплекса между ионом кобальта(II) и фенилаланином (Phe) состава 1:1 – [CoPhe]$^+$, проявляющего себя как гомогенный катализатор при распаде гидропероксида кумола (ROOH) в водной среде (pH>7). Выведены кинетическое уравнение скорости каталитической реакции, протекающей в системе Co^{2+}+Phe+ROOH+H$_2$O под действием комплексного катализатора [CoPhe]$^+$, а также аррениусовское уравнение, описывающее температурную зависимость эффективной константы скорости $K_{эфф.}$ ($=K_{кат.}$[Co^{2+}]$_0$[Phe]$_0$) каталитического распада ROOH в интервале 323–343 K.