Chemistry

KINETICS OF CUMENE HYDROPEROXIDE CATALYTIC DECAY IN AQUEOUS SOLUTION IN THE PRESENCE OF COPPER ION (II) AND TRYPTOPHAN

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The formation of Cu^{2+} : Tryptophan (Trp) = 1 : 1 complex, which acts as a model catalyst for decomposition of cumene hydroperoxide (ROOH) in $H_2O+Cu^{2+}+Trp+ROOH$ system, has been confirmed via kinetic study in aqueous solution at pH > 7. Kinetic equation of single catalytic decomposition reaction of ROOH under the influence of $[CuTrp]^+$ complex was derived:

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

The temperature dependence of the effective rate constant K_{eff} ($K_{eff} = K_{cat}[Cu^{2+}]_0[Trp]_0$ = const) for ROOH decay in the temperature range from 323 to 343 K can be expressed by Arrhenius equation (K_{eff} is in *kJ/mol*):

$$K_{eff} = (7.45 \pm 0.02) \cdot 10^6 \exp[-(56.5 \pm 0.2)/RT]\ 1/min.$$

Keywords: amino acid, tryptophan, complex, cumene hydroperoxide, catalytic decay, kinetics.

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

We have shown that unlike 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].

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In this work the heterocyclic amino acid tryptophan (α-2-amino-3-(1H--indol-3-il) propionic acid) [structure] which is one of the essential amino acids and cannot be synthesized in organism [10, 11] is used as a ligand for the first time. It should be noted, that regardless of its low solubility in water (1.14 g/100 g H_2O at 298 K) and low concentration, the complex of Cu^{2+} with Trp formed in the system $H_2O + M^{2+} + Ac + ROOH$ shows significant catalytic activity in the reactions of decomposition of ROOH compared with the complexes of Cu^{2+} with some other amino acids [5, 6].

The purpose of this work was to study the catalytic activity of the complex formed due to the interaction between copper (II) ion and tryptophan with 1:1 composition in the decomposition reaction of ROOH in aqueous solution. Moreover, the kinetic regularities of this catalytic reaction under the most optimal conditions for the formation of complex catalyst pH=9.5–9.7 and temperature range from 323 to 343 K have been studied as well.

Experimental Part. Experiments were carried out in aqueous solutions. Heterocyclic amino acid tryptophan was used as ligand, copper (II) ion in form of $CuSO_4 \cdot 5H_2O$ was used as complex forming agent, and cumene hydroperoxide (99.8% purity) was used as substrate-reagent. The initial concentrations of the reagents were $[Cu^{2+}]_0 = 1.0 \cdot 10^{-4}$, $1.5 \cdot 10^{-4}$, $2.0 \cdot 10^{-4}$ M; $[Trp]_0 = 4.0 \cdot 10^{-3}$, $5.0 \cdot 10^{-3}$, $6.0 \cdot 10^{-3}$ M; $[ROOH]_0 = 4.0 \cdot 10^{-2}$ M.

The rate of catalytic decomposition reaction was determined via iodometric titration according to the method developed for the analysis of ROOH in aqueous solution and described in [1, 6]. In single experiments the probability of decomposition of ROOH was studied under the influence of system components separately – Cu^{2+} 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 copper (II) ion and tryptophan in the system and in the case of complex formation.

Experiments were carried out in aqueous solutions at pH=9.5–9.7 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). pH of solutions were measued using JENWAY 4330 pH-meter. Experiments were carried out in the temperature range from 323 to 343 K. The temperature of the system was kept constant using thermostate with accuracy ± 0.1 K.

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

The dependence of ROOH consumption on the initial concentration of copper (II) ion (i.e. the order of reaction with respect to Cu^{2+}) was determined in the concentration range $[Cu^{2+}]_0 = 1.0 \cdot 10^{-4} - 5.0 \cdot 10^{-4}$ 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 are calculated via graphical differentiation drawing tangents to the kinetic plots (Fig. 1, a).

