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THERMAL DECOMPOSITION OF ORGANO-ZINC AND -CADMIUM PEROXIDES IN HYDROCARBONS *

Yu.A. ALEXANDROV *, S.A. LEBEDEV and R.V. KUZNETSOVA
Chemistry Institute, N.I. Lobachevsky State University, Gorky (U.S.S.R.)

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Summary

The thermal decomposition of methyl(methylperoxy)zinc, methyl(tert-butylperoxy)zinc and methyl(tert-butylperoxy)cadmium has been investigated in n-hydrocarbons at 60—90°C. The process occurs heterolytically without free-radical formation. The main metal-containing products of thermal decomposition are $\text{AlkOZnOC(O)H} \cdot \text{ZnO}$ and $\text{CH}_3\text{CdOC(O)H} \cdot \text{CdO}$, respectively. The possible decomposition mechanism of the peroxides studied is discussed.

Results and discussion

As it has been shown [1], Alk_2M auto-oxidation, where Alk is alkyl radical and M is Zn or Cd, in hydrocarbons leads to successive formation of AlkOOMAlk and $(\text{AlkOO})_2\text{M}$, which under Alk_2M auto-oxidation conditions (initial concentration from 0.02 to 0.08 mol/l and reaction temperature from 50 to —65°C) practically do not convert to non-peroxide products through intramolecular rearrangement or interaction with initial Alk_2M. These reactions were proposed earlier by many investigators [2], for example, in the case of AlkMOOAlk they are of the form:

$$\text{AlkMOOAlk} \rightarrow \text{AlkOMOAlk} \tag{1}$$

$$\text{AlkMOOAlk} + \text{Alk}_2\text{M} \rightarrow 2\ \text{AlkMOAlk} \tag{2}$$

In the this work we have undertaken the detailed investigation of the thermal organo-zinc and -cadmium peroxide decomposition in paraffin hydrocarbons. Methyl(methylperoxy)zinc, methyl(tert-butylperoxy)zinc and methyl(tert-butylperoxy)cadmium (peroxides I, II, III, respectively) were investigated. The decompositions were carried out in evacuated glass tubes, eliminating contact with atmospheric oxygen and water vapour, and in the absence of light.

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* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

TABLE 1

THERMAL DECOMPOSITION PRODUCTS OF AlkEOOAlk (E = Zn, Cd) IN n-HEPTANE AT 80°C (in mole per mole of peroxide decomposed)

Peroxide AlkEOOAlk	$C_0 \times 10^2$ (mol/l)	CH_4	$(CH_3)_3COH$	$(CH_3)_3COECH_3$	$(CH_3O)_2Zn$ [a]	$CH_3OEOC(CH_3)_3$ [a]	$CH_3OZnOC(O)H \cdot ZnO$	$(CH_3)_3COZnOC(O)H \cdot ZnO$ [a]	$CH_3CdOC(O)H \cdot CdO$ [a]
$CH_3ZnOOCH_3$	6	0.8	—	—	0.22	—	0.4	—	—
$CH_3ZnOOC(CH_3)_3$	8	0.31	0.2	0.22	—	0.17	—	0.31	—
$CH_3CdOOC(CH_3)_3$	6	—	0.46	0.38	—	0.05	—	—	0.32

[a] According to solvolysis product.

