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DECOMPOSITION OF ORGANIC PEROXIDES IN THE PRESENCE OF ALKALIS

IN NONAQUEOUS MEDIA

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It is known that the thermal decomposition of organic peroxides in neutral media is accompanied by homolysis of the O-O bond and that it leads to the formation of free radicals in the system [1, 2]. In the presence of strong mineral acids, peroxides may be subjected to isomerization and heterolytic decomposition [2]. The nonradical thermal decomposition of peroxides in the presence of catalytic quantities of Cl⁻, Br⁻, CN⁻, or other ions, as has been shown in the example of decomposition of organometallic peroxides, can be accomplished as a result of solvolysis of the M-O bonds (M = Si, Tl, Ge) and by means of intramolecular rearrangements [3-6].

In the present work, we investigated the influence of OH⁻ ions on the mechanism of decomposition of organic peroxides in nonaqueous media.

The decomposition of benzoyl peroxide (BP), α -phenylethyl hydroperoxide (PEHP), cumyl hydroperoxide (CHP), and dicyclohexylperoxydicarbonate (DCPC) was carried out in the presence of potassium hydroxide at 50-90°C. Ethylbenzene and chlorobenzene were used as solvents; in order to increase the solubility of the KOH in the aromatic hydrocarbons, 18-crown-6 was used in accordance with a procedure analogous to that of [7]. The KOH and 18-crown-6, in amounts of 0.01 mole each, were dissolved at 50°C in 3 ml of MeOH. The solution was evaporated to dryness at 50-60°C under a pressure ≤ 1 torr. The solid residue was dissolved in 30 ml of the solvent and filtered through a glass filter, obtaining a solution with [OH⁻] = 0.25 M.

The BP and DCPC were purified by recrystallization from acetone, the CHP by a procedure given in [8]. The PEHP was obtained by oxidation of ethylbenzene at 105° C to a low conversion with subsequent concentration under vacuum to [PEHP] ~ 0.2 M.

The content of peroxides in the solution was determined iodometrically. The decomposition products were analyzed by GLC in an LKhM-8M chromatograph using a 1 m \times 3 mm column with 15% XE-60 on Gas-Chrom-S (100-200 mesh), column temperature 80°C, vaporizer temperature 125°C. Benzoic acid was determined in a 0.5 m \times 3 mm column with Polysorb 1, column temperature 175°C, vaporizer temperature 200°C.

The rate of radical decomposition of the peroxides (W_R) was calculated from the rate of ethylbenzene oxidation from the formula

$$W_{\rm R} = \frac{k_6 W^2}{k_2^2 [\rm RH]^2} \tag{1}$$

UDC 541.124:542.92:547.582.3

where k_2 and k_6 are the rate constants of chain extension and breaking in the case of ethylbenzene oxidation ($k_2 = 1.7$, $k_6 = 1.9$ liters/mole•sec [9]); [RH] is the concentration of hydrocarbon; W is the oxidation rate. The ethylbenzene oxidation rate was measured according to the rate of oxygen uptake in a manometric unit [1].

It is known that in nonaqueous media, BP, DCPC, and PEHP are quite thermally stable; the half-decomposition periods of BP at 90°C and of DCPC at 70°C are approximately 2 h, and that of PEHP at 120°C is 300 h. In the presence of an equimolar quantity of KOH, the decomposition

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2223-2226, October, 1983. Original article submitted December 3, 1982.



Fig. 1. Kinetic curves for decomposition: 1) PEHP in ethylbenzene, 50° C, [KOH] = 0.035 M, [18-crown-6] = 0.07 M; 2) CHP in chlorobenzene, 60° C, [KOH] = 0.037 M, [18-crown-6] = 0.1 M; 3) PEHP; 4) CHP in the absence of additives.

Fig. 2. Kientics of PEHP accumulation in ethylbenzene oxidation at 120°C in the absence of additives (1) and in the presence of [KOH] = $7 \cdot 10^{-2}$ M and [18-crown-6] = $8 \cdot 10^{-2}$ M (2).

of the BP, DCPC, and PEHP is greatly accelerated: 93-98% conversion is reached in 0.5-10 min; i.e., the decomposition rates are increased by a factor of 10^2 to 10^4 in comparison with the thermal decomposition.