The data of the effective rate constant (K_{eff}) for different initial concentrations of copper (II) ion were also obtained graphically from the dependence of the first order reaction rate with respect to ROOH ($\lg(P/(P–x))$ 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 Cu^{2+} ion and ROOH are determined. In both cases the orders of reaction are 1, because $W_0/[Cu^{2+}]$=const and $K_{eff}/[Cu^{2+}]$=const (Fig. 1, b).
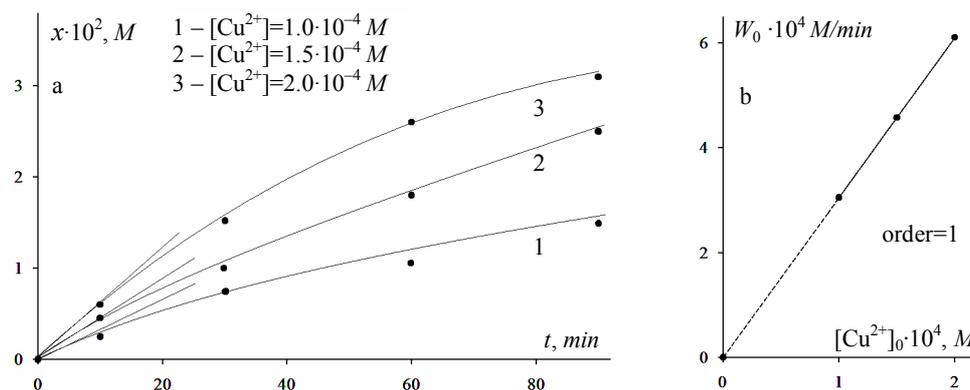
Fig. 1. a) The kinetic curves of ROOH consumption in the catalytic decomposition reaction at different initial concentrations of Cu^{2+}. b) Illustration of the first order of reaction with respect to copper (II) ion at T=343 K; $[ROOH]_0$=0.04 M; $[Trp]_0$=$[KOH]_0$=0.006 M.

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 tangent of the plots were depicted and the slope gives W_0. From the data obtained the plot of dependence of W_0 on $[Trp]_0$ is depicted (Fig. 2, b). These data show that reaction is also first order with respect to amino acid ($W_0/[Trp]$=const).

Table 1

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

$[Cu^{2+}]_0 \cdot 10^4$, M	$W_0 \cdot 10^4$, M/min	$W_0/[Cu^{2+}]$	K_{eff}, min^{-1}	$K_{eff}/[Cu^{2+}]_0$
1.0	3.15	3.15	0.0086	86.0
1.5	4.75	3.16	0.0129	86.0
2.0	6.25	3.13	0.0173	86.5

Thus, as it can be seen from the obtained data (Figs. 1, 2 and Tab. 1), the reaction order with respect to components is equal to one. Straight line dependencies passing through the coordinates origin (Fig. 1, 2) mean not only the first order with respect to components, but also the fact that in $H_2O+Cu^{2+}+Trp+ROOH$ system only a single ROOH decomposition reaction takes place. This reaction is catalyzed by the complex of copper (II) ion with Trp, as in the case of 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 the decomposition of ROOH in aqueous solutions.
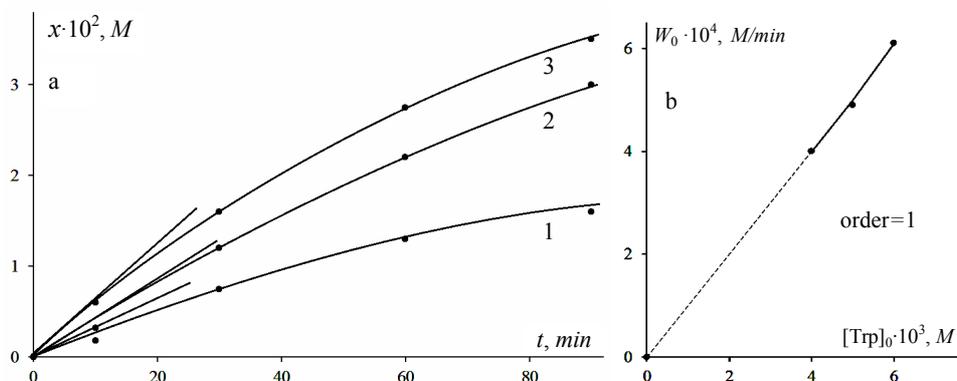
Fig. 2. a) The dependence of ROOH consumption on the initial concentration of Trp, M: 0.004 (1), 0.005 (2), 0.006 (3). b) Illustration of the first order of reaction with respect to Trp at T=343 K.

The established first order of ROOH catalytic decomposition reaction with respect to Cu^{2+} and Trp confirms that the complex catalyst formed in the system actually has 1:1 composition $[CuTrp]^+$, as in the cases of other M^{2+} and amino acids [1–9]. It should be noted that although the initial concentration of Ac is 1–2 orders of magnitude greater than the initial concentration of the copper (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 $[CuTrp]^+_0$ maximum concentration will be equal to the $[Cu^{2+}]_0$.

