Catalysis of Cumyl Hydroperoxide Decomposition by Calcium Salts and Complexes: A Kinetic Experiment and Quantum Chemical Modeling

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Abstract—The kinetic and thermodynamic parameters of the decomposition of cumyl hydroperoxide in a chlorobenzene medium in the presence of calcium 2-ethylhexanoate and a complex of $CaCl_2$ with crown ether were experimentally obtained. The formation of intermediate complexes in the catalyst—hydroperoxide system was kinetically established. The formation of intermediate complexes was confirmed using quantum chemical modeling, their structure was optimized, and the thermodynamic characteristics of reactions with their participation were found. A mechanism of the stepwise decomposition of the intermediate was proposed.

Keywords: cumyl hydroperoxide, catalytic decomposition, organic calcium salts, dibenzo-18-crown-6, complexation, quantum chemical modeling

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INTRODUCTION

In a developed process of the oxidation of alkylaromatic hydrocarbons by molecular oxygen, transition metal compounds noticeably accelerate the process by decomposing a small hydroperoxide portion [1-3]. A disadvantage of the use of these compounds is their low solubility in alkylaromatic hydrocarbons and a tendency to form colloidal solutions [1].

The need to compare the catalytic activity of various metals under identical conditions and to relate it to the atomic properties of metals has led us to a search for a solubilizing ligand that is equally suitable for all nontransition metals. The residue of 2-ethylhexanoic acid was found as such a ligand for IIb subgroup metals [4]. However, it was found that the ethyl hexanoates of not all metals of interest are soluble in chlorobenzene, a standard solvent for studying the decomposition of hydroperoxides. A more universal ligand, crown ether, was found, the main advantage of which is the ability to transfer salts initially insoluble in an organic medium into solution [5-7]. This allowed us to study in detail the decomposition of *tert*-butyl hydroperoxide in the presence of the chloride complexes of IIa subgroup metals [8].

This article presents the results of a study of the catalytic decomposition of cumyl hydroperoxide (CHP) in the presence of calcium 2-ethylhexanoate (Ca(EH)₂) and a complex of calcium chloride with dibenzo-18-crown-6 (CaCl₂ · DBC).

EXPERIMENTAL

To avoid solvent entrainment, the catalytic decomposition of CHP was studied using an ampoule method [8] at $[CHP]_0 = 0.1-1.5 \text{ mol/L}$ and $[Cat]_0 =$ $(0.5-7) \times 10^{-3} \text{ mol/L}$ over a temperature range of $100-130^{\circ}$ C. The hydroperoxide concentration was monitored by an iodometric method [9]. Kinetic curves were approximated by a cubic polynomial and differentiated with respect to time. The initial rates of decay were determined as the derivative as $\tau \rightarrow 0$.

Cumyl hydroperoxide was purified through a sodium salt [10]. The concentration of CHP was 6.98 mol/L (99.8%). The solvent (chlorobenzene) was purified by an acid—base method [11]. The procedure used for the preparation of 2-ethylhexanoates was described in detail earlier [12]. Unlike naphthenates and stearates, ethylhexanoates are not prone to self-association, and they are homogeneous in organic solutions over wide ranges of concentrations and temperatures.

Abbreviations: CHP, cumyl hydroperoxide; Ca(EH)₂, calcium 2-ethylhexanoate; CaCl₂ · DBC, a complex of calcium chloride with dibenzo-18-crown-6; PBE, density functional theory method; [CHP]₀, the initial concentration of CHP; [Cat]₀, the initial catalyst concentration; *n*, the number of hydroperoxide molecules bound in a complex; *K*, the equilibrium constant of complex formation; *k*, the rate constant of decomposition of the complex; w_{0} , the overall rate of decay of CHP; w, the rate of CHP decay; w_{max} , the maximum rate of CHP decay obtained experimentally; E_{a} , the activation energy of decomposition.



Fig. 1. Dependence of the rate of decay of cumyl hydroperoxide on the concentration of CHP in the presence of different catalysts ($[Cat]_0 = 5 \times 10^{-3} \text{ mol/L}$; $T = 130^{\circ}$ C; chlorobenzene): (1) CaCl₂ · DBC and (2) Ca(EH)₂.

The quantum chemical calculations were performed with the Priroda program suite [13] using the PBE density functional theory method [14]. The atomic orbitals were described using the 6-31G(d,p) basis set [15]. All of the geometric parameters were optimized; thereafter, the frequencies of normal vibrations were calculated. The absence of imaginary modes indicated the achievement of a minimum energy. The enthalpy, entropy, and Gibbs free energy values for the test compounds were calculated using a standard thermochemical procedure in the Priroda program suite.

