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Dialkyl Peroxides Decomposition in the Presence of Quaternary Ammonium Halides

N. V. Maksyuta[1], V. Ya. Suprun[2], I. A. Opeida[1], and N. A. Turovskii[1]

[1]*Litvinenko Institute of Physical Organic and Coal Chemistry, Ukrainian Academy of Sciences, Donetsk, 183114 Ukraine*
[2]*Martin-Luther Universität, Halle-Wittenberg, Merseburg, BRD*

Abstract—Decomposition of dicumyl peroxide and cumyl *tert*-butyl peroxide was studied in the presence of tetraethylammonium halides in acetonitrile, dimethylformamide, 2-propanol, and acetic acid. The tetraethylammonium halides accelerate the decomposition of dialkyl peroxides in 2-propanol and acetic acid, but do not affect the reaction velocity in dimethylformamide and acetonitrile. The decomposition products character depends on the solvent nature.

In a number of publications [1] was reported on considerable acceleration of diacyl peroxides decomposition effected by quaternary onium salts (chlorides, bromides, iodides, picrates of tetraethylammonium, triethylbenzylammonium, etc.).

The investigation of effect of the quaternary ammonium salts on the benzoyl peroxide decomposition established that the rate of reaction became 2–3 orders of magnitude greater than the thermolysis velocity, and therefore it was possible to carry out the peroxide decomposition at lower temperature (298–303 K). The process activation is effected by anion as shows the increase of the reaction rate in the halide series I > Br > Cl. The role of cation consists in electrophilic assistance to the peroxide decomposition. The acceptor characteristics of the solvent notably affect the rate of the activated decomposition [2]. It is also known that the oxidation of hydrocarbons in the presence of the quaternary onium salts is accelerated [3] due to the interaction of the forming hydroperoxides with the salts.

Thus obviously the decomposition of peroxides of RC(O)OO(O)CR and ROOH type is significantly affected both by the structure of salts and the medium characteristics.

Under thermolysis conditions dialkyl peroxides are more stable than hydroperoxides and diacyl peroxides [4]. The target of this study was evaluation of the possibility to activate the decomposition of dialkyl peroxides with quaternary ammonium halides and investigation of the medium effect on the kinetic parameters and mechanism of the process. As objects of the study we selected the most accessible dicumyl peroxide (**I**) and cumyl tert-butyl peroxide (**II**).

The decomposition thereof was already studied in cumene and chlorobenzene [5] where the products composition was limited to acetophenone and 2-phenylpropan-2-ol. Yet it is known [6] that at induced decomposition of dialkyl peroxides (*tert*-butyl peroxide) arise epoxy derivatives which can produce quite a few secondary products depending on the experiment conditions. Besides the quaternary ammonium halides are sparingly soluble in the solvents of low polarity. Therefore we chose a series of solvents with different properties that were sufficiently good solvents both for peroxides and quaternary ammonium salts.

The thermal decomposition of peroxides was studied at 90°C. We chose this temperature to reduce the contribution from the thermal decomposition. The curves of peroxide **I** consumption are given on Fig. 1. The initial rates of the thermal and activated decompositions were evaluated by graphical differentiation of the curves *c* vs time till conversion 10% (Table 1).

It turned out that the rate of the thermal decomposition considerably depended on the character of solvent and changed in the series AcOH> *i*-PrOH> MeCN > DMF. This fact is well consistent with the literature data. For instance, in [5] was established that the rate of thermal decomposition of the *tert*-butyl peroxide in the temperature range 120–135°C decreased in the solvent series acetic acid > acetonitrile > 2-propanol. The alteration of the thermal decomposition rate corresponds to the change in the electrophilicity factor and dielectric constant [7]. Thus just the electrophilic characteristics of the solvent influence the most the rate of thermal decomposition.

Table 1. Initial decomposition rates of dialkyl peroxides in various solvents, 90°C

Peroxide	[Et₄NBr], mol l⁻¹	Solvent	ε [a]	E [a]	$W_0 \times 10^8$, mol l⁻¹ s⁻¹ [b]
CumOOCum	–	MeCN	37.5	5.2	4.1 ±0.7
	–	DMF	36.7	2.6	5.2 ±1.1
	–	*i*-PrOH	18.3	8.7	10.8 ±0.5
	0.1	*i*-PrOH			11.6 ±0.6
	–	AcOH	6.15	14.6	26.5 ±3.6
	0.1	AcOH			92.9 ±4.1
CumOOBu-*t*	–	MeCN			0.97 ±0.12
	0.1	MeCN			1.93 ±0.43
	–	*i*-PrOH			10.8 ±0.6
	–	AcOH			286 ±22

[a] Data from [7]. [b] W_0 was determined up to 10% conversion.

