

Homolytic Decomposition of Cumyl Hydroperoxide under the Action of Zinc, Cadmium, and Mercury 2-Ethylhexanoates

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Abstract—The free-radical decomposition of cumyl hydroperoxide (CHP) and the overall CHP decomposition process proceed via the same mechanism with similar kinetic parameters through the formation of a hydroperoxide–metal compound intermediate. The catalytic activity of metal ethylhexanoates decreases in the order $\text{Cd} > \text{Zn} > \text{Hg}$. The complex formation thermodynamics and decomposition kinetics are correlated with the metal ionization potentials, which are the lowest for cadmium. The zinc-family metals are catalytically more active than the Group IIA metals owing to their polarization effect. Within Group IIA, the catalytic properties are mainly determined by the nature of the interaction in the intermediate complex.

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In our earlier works [1–3], we demonstrated kinetically that, in the overall cumyl hydroperoxide (CHP) decomposition process in the presence of zinc naphthenate or zinc, cadmium, or mercury 2-ethylhexanoate (EH), the primary event is the formation of the intermediate complex ROOH-M(EH)_2 (1 : 1), where M is a metal. This finding, which is rather trivial for polyvalent metals, required further confirmation for salts of Group IIB metals.

For zinc and cadmium naphthenates as catalysts, Kozlov et al. [4–6] postulated that the reaction is first-order with respect to the catalyst and hydroperoxide concentrations. This conclusion was based on kinetic data for a narrow CHP concentration range limited by 0.1 mol/l. However, we found that a plateau in the decomposition rate versus the CHP concentration curve, which is characteristic of reactions with intermediate complex formation, occurs at much higher hydroperoxide concentrations of 0.5–1 mol/l [1–3]. This is the reason why Kozlov et al. [4–6] did not detect any caprylate, stearate, or acetylacetonate complex of these metals. Other authors assumed, without any kinetic substantiation, the formation of a Zn–dithiocarbamate–CHP complex [7]. This assumption was not confirmed by a later study of this system [8]. It was proved reliably by kinetic methods that the complex Zn-2ROOH forms in the tetralin hydroperoxide–zinc dithiophosphate system [9]. Note that, among the non-transition metal compounds, only alkali metal carboxylates form $\text{M-}n\text{ROOH}$ complexes in the absence of an activating agent [10–12]. There are only a few publications [13–15] in which the formation of such complexes with alkaline-earth metals (Mg, Ca, Ba, Sr) is reported to be possible.

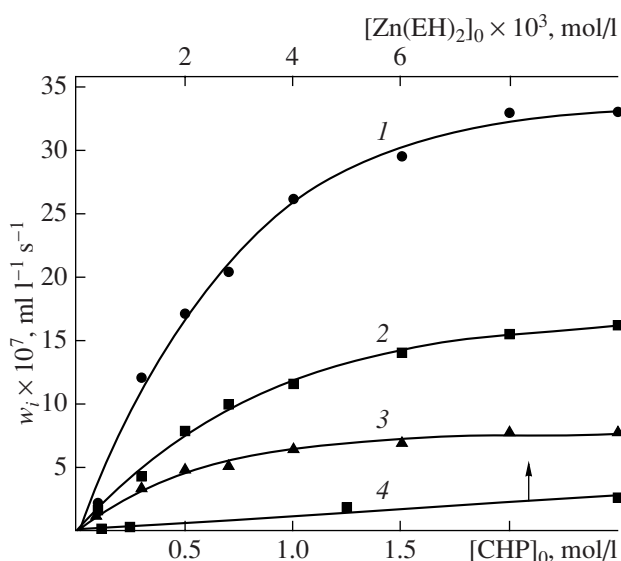
It has been convincingly demonstrated by numerous examples that the formation of an intermediate necessarily takes place in the catalytic decomposition of peroxides. The absence of such information for Group II metals is explained not by the specific properties of these metals, but by the small values of the stability constants of their complexes and by the inappropriate choice of reactant concentrations.

Here, we report the free-radical decomposition of CHP in the presence of zinc, cadmium, and mercury 2-ethylhexanoates and attempt to relate the catalytic activity of the metals to their atomic properties.