RESULTS AND DISCUSSION

As can be seen in Fig. 1, calcium compounds accelerate the decomposition of the test hydroperoxide. The rate of decay tends to a limiting value as the hydroperoxide concentration $[CHP]_0$ is increased. In the concentration range presented, the curve characterizing the rate of the process in the presence of $CaCl_2 \cdot DBC$ is S-shaped, and it first reaches a plateau. The flattening out (Fig. 1) is a kinetic sign of the formation of an intermediate hydroperoxide complex with the catalyst [16].

The nearly first order of reactions with respect to the catalyst in the test systems was determined from the linearity of plots in the $\ln (w_0)$ -ln ([Cat]₀) coordinates.

The formal kinetic reaction scheme of hydroperoxide decomposition can be represented as follows:

$$nCHP + Cat \xleftarrow{K} [nCHP - Cat],$$
 (I)

$$[nCHP-Cat] \xrightarrow{k} Cat + products, \qquad (II)$$

where n is the number of hydroperoxide molecules bound in a complex; K is the equilibrium constant of complex formation, and k is the rate constant of decomposition of the complex.

The processing of the formal kinetic reaction scheme in a quasi-equilibrium approximation led to the Michaelis-Menten equation for the overall rate of decay of CHP (w_0):

$$w_0 = \frac{kK[Cat]_0[CHP]_0^n}{1 + K[CHP]_0^n}.$$
 (1)

Equation (1) shows that the rate of decomposition is a hyperbolic function of hydroperoxide concentration, and it tends to a limiting value.

To determine the stoichiometry of the complexes, we used the following equation [17]:

$$\ln\left(\frac{1}{w} - \frac{1}{w_{\max}}\right) = \ln\left(\frac{1}{w_{\max}K}\right) - n \times \ln\left[\text{CHP}\right]_{0}, \quad (2)$$

where w is the rate of hydroperoxide decay, and $w_{\text{max}} = k \times [\text{Cat}]_0$ is the maximum rate of decay of CHP measured experimentally.

The numbers of CHP molecules included in the intermediate complexes were determined from the slopes of the corresponding straight lines in the coordinates of Eq. (4). It was found that $Ca(EH)_2$ retains only one CHP molecule. The complex with $CaCl_2 \cdot DBC$ contains two hydroperoxide molecules (Fig. 2).

In the formation of organic hydroperoxide complexes with group II metal salts, hydrogen bonds at the oxygen atoms of the acid residue can be formed. Theoretically, up to four hydroperoxide molecules can be attached to one calcium carboxylate molecule. However, based on the above kinetic data, we can assume that, on the formation of organic hydroperoxide complexes with group II metal salts, a hydrogen bond of cumyl hydroperoxide with oxygen of the acid residue is initially formed; then, a six-membered ring is closed with the formation of a metal–oxygen bond. As a result, the 1 : 1 complex of Ca(EH)₂ with CHP is formed (Scheme 1):



Scheme 1.

The formation of complexes with crown ethers is facilitated by the possibility of the formation of numerous hydrogen bonds with the crown atoms of an ether and coordination bonds with the central metal atom.

The kinetic parameters of overall decay (k, K) were determined by the linearization of Eq. (1) according to the Lineweaver–Burk method [18]:

$$\frac{1}{w} = \frac{1}{w_{\max}} + \frac{1}{w_{\max}K} \times \frac{1}{[CHP]_0^n}.$$
 (3)

Then, the activation parameters of decay were determined from the temperature dependence of the rate constant of decomposition of the complex.

Below are given the Arrhenius expressions obtained for the rate constants in a chlorobenzene medium:

$$k = 1.82 \times 10^{10} \times \exp\left(-\frac{81.55 \times 10^3}{RT}\right) (s^{-1})$$
 (4)

for Ca(EH)₂ and

$$k = 5.44 \times 10^{15} \times \exp\left(-\frac{125.26 \times 10^3}{RT}\right) (s^{-1}) \qquad (5)$$

for $CaCl_2 \cdot DBC$.