Note the significant difference in products arising at peroxide **I** decomposition in various solvents (Table 2). In the literature as the main products of peroxide **I** decompositions were described 2-phenyl-propan-2-ol and acetophenone, however we detected in the reaction mixture also 2-phenylpropene, 2-phenyl-1,2-epoxypropane, and 1-acetoxy-2-phenyl-propan-2-ol. The selectivity of decomposition product formation we calculated in moles per 1 mole of decomposed peroxide.

In 2-propanol and dimethylformamide the main decomposition product is 2-phenylpropan-2-ol, in acetic acid alongside this compound and acetophenone arise 2-phenylpropene, 2-phenyl-1,2-epoxypropane, and also 1-acetoxy-2phenylpropan-2-ol.
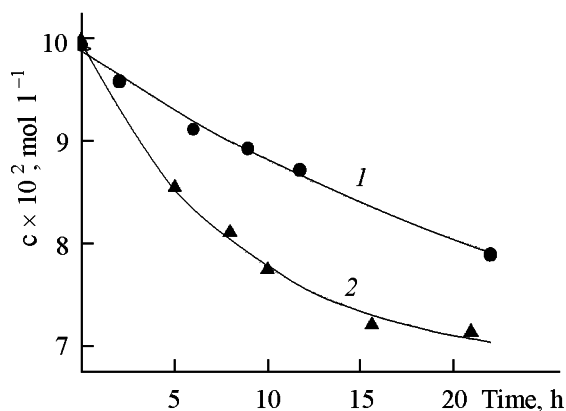

Fig. 1. DEcomposition of dicumyl peroxide in acetic acid, 90°C. (*1*) Thermal decomposition; (*2*) Decomposition in the presence of tetraethylammonium bromide.

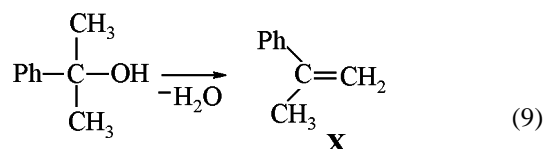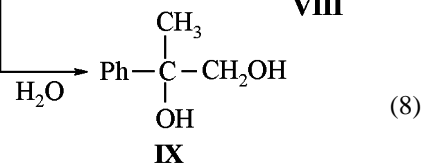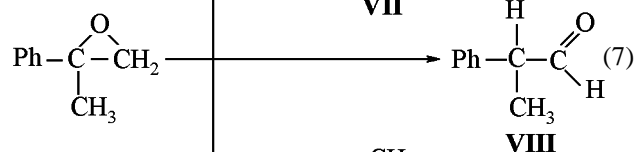From the above data may be constructed the following hypothetical scheme of peroxide **I** decomposition.
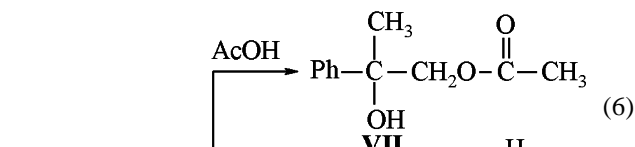
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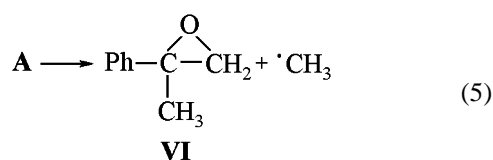
Table 2. Selectivity of products formation in decomposition of dialkyl peroxides, 90°C, c_0 0.1 mol l^{-1}
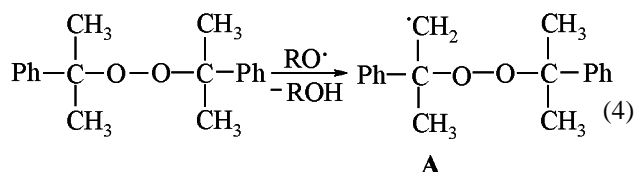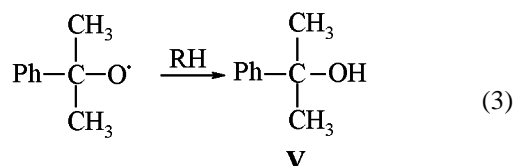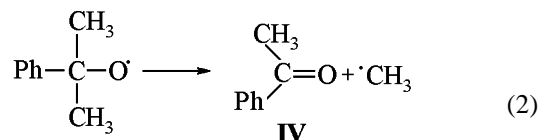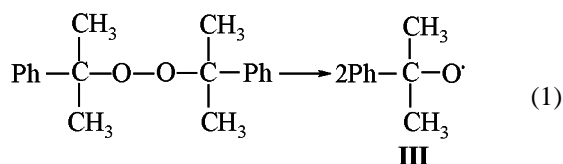
Solvent	[Et$_4$NBr], mol/l	ΔX, %	Decomposition products, mol mol^{-1} of decomposed peroxide					
			aceto-phenone	2-phenylpro-pan-2-ol	2-phenyl-propene	2-phenyl-1,2-epoxypropane	1-acetoxy-2-phe-nylpropan-2-ol	2-phenylpro-pane-1,2-diol
			Dicumyl peroxide[a]					
DMF	0	4	0.25	1.75	0	0	0	0
DMF	0.1	7.8	0.22	1.78	0	0	0	0
MeCN	0	0.9	1.55	0.45	0	0	0	0
i-PrOH	0	11	0.19	1.81	0	0	0	0
i-PrOH	0.1[b]	6.4	0.35	0.63	1.01	0	0	0
i-PrOH	0.1	9.7	0.11	1.89	0	0	0	0
AcOH	0	21.5	0.69	0.13	0.98	0.06	0.15	0
AcOH	0.1	17	0	1.5	0.041	0.05	0.41	0
			Cumyl *tert*-butyl peroxide[c]					
MeCN	0	2.5	0.78	0.22	0	0	0	0
i-PrOH	0	45.5	0.12	0.1	0.49	0	0	0.29
AcOH	0	~100	0.11	0.05	0.34	0.31	0.2	–
AcOH	0.1	~100	0.14	0.14	0.2	0.23	0.29	0

