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THE CHEMISTRY OF HYDROPEROXIDES I. THE ACID-CATALYZED DECOMPOSITION OF α,α-DIMETHYLBENZYL (α-CUMYL) HYDROPEROXIDE[1]

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The decomposition of α-cumyl hydroperoxide, under a variety of conditions, has yielded the following compounds:

1. Phenol
2. Acetophenone
3. α,α-Dimethylbenzyl alcohol
4. Acetone
5. 2,4-Diphenyl-4-methyl-2-pentene
6. α-Cumyl peroxide (α,α-dimethylbenzyl peroxide)
7. Methane
8. Methanol
9. Oxygen
10. Water
11. Ethane
12. Hydrogen peroxide

Obviously such a diversity of products cannot be formed by a single mechanism. The purpose of this and of succeeding papers is to demonstrate that the chemistry of hydroperoxides can best be understood if it be assumed that they may undergo disintegration of any one of the three following independent types: (a) acid-catalyzed decomposition, which proceeds by an ionic mechanism; (b) free-radical decomposition; and (c) decomposition by a reagent which causes evolution of oxygen. Which course the reaction actually follows depends on the reagents used.

Failure to recognize these different mechanisms has hitherto made it impossible to interpret much of the experimental data recorded in the literature. For example, in many instances acid decomposition was carried out at an elevated temperature, and thus a free-radical reaction was superimposed upon the ionic reaction. A general method for carrying out exclusively ionic decompositions of hydroperoxides has now been perfected, and the products formed in many such reactions have been carefully determined.[2] The hydroperoxides were decomposed by dissolving them in glacial acetic acid and adding to the solution a small amount (0.01–0.2%, depending upon the hydroperoxide used) of perchloric acid. Under these conditions, *tertiary* hydroperoxides containing at least one aromatic group decompose rapidly at room temperature. Since these decompositions are exothermic, it is necessary, in some cases, to cool the reaction mixture. In the present paper, the decomposition of α-cumyl hydroperoxide is discussed.

DECOMPOSITION OF α-CUMYL HYDROPEROXIDE

The decomposition of α-cumyl hydroperoxide by strong acids is highly exothermic, and proceeds at an appreciable rate even at $-80°$. In order to minimize

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[2] These will be reported in succeeding articles.

undesirable side-reactions, the decompositions here reported were carried out in acetic acid (in which the hydroperoxide is stable at room temperature) in the presence of 0.1 mole-per cent of perchloric acid.[3] Under these conditions, α-cumyl hydroperoxide decomposes quantitatively into phenol and acetone. The formation of these products is best accounted for by the following (perhaps oversimplified) chain-reaction mechanism.[4] In this scheme, "A" is an acid in the Lewis sense (1).

1. $C_6H_5(CH_3)_2C{-}OOH + A \rightarrow [C_6H_5(CH_3)_2CO]^+ + AOH^-$
2. $[C_6H_5(CH_3)_2CO]^+ \rightarrow [(CH_3)_2C{-}OC_6H_5]^+$
3. $C_6H_5(CH_3)_2C{-}OOH + [(CH_3)_2C{-}OC_6H_5]^+ \rightarrow [C_6H_5(CH_3)_2CO]^+ + (CH_3)_2CO + C_6H_5OH$

The validity of the idea that only (strong) acids in the Lewis sense cause decomposition of α-cumyl hydroperoxide is attested by the following facts: (a) hydrogen chloride, which is a weak acid in acetic acid, in acetic acid is a relatively ineffective agent for the decomposition;[5] (b) ferric chloride, which in alcohol is a weak acid, causes no decomposition of α-cumyl hydroperoxide in that solvent. However, ferric chloride in benzene is, in the Lewis sense, a relatively strong acid, and, in this solvent, it readily converts α-cumyl hydroperoxide into phenol and acetone. Similar results were obtained with other solvents (dioxane, benzene) and other acids (boron fluoride, aluminum chloride, sulfuric acid). This indicates the absence of a specific solvent or anion effect.

Furthermore, the decomposition of α-cumyl hydroperoxide can be substantially altered by introducing substances which compete for the acid "A." Thus, the addition to the acetic acid solution of varying amounts of α,α-dimethylbenzyl alcohol, or α-methylstyrene, followed by the addition of 70% perchloric acid to the extent of 0.1 mole per mole of the α-cumyl hydroperoxide used, causes the formation of correspondingly varying amounts of 2,4-diphenyl-4-methyl-2-pentene (α-methylstyrene dimer),[6] and correspondingly decreased amounts of phenol and acetone. When a large amount of α,α-dimethylbenzyl alcohol (2 or 3 moles per mole of hydroperoxide) is added to the α-cumyl hydroperoxide in the presence of the acid "A," the reaction which favors phenol and acetone formation (steps 1, 2, and 3) is completely suppressed; the dimer of α-methylstyrene and hydrogen peroxide are the sole products.[7] These data are interpreted upon

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[3] As is well known, perchloric acid in acetic acid forms a "superacid solution" see, *e.g.*, Hall and Conant, *J. Am. Chem. Soc.*, **49**, 3047 (1927).