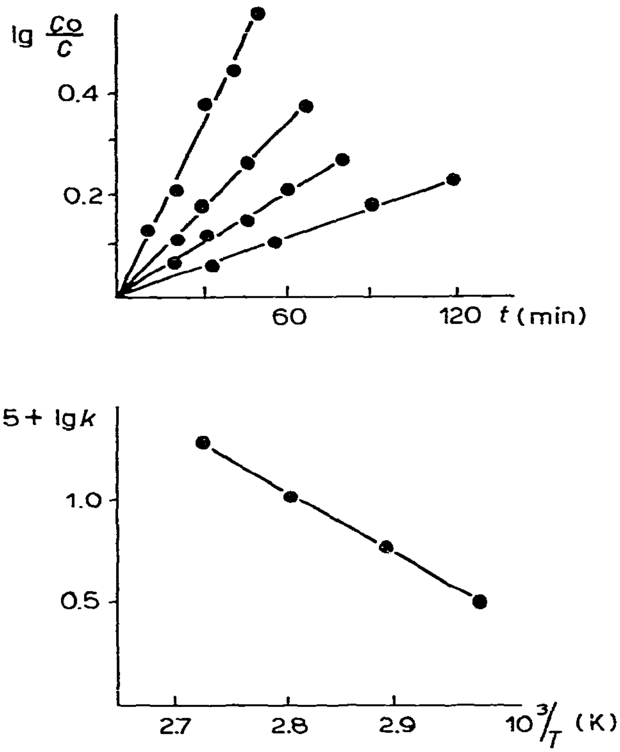


Fig. 1. (a) Kinetic curves for $CH_3OOZnCH_3$ decomposition in hexane (C_0 = 0.066 mol/l) at various temperatures. 1, 65°C; 2, 75°C; 3, +85°C; 4, 95°C. (b) Corresponding semilogarithmic plot.

The thermal decomposition of peroxides I—III proceeds at conveniently measured rates at temperatures above 50°C. The composition and the yield of the reaction products are given in Table 1.

The decomposition of peroxides I—III in paraffin hydrocarbons proceeds

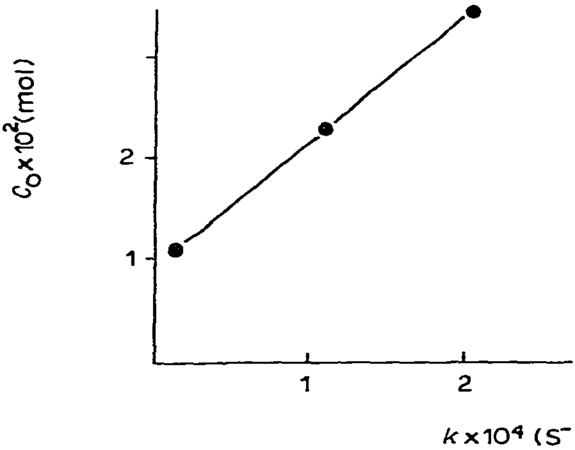


Fig. 2. The dependence of thermal decomposition rate constant upon initial $(CH_3CdOOC(CH_3)_3)_4$ concentration.

according to a kinetic law of a first order reaction relative to the present peroxide concentration (Fig. 1). With increasing initial peroxide concentration the reaction rate constant (k) increases (Fig. 2). A semilogarithmic plot of the k-temperature dependence is linear in a set of experiments with constant peroxide concentration (Fig. 1). The total appearance of k for peroxide I ($C_0 = 0.054$ mol/l) is: $k = 10^5 \times \exp\{-14200/RT\}$ sec^{-1}, for peroxide II ($C_0 = 0.09$ mol/l) $k = 2.8 \times 10^8 \exp\{-20800/RT\}$ sec^{-1}, for peroxide III ($C_0 = 0.066$ mol/l) $k = 4.7 \times 10^7 \exp\{-17500/RT\}$ sec^{-1}.

Organic peroxide compounds of non-transition elements containing a α-hydrogen at the peroxy group are known to rearrange with formation of aldehyde and metal hydroxide [2], and aldehydes react readily with peroxide with formation of appropriate acylates and alcohol:

$$R_3EOOCH_2R_2' \rightarrow R_3EOH + R'C(O)H \qquad (3)$$

$$R_3ECOR'' + R'C(O)H \rightarrow R_3EOC(O)R' + R''OH \qquad (4)$$

We investigated the possibility of similar reactions for peroxides I—III with methyl(methylperoxy)zinc as example. In the thermal decomposition of this peroxide in hexadecane, formaldehyde was qualitatively found, pointing to rearrangement proceeding with migration of the α-hydrogen atom. The interaction of peroxide I with the aldehyde proton in n-hexane occurs readily at room temperature and is accompanied by formation of the appropriate acylate and methane in quantitative yield. This suggests that the thermal decomposition of methyl(methylperoxy)zinc may be written in the following terms:

$$CH_3ZnOOCH_3 \rightarrow CH_3ZnOH + OCH_2 \qquad (5)$$

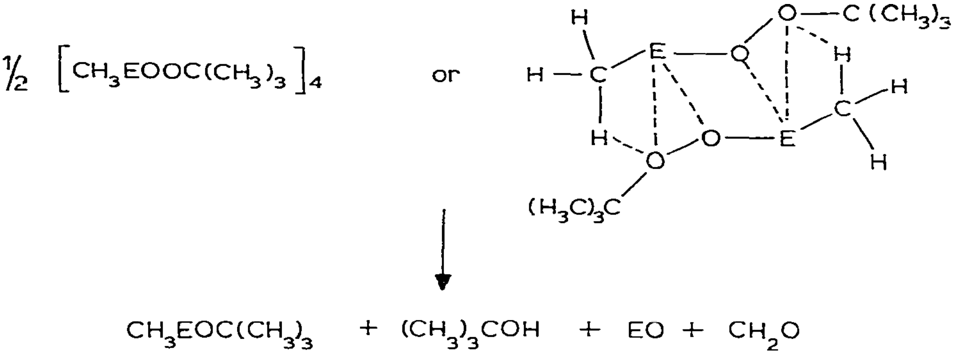
$$CH_3ZnOOCH_3 + CH_3ZnOH \rightarrow CH_3ZnOZnOOCH_3 + CH_4 \qquad (6)$$

$$CH_3ZnOZnOOCH_3 + CH_2O \rightarrow CH_3ZnOZnOC(O)H + CH_3OH \qquad (7)$$

$$CH_3ZnOZnOC(O)H + CH_3OH \rightarrow \begin{array}{c} CH_3OZnOZnOC(O)H + CH_4 \\ \downarrow \\ CH_3OZnOC(O)H + ZnO \end{array} \qquad (8)$$

It should be noted that reactions of type 6 have been observed earlier [3]. Expressions 5—8 are formal in nature, since peroxides I—III are strongly associated in the solvents used. Thus, according to cryoscopy, peroxide III in benzene is tetrameric under ordinary conditions $[(CH_3)_3COOCdCH_3]_4$ (molecular weight for monomer is 216.4; determined 854). Based on the association of peroxides I—III, the selectivity of reactions 5—8 could be explained as being due to peroxide decomposition occurring in the associate complex, the structure of which is assumed to be similar to the cubane structure of tetrameric methylmethoxyzinc [4].

The decomposition of the associated complexes of peroxides II—III was assumed to occur through a concerned mechanism, as given below for a dimeric fragment of the complex:



(9)

$$CH_3EOOC(CH_3)_3 + CH_2O \rightarrow CH_3EOC(O)H + (CH_3)_3COH \quad (10)$$

It should be mentioned that hydrogen donors (compounds with "active" hydrogen atoms) might break the intramolecular O- -H bonds at the expense of intermolecular O- -H bond formation. So peroxide III decomposition in tetrahydrofuran is accompanied by a more than two fold increasing yield of tert-butyl alcohol, formate being present in traces.

Substitution of one alkyl group by the acyloxy fragment in the organozinc compound increases the zinc—carbon bond polarity and promotes more rapid displacement of it by the alkoxy group [4]. Therefore, in the case of peroxide II, the tert-butyl alcohol being formed reacts with methylzinc formate.

$$CH_3EOC(O)H + t\text{-}BuOH \rightarrow CH_4 + t\text{-}BuOEOC(O)H \quad (11)$$

The presence of dimethoxyzinc and methoxy(tert-butoxy)zinc, respectively, in the peroxide I and II decomposition products points to the occurrence of an intramolecular rearrangement:

$$Me{-}Zn{-}O{-}O{-}R \rightarrow MeO{-}Zn{-}OR \quad (12)$$

In the case of peroxide III the rearrangement practically does not occur.

Variation of the initial concentration of peroxide compound influences the constant value of thermal decomposition rate of peroxides I—III. We think that this effect is due to the catalytic influence of the zinc and cadmium oxides. Similar effects have been mentioned earlier in an investigation of the thermal decomposition of organo-tin and -mercury peroxides [2]. $E^{\delta+}{-}O^{\delta-}$ may act as an electron-donor ligand, decreasing the effective electronegativity of the hetero atom and facilitating the reaction.

The general view of the peroxide decomposition scheme is of the form:

$$X \xrightarrow{k_0} \text{oxide}_{\text{solv}} + P \quad (13)$$

$$\text{oxide}_{\text{solv}} \underset{k_2'}{\overset{k_1}{\rightleftharpoons}} \text{oxide}_{\text{solid}} \quad (14)$$

$$X + \text{oxide}_{\text{solv}} \overset{k_3'}{\rightleftharpoons} \text{oxide}_{\text{solv}} + P \quad (15)$$

with $k_3' >> k_0'$.