[a] Conversion in 29 h. [b] Et$_4$N–Cl. [c] Conversion in 60 h.

It is expectable that the primary product of peroxide **I** decomposition would be cumyloxy radical **III** that can undergo fragmentation into acetophenone **IV** and a methyl radical or can abstract hydrogen atom from solvent or another species. This hydrogen abstraction provides 2-phenylpropan-2-ol (**V**) [8]. The ratio of compounds **IV** and **V** shows the rate ratio of the two processes; the latter is governed by the temperature and energy of rupture of the C–H or O–H bonds in the solvent molecules [9]. For instance, at peroxide **I** decomposition in 2-propanol alcohol **V** forms considerably faster than occurs fragmentation of radical **III** (Table 2). In acetonitrile the fragmentation rate is higher than that of alcohol **V** formation, and acetophenone becomes the major product of the reaction.

When alkoxy radical attacks the peroxide molecule may occur hydrogen abstraction from a methyl group resulting in a β-peroxy radical (A) [reaction (4)] [6, 9]. The intermolecular homolytic substitution within β-peroxy radical affords 2-phenyl-1,2-epoxypropane (**VI**). The epoxy ring is unstable and depending on the solvent and temperature it may open to provide secondary products: 2-phenyl-2-methyl-propanal, 1-acetoxy-2-phenylpropan-2-ol, and also 2-phenylpropane-1,2-diol [reactions (6, 7, 8)]. Ester **VII** readily forms in acetic acid at 60°C within 1 h as show special experiments. Diol **IX** can arise in the presence of water; thus the water content in the

solvents in the course of reaction was sufficient for ring opening along this path. Aldehyde **VIII**, product of epoxy ring rearrangement, was not detected in the reaction mixture.

The dehydration of alcohol **V** furnishes 2-phenylpropene [reaction (9)] as is confirmed by the form of product accumulation curves (Fig. 2).

The composition of products of peroxide **II** thermolysis (expressed in mol mol^{-1} of peroxide decomposed) is given in Table 2. We did not investigate the volatile products originating from the *tert*-butyl part of the molecule.

The peroxide decomposition in the presence of quaternary ammonium halides was carried out at equimolar concentration of peroxide and salt. We established that the solvent character considerably affected the salt activity in the peroxide decomposition.

