Effect of the Solvent Nature on the Magnesium 2-Ethylhexanoate-Catalyzed Decomposition of Cumene Hydroperoxide

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Abstract—Decomposition of cumene hydroperoxide (CHP) in benzene, chlorobenzene, and carbon tetrachloride in the presence of magnesium 2-ethylhexanoate has been investigated. It has been determined and kinetically proved that the degradation is preceded by the formation of an intermediate hydroperoxide−catalyst complex; the thermodynamic parameters of the complex formation have been determined. It has been found that the catalytic activity of magnesium 2-ethylhexanoate in carbon tetrachloride is higher than in chlorobenzene and benzene. The stability of the complex depending on the nature of the solvent decreases in the order $C_6H_5Cl > CCl_4 > C_6H_6$.

Oxidative transformations of alkylaromatic hydrocarbons form the basis for promising methods for preparing various oxygenated organic compounds. One of the ways to improve the process of oxidation of hydrocarbons with molecular oxygen is the choice of new efficient catalysts. The use of homogeneous oxidation catalysts and, in particular, transition metal compounds seems the most promising. Another focus is the rational selection of the solvent in which the oxidation process occurs.

Conflicting information on the role and mechanism of action of main-group metals, marking both acceleration [1−4] and inhibition [5−7] of the hydrocarbon oxidation reactions, the absence of a general theory of the influence of the medium on the kinetics of chemical reactions prompted us to investigate the efficiency of the catalytic action of magnesium 2-ethylhexanoate in the reactions of cumene hydroperoxide (CHP) decomposition in various media.

EXPERIMENTAL

Magnesium 2-ethylhexanoate $(Mg(EH)_2)$ was obtained according to the procedure detailed in [8] by the reaction of freshly distilled acid of the "chemically pure" grade and reagent-grade magnesium oxide in boiling benzene. The water formed was separated using a Dean−Stark trap. For the complete involvement of the acid in the reaction a small (1−2%) excess of magnesium oxide was used. After separating the excess oxide and evaporating benzene in vacuo, magnesium 2-ethylhexanoate was obtained as a white solid. The magnesium 2-ethylhexanoate content of

the product was 99.44 wt % as determined by chelatometry [9].

Gross decomposition of CHP was performed by the ampoule method at temperatures of 110−130°C, [CHP] = 0−2 mol/L, and $[Mg(EH)_2]$ of 0 to 5 × 10^{-3} mol/L. The contribution of thermal degradation was subtracted from the total rate found experimentally.

RESULTS AND DISCUSSION

For all the solvents, the dependences of the rate of the overall decomposition of hydroperoxide on the catalyst concentration are linear over the entire range of temperatures, indicating the first order of the reaction with respect to the catalyst.

The change of the rate order of the CHP decomposition reaction with respect to the hydroperoxide in the concentration range of 0 to 2 mol/L from the first to near zero order is a kinetic signature of the formation of a hydroperoxide−catalyst intermediate. The concentration dependence curves for the initial rate of the catalytic decomposition of cumene hydroperoxide in all the media exhibit the "saturation" behavior.

Figure 1 shows the plots of the cumene hydroperoxide degradation rate in various solvents; from these plots, it is seen that magnesium 2-ethylhexanoate is the most active in the carbon tetrachloride medium (curve *1*).

The main products of CHP decomposition in any of the solvents examined are dimethylphenylcarbinol (DMPC), acetophenone (AP), α-methylstyrene (α-MS), methanol, phenol, and acids (GLC; a Chro-
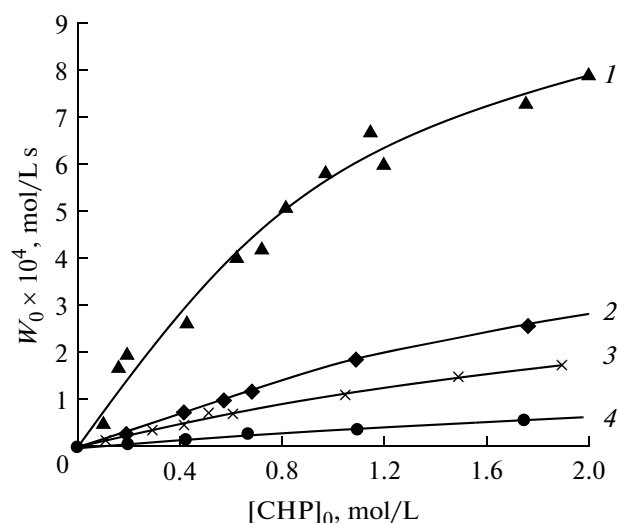
Fig. 1. Dependence of the initial rate of cumene hydroperoxide decomposition on the CHP concentration ($T = 130°C$, $[Mg(EH)_2]_0 = 1 \times 10^{-3}$ mol/L) in various solvents: *1*, CCl_4; *2*, C_6H_6 ($[Mg(EH)_2]_0 = 5 \times 10^{-3}$ mol/L); *3*, C_6H_5Cl; *4*, C_6H_6.