In chelate complexes of 1:1 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 previous studies [1–7], 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 Cu^{2+} with other amino acids, the structure of the chelate, catalytically active complex of copper (II) ion with tryptophan anion can be represented by the following scheme:

$$\begin{matrix} R-CH-COO^- \\ | \\ H_2N: \end{matrix} + Cu^{2+} \rightarrow \left[\begin{matrix} R-CH-COO^- \\ | \quad\quad | \\ H_2N: \rightarrow Cu^{2+} \end{matrix} \right], [CuTrp]^+.$$
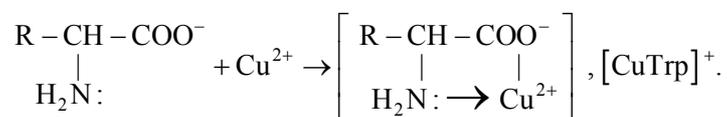
In the second part of experiments, the temperature dependence of ROOH decomposition reaction rate under the influence of the $[CuTrp]^+$ complex catalyst was determined. The kinetic curves of the ROOH catalytic decomposition reaction at temperatures of 323, 328, 333 and 343 K are presented in Fig. 3, a. According to the Figure, the values of effective rate constant (K_{eff}) are graphically calculated at the indicated temperatures. And from the graphical dependence $\lg K_{eff}$ versus $1/T$ (Fig. 3, b) the value of the effective activation energy (E_{eff}) and the average PZ value are calculated. The calculated values of K_{eff}, E_{eff} and PZ are given in Tab. 2.
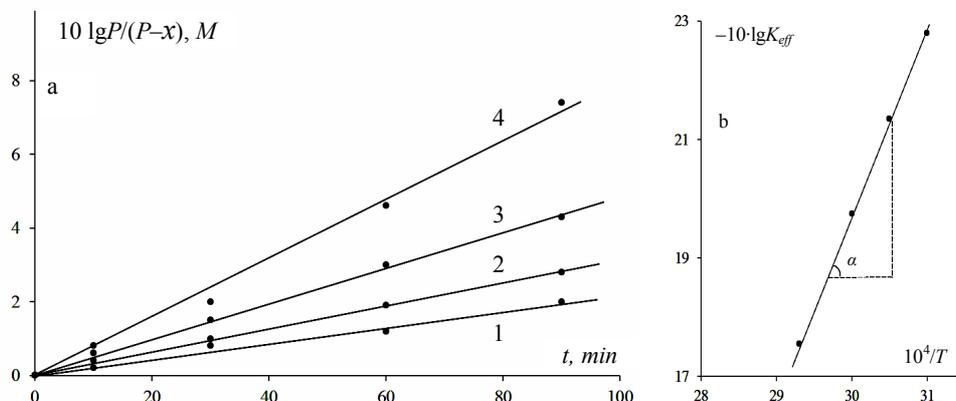
Fig. 3. a) The kinetic curves of ROOH catalytic decomposition reaction at T = 323 (1), 328 (2), 333 (3), 343 K (4), $[ROOH]_0$=0.04 M, $[Trp]_0$=$[KOH]_0$=0.006 M, $[CuTrp]^+_0$=$[Cu^{2+}]_0$=2.0·10^{-4} M. b) The dependence lg K_{eff} versus 1/T.

T a b l e 2

The values of K_{eff}, E_{eff} and PZ, $[ROOH]_0$=0.04 M, $[Trp]_0$=$[KOH]_0$=0.006 M, $[Cu^{2+}]_0$=$[CuTrp]^+_0$= 2.0·10^{-4} M

T, K	$10^4/T$, K^{-1}	$K_{eff} \cdot 10^2$, min^{-1}	$-10 \cdot lg K_{eff}$	E_{eff} and $\overline{PZ}$
323	30.96	0.52	22.84	
328	30.49	0.71	21.50	E_{eff}=56.5 ± 0.2 *kJ/mol*
333	30.03	1.04	19.83	PZ=(7.45 ± 0.02)·10^6
343	29.15	1.73	17.60	

Conclusion. Thus, on the basis of the obtained experimental and calculated results, in the H$_2$O+Cu^{2+}+Trp+ROOH system the initial rate of ROOH catalytic decomposition under the influence of [CuTrp]$^+$ complex catalyst is expressed by the following kinetic equation:

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

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

$$K_{eff} = (7.45 ± 0.02)·10^6 exp[-(56.5 ± 0.2)/RT],\ min^{-1}.$$

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