[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

THE CHEMISTRY OF HYDROPEROXIDES. VII. THE IONIC AND FREE RADICAL DECOMPOSITION OF α-PHENYLETHYL HYDROPEROXIDE

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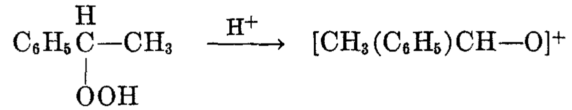
Preparation of α-phenylethyl hydroperoxide. α-Phenylethyl hydroperoxide has been prepared by Hock and Lang (1) by illuminating and agitating ethylbenzene in an atmosphere of oxygen at 75°. The yield of the hydroperoxide is poor—about one per cent at the end of 60 hours. No mention is made of the effect of light on the rate of oxygen uptake, although the authors illuminated the ethylbenzene throughout the period of oxidation. A somewhat better yield (10%) was obtained by us by slowly adding hydrogen peroxide (30%) to cooled α-phenylethanol containing a few drops of concentrated sulfuric acid.

Decomposition of α-phenylethyl hydroperoxide by strong acids. The acid decompositions of secondary hydroperoxides, *e.g.*, 3-cyclohexenyl (2), 2-*p*-menthenyl (3), α-tetralyl (4), and benzhydroxyl (4) with aqueous acid (in a two-phase system) at elevated temperatures have been investigated. Because our experience has indicated that such conditions favor secondary reactions, the homogeneous liquid-phase decomposition of α-phenylethyl hydroperoxide was investigated at 20–25°. The best results were obtained by allowing a mixture of the hydroperoxide, acetic acid, and a trace of perchloric acid to stand at room temperature until the presence of hydroperoxide could no longer be detected iodometrically. The reaction products isolated were phenol (45%) and α-phenylethyl peracetate (probably admixed with some other peroxidic material, which by inference may be α-phenylethyl peroxide). The remarkable feature of this decomposition is the non-formation of acetophenone. These results indicate that in acid-catalyzed decomposition of hydroperoxides containing an aromatic group and a hydrogen atom on the same carbon atom, the aromatic group, and not the hydrogen atom, migrates.

1.


$$C_6H_5\overset{H}{\underset{OOH}{C}}-CH_3 \xrightarrow{H^+} [CH_3(C_6H_5)CH-O]^+$$

2. $[CH_3(C_6H_5)CH-O]^+ \rightarrow [C_6H_5O(CH_3)CH]^+$

3. $[C_6H_5O(CH_3)CH]^+ + C_6H_5CH(CH_3)OOH \rightarrow$
$C_6H_5OH + CH_3CHO + [CH_3(C_6H_5)CH-O]^+$

The ketones formed when secondary hydroperoxides are heated with dilute acids do not arise from the acid-catalyzed decomposition but from the thermal decomposition of the secondary hydroperoxide or some derivative of the latter. Thus, if the decomposition of the α-phenylethyl hydroperoxide is carried out in acetic acid (in the presence of a very small amount of perchloric acid) at elevated temperatures one obtains, in addition to phenol, some acetophenone. The latter product is probably formed as follows:

4. $CH_3(C_6H_5)CHOOH + CH_3CO_2H \xrightarrow{H^+} CH_3(C_6H_5)CHOOC(=O)CH_3$

5. $CH_3(C_6H_5)CHOOC(=O)CH_3 \xrightarrow{\Delta} CH_3COC_6H_5 + CH_3CO_2H$[1]

Free-radical decomposition of α-phenylethyl hydroperoxide. When α-phenylethyl hydroperoxide, suspended in water, is treated with a solution of a ferrous salt (10 mole-%), about 93% of the hydroperoxide is decomposed. The acetophenone formed corresponds to 88% of the hydroperoxide originally present, and the α-phenylethanol to 5%. Since only 10 mole-% of ferrous salt is used in the decomposition of 93% of α-phenylethyl hydroperoxide the process involved must be a chain reaction. Provisionally, the reaction scheme may be formulated as follows:

6. $CH_3(C_6H_5)CHOOH + Fe^{++} \rightarrow CH_3(C_6H_5)CHO\cdot + Fe^{++}OH$

7. $CH_3(C_6H_5)CHO\cdot + CH_3(C_6H_5)CHOOH \rightarrow CH_3COC_6H_5 + H_2O + CH_3(C_6H_5)CHO\cdot$

8. $CH_3(C_6H_5)CHO\cdot + Fe^{++} \xrightarrow{HOH} CH_3(C_6H_5)CHOH + Fe^{+++} + OH^-$

9. $2\ CH_3(C_6H_5)CHO\cdot \rightarrow CH_3COC_6H_5 + CH_3(C_6H_5)CHOH$

Reactions 8 and 9 are chain-terminating steps and account for the relatively short chain (*ca.* 20) for reaction 7. It should be mentioned that the chain decomposition of α-phenylethyl hydroperoxide by ferrous salts into acetophenone and water is similar to the chain decomposition by ferrous salts of α-cumyl hydroperoxide into acetophenone and methanol (5).