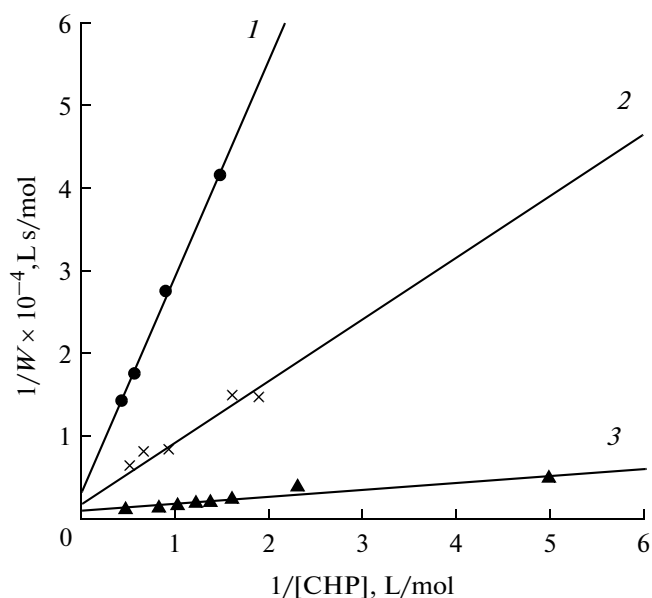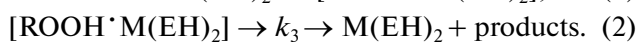**Fig. 2.** Type of the dependences in the Lineweaver–Burk coordinates at 130°C in various media ($[Mg(EH)_2]_0 = 1 \times 10^{-3}$ mol/L): *1*, benzene; *2*, chlorobenzene; *3*, CCl_4.

matec-Crystal chromatograph; capillary column with a polar phase (polyethylene glycol)). The table shows the amounts (%) of the main CHP degradation products. The acids (formic and benzoic) that present in the products of the catalytic decomposition are responsible for the heterolytic degradation of CHP yielding phenol.

Formally, the kinetic scheme of the process involves the formation of the intermediate complex:

$$ROOH + M(EH)_2 \leftrightarrow [ROOH \cdot M(EH)_2], \quad (1)$$

$$[ROOH \cdot M(EH)_2] \rightarrow k_3 \rightarrow M(EH)_2 + \text{products.} \quad (2)$$

The degradation rate is described by the Michaelis–Menten equation [10]:

$$W = \frac{k_3 K [Mg(EH)_2]_0 [CPH]_0}{1 + K[CPH]_0}, \quad (3)$$

where W is the rate of CHP degradation, k is the decay rate constant of the complex, and K is the complexation equilibrium constant.

Using the Lineweaver–Burk method [10] (linearization of the Michaelis–Menten equation), we determine the kinetic parameters of the overall decomposition (Fig. 2).

Arrhenius expressions for the rate constants in different media are as follows:

$$k_3 = (7.44 \pm 0.37) \times 10^{14} \exp((-114.77 \pm 5.74) \times 10^3 / RT) \text{ s}^{-1} \quad \text{(for } CCl_4), \quad (4)$$

$$k_3 = (2.16 \pm 0.05) \times 10^{17} \exp((-134.45 \pm 2.90) \times 10^3 / RT) \text{ s}^{-1} \quad \text{(for } C_6H_5Cl), \quad (5)$$

$$k_3 = (2.49 \pm 0.12) \times 10^{10} \exp((-83.93 \pm 4.20) \times 10^3 / RT) \text{ s}^{-1} \quad \text{(for } C_6H_6). \quad (6)$$

Note that the pre-exponential factors, as expected, have values typical of unimolecular reactions.