Tertiary hydroperoxides (tert-butyl hydroperoxides and CHP) are more resistant to the action of the caustic; the half-decomposition period of these compounds amounts to several hours at 60-70°C.

The rate of PEHP decomposition $(3.5 \cdot 10^{-4} \text{ mole/liter} \cdot \text{sec}, 50^{\circ}\text{C})$ in the presence of KOH and 18-crown-6 is more than an order of magnitude greater than the rate of decomposition of CHP $(1.5 \cdot 10^{-5} \text{ mole/liter} \cdot \text{sec}, 60^{\circ}\text{C})$ (Fig. 1). The CHP decomposes at rates commensurate with the rates of its thermal decomposition. In the absence of alkali, the crown ether does not affect the decomposition rates of the hydroperoxides.

In the absence of alkaline additives, all of the peroxides that we have investigated decompose mainly at the O-O bond, forming radicals that are capable of initiating the oxidation of hydrocarbons through a chain mechanism [1, 2]. In evaluating the contribution of radical decomposition of hydroperoxides in the presence of KOH and 18-crown-6, we used a liquid-phase oxidation technique. If the peroxides decompose in the radical direction, the average ethylbenzene oxidation rate at 50°C in the presence of 0.1 M PEHP, 0.035 M KOH, and 0.07 M 18-crown-6 (see Fig. 1) should be $6.90 \cdot 10^{-5}$ mole/liter·sec. The experimentally measured oxygen uptake rate under these conditions $W \leqslant 2 \cdot 10^{-6}$ mole/liter·sec. The maximum possible rate of formation of radicals by decomposition of PEHP, as calculated by the use of Eq. (1), in this case is $W_{\rm R} \leqslant 4.2 \cdot 10^{-8}$ mole/liter·sec, i.e., less than 0.01% of the PEHP decomposition rate.

The high rates of hydroperoxide decomposition without the formation of free radicals in the presence of KOH and 18-crown-6 are apparently the reason for the complete retardation of ethylbenzene oxidation at 120°C that we have observed (Fig. 2).

In the oxidation of cumene, the addition of KOH and 18-crown-6 also has a retarding effect, but the degree of retardation of the oxidation is considerably less than in the case of ethylbenzene oxidation. Apparently the reason for this difference is that the fraction of the radical decomposition of CHP in the presence of the bases is higher than in the case of the PEHP.

The BP and DCPC, in the presence of the alkaline additives, do not increase the rate of ethylbenzene oxidation during the time of practically complete conversion of these substances, whereas in the absence of the alkaline additives, these peroxides effectively accelerate the ethylbenzene oxidation (Fig. 3). This means that the BP and DCPC also decompose without the formation of free radicals.



Fig. 3. Oxygen uptake in ethylbenzene oxidation: 1) initiator BP, 90°C, $W_i = 4.14 \cdot 10^{-5}$ mole/liter•sec; 2) initiator DCPC, 70°C, $W_i = 2.02 \cdot 10^{-5}$ mole/liter•sec; 3) initiator BP, 90°C, $W_i = 4.14 \cdot 10^{-5}$ mole/liter•sec; [18-crown-6] = 0.22 M, [KOH] = 0.125 M; 4) initiator DCPC, 70°C, $W_i = 2.02 \cdot 10^{-5}$ mole/liter•sec; [18-crown-6] = 0.57 M, [KOH] = 0.11 M.

In order to establish the mechanism of decomposition of these peroxides, we analyzed the composition of the conversion products. If the decomposition is accomplished by a preliminary rearrangement of the type [3-6]

PhCH(Me)OOH → PhOCH(Me)OH PhC(O)OOC(O)Ph → PhOC(O)OC(O)Ph

then phenol should be formed as one of the principal products from the decomposition of PEHP and $\ensuremath{\mathtt{BP}}\xspace$.