EXPERIMENTAL

The synthesis of the 2-ethylhexanoates is detailed elsewhere [2, 3]. The free-radical decomposition of CHP was studied using a manometric setup under conditions of radical-chain styrene oxidation [16]. The initial reactant concentrations were $[\text{CHP}]_0 = 0\text{--}2.5$ mol/l and $[\text{M(EH)}_2]_0 = 0\text{--}1 \times 10^{-2}$ mol/l. The reaction was carried out in the temperature range of 70–90°C. The solvent was chlorobenzene. Using the mixed initiation method [17] with dicumyl peroxide (DCP) and the ROOH-M(EH)_2 as initiators, it was established that Zn, Cd, and Hg 2-ethylhexanoates do not affect chain propagation or termination in oxidation. For this reason, the following simple equation can be used in the calculation of the radical formation rate:

$$w_0 = (k_2/\sqrt{k_6})[\text{RH}]\sqrt{w_i}, \quad (1)$$



Rate of the free-radical CHP decomposition ($T = 80^\circ\text{C}$; [styrene] = 0.1 mol/l; chlorobenzene as the solvent) versus (1–3) the CHP concentration at a constant ethylhexanoate concentration of $[M(\text{EH})_2]_0 = 5 \times 10^{-3}$ mol/l ($M = (1)$ Cd, (2) Zn, and (3) Hg) and (4) the $\text{Zn}(\text{EH})_2$ concentration at $[\text{CHP}]_0 = 0.1$ mol/l.

where w_0 is the oxidation rate, w_i is the radical formation rate, $k_2/\sqrt{k_6}$ is the propagation-to-termination rate constant ratio, and $[\text{RH}]$ is the styrene concentration (mol/l).

The w_0 and w_i values were derived from oxygen consumption curves. The stoichiometry of the decomposition reaction is such that the rate of CHP decomposition into free radicals is half the observed chain initiation rate.

It was established by special experiments that the radical formation rate in the thermal decomposition of CHP in chlorobenzene is given by the equation

$$w_{i, \text{therm}} = 1.043 \times 10^9 \exp(-110.73/RT) [\text{CHP}]^2 \quad (2)$$

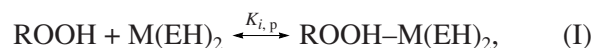
and is ~9% of the overall decomposition rate. The thermal decomposition rate was subtracted from the overall rate. The latter was derived from the chain initiation rate observed for styrene oxidation. The thermal and catalytic decomposition products were identified by GLC (HP-6890 Series GC System chromatograph, capillary column packed with poly(ethylene glycol)).

RESULTS AND DISCUSSION

The rate of radical formation as a function of the reactant concentrations is plotted in the figure. Clearly, the most efficient catalyst for this reaction, as well as for the overall decomposition process, is cadmium carboxylate.

The radical formation rate is a linear function of the catalyst concentration for all of the catalysts throughout the temperature range examined. This indicates that the reaction is first-order with respect to the catalyst.

The order of the CHP decomposition reaction with respect to the hydroperoxide ranges between 1 and ~0 at hydroperoxide concentrations of 0–2.5 mmol/l (figure). This is a kinetic indication of the formation of a hydroperoxide–catalyst intermediate. The mechanism of CHP decomposition into free radicals can be represented as



The kinetic parameters of free-radical decomposition obtained by Lineweaver–Burk processing of experimental data [19], refined overall decomposition data, the thermodynamic functions of formation of the complex derived from the temperature dependence of the equilibrium constant, and the activation parameters of the decomposition of the complex derived from the temperature dependence of the decomposition rate are listed in Table 1.

Both the overall decomposition rate and the free-radical decomposition rate are described by the Michaelis–Menten equation. Therefore, irrespective of the metal, free-radical decomposition and the overall decomposition process proceed via the same mechanism, yielding the intermediate complex $\text{ROOH-M}(\text{EH})_2$, and are characterized by similar kinetic parameters.

The reaction orders with respect to the reactants are the same in both cases. It is, therefore, possible to evaluate the contributions from the molecular and free-radical pathways (Table 1) as the rate constant ratio for the corresponding reactions ($k_{\text{rad}}/k_{\text{overall}}$). For comparison, we present thermal decomposition data as $100w_i/w_{\text{overall}}$ at $[\text{CHP}]_0 = 1.5$ mol/l and $T = 110^\circ\text{C}$. The contribution from free-radical decomposition in the presence of zinc or cadmium ethylhexanoate is ~30% at 80°C and 45% at 120°C . In the presence of mercury ethylhexanoate, this contribution is 3 times larger (88.9%) at 80°C and decreases to 68% as the temperature is raised.

