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V. A. SHUSHUNOV, V. A. YABLOKOV

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V. A. SHUSHUNOV, V. A. YABLOKOV

ON THE MECHANISM OF THE ACID-CATALYTIC DECOMPOSITION OF ALKYL HYDROPEROXIDES

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Although the mechanism of the acid-catalytic decomposition of alkyl hydroperoxides has been studied repeatedly ($^{1-8}$), there are still no fully convincing data confirming the schemes proposed earlier. In several studies ($^{1-5}$) it is assumed that, when alkyl hydroperoxides (R_3COOH) interact with strong acids (HA), peresters are formed in which the O—O bond is so strongly polarized that in limiting cases it is transformed into an ionic one

$$R_3COOH + HA \rightarrow [R_3CO]^+A^- + H_2O. \qquad (1)$$

In earlier works ($^{1-3}$) the existence of free ions with a positive charge on the oxygen atom was admitted, whereas later (^{4,5}) only the formation of an ion pair was assumed. An ion with a positive charge on the oxygen atom, regardless of whether it is in the free state or in an ion pair, is unstable and rapidly rearranges

$$[R_3CO]^+A^- \rightarrow [R_2(RO)C]^+A^-. \qquad (2)$$

It was assumed that the newly formed compound is capable of entering into reaction with alkyl hydroperoxides (1), as well as with water (4)

$$[R_2(RO)C]^+A^- + R_3COOH \rightarrow R_2(RO)COH + [R_3CO]^+A^-, \qquad (3)$$

$$[R_2(RO)C]^+A^- + H_2H \rightarrow R_2(RO)COH + HA. \qquad (4)$$

The hemiacetal formed in this process is subsequently converted into the corresponding hydroxyl and carbonyl compounds.

Reaction (3) may be regarded as propagation, and reaction (4) as termination, of a chain proceeding by an ionic mechanism.

Figure 1. Decomposition of cumene hydroperoxide and cumyl pertrichloroacetate. $\alpha = C/C_0$, where C_0 is the initial concentration and C is the current concentration of peroxide oxygen in solution

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However, these ideas concerning the mechanism of the chain acid-catalytic decomposition of alkyl hydroperoxides have still not been convincingly confirmed. The principal and almost the only fact used to prove the validity of the above views on the mechanism of the acid-catalytic decomposition of alkyl hydroperoxides is the readily occurring rearrangement of certain peresters (9–12). We set ourselves the goal of confirming or refuting the above scheme for the mechanism of the heterolytic decomposition of alkyl hydroperoxides; for this purpose we carried out an experimental study of the acid-catalytic decomposition of cumene hydroperoxide.

We have shown that, when sodium salts of alkyl hydroperoxides react with acid chlorides of carboxylic acids, peresters are formed instantaneously, the rate of heterolytic rearrangement of which depends strongly on the nature of their acid residues. If the peresters formed are derivatives of strong acids, they undergo a very rapidly proceeding heterolytic rearrangement and therefore may serve as initiators of chain heterolytic decomposition of alkyl hydroperoxides, if it in fact takes place.

We carried out an experimental test of this proposition in studying the heterolytic decomposition of cumene hydroperoxide in the presence of several peresters.

Cumene hydroperoxide in a mixture with trichloroacetic acid chloride in benzene at 40° does not undergo chemical transformation for a long time (Fig. 1, 1). The anhydrous sodium salt of cumene hydroperoxide in ben—

in benzene at this temperature is also fairly stable. But this compound, in a mixture with trichloroacetic acid chloride under the same experimental conditions, undergoes a rapid transformation, which can readily be detected from the precipitation of sodium chloride and from the sharp decrease in the solution concentration of compounds containing peroxide oxygen (Figs. 1, 2). After completion of the reaction and subsequent hydrolysis of its products, the reaction mixture was found to contain 0.6 mole of phenol, 0.13 mole of dicumyl peroxide, and 0.1 mole of α-methylvinyl phenyl ether per mole of decomposed sodium salt of cumene hydroperoxide.

Fig. 1. Decomposition of cumene hydroperoxide and cumyl pertrichloroacetate.
$\alpha = C/C_0$, where C_0 is the initial concentration and C is the current concentration of peroxide oxygen in solution.

If the reaction of the sodium salt of cumene hydroperoxide with trichloroacetic acid chloride is carried out under the same conditions, but in the presence of cumene hydroperoxide, then, as in the preceding case, sodium chloride is rapidly precipitated and the concentration in solution of compounds containing peroxide oxygen decreases. However, the decrease in peroxide-oxygen concentration occurs only to an extent that accounts for the formation and heterolytic rearrangement of the perester, without noticeable participation in the reaction of the cumene hydroperoxide present in the solution. Curve 3 (Fig. 1) shows that, in an experiment with equimolar amounts (0.1 mole/liter) of trichloroacetic acid chloride, cumene hydroperoxide, and its sodium salt, the concentration of compounds containing peroxide oxygen decreased only by a factor of two.