Studies of the peroxide decomposition products showed that the decomposition of the PEHP gives acetophenone; the decomposition of the BP gives benzoic acid and methyl benzoate. No phenol was found in the reaction products. In the decomposition of DCPC, the principal products are CO_2 and cyclohexanol. The decomposition of BP and DCPC also gives gaseous products that are not absorbed by aqueous caustic solution.

These data suggest that the decomposition of BP and DCPC includes a stage of nucleophilic substitution at the carbonyl carbon atom. The nucleophilic species are apparently OH⁻ ions or methylate ions. In accordance with the known method of obtaining peroxybenzoic acid by the interaction of BP with sodium methylate, it is possible that a peroxybenzoate ion is formed in the first stage [2], and that this ion then decomposes rapidly to release oxygen

PhC(0)OOC(0)Ph + RO⁻ \rightarrow PhC(0)OR +PhC(0)OO⁻ PhC(0)OO⁻ \rightarrow PhC(0)O⁻ + $\frac{1}{2}O_2$ R = H, Me.

In the decomposition of the PEHP, the acetophenone is evidently formed by a reaction in which the peroxide ion participates:

PhCH(Me)OOH + OH⁻ \rightleftharpoons H₂O + PhCH(Me)OO⁻(RO⁻₂) PhCH(Me)OOH $\xrightarrow{\text{RO}_2^-}$ PhC(O)Me + H₂O

The relative stability of tert-butyl hydroperoxide and CHP to the action of alkalis in nonaqueous media is apparently related to the absence of any hydrogen atom on the α -carbon atom relative to the peroxy group.

CONCLUSIONS

1. In nonaqueous media in the presence of caustic and a crown ether, diacyl peroxides and hydroperoxides decompose at high rates without the formation of free radicals. The hydroperoxide decomposition rate is determined by its structure.

2. It is suggested that the decomposition of peroxy compounds in the presence of alkaline additives proceeds through a stage of nucleophilic substitution at the carbonyl carbon atom.

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REACTIONS OF FORMATION AND DECOMPOSITION OF TETRACYANOCYCLOBUTANE

DERIVATIVES OF CARBAZOLE AND PHENOTHIAZINE

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and E. G. Pal'chuk	547.759.32+547.869

The reactions of cycloaddition of 9-vinylcarbazole (I) and 10-vinylphenothiazine (II) to tetracyanoethylene (III) have been adequately examined in detail in [1-3]. In these sources the no less specific details of the complex mechanism of the formation and decomposition of 9-(2,2,3,3-tetracyano-1-cyclobutyl) carbazole (VI) and 10-(2,2,3,3-tetracyano-1-cyclobutyl)phenothiazine (VII) were not completely clarified. The reactions competitive with cycloaddition, i.e., dehydrocyanation, polymerization, and hydrolysis, also remain inade-quately studied. In the present research we investigated the kinetics and the basic principles of the above mentioned processes. In agreement with [1] and [2] the synthesis and decomposition of the cycloaddition products (VI) and (VII) can proceed without the intermediate steps of formation of zwitterions (IV) and (V), the actual existence of which has not been established experimentally up to this time

The equilibrium character of this reaction in nonpolar aromatic hydrocarbons was logically based on the example of the reaction of compound (I) in [2]. The tendency of compound (VII) to break down to the starting compounds (II) and (III) by heating in a vacuum has previously been shown by us [3]: The process occurs very readily in anhydrous dimethoxyethane at room temperature. In the UV spectrum of freshly prepared solutions of (VII) in dimethoxyethane, the recorded absorption maximum at 282 nm results from electronic transfer to the chromophore system of compound (II) [4]. The presence in the reaction medium of electronaccepting (III) is established by an absorption band in the 506 nm region appearing on introduction into it of the electron-donor anisole [2].

The investigation which we made of the electronic spectra of aqueous dimethoxyethane solutions (ϵ 26) of compounds (VI) and (VII) revealed new maxima at 336 and 417 nm, corresponding to the zwitterions (IV) and (V). The correctness of this definition is shown by

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2227-2231, October, 1983. Original article submitted December 28, 1982.

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