The presence of tetraethylammonium bromide (Et$_4$N–Br) during the decomposition of peroxide **I** in dimethylformamide does not affect the process rate or products composition. The difference in the reaction rates is within the accuracy of gas-chromatographic analysis. The qualitative composition and ratio of reaction products are identical to the data obtained with thermal degradation. In the presence of Et$_4$N–Cl in 2-propanol the ratio of degradation

products changes, and arises additionally olefin **X** originating from dehydration of alcohol **V**. However in the presence of Et_4N-Br the set of decomposition products of peroxide **I** remains the same.

Et_4N-Br considerably affects the rate and decomposition products when the reaction is carried out in acetic acid. In the presence of the salt grows the rate of alcohol **V** formation as compared to the rate of fragmentation, decreases the fraction of olefin **X**, increases the amount of ester **VII**, and that of epoxide **VI** is reduced. The rate of the activated decomposition is similar to that of thermolysis (Table 1).

Thus the data of this study show that the solvent character significantly affects the activity of tetraethylammonium halides in the decomposition process of dialkyl peroxides. The series of alteration in the thermal decomposition rate is in agreement with the change in the solvent electrophilicity.

The effect of salts on the kinetic parameters and decomposition mechanism in dimethylformamide and acetonitrile is negligible, and only the decomposition in acetic acid and 2-propanol is accelerated in the presence of salts. The presence of salts considerably affects the reaction products composition indicating that the transformation of the cumyloxy radical shifts in the direction of proton abstraction.

EXPERIMENTAL

Acetonitrile (Aldrich, 99.3%) was used without further purification. 2-Propanol, acetic acid, and dimethylformamide were purified as in [10].

Tetraethylammonium bromide (Aldrich, 99%) was dried at reduced pressure at 353 K in Fisher gun. Tetraethylammonium chloride was purified by reprecipitation with cold ethyl ether from hot ethanol solution. The precipitate was collected on glass frit filter and dried at 329 K in Fisher gun at reduced pressure over P_2O_5. The salts were kept in a glove box containing P_2O_5.

Dicumyl peroxide was purified by recrystallization from ethanol. Cumyl tert-butyl peroxide (Peroxid-Chemie, 99%) was used without further purification.

The decomposition products were identified by GLC according to the retention time of the authentic samples. 2-Phenyl-1,2-epoxypropane was prepared by epoxydation of 2-phenylpropene *in situ* along procedure [6], 1-acetoxy-2-phenylpropan-2-ol was obtained by heating the 2-phenyl-1,2-epoxypropane in acetic acid to 60°C for 1 h.
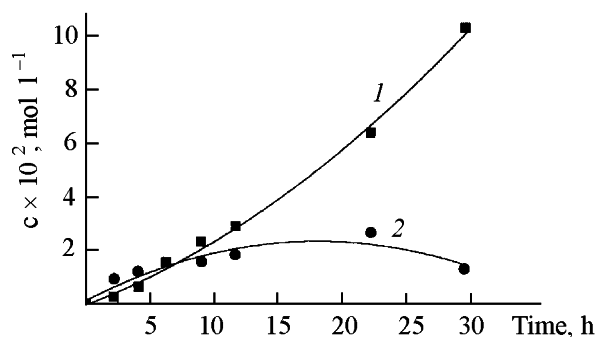

Fig. 2. Accumulation of 2-phenylpropene (*1*) and 2-phenylpropan-2-ol (*2*) at the thermal decomposition of dicumyl peroxide in acetic acid, 90°C.

The solutions of the peroxides under study were maintained at constant temperature in the sealed ampules. The temperature 90°C was maintained with the accuracy 0.05°C. The initial reagents concentrations were as follows: ROOR, 0.1 mol l^{-1}; Et_4N-Hlg, 0.1 mol l^{-1}.

The consumption of peroxides and accumulation of decomposition products was determined by GLC using a capillary column CP-Sil 5CB Film-0.12 µm, 10 m long, internal diameter 0.25 mm. It was preliminary shown at that the use of capillary columns at evaporator temperature less than 200°C the chromatographic separation of peroxides was not accompanied by their thermal decomposition [11]. The analysis was carried out on a Chrompack chromatograph equipped with the flame-ionization detector, evaporator temperature 170°C, detector at 250°C, oven temperature programmed from 50 till 170°C at a rate 7°C/min. The reactant concentrations was evaluated by internal standard method, biphenyl standard.

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