

CATALYTIC ACTIVITY OF COBALT(II) ION AND ISOLEUCINE COMPLEX ON DECAY OF CUMENE HYDROPEROXIDE IN AQUEOUS SOLUTION

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Formation of complex between cobalt ion (Co^{2+}) and isoleucine (Ile) with composition 1:1, which reveals itself as a model catalyst for decay of cumene hydroperoxide (ROOH) in the studied $\text{Co}^{2+}+\text{Ile}+\text{ROOH}+\text{H}_2\text{O}$ system, has been established by kinetic method. The kinetic equation of rate of catalytic decay of ROOH under the action of $[\text{Co}\cdot\text{Ile}]^+$ complex catalyst has been derived:

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

Temperature dependence of the effective rate constant ($K_{\text{eff}}=K_{\text{cat}}[\text{Co}^{2+}]_0[\text{Ile}]_0$) of decay of ROOH in the interval 323–353 K is expressed by Arrhenius equation (E_{eff} in kJ/mol): $K_{\text{eff}} = (2.50 \pm 0.02) 10^8 \exp[-67.0 \pm 0.3/RT] \text{ min}^{-1}$.

Keywords: catalysis, complex formation, hydroperoxide, amino acid, isoleucine, reaction kinetics.

In order to obtain comparative experimental and generalizing results of the influence of naturally derived amino acids (glycine, alanine, proline, leucine, isoleucine, etc.) and metal ions(II) of the first transition series (Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , etc.) on the kinetics of catalytic decay of cumene and *tert*-butyl hydroperoxides (ROOH) in the aqueous solution we conducted studies of complex formation between the components of the systems and the kinetic regularities of the reactions [1–8]. Using spectroscopic and kinetic methods we have found previously the formation of binary complexes in the system with compositions 1:1 and 1:2 at $\text{pH} > 7$ [1, 2, 6–9]. Among these complexes the complex with the composition 1:1 prevails in the studied systems, which is a catalase type homogeneous model catalyst for ROOH decomposition reaction in water. Recently, we have studied both above mentioned complex formation of metal ions(II) with leucine [4–8] and isoleucine (Ile) [4, 7] and catalytic decomposition of ROOH in an aqueous basic solution under the influence of complex with the composition 1:1 [5, 6, 8].

This paper presents the results of a study of catalytic decomposition of ROOH under the influence of $[\text{Co}\cdot\text{Ile}]^+$ complex with composition 1:1, which is formed in the system $\text{Co}^{2+}+\text{Ile}+\text{ROOH}+\text{H}_2\text{O}$, and kinetic parameters of the reaction at the temperature range 323–353 K. It should be noted that, in the cases of prior studies, amino acid (Ac) and metal ions M(II) do not cause decomposition of ROOH separately, which occurs at their jointly presence in the reaction solution

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with the formation of complexes $[\text{MAc}]^+$ in alkaline medium. Because of catalytic action of the formed complex on ROOH the latter decomposes into oxygen and corresponding alcohol [9].

Kinetic results of catalytic decomposition of ROOH under the influence of complex $[\text{Co}\cdot\text{Ile}]^+$. The amino acid isoleucine, mark “Chemically Pure”, is used as a ligand, Co(II) ion in the form of salt $\text{CoCl}_2\cdot 7\text{H}_2\text{O}$, mark “Analytical Grad”, is used as an adjustable complex former. The purified and distilled cumene hydroperoxide, mark “Pure”, is used in the experiments. The rate of the reaction was monitored by the consumption of hydroperoxide using the indirect iodometry titration method.

As it was noted above, in the presence of Co^{2+} and Ile separately ROOH does not decay, and only when they both are present (at $\text{pH}>7$) the formed complex with composition 1:1 causes catalytic decomposition of hydroperoxide. Kinetic studies are carried out at temperatures 323, 333, 343 and 353 K. The accuracy of temperature measurement was ± 0.2 K.