The values of the thermodynamic parameters of complex formation in the interval of $[CHP]_0 = 0–2$ mol/L were calculated by the van't Hoff equation:

$$\ln K = (45.91 \pm 2.30) \times 10^{10} / RT + (-123.06 \pm 6.15)/R \text{ L/mol} \quad \text{(for } CCl_4), \quad (7)$$

Main products of cumene hydroperoxide decomposition ($T = 130°C$, $[Mg(EH)_2]_0 = 1 \times 10^{-3}$ mol/L, $[CHP]_0 = 1.5$ mol/L)

Solvent	Time to reach 100% CHP conversion, τ, h	Products, wt %				
		AF	DMPC	phenol	α-MS	methanol
CCl_4	4	26.37	2.49	15.72	35.31	11.03
C_6H_5Cl	6	43.41	10.2	5.53	25.83	3.47
C_6H_6	10	22.09	40.28	18.41	0.91	6.14

$$\ln K = (106.78 \pm 5.34) \times 10^3 / RT$$
$$+ (-282.76 \pm 14.14)/R \text{ L/mol} \quad \text{(for } C_6H_5Cl\text{)}, \quad (8)$$

$$\ln K = (37.33 \pm 1.87) \times 10^3 / RT$$
$$+ (-110.58 \pm 5.53)/R \text{ L/mol} \quad \text{(for } C_6H_6\text{)}. \quad (9)$$

The formation mechanism and the structure of the hydroperoxide complexes with Zn, Cd, and Hg ethylhexanoates are discussed in detail in [11]: the formation of a hydrogen bond between hydroperoxide and the carbonyl group of the acid residue followed by the closure of a six-membered ring via forming a metal–oxygen bond. In the case of $Mg(EH)_2$, the formation of a similar cyclic complex is supposed:
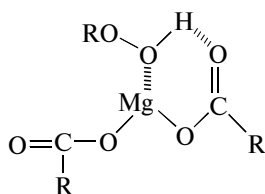
As a result of the formation of the six-membered cyclic intermediate, covalent O–O bond in the ROOH molecule weakens and its breaking is facilitated. This is evidenced by a decrease in the activation energy of the degradation (84–134 kJ/mol) compared to the O–O bond strength in hydroperoxides (163 kJ/mol) [12].

Comparing activation energies for the catalytic decomposition of CHP in different media, it can be noted that E_a in benzene (83.93 kJ/mol) is lower than in CCl_4 (114.77 kJ/mol) and chlorobenzene (134.45 kJ/mol). Such a decrease in the energy barrier should result in quite significant acceleration of the CHP degradation reaction, but low values of the complex formation equilibrium constant to some extent compensate for the weakening of the O–O bond. In fact, the $Mg(EH)_2$–CHP complex more quickly decomposes to the initial components than further reacts to result in hydroperoxide degradation.

The intermediate catalytic complex is formed exothermically ($\Delta H < 0$). The enthalpy change can be a measure of the stability of the complex; the stability, in turn, is due to the strength of the newly formed
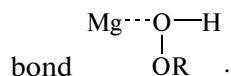
bond

It seems clear that the greater the Mg–O bond strength in the ROOH–Mg intermediate, the stronger should weaken the hydroperoxide O–O bond in the coordination sphere of the metal, making the homolysis of this bond easier. Judging from the enthalpy of complex formation (ΔH), the complex is the most stable and decomposes at the highest rate in CCl_4.

In chlorobenzene, the entropy change upon complex formation has a large negative value in comparison with CCl_4 and benzene, indicating the formation of a more ordered structure. The change in entropy

(ΔS) upon the formation of the intermediate increases in the order $C_6H_6 < CCl_4 < C_6H_5Cl$. The carboxylate–hydroperoxide complex in benzene has the least ordered loose structure.

The low values of ΔS in conjunction with the minimal complex formation enthalpy lead to the fact that the CHP degradation rate in benzene at operating temperatures of 110–130°C and a fixed catalyst concentration is minimal. The lower values for the equilibrium constant of complexation in benzene in comparison with CCl_4 indicate that the complex faster dissociates into the reactants in benzene.