[4] The intermediate formation of a positively-charged oxygen atom in the oxidation of carbinols has been suggested by many investigators. The postulate that molecules containing a positive charge on the oxygen atom may undergo a rearrangement of the carbon skeleton was first emphasized by Criegee, *Ann.*, **560**, 127 (1948).

[5] Minute traces of hydrogen chloride in otherwise pure α-cumyl hydroperoxide induce a violent decomposition.

[6] This product wherever formed was identical with the dimer of α-methylstyrene prepared by the method of Bergmann, Taubadel, and Weiss, *Ber.*, **64**, 1493 (1931).

[7] α-Cumyl peroxide in acetic acid decomposes in the presence of small amounts of perchloric acid to give the dimer of α-methylstyrene, phenol, and acetone. However, here too, the addition of α,α-dimethylbenzyl alcohol suppresses completely the formation of phenol and acetone. The dimer of α-methylstyrene and hydrogen peroxide are the only reaction products.

the assumption that α,α-dimethylbenzyl alcohol is a stronger base than α-cumyl hydroperoxide; hence the reaction indicated in step 1 cannot take place.

On the other hand, when α,α-dimethylbenzyl alcohol, dissolved in glacial acetic acid, is treated, in the presence of acid, with a 3–5-mole excess of hydrogen peroxide, a quantitative yield of phenol and acetone is obtained. Similarly, when α-methylstyrene, dissolved in glacial acetic acid, is treated with hydrogen peroxide in the presence of concentrated hydrochloric acid (or any strong acid) a nearly quantitative yield of phenol is formed. These facts are not incompatible with the scheme postulated for the decomposition of α-cumyl hydroperoxide, for it must be remembered that under the conditions cited two of the equilibrium reactions are followed by further irreversible reactions (Chart I).

CHART I

4. $C_6H_5(CH_3)_2COH + A$[a] $\rightleftharpoons C_6H_5(CH_3)_2C^+ + B + H_2O$
5. $C_6H_5(CH_3)_2C^+ + B \rightleftharpoons C_6H_5(CH_3)C{=}CH_2 + A$
6. $C_6H_5(CH_3)_2C^+ + H_2O_2 + B \rightleftharpoons C_6H_5(CH_3)_2C{-}OOH + A$
7. $C_6H_5(CH_3)_2C{-}OOH + A'$[b] $\rightarrow C_6H_5(CH_3)_2C{-}O^+ + B' + H_2O$
8. $C_6H_5(CH_3)_2C^+ + C_6H_5(CH_3)C{=}CH_2 + B \rightarrow$ Dimer[c] $+ A$

[a] A is an acid and B its conjugate base ($B + H^+ \rightleftharpoons A$). [b] In reactions 4 to 6 the acid A is a stronger acid than dimethylbenzyl alcohol, and in reaction 7 A′ is a stronger acid than the hydroperoxide. [c] Dimer of α-methylstyrene, namely, 2,4-diphenyl-4-methyl-2-pentene.

The final product depends, therefore, largely upon the experimental conditions used.[8] The observation of Hock and Lang (2) that α,α-dimethylbenzyl alcohol is formed when α-cumyl hydroperoxide is treated with dilute acids may readily be interpreted in accordance with the reaction scheme outlined above: namely, the carbinol arises by the hydrolytic attack of hydronium ion on the hydroperoxide with the simultaneous formation of hydrogen peroxide.[9]

Of considerable relevance to a general understanding of the reactions cited above is the observation that when α-methylstyrene, dissolved in acetic acid, is treated with hydrogen peroxide in the presence of catalytic quantities of perchloric acid, a different compound is obtained, namely α-phenyl-α-methylethylene glycol. The reactions of olefins with hydrogen peroxide to yield a variety of different products will be discussed in a future publication.

EXPERIMENTAL PART

Materials used. Commercial 72% α-cumyl hydroperoxide (Hercules Powder Company) was purified by the method of Hock and Lang (2). Extreme care was taken to insure com-

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[8] These considerations made it possible to select various aryl tertiary alcohols to compare a number of aryl and other groups with respect to their tendency to migrate from carbon to oxygen. The results will be reported shortly.