To determine the reaction order with respect to the components and the complex catalyst dependence of the initial rate (W_0) of the reaction from the initial concentrations of reacting components of the studied system was investigated.

The rate dependence of catalytic reaction from the initial concentration of Co(II) ion was studied in the concentration range $[\text{Co}^{2+}]_0 = 1\cdot 10^{-3} - 3\cdot 10^{-3}$ mol/L at the constant concentration of $[\text{ROOH}]_0 = [\text{Ile}]_0 = 0.050$ mol/L and the temperature 353 K. In the studied systems the concentration of alkali (KOH) is taken to be equal to the concentration of amino acid $[\text{Ile}]_0 = [\text{KOH}]_0 = 0.050$ mol/L. The experimental data are presented in Fig. 1, according to which the values of the effective rate constant (K_{eff}) have been determined.

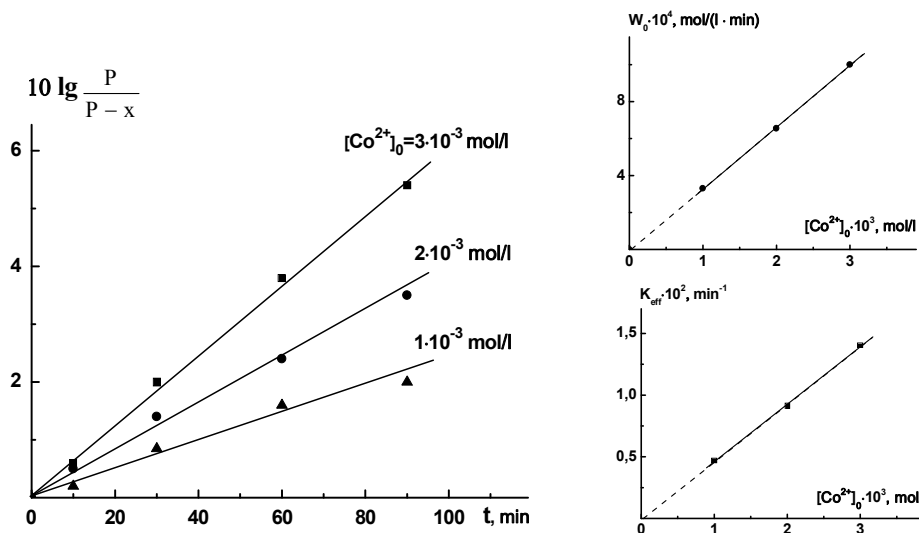


Fig. 1. Illustration of the first-order reaction with respect to Co^{2+} and ROOH: P , x , $P-x$ are initial, consumed and current ROOH concentration respectively, mol/L; $[\text{ROOH}]_0 = [\text{Ile}]_0 = 0.05$ mol/L; $T = 343$ K.

The values of W_0 of reaction are calculated by graphical differentiation of consumption ROOH (x) depending on time and are presented in Table 1.

Table 1

The values of W_0 and K_{eff} at different initial concentrations of Co^{2+} :
 $[\text{ROOH}]_0 = [\text{Ile}]_0 = 0.050 \text{ mol/L}$, $[\text{KOH}]_0 = 0.050 \text{ mol/L}$, $T = 343\text{K}$

$[\text{Co}^{2+}]_0 \cdot 10^3$, mol/L	$W_0 \cdot 10^4$, mol · L ⁻¹ · min ⁻¹	$W_0/[\text{Co}^{2+}]_0 = \text{const}$, min ⁻¹	$K_{\text{eff}} \cdot 10^2$, min ⁻¹	$K_{\text{eff}}/[\text{Co}^{2+}]_0 = \text{const}$, L · mol ⁻¹ min ⁻¹
3	10.20	0.340	1.430	4.766
2	6.75	0.338	0.952	4.760
1	3.40	0.340	0.477	4.770

The rectilinear dependence of $\lg P/(P-x)$ from t (Fig. 1) shows that the order of the reaction with respect to ROOH is equal to one ($n_{\text{ROOH}}=1$). The reaction order with respect to Co^{2+} is also equal to one, which is obtained from the following constant relations: $W_0/[\text{Co}^{2+}]_0 = \text{const}$ and $K_{\text{eff}}/[\text{Co}^{2+}]_0 = \text{const}$ (Tab. 1). It should be noted that according to the straight, passing through the beginning of Fig. 1, the linear curves represent not only the first order with respect to Co^{2+} , but also the fact that in the complex reaction system $\text{Co}^{2+} + \text{Ile} + \text{ROOH} + \text{H}_2\text{O}$ only one reaction occurs catalytic decomposition of ROOH.