The values of the thermodynamic characteristics of the complexation reaction are presented in the forms of the corresponding van't Hoff equations:

$$\ln K = \frac{65.09}{RT} - \frac{172.37}{R} \, (\text{L/mol}) \tag{6}$$

for $Ca(EH)_2$ and

$$\ln K = \frac{74.28}{RT} - \frac{179.78}{R} \, (\text{L}^2/\text{mol}^2) \tag{7}$$

for $CaCl_2 \cdot DBC$.

Note that the complexation of calcium compounds, as well as of other group II metals, is an exothermic reaction [16]; therefore, equilibrium is shifted in the opposite direction with increasing temperature, and the concentration of the complex decreases.

Hydroperoxide molecules are bound in the complex with the oxygen atoms of the catalyst by hydrogen bonds. For all of the test compounds, the heat of complexation significantly exceeds the strength of hydrogen bonds in hydroperoxides (8–13 kJ/mol). Consequently, an oxygen atom of the hydroperoxide O–O group is also coordinated to the central metal atom.

The formation of hydrogen bonds weakens the O–O bond in the hydroperoxide and facilitates its homolytic cleavage. Note that, for all of the catalysts under consideration, the activation energy E_a of decomposition is much lower than the O–O bond strength in hydroperoxides (167 kJ/mol) [19], and this decrease in E_a cannot be explained only by the appearance of hydrogen bonds. This fact is additional evidence of the coordination of CHP with the metal.

Hydroperoxide decomposition in the presence of a crown ether catalyst proceeds sequentially; a complex chain of decomposition reactions and the formation of complexes of different stoichiometry occurs in the system, and it can be expressed by the following reaction scheme (Scheme 2) (the formation of products is not shown for simplicity):



 k_1 is the rate constant of decay of the 2ROOH–Cat complex; k_2 is the rate constant of decay of the ROOH–Cat complex. Scheme 2.

It can be seen in Scheme 2 that, in the case of using the crown ether catalyst, two complexes of different stoichiometry, $ROOH-CaCl_2 \cdot DBC$ and $2ROOH-CaCl_2 \cdot DBC$, can decompose simultaneously to lead to higher observed values of the rate constants of decay (Fig. 1) than those in the catalysis by $Ca(EH)_2$.

In the course of quantum chemical calculations, we primarily optimized the structures of the reagents: the molecules of CHP, $Ca(EH)_2$, and $CaCl_2 \cdot DBC$. Based on an analysis of the structures of these compounds, we proposed and modeled the structures of

catalyst complexes with hydroperoxide (intermediates).

Figure 3 shows the optimized geometric structure of the intermediate complex $CHP-Ca(EH)_2$. As expected, a six-membered ring is formed with the participation of a calcium ion. The correspondence of this intermediate to reaction (I) was verified by calculating the internal reaction coordinate (IRC). The calculations in both descent directions led to the structures of reagents and reaction products, respectively, which were identical to those optimized previously.



Fig. 2. Determination of the stoichiometry of the *n*CHP–Cat complexes: (1) Ca(EH)₂ and (2) CaCl₂ \cdot DBC.

Figure 4 shows an optimal conformation of the intermediate complex formed with the participation of CHP and a catalyst containing crown ether. It is interesting to note that, here, the hydroperoxide molecules are directly bound to the metal atom through their hydroxyl oxygen atoms without forming additional hydrogen bonds and cyclic structures. In this case, one CHP molecule is attached on the side of crown oxygen atoms and the other molecule, on the back side of the crown ether, where hydrogen bonds cannot be formed.

Using special calculations, we found that the crown ether itself retains two CHP molecules on the side of crown oxygen atoms in a hydrogen-bound complex. Thus, the introduction of an ion of calcium (or, probably, any other metal) into the internal cavity of the crown ether creates steric hindrances to the formation of hydrogen bonds between the hydroperoxide and the oxygen atoms of the crown ether due to a large size of the central ion and the branched molecular structure of CHP.

According to the quantum chemical calculations, changes in the enthalpy of reaction of the formation of an intermediate complex (reaction (I)) were negative for all of the catalysts, and this is consistent with the experimental data. Thus, the calculated enthalpies of formation were -117.88 kJ/mol for the CHP–Ca(EH)₂ complex and -103.40 kJ/mol for the 2CHP–CaCl₂ · DBC complex.

Taking into account the effect of solvation, in the framework of this study, we obtained the values of ΔG_s for the solvation of the reaction mixture components. Based on these values, we found a change in the Gibbs free energy taking into account the solvation of molecules in chlorobenzene. Table 1 shows the values of ΔG for complex formation and decomposition reactions (for calcium 2-ethylhexanoate).