Under the same experimental conditions, in the presence of trichloroacetic acid, cumene hydroperoxide decomposes comparatively rapidly with formation of acetone and phenol, the yields of which reach 90–95%.

It had previously been established (^{1}) that cumene hydroperoxide in glacial acetic acid, in the absence of additions of other acids, decomposes heterolytically with formation of acetone and phenol, whose yield reaches 80% of the theoretically calculated amount. We found that this reaction in the same solvent at 90° proceeds very slowly, and over 6 hours the hydroperoxide concentration decreases only by a factor of two. Additions of cumyl peracetate up to 50% of the initial concentration of cumene hydroperoxide (0.1 mole/liter) have no effect on the rate of decomposition of the hydroperoxide, although the perester itself under these conditions undergoes a rapidly proceeding heterolytic rearrangement. Consequently, in this case as well, the perester, which according to (^{1}) should have been an intermediate compound in the acid-catalyzed decomposition of cumene hydroperoxide in glacial acetic acid, takes no part in this reaction.

Thus, the absence of an accelerating effect of cumyl pertrichloroacetate and cumyl peracetate in the heterolytic decomposition of cumene hydroperoxide gives grounds for asserting that the acid-catalyzed decomposition of it, as well as of other alkyl hydroperoxides, proceeds without the participation of ionic chains.

Cumene hydroperoxide (0.1 mole/liter) in benzene at 40° does not react with benzenesulfonic acid chloride (0.2 mole/liter), as is evident from Fig. 2, 2. The anhydrous sodium salt of this hydroperoxide (0.1 mole/liter), under the same reaction conditions, reacts at a high rate with benzenesulfonic acid chloride (0.2 mole/liter), with loss of peroxide oxygen (Fig. 2, 2). It is characteristic that the initial concentration of peroxide oxygen in this case decreases only by a factor of two, although the initial reaction mixture contained a twofold excess of the acid chloride relative to the salt.

hydroperoxide. This is explained by the fact that the initially formed cumyl perbenzenesulfonate is very rapidly rearranged into an isomeric compound containing no peroxide oxygen, which also rapidly decomposes with the formation of α-methylvinyl phenyl ether and benzenesulfonic acid. The latter very readily

Fig. 2. Decomposition of cumene hydroperoxide and cumyl perbenzenesulfonate

Figure 2: Fig. 2. Decomposition of cumene hydroperoxide and cumyl perbenzenesulfonate

reacts with the sodium salt of cumene hydroperoxide, forming the corresponding benzenesulfonic acid salt and free hydroperoxide.

In the products of interaction of equivalent amounts (0.2 mole/l) of the sodium salt of cumene hydroperoxide and benzenesulfonyl chloride, equivalent amounts of sodium chloride and sodium benzenesulfonate were found, explaining the twofold decrease in the concentration of peroxide oxygen. In the same reaction mixture, α-methylvinyl phenyl ether was found in a yield of about 50%, and cumene hydroperoxide—about 50% of the initial amount of its sodium salt. Admixtures of small amounts of water in the initial reaction mixture did not substantially change the composition of the final products of this reaction.

Fig. 2. Decomposition of cumene hydroperoxide and cumyl perbenzenesulfonate

Extremely characteristic is the complete absence of phenol in the products of hydrolysis of the reaction mixture formed in the interaction of the sodium salt of cumene hydroperoxide with benzenesulfonyl chloride. At the same time, the decomposition of cumene hydroperoxide catalyzed by benzenesulfonic acid under the same reaction conditions is accompanied by the formation of phenol in quantitative yield.

Thus, the results of the investigation of the products of these two reactions indicate that their mechanisms differ fundamentally and that, in the acid-catalytic decomposition of alkyl hydroperoxides, the corresponding peresters are not formed as intermediates, as had been assumed in previously published works (1-5).

Curve 3 (Fig. 2) shows that the decomposition of cumene hydroperoxide (0.1 mole/l) is not accelerated by the simultaneously occurring interaction of its sodium salt (0.1 mole/l) with benzenesulfonyl chloride (0.2 mole/l). This once again confirms our conclusion that there is no chain ionic transformation of alkyl hydroperoxides during their acid-catalytic decomposition.

A study of the isotopic composition of the products of the acid-catalytic decomposition of triphenylmethyl hydroperoxide in a mixture of dioxane with water enriched in O^{18} also showed that this reaction proceeds without formation of a perester playing the role of an intermediate compound.

In a recently published work (13), the decomposition of 2,4,6-trimethylbenzyl hydroperoxide in the presence of hydrochloric or benzoic acids was studied. The results obtained therein do not contradict the results set forth in our work.

Gorky State University

named after N. I. Lobachevsky

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