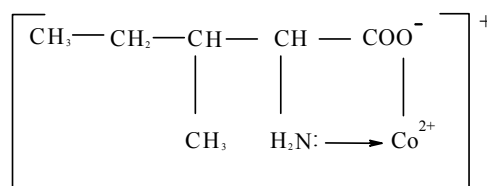
The reaction order with respect to isoleucine was also determined by graphical differentiation of the curves of consumption of hydroperoxide depending on time, defining W_0 at various initial concentrations of amino acid (Tab. 2). The constancy of the ratio $W_0/[\text{Ile}]_0 = \text{const}$ shows that the order of reaction with respect to isoleucine is also equal to one ($n_{\text{Ile}}=1$).

Table 2

The dependence of the initial rate from the initial concentrations of isoleucine:
 $[\text{ROOH}]_0 = 0.050 \text{ mol/L}$, $[\text{Co}^{2+}]_0 = 2 \cdot 10^{-3} \text{ mol/L}$, $T = 343\text{K}$

$[\text{Ile}]_0 \cdot 10^2$, mol/L	$W_0 \cdot 10^4$, mol/(L · min)	$(W_0 \cdot 10^2) / [\text{Ile}]_0 = \text{const}$
5	6.75	1.35
4	5.32	1.33
3	4.05	1.35

It should be noted that the first order of the reaction with respect to the ion of Co(II) and amino acid confirms that in the studied system the formed complex catalyst has a composition 1:1. In the chelate complex cobalt ion is bound with carboxyl group of Ile by an electrostatic interaction, and with an amine group – by coordination bond. These results have been obtained both by our early spectroscopic and kinetic studies for other Ac and M^{2+} [1–8], and by the works of other authors [10–15]. According to these results, the complex of Co^{2+} with isoleucine, which has the composition 1:1, may be expressed by the following scheme:



Taking into account that the initial concentration of Co^{2+} in the studied system is 1–2 order less than comparing with the concentration of ligand (isoleucine),

the initial concentration of the resulting catalytic active homogeneous complex catalyst with composition 1:1 can be considered to be equal to the initial concentration of the complexing agent Co(II) ion: $[\text{Co}\cdot\text{Ile}]^+ = [\text{Co}^{2+}]_0$, which also follows from the first-order reaction with respect to the amino acid and metal ion.

Thus, based on the obtained results, the rate of the catalytic decomposition reaction of ROOH in the studied $\text{Co}^{2+} + \text{Ile} + \text{ROOH} + \text{H}_2\text{O}$ system is expressed by the following presented according to the following first-order kinetic equation:

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

where $K_{\text{eff}} = K_{\text{kat}}[\text{Co}^{2+}]_0[\text{Ile}]_0 = \text{const}$ at given temperature and initial constant concentrations of Co^{2+} and Ile (during the reaction they do not consume).

We have also determined the temperature dependence of the effective rate constant of decomposition of ROOH (K_{eff}). With this purpose the catalytic reaction has been studied at the temperature range 323–353K and constant initial concentrations of reagents: $[\text{ROOH}]_0 = [\text{Ile}]_0 = 0.050 \text{ mol/L}$, $[\text{Co}\cdot\text{Ile}]^+ = 2 \cdot 10^{-3} \text{ mol/L}$. From the linear dependence of $\lg P/(P-x)$ versus t the values of effective rate constant of reaction have been graphically calculated at the temperatures 323, 333, 343 and 353 K (Tab. 3).