Thus, the solvent (chlorobenzene) did not significantly affect the course of the main stages of the



Fig. 3. Optimized geometric structure of the intermediate complex CHP–Ca(EH)₂.



Fig. 4. Optimized structure of the complex $2CHP-CaCl_2 \cdot DBC$.

decomposition process. The discrepancy between the thermodynamic potentials of the main stages of the process under study in a gas phase and in chlorobenzene was 3-7%.

The decomposition of the intermediate complex nROOH-Cat proceeded with the formation of radicals and then the molecules of CHP decomposition products and the restoration of the initial catalyst structure. The lifetime of the intermediate complex, the reaction paths of its decomposition, and the acti-

Reaction conditions	Reaction	Parameter	
		ΔG of the system in a gas phase, kJ/mol	ΔG of the system in chlorobenzene, kJ/mol
No catalyst	$ROOH \rightarrow RO' + OH'$	160.41	158.40
Ca(EH) ₂	$ROOH + Cat \rightleftharpoons ROOH-Cat$	-64.79	-60.60
	$ROOH-Cat \rightarrow RO' + OH' + Cat$	225.20	219.00

Table 1. Comparison of the Gibbs free energies of the main reactions in a gas phase and in a solvent

Table 2. Thermodynamic characteristics of the main stages of CHP decomposition

Deartian	Parameter		
Reaction	ΔH , kJ/mol	ΔG , kJ/mol	
$ROOH + Cat \rightleftharpoons [ROOH-Cat]$	-117.88	-57.87	
$[ROOH-Cat] \rightarrow RO' + OH' + Cat$	327.71	225.20	
$[ROOH-Cat] \rightarrow [RO' \cdot Cat] + OH'$	231.10	185.11	
$[\mathrm{RO}^{\bullet} \cdot \mathrm{Cat}] \rightarrow \mathrm{RO}^{\bullet} + \mathrm{Cat}$	96.61	40.09	
$[\text{ROOH-Cat}] \rightarrow [\text{OH}^{\bullet} \cdot \text{Cat}] + \text{RO}^{\bullet}$	202.55	135.70	
$[OH' \cdot Cat] \rightarrow OH' + Cat$	125.16	89.50	

vation energy of hydroperoxide decomposition depend on many factors: the nature of the catalyst, the concentrations of components, the nature of the solvent, the conditions of the experiment, etc.

We have optimized various structures of decay products, including the catalyst and RO' and OH' radicals.

As a test reaction, we considered the primary act of hydroperoxide decomposition

$$n$$
ROOH–Cat $\rightarrow n$ RO' + n OH' + Cat. (III)

Obviously, the decay proceeded stepwise because the process requires high energy consumption. Moreover, this mechanism is valid for both of the catalysts (ethylhexanoate and crown ether-metal complex):

$$ROOH + Cat \rightleftharpoons [ROOH-Cat],$$
 (IV)

 $[ROOH-Cat] \rightarrow [OH' \cdot Cat] + RO', \qquad (V)$

$$[OH' \cdot Cat] \rightarrow OH' + Cat.$$
 (VI)

In this reaction scheme, the first stage is complex formation, the second is O–O bond cleavage with the release of an RO[•] radical, and the third is catalyst regeneration with the release of the hydroxyl radical into the volume. According to the results of the quantum chemical calculations, the simultaneous elimination of both RO[•] and OH[•] radicals from the intermediate complex with catalyst regeneration requires much more energy than the sequential one (Table 2).

Based on the enthalpies calculated for each particular stage in the studied catalytic systems, we found that reaction (VI) is a rate-limiting stage. The subsequent stage of decay requires less energy. The values of ΔH for the limiting stages of decomposition in the presence of Ca(EH)₂ and CaCl₂ · DBC are 202.50 and 117.88 kJ/mol, respectively.

CONCLUSIONS

Thus, based on an analysis of the data obtained in two different ways (experimental and theoretical), we can note that the formation of activated intermediate complexes is possible and energetically favorable. Both methods confirm the catalytic properties of the test catalytic systems: calcium compounds accelerate the decomposition of CHP by reducing the activation energy of O–O bond cleavage in the hydroperoxide.

The results of the quantum chemical calculations confirm the proposed mechanism of intermediate formation.

In the course of a theoretical study, we determined a stepwise mechanism of the formation and decay of the intermediate and a rate-limiting stage of CHP decomposition.

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No. 6

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