The products of the overall catalytic CHP decomposition process include methanol, acetophenone, 1-methyl-1-phenylethanol, α -methylstyrene, phenol, and traces of benzoic and formic acids. The total yield of the products per mole of CHP decomposed is 1.6 mol (in the presence of the cadmium catalyst) to 2.1 mol (in the presence of the mercury catalyst). The contribution from the heterolytic pathway (the ratio of the phenol yield to the total product yield), which is associated with the acid decomposition of CHP, does not exceed 17–20%.

Investigating the catalytic decomposition of CHP, we found that the activation energy of the decomposition of the complex, the contribution from the free-rad-

Table 1. Kinetic parameters of the catalytic overall and free-radical decomposition of CHP

M(EH) ₂	K_p , l/mol (120°C)	$k_3 \times 10^3$, s ⁻¹ (100°C)	$-\Delta H$, kJ/mol	$-\Delta S$, e.u.	k_0 , s ⁻¹	E_a , kJ/mol	Free-radical decomposition fraction, % (80°C)
Overall decomposition process							
No catalyst	—	—	—	—	9.77×10^8	106.37	38*
Zn(EH) ₂	0.71	11.33	74.15	191.45	1.82×10^8	77.84	27.2
Cd(EH) ₂	1.61	11.03	60.70	150.72	2.84×10^8	74.27	32.2
Hg(EH) ₂	0.60	3.39	117.89	303.71	2.94×10^{14}	120.89	88.9
Free-radical decomposition							
No catalyst	—	—	—	—	1.04×10^9	110.73	—
Zn(EH) ₂	0.04	3.6	71.34	207.70	1.26×10^{11}	96.66	—
Cd(EH) ₂	0.60	4.10	62.12	174.80	9.43×10^8	81.05	—
Hg(EH) ₂	0.08	2.61	124.68	349.25	1.92×10^{13}	113.24	—

Note: $[M(EH)_2] = 5 \times 10^{-3}$ mol/l; the solvent is chlorobenzene.

* Calculated as $w_i/w_{\text{overall}} \times 100$ for $[CHP]_0 = 1.5$ mol/l and $T = 110^\circ\text{C}$.

ical decomposition pathway at 120°C, the M–O bond strength in the complex [2], and the contribution from the heterolytic decomposition pathway (the ratio of the phenol yield to the total product yield) increase in the order Cd < Zn < Hg. The alcohol : ketone ratio in the decomposition products and CHP conversion under fixed condition decrease in the same order.

Clearly, the catalytic properties of the ethylhexanoates depend strongly on the metal cation. It is significant that the trends observed for the Group IIB metals are nonmonotonic.

Up to now, research in this field has generally been limited to the properties of zinc and cadmium. The literature contains only a limited number of publications concerning the role of mercury in such processes. For example, it was reported that mercury compounds participate in hydroperoxide decomposition reactions in an acylating solvent [20] and that hydroperoxides can react non-oxidatively with organomercuric compounds [21].

Limiting the correlation between the properties and the catalytic activity to the first two representatives of Group IIB would certainly provide only incomplete information concerning the behavior of the Group IIB elements. Only examination of the entire zinc family enabled us to discover that many of the catalytic decomposition parameters vary nonmonotonically in going from zinc to mercury.

As was noted above [1, 2], the irregular variation of the properties of the metals and their compounds in the order Zn–Cd–Hg is well known in inorganic chemistry and is explained by the fact that the electron shells of zinc-family d^{10} elements are readily deformable. This causes an extra polarization effect, which makes possible the formation of covalent bonds. Cadmium is much inferior to zinc and mercury in this respect. This specific feature of cadmium is due to the interplay between the increase of the d^{10} shell deformability in the order

Zn < Cd < Hg and the decrease of the atomic radius in the order Hg > Cd > Zn [22]. Thus, it is due to the weakness of its polarization effect that cadmium is the outlier from the Group IIB series.

In view of this, one might expect the zinc and mercury compounds to be the most active in hydroperoxide decomposition. In fact, it was found experimentally that cumyl hydroperoxide decomposition is most rapid in the presence of the cadmium salt and the activation energy of this process is constant through the zinc family.

In the zinc family, as distinct from the alkaline-earth metals, activity and complex formation ability are not correlated with the ionic radii of the elements. For example, cadmium and mercury have similar ionic radii (Table 2), but they show very different complex formation and decomposition behaviors.