In this scheme $X = (OEPC)_n$, oxide_{solv} = dissolved metal oxide, oxide_{solid} = metal oxide in residue, P = reaction products.

In accordance with the scheme the expression for the thermal decomposition rate is of the form:

$$W = k' \cdot [X] + k'[X] \cdot [\text{oxide}_{solv}]$$

Assuming a stationary concentration of the dissolved metal oxide, $k'_1 >> k'_3[X]$ and $[\text{oxide}_{solid}] >> [\text{oxide}_{solv}]$

$$W = k_{eff}[X], \text{ where } k_{eff} = k'_0 + \frac{k'_0 k'_3}{k'_1}[X]_0$$

The k_{eff} dependence upon initial concentration of OEPC (with $n = 4$) for the case of peroxide III is given in Fig. 2. It follows from Fig. 2, that the linear dependence of k_{eff} upon $[X]_0$ is disturbed in the small concentration range of the peroxide compounds. It is due to a decreasing association extent of peroxide compound and as a consequence to a decreasing thermal decomposition rate.

Experimental

Methyl(methylperoxy)zinc (I) was prepared by dimethylzinc oxidation [5] and recrystallized from hexane. Elemental analysis results are given in Table 2. Methyl(methylperoxy)zinc is a white crystalline readily hydrolyzable compound. It is tetrameric in benzene solution with $C_0 = 0.053$ mol/l.

Methyl(tert-butylperoxy)zinc(II) and methyl(tert-butylperoxy)cadmium(III) were synthesized by reaction of equimolar Me_2M and tert-butyl hydroperoxide. The synthesis was carried out under inert atmosphere at 0°C; the stoichiometry of the reaction is the following:

$$(CH_3)_2M + (CH_3)_3COOH \rightarrow CH_3MOOC(CH_3)_3 + CH_4$$

Analysis data of these peroxide compounds, recrystallized from hexane, is given in Table 2.

Thermal decomposition product analysis of peroxides I—III

(a) Gaseous and hexane-soluble decomposition products: Methane was analysed by gas-liquid chromatography on a "Tsvet-102" chromatograph. Analysis condi-

TABLE 2

ANALYSIS DATA OF ZINC AND CADMIUM PEROXIDES

Compound	Found (calcd. (%))			Empirical formula
	CH_3	—O—O—	E	
$CH_3ZnOOCH_3$	11.5 (11.77)	25.0 (25.1)	50.7 (51.3)	$C_2H_6O_2Zn$
$CH_3ZnOOC(CH_3)_3$	8.5 (8.85)	18.7 (18.9)	38.0 (38.6)	$C_5H_{12}O_2Zn$
$CH_3CdOOC(CH_3)_3$	6.8 (6.93)	14.5 (14.78)	51.3 (59.94)	$C_5H_{12}O_2Cd$

tions: $l_0 = 1.5$ m, $d = 4$ mm, sorbent was annealed molecular sieve NaX, $V_{He} =$ 35 ml/min. t-BuOH was analysed by GLC. Analysis conditions: $l = 3$ m, $d =$ 3 mm, sorbent "Polysort", $T_v = 120°C$, $T_c = 80°C$, $V_{He} = 35$ ml/min. CH_3MOt-Bu: The product isolated from hexane was solvolyzed by diethyl ether and propionic acid mixture. The CH_4 and t-BuOH formed were quantitatively analysed by GLC and M^{2+} by complexometric titration. The product structure was also confirmed by IR-spectra. (UR-20 apparatus, suspension in vaseline oil).

(b) Hexane-insoluble thermal decomposition products of peroxides I—III were treated with a mixture of diethyl ether and propionic acid. Solvolysis products were analysed by GLC. Formic acid was displaced out of the decomposition product by diethyl ether saturated with HCl and analysed by GLC ($l = 1$ m, $d = 3$ mm, $T_v = 160°C$, $T_e = 140°C$, $V_{He} = 35$ ml/min, sorbent = 15% PEG-6000 on chesasorb AW 0.25—0.36 mm. In addition the formation of the appropriate formates was confirmed by IR spectroscopy. The presence of zinc and cadmium oxide was shown by X-ray diffraction.

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