[9] The decomposition of the hydroperoxide with 10% sulfuric acid according to the method of Hock and Lang was repeated. The water solution contained peroxidic material which was considerably more soluble in water than ether. When the neutralized aqueous solution was treated with potassium iodide, oxygen was liberated. The presence of hydrogen peroxide is thus demonstrated.

plete removal of acid during the purification. Under these conditions the final product is stable and may be distilled at pressures between 0.01–0.3 mm. The peroxide thus obtained had an iodometric titre of 98–99% of the calculated value. The glacial acetic acid used was reagent grade (99.5%) supplied by the General Chemical Company; this material was employed without further purification. α,α-Dimethylbenzyl alcohol was prepared by the reduction of α-cumyl hydroperoxide by the method of Hock (2). The compound was purified by crystallization from cold petroleum ether; the fraction used melted at 36°. In some instances, α-methylstyrene was prepared by dehydrating the carbinol with potassium bisulfate. In other instances, redistilled commercial α-methylstyrene (supplied by the Dow Chemical Company) was used. Commercial perchloric acid (70%) and hydrogen peroxide (Merck's 30% reagent grade) were used.

Decomposition of α-cumyl hydroperoxide in the presence of acetic acid and catalytic quantities of perchloric acid. α-Cumyl hydroperoxide (15.2 g., 0.1 mole), dissolved in 100 cc. of glacial acetic acid was treated with 0.1 cc. of a 5% solution of 70% perchloric acid in acetic acid. The temperature of the reaction mixture was kept below 22°. The peroxide titre of the mixture fell to zero after 5 minutes. *Phenol* (9 g., 95% yield) was isolated in crystalline form. *Acetone* was identified and estimated by means of its dinitrophenylhydrazone. An unidentified neutral oil (amounting to less than 3% of the starting material) was also obtained.

Similar results were obtained with dioxane or benzene as solvents, and with ferric chloride, boron fluoride, aluminum chloride, or sulfuric acid as acids. In the presence of traces of hydrogen sulfide, anhydrous ferrous salts or sulfur dioxide, violent decomposition to phenol and acetone occurred only after an induction period. During this period the catalysts were oxidized to their higher valence states, in which form they are stronger acids. With ceric sulfate a similar induction period was observed; here, however, the ceric sulfate is reduced to a lower valence state, thereby liberating sulfuric acid.

Acid decomposition of α-cumyl hydroperoxide in the presence of α,α-dimethylbenzyl alcohol. α-Cumyl hydroperoxide (15.2 g., 0.1 mole), and α,α-dimethylbenzyl alcohol (30 g.) were dissolved in 100 cc. of glacial acetic acid. To this solution was added 0.1 cc. of 5% perchloric acid in acetic acid. The temperature was maintained below 25°. The following fractions were isolated: phenol, less than 5%; α-methylstyrene, 12 g.; dimer of α-methylstyrene (b.p. 65°/0.001 mm., n_D^{20} 1.5790), 27 g.

Anal. Calc'd for $C_{18}H_{20}$: Mol wt., 236; C, 91.3; H, 8.7.

Found: Mol. wt., (cryoscopic, benzene), 225; C, 90.8; H, 8.7.

When 30 g. of the carbinol was similarly treated in acetic acid with perchloric acid, in the absence of α-cumyl hydroperoxide, the dimer of α-methylstyrene (12 g.) was obtained. When α-methylstyrene was used in place of the carbinol the results were similar.

Oxidation of α,α-dimethylbenzyl alcohol to acetone and phenol. α,α-Dimethylbenzyl alcohol (5 g.) in 75 cc. of glacial acetic acid was treated with 30% hydrogen peroxide (10 cc.) and 1 cc. of 70% perchloric acid. The reaction mixture was maintained below 30°. Phenol (3.3 g., 93%) was isolated in crystalline form.

Oxidation of α-methylstyrene. α-Methylstyrene 2.36 g. (0.02 mole), dissolved in glacial acetic acid (4.0 cc., 0.06 mole) was cooled to 5°. To this solution was added 1.72 cc. (0.02 mole) of concentrated hydrochloric acid. After 15 minutes, 30% hydrogen peroxide (2.5 cc., 0.023 mole) was added. The suspension was shaken, and the temperature of the reaction mixture was maintained below 50° by cooling until a homogeneous light-purple solution resulted. The reaction mixture was treated with 100 ml. of water, and the phenol was precipitated with bromine.

The melting point of this material was 93–95°. The yield of tribromophenol thus obtained was 90%, calculated upon the amount of α-methylstyrene used in the reaction.

SUMMARY

1. The variety of products obtained by the decompositions of α-cumyl hydroperoxide is due to the superimposition of different modes of decomposition.

2. It is shown that one mode of decomposition is that catalyzed by traces of strong acids (in the Lewis sense). With α-cumyl hydroperoxide the decomposition products are exclusively phenol and acetone.

3. In the presence of excess α-methylstyrene or α,α-dimethylbenzyl alcohol the acidic decomposition results in the exclusive formation of 2,4-diphenyl-4-methyl-2-pentene (α-methylstyrene dimer).

4. In the presence of a large excess of hydrogen peroxide 2,2-dimethylbenzyl alcohol gave exclusively phenol and acetone.

5. In the presence of equivalent amounts of concentrated hydrochloric acid, α-methylstyrene when treated with an equivalent amount of hydrogen peroxide gave 90 per cent phenol.

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REFERENCES

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