It seems obvious that M–O bond strengthening in the ROOH–M intermediate will weaken the hydroperoxide O–O bond in the coordination sphere of the metal, thus favoring the homolysis of this bond. In terms of the enthalpy of formation (ΔH), the zinc and mercury complexes are the most stable. The decomposition of these complexes proceeds at the lowest rate and is characterized by the highest activation energy.

In inorganic chemistry, it has been established by examination of many examples that cadmium complexes are less stable than their zinc and mercury counterparts. This point is supported by our finding that the Cd(EH)₂CHP complex has the lowest enthalpy of formation.

The contradiction between the low stability of the cadmium complex and the high peroxide decomposition rate in the presence of the cadmium salt suggests that catalytic activity is governed by the nature of the M–O bond in the intermediate rather than by the strength of this bond.

Table 2. Some properties of Group IIA and IIB elements [22]

Element	Radius of the M^{2+} , nm	Standard electrode potential E_{M^{2+}/M^0}^0 , V	Ionization potential, eV	
			$M^0 \rightarrow M^+$	$M^+ \rightarrow M^{2+}$
Zn	0.083	−0.763	9.39	17.89
Cd	0.103	−0.403	8.99	16.84
Hg	0.112	+0.850	10.43	18.65
Ca	0.104	−2.87	6.11	11.87
Ba	0.138	−2.90	5.21	10.0

While the coordination bond in the zinc and mercury complexes is highly covalent, the same bond in the cadmium complex, a more active catalyst, is more ionic. This might lead one to conclude that the higher the degree of ionicity of the bond, the more active the catalyst. However, if this were true, the purely ionic complexes of calcium and barium would be more active than the complexes of the zinc-family metals, particularly since the ionic radii of Ca and Cd are nearly equal (Table 2). In fact, the compounds of zinc-family metals are more active in decomposition reactions [23]. Therefore, the existence of a correlation between catalytic activity and the ionic radius of the metal or the degree of ionicity of the M–O bond does not suggest an unambiguous inference as to the true mechanism of the process.

The higher activity of the zinc-family versus the alkaline-earth metals is undoubtedly due to the extra polarization effect. However, the entropy factor should be taken into account in order to explain the variation of catalytic activity within the zinc family itself.

The entropy of formation (ΔS) of the intermediate increases in the order $Cd < Zn < Hg$ (Table 1). Thus, the complex between cadmium ethylhexanoate and CHP, in which the properties of the Cd–O–O bond are mainly determined by electrostatic factors, has the least ordered, loose structure at the same time.

From activation entropy data for CHP decomposition in the presence of a zinc pyrazolone complex and various activators, Kozlov and Potekhin [24] inferred that, as the degree of order of the system decreases, the rate of CHP exchange between the coordination sphere of the metal and the reaction medium increases. Activated $ROOH^*$ molecules build up in the solution, which decompose spontaneously into radicals, thus raising the overall decomposition rate. However, the work quoted above considers, in the framework of absolute rate theory, some dynamic state that must turn into products within $\sim 10^{-13}$ s [25], not an individual compound. Obviously, this period of time is too short for molecular exchange to take place. The preexponential factors reported by Kozlov and Potekhin [24] are very different from the preexponential factors typical of monomolecular and bimolecular reactions. This is apparently due to the fact that, in the calculation of the

decomposition rate constant, the experimental data were fitted to a second-order equation, without taking into account complex formation.

The formation of the intermediate catalytic complex, which is a rather stable compound, is an exothermic process ($\Delta H < 0$). The hydroperoxide molecule in the complex is indeed activated since its O–O bond is weakened. The exchange of molecules between the coordination sphere and the environment undoubtedly takes place, if for no other reason than the reversibility of the complex formation reaction. However, an activated CHP molecule that has left the coordination sphere of the metal must immediately return to the ground state because the M–O–O bond is broken and, therefore, there is no longer any cause of activation.

Owing to the combination of the above factors (electronic configuration, polarization effect, ionic radius, etc.), cadmium forms a loose, comparatively unstable complex characterized by a low entropy of formation. It is the low ΔS value, in combination with the low enthalpy of formation of the complex, that makes the equilibrium constant K_p only slightly sensitive to temperature variations. In the working temperature range (90–120°C), it is the cadmium complex that is characterized by the largest K_p value (Table 1). Simple calculations supported the a priori assumption that the highest concentration of the intermediate is reached in the reaction involving the cadmium complex. According to the law of mass action, this implies the highest decomposition rate. At certain temperatures, the K_p value for the cadmium complex is close to or even significantly smaller than the K_p values for the complexes of the other metals. Nevertheless, the activity order remains the same at these temperatures because of the dramatic decrease in the decomposition rate constants of the zinc and cadmium complexes, which are more temperature-sensitive, and the corresponding increase in the activation energy.