EXPERIMENTAL

Preparation of α-phenylethyl hydroperoxide. α-Phenylethyl hydroperoxide was prepared by the method described by Hock and Lang (1), except that the temperature was maintained at 80–90°, and the mixture was internally illuminated with visible light by means of a mercury vapor-neon fluorescent coil for 48 hours. The yield of the α-phenylethyl hydroperoxide was, however, still poor (5%). It was also prepared by slow addition of a solution of 30% hydrogen peroxide to cold α-phenylethanol (containing a few drops of concentrated sulfuric acid). The crude hydroperoxide was purified by converting it first te the sodium salt. The hydroperoxide, purified by this procedure, distilled at 52°/0.03 mm.; n_D^{20} 1.5266. An iodometric titration gave 99.6% of the calculated value.

Anal. Calc'd for $C_8H_{10}O_2$: C, 69.8; H, 7.1.
Found: C, 69.6; H, 7.2.

Decomposition of α-phenylethyl hydroperoxide by perchloric acid in acetic acid solution. To a solution of α-phenylethyl hydroperoxide (4 g.) in glacial acetic acid (20 ml.), perchloric acid (0.04 ml. of a 70% solution) was added. The mixture was allowed to stand at room temperature (20–25°) for 16 hours, was then diluted with 80 ml. of water, and the

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[1] The mechanism of the thermal decomposition of the peracetate is not indicated here. It will be discussed in a subsequent publication.

whole was extracted with ether. The presence of acetaldehyde was demonstrated in the water layer. The ether layer was washed with bicarbonate solution and then with aqueous sodium hydroxide (5%). The alkaline solution was acidified and treated with bromine water. The tribromophenol which separated was dried. The amount of phenol, calculated from the tribromophenol formed, corresponded to about 45% of the α-phenylethyl hydroperoxide used.

The ether extract was dried and the ether was removed. The residue gave no test for acetophenone (dinitrophenylhydrazine) or α-phenylethyl hydroperoxide (acidified potassium iodide in isopropanol). That it was a mixture of peroxidic material was clearly indicated by the elementary analyses for carbon and hydrogen, and titrations with (a) concentrated hydrogen iodide in acetic acid in the hot, and (b) potassium iodide in acetic acid in the cold.

The mixture could not be separated into its components by the usual means. However, the presence of the α-phenylethyl peracetate was demonstrated in two ways. (*a*) Some of the material was heated *in vacuo* at 120–140°. From the decomposition products about 60% by weight of acetophenone was obtained. (*b*) Some of the mixture was dissolved in absolute ether and treated with sodium metal and allowed to stand for two days. At the end of that time the mixture was analyzed. It was shown to contain α-phenylethyl alcohol (24% by weight) and acetic acid (*ca.* 20% by weight). The α-phenylethyl alcohol was determined by oxidation of the alcohol to acetophenone. The acetic acid was estimated from the color intensity of the solution with lanthanous hydroxide in the presence of iodine. It should be mentioned that while α-cumyl peroxide is quantitatively reduced by sodium to α-cumyl alcohol, the reduction of α-phenylethyl α-cumyl peroxide is not quantitative (6).

Decomposition of α-phenylethyl hydroperoxide by ferrous salts. Ferrous ammonium sulfate solution (1 *N*) was added dropwise to a well-agitated suspension of α-phenylethyl hydroperoxide (1 g.) in 10 ml. of water. The reaction was interrupted when 10 mole-% of the ferrous salt had been added. A titration showed that 93% of the hydroperoxide had decomposed. From the reaction mixture acetophenone was obtained (as the 2,4-dinitrophenylhydrazone) in 88% yield on the basis of the hydroperoxide originally present. The other decomposition product was α-phenylethyl alcohol (5%).

SUMMARY

1. The decomposition of α-phenylethyl hydroperoxide in strong acid (at room temperature or lower) gives phenol and a mixture of peroxidic materials, indicating migration of a phenyl group from carbon to oxygen. No acetophenone is formed under these conditions.

2. Ferrous ion decomposes α-phenylethyl hydroperoxide by a chain mechanism. The major reaction product is acetophenone.

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