Table 3

The values of effective rate constant of decay of ROOH (K_{eff}) at different temperatures:
 $[\text{ROOH}]_0 = [\text{Ile}]_0 = 0.05 \text{ mol/L}$, $[\text{Co}\cdot\text{Ile}]^+ = [\text{Co}^{2+}]_0 = 2 \cdot 10^{-3} \text{ mol/L}$

T, K	$1/T \cdot 10^4, K^{-1}$	$K_{\text{eff}} \cdot 10^2, \text{min}^{-1}$	$-10 \cdot \lg K_{\text{eff}}$	$E_{\text{eff}}, \overline{PZ}$
353	28.30	1.49	17.13	$E_{\text{eff}} = 67.0 \text{ kJ/mol}$, $\overline{PZ} = 2.50 \cdot 10^8$
343	29.15	0.95	20.22	
333	30.00	0.46	23.37	
323	30.96	0.21	26.78	

The data shown in Table 3 satisfy Arrhenius equation (Fig. 2). Using these values the pre-exponential factor (\overline{PZ}) and the effective activation energy (E_{eff}) of the catalytic reaction are graphically calculated.

The temperature dependence of the effective rate constant of the catalytic decomposition reaction of cumene hydroperoxide is expressed by the following equation (E_{eff} in kJ/mol): $K_{\text{eff}} = (2.50 \pm 0.02) 10^8 \exp[-67.0 \pm 0.3/RT] \text{ min}^{-1}$.

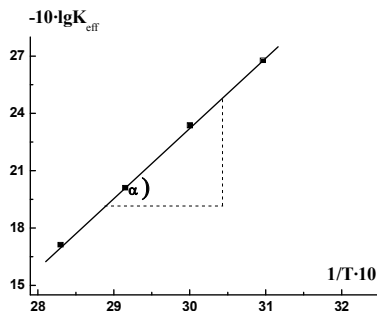


Fig. 2. Illustration of the temperature dependence of the catalytic reaction $[\text{ROOH}]_0 + [\text{Co}\cdot\text{Ile}]^+$:

$$[\text{ROOH}]_0 = [\text{Ile}]_0 = 0.050 \text{ mol/L},$$

$$[\text{Co}\cdot\text{Ile}]^+ = [\text{Co}^{2+}]_0 = 2 \cdot 10^{-3} \text{ mol/L}.$$

Conclusion. Due to the obtained results the following conclusion can be made:

1. It has been shown kinetically that in the $\text{Co}^{2+} + \text{Ile} + \text{ROOH} + \text{H}_2\text{O}$ system catalytically active complex $[\text{Co}\cdot\text{Ile}]^+$ with the composition 1:1 is formed, which is

a model of homogeneous catalase type catalyst for the decay of cumene hydroperoxide in the aqueous solution. In the same conditions the complexing components do not cause the decay of hydroperoxide separately.

2. The kinetic rate equation of the catalytic decay of ROOH in water under the action of $[\text{Co}\cdot\text{Ile}]^+$ complex catalyst has been derived:

$$W_0 = -d[\text{ROOH}]_0/dt = K_{\text{cat}}[\text{Co}^{2+}]_0[\text{Ile}]_0[\text{ROOH}]_0 = K_{\text{eff}}[\text{ROOH}]_0.$$

3. Temperature dependence of the effective rate constants of decay of ROOH satisfying Arrhenius equation has been determined (E_{eff} in kJ/mol):

$$K_{\text{eff}} = (2.50 \pm 0.02) 10^8 \exp[-67.0 \pm 0.3/RT] \text{ min}^{-1}.$$