An analysis of the activation energies of hydroperoxide decomposition in the presence of the zinc-family metal compounds (which are less active than the compounds of polyvalent metals) shows that E_a for $Cd(EH)_2$ is abnormally low. By contrast, for vanadyl acetylacetonate, which is among the strongest hydroperoxide decomposers and is active at room tempera-

ture, $E_a = 88.7$ kJ/mol [26]. Therefore, it should not be expected that the activation energy of hydroperoxide decomposition in the presence of cadmium compounds will be much lower than the O–O bond dissociation energy (163 kJ/mol). We believe that the low E_a value observed in the presence of $\text{Cd}(\text{EH})_2$ is only apparent and is explained by the speedup of decomposition due to the increased concentration of the intermediate complex.

The preexponential factor k_0 for the reaction catalyzed by $\text{Cd}(\text{EH})_2$ is also rather small, while the k_0 values for the zinc and mercury compounds are close to the values typical of elementary monomolecular reactions. In view of this, the activation parameters determined for the decomposition of the cadmium complexes should be regarded as apparent.

Thus, the zinc and mercury salts, which are characterized by large complex formation parameters (ΔH , ΔS , and M–O bond strength) might be expected to be catalytically more active than the cadmium carboxylates. However, because of the thermodynamic factor (the more rapid decrease of the equilibrium with an increase in temperature) and the kinetic factor (the more rapid decrease of the rate constant with a decrease in temperature), the zinc and mercury carboxylates appear to be less active than the cadmium carboxylates.

The only possible alternative to this explanation is that the formation of a strong, more covalent M–O bond in the zinc and particularly mercury complexes almost does not weaken the O–O bond in the coordinated hydroperoxide, thus favoring the homolysis of this bond.

As was noted above, not only zinc and cadmium, but also mercury, should necessarily be considered when correlating the catalytic properties of metal salts and the atomic properties of metals for Group IIB. In passing from zinc to cadmium, catalytic activity increases along with the atomic radius, the ionic radius of M^{2+} , and the ionization potential. However, no such symbasis is observed for the entire zinc family (Table 2).

An analysis of the data presented in Tables 1 and 2 suggests that nearly all of the parameters of catalytic decomposition in the presence of $\text{Cd}(\text{EH})_2$ pass through a minimum. This correlates well with the Cd ionization potentials being the lowest. The existence of the few peaking parameters (rate constant, ROOH conversion) is not in conflict with the general trend since these parameters are derivatives of parameters passing through a minimum (ΔH , ΔS , E_a , etc.). It follows from Table 2 that mercury, not cadmium, is the outlier differing greatly in some properties from the other Group IIB metals [27]:

(1) The radius of the doubly charged ion Hg^{2+} is nearly equal to the radius of the Cd^{2+} ion because of lanthanide contraction.

(2) The standard electrode potential $E_{\text{Hg}^{2+}/\text{Hg}}^0$ is positive because the $6s^2$ electrons are screened by both the

$5d^{10}$ -electrons and the $4f^{14}$ electrons. It is due to this circumstance that, as compared to the other zinc-family elements, mercury forms much less stable heteroatomic compounds and is more capable of forming covalent bonds.

Thus, the free-radical decomposition of CHP and the overall decomposition process under the action of the zinc-family metal salts proceed via the same mechanism involving the formation of an intermediate complex. The catalytic activity of the salts decreases in the order $\text{Cd} > \text{Zn} > \text{Hg}$. The thermodynamic parameters of formation and the decomposition kinetics of this complex are correlated with the metal ionization potentials, which are the lowest for cadmium. The zinc-family metals are more active than the Group IIA metals owing to the polarization effect. Within Group IIB, the catalytic properties are mainly determined by the nature of the interaction in the $\text{ROOH-M}(\text{EH})_2$ intermediate. In particular, the electrostatic factors are crucial in the formation of the Cd–O bond, as in the case of Group IIA metals. In the zinc and mercury intermediates, a significant role is played by bond covalence. However, the capacities of Zn and Hg to form covalent bonds are due to different factors, namely, the extra polarization effect in the case of mercury and the small ionic radius in the case of zinc.

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