Thus, the catalyst activity and the mode of occurrence of the reactions of hydroperoxides, in particular, their degradation are largely determined by the medium. Depending on the properties of the solvent, both homolytic and heterolytic decomposition are possible [13]. In the reactions of radical degradation, the solvent can affect the rate and direction of the process through both specific solvation [14–17] and direct participation in the degradation step. In the heterolytic degradation reactions, the effect of the solvent is mainly due to specific solvation [18, 19].

In low-polarity solvents (benzene and chlorobenzene), the decomposition of hydroperoxides predominantly follows the radical chain mechanism [20]. In solvents with a high dielectric constant, ionic reactions along with the radical decomposition are possible, the probability of occurrence of the former being determined by the polarity of the solvent.

In inert solvents, which should not affect the monomolecular reaction of the hydroperoxide decomposition, the cage effect manifests itself [21] resulting in an increased probability of the combination reaction of $RO^{\cdot}$ and $^{\cdot}OH$ radicals to give RO–OH. Thus, the experimentally determined rate of hydroperoxide decomposition is lower than the true one. In addition to the aforementioned cage effect, the solvent may be involved in degenerate chain branching by reacting with hydroperoxide (solvent as a reactant).

In [22] it was shown that the solvents used in this study are capable of solvating hydroperoxides. The ROOH oxygen becomes hydrogen-bonded to the π-system of the benzene ring or the chlorine atom.

Experimental data show that benzene, compared with CCl_4 and chlorobenzene, stronger solvates CHP molecules, thereby hindering the formation of the CHP–$Mg(EH)_2$ complex. Therefore, the rate of the hydroperoxide decomposition in benzene is lower than in other solvents, despite the lowest activation energy. Comparing the decomposition rates, it can be argued that CCl_4 almost does not solvate the hydroperoxide.

The discovery of the catalytic properties of Group IIA and IIB metals has led to an interesting conclusion: the nature of the metal affects the catalytic activity. Exploring the role of Zn, Cd, and Hg 2-ethylhexanoates in the CHP decomposition [4, 8, 11], we

concluded that the decomposition of hydroperoxide occurs via the formation of a complex with the salt, which complex is thermally less stable and easily decomposes to give $RO^{\cdot}$ and $ROO^{\cdot}$ free radicals. Thus, non-transition metals in their catalytic activity are arranged in the order: $Cd(EH)_2 > Zn(EH)_2 > Hg(EH)_2$.

The catalytic functions of compounds of Group IIA and IIB metals, which differ in electronic structure and chemical nature are likely realized by various mechanisms.

Magnesium is markedly different from the IIB subgroup metals by the atomic and ionic radii. Magnesium exhibits stronger metallic properties, the formation of covalent bonds is less typical of Mg than Zn or Hg, and the formation of ionic bond is more typical. In this regard, Mg is closer to Cd. The kinetic and thermodynamic parameters of CHP decomposition in the presence of magnesium 2-ethylhexanoate are comparable in value to those for the Zn subgroup carboxylates.

In the complexes of Zn and Hg, the proportion of covalency is high and these metals are less reactive, but this bond is more ionic for active Cd; therefore, an obvious conclusion is that the greater the stronger the ionic character of the bond, the more active is the catalyst. According to this conclusion, purely ionic Mg complexes should surpass complexes of the zinc subgroup metals in activity.

However, it is the Zn subgroup metals that are noted to exhibit a high catalytic activity [23], which is undoubtedly due to the effect of additional polarization. Within the IIB subgroup, the catalytic properties depend mainly on the nature of interaction forces acting during the formation of the $ROOH-M$ intermediate (M = metal). As in the case of the main subgroup, the bond for Cd compounds is determined mainly by electrostatic factors. In the case of Zn and Hg, covalency plays an important role in the interaction. However, the reasons behind the tendency of Zn and Hg to form covalent bonds are different: it is due to the additional effect of polarization for Hg and to a small ionic radius for Zn.

Thus, the overall decomposition of CHP mediated by Mg carboxylate proceeds through the formation of an intermediate activated complex, as in the case of catalysis with Zn, Cd, or Hg 2-ethylhexanoate. The kinetic and thermodynamic characteristics of the CHP decomposition are close for Mg and Zn subgroup metals. The catalytic activity of Mg 2-ethylhexanoate in a CCl_4 medium is higher than in chlorobenzene and benzene. The stability of the complex, depending on the solvent, decreases in the order $C_6H_5Cl > CCl_4 > C_6H_6$.

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