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REFERENCES

1. **Grigoryan S.K., Babayan M.A., Vardanyan E.Ya., Grigoryan G.S.** Catalytic Activity of Copper(II) and Histidine Complexes on Decay of Cumene Hydroperoxide in Aqueous Solutions. // *Chem. J. of Armenia*, 1997, v. 50, № 3–4, p. 15 (in Russian).
2. **Grigoryan S.K., Petrosyan G.G., Grigoryan G.S., Vardanyan E.Ya.** The Complex Formation of Lysine with Metal(II) Ions and the Action of the Complexes on Cumene Hydroperoxide Decomposition in Aqueous Solution. // *Chem. J. of Armenia*, 2005, v. 58, № 4, p. 12 (in Russian).
3. **Grigoryan G.S., Petrosyan G.G., Vardanyan E.Ya., Grigoryan S.K.** The Catalytic Action of Cobalt(II) Ion on The Kinetics of the Reaction of Cumene Hydroperoxide with Methionine in Aqueous Solutions. // *Uchenie zapiski EGU*, 2008, v. 3, p. 112 (in Russian).
4. **Grigoryan G.S.** The Study of Complex Formation of Copper(II) Ion with Leucine And Isoleucine in Aqueous Solutions. Thesis at XI International Conference “Problems of Solvation and Complex Formation in Solutions”. Russian Federation, Ivanovo, October 2011, p. 165–166.
5. **Grigoryan G.S., Petrosyan G.G., Grigoryan G.L., Harutyunyan M.G., Grigoryan S.K.** Cu (II)–Leucine Complex as Homogeneous Catalyst for Cumene Hydroperoxide Decomposition in Aqueous Medium. // *Uchenie zapiski EGU, Chemical and Biological Sciences*, 2012, № 1, p. 26 (in Russian).
6. **Grigoryan S.K., Harutyunyan M.G., Grigoryan G.S.** Study of Catalytic Activity of Nickel(II)–Leucine Complex on the Decay of Cumene Hydroperoxide in Aqueous Solution. // *Uchenie Zapiski EGU, Chemical and Biological Sciences*, 2012, № 3, p. 13 (in Russian).
7. **Grigoryan G.S.** The Complex Formation between Copper(II) Ion with Leucine and Isoleucine in Aqueous Solution. // *Chem. J. of Armenia*, 2013, v. 66, № 1, p. 148 (in Russian).
8. **Grigoryan S.K., Harutyunyan M.G., Grigoryan G.S.** Study of Catalytic Activity of the Complex Formed between Co(II) and Leucine on the Decay of Cumene Hydroperoxide in Aqueous Solution. // *Chem. J. of Armenia*, 2013, v. 66, № 2, p. 208 (in Russian).
9. **Grigoryan G.S.** The Method of Oxygen Obtaining. Patent of Armenia № 2286A. Request № AM 20080210. Yerevan, 2009.
10. **Nakamoto K.** Infrared and Raman Spectra of Inorganic and Coordination Compounds (4th ed.). New York: John Wiley and Sons Inc., 1986, 464 p.
11. **Bolotin S.N., Vashchuk A.B., Panyushkin V.T.** Study of Complex Formation with Copper Chloride and Amino Acids in Aqueous Solutions According to EPR Spectra. // *J. of General Chem.*, 1996, v. 66, № 8, p. 1360 (in Russian).
12. **Bolotin S.N., Panyushkin V.T., Nikolaenko I.A., Sklyar A.A.** Complexing of Copper (II) with L-histidine in an Aqueous Solution According to EPR Spectra. // *J. Inorg. Chem.*, 2004, v. 49, № 11, p. 1838–1842 (in Russian).
13. **Stacenko O.V., Bolotin S.N., Panyushkin V.T.** Complexing of Copper (II) c L- and DL-Threonine According EPR. // *J. of General Chem.*, 2004, v. 74, № 8, p. 1388–1391 (in Russian).
14. **Marru A., Stanila A., Rusu D., Rusu M., Cazar O., David L.** // *J. of Optoelectronics and Advanced Materials*, 2007, v. 9, № 3, p. 741.

15. **Rusu D., Stanila A., Marian I.O., Marian C.O., Rusu M., Lucaciu R.** // *Rev. Chim.*, 2009, v. 60, № 9, p. 939.