[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Studies in Organic Peroxides. XXVI. Organic Peroxides Derived from Acetone and Hydrogen Peroxide

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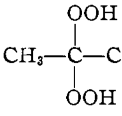
The reaction of hydrogen peroxide with acetone was studied in the presence and absence of hydrogen ion. In both cases the initial stable peroxide formed was the hitherto unknown 2,2-dihydroperoxypropane (I). Without hydrogen ion this peroxide is the main product which slowly undergoes a free radical change to 2,2'-dihydroperoxydipropyl peroxide (III) and other higher peroxides. In the presence of hydrogen ion and excess of acetone peroxide I is converted *via* peroxide III into a cyclic trimer in high yields.

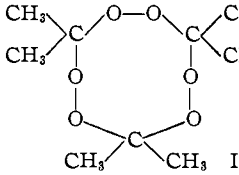
Organic peroxides derived from acetone have been extensively studied by several investigators.[2-5] In view of our recent extensive investigations on organic peroxides derived from simple ketones,[6] we have decided to reinvestigate the peroxides derived from acetone and hydrogen peroxide with the hope of isolating the hitherto unknown 2,2-dihydroperoxypropane (I) and study its decomposition by means of paper chromatography.[7]

When acetone was allowed to react at 0 to −5° with 50% hydrogen peroxide in the presence of hydrogen ion, a mixture of peroxides was obtained which showed four different peroxides on a paper chromatogram. Three of these have low *R*f's: 0.052, 0.110 and 0.168, and one a high *R*f, 0.918. The one with the high *R*f was identified as the cyclic trimer II and is the predominant (90%) peroxidic product of the mixture. The peroxide with the lowest *R*f was identified as 2,2'-dihydroperoxy-2,2'-diisopropyl peroxide (III). No peroxide corresponding to formula I was found present in the pentane extract which had been washed with ammonium sulfate solution and with water. However, when the combined washings were extracted with ethyl ether, dried and the ether removed, a peroxide was isolated which gave a single spot on the paper chromatogram with an *R*f of 0.01, and was shown to be different from peroxide III as well as from hydrogen peroxide. By analysis and by the preparation of derivatives this peroxide was shown to be the hitherto unknown peroxide I.

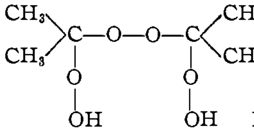


$$CH_3-\overset{OOH}{\underset{OOH}{C}}-CH_3$$

I

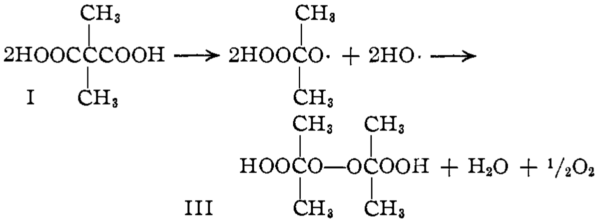


II



III

Moreover, peroxide I was the only peroxide formed in about 12% when hydrogen peroxide (50%) was allowed to react with acetone at 0° in a mole ratio of 1:1 in the absence of hydrogen ion. When the same mixture was allowed to stand at room temperature for twenty-four hours peroxide I was formed in excess of 95% together with traces of peroxide III. When paper chromatograms were taken daily for several days, the amount of peroxide III increased and, after seven days, traces of two new peroxides appeared on the chromatograms, the *R*f's of which were near to that of peroxide III. Identical results were obtained when pure peroxide I was allowed to decompose slowly for 500 hours at 30–32° in a closed system similar to that used for the study of the decomposition of the corresponding peroxides from diethyl and methyl ethyl ketones. In addition to the small evolution of oxygen, the paper chromatograms of the residue showed the same pattern as those taken during the decomposition of similar peroxides. No cyclic trimer was found. The results seem to indicate that 2,2-dihydroperoxypropane is the parent stable peroxide of the acetone series and undergoes spontaneous decomposition in accordance with the following equation.



$$\underset{\text{I}}{2HOOC\overset{CH_3}{\underset{CH_3}{C}}COOH} \longrightarrow 2HOO\overset{CH_3}{\underset{CH_3}{C}}O\cdot + 2HO\cdot \longrightarrow \underset{\text{III}}{HOO\overset{CH_3}{\underset{CH_3}{C}}O-O\overset{CH_3}{\underset{CH_3}{C}}OOH} + H_2O + {}^1/_2O_2$$

Moreover, it is significant that this peroxide undergoes these changes even in aqueous solution, and it is therefore possible that such changes may also occur in biological systems in which hydrogen peroxide and ketones or aldehydes are present at the same time.

Experimental

These peroxides are dangerously explosive and should be handled with extreme care.

2,2-Dihydroperoxypropane (I).—To 11.3 cc. (0.2 mole) of 50% hydrogen peroxide cooled to 0° was added dropwise in the course of one hour with stirring 14.7 cc. (0.2 mole) of acetone. Stirring was continued at 0° for three additional hr. then 50 cc. of ether was added and the mixture was shaken with 2 × 50 cc. of saturated solution of ammonium sulfate followed by 2 × 10 cc. of water. The final mixture was dried over magnesium sulfate, filtered and the ether removed in vacuum. The viscous residue (2.4 g.) failed to crystallize but it gave a single spot on a paper chromatogram with an R_f of 0.01 and was different when com-

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[2] K. Wolffenstein, *Ber.*, **28**, 2265 (1895).

[3] A. Baeyer and V. Villiger, *ibid.*, **32**, 3628, 3692 (1899); **33**, 124, 858 (1900).

[4] A. Rieche, "Alkyl Peroxyde und Ozonide," Steinkopff, Dresden, 1931.

[5] (a) R. Criegee, W. Schnorrenberg and J. Becke, *Ann.*, **565**, 7 (1949); (b) R. Criegee and K. Metz, *Chem. Ber.*, **89**, 1714 (1956)

[6] (a) N. A. Milas and A. Golubović, THIS JOURNAL, **81**, 3361 (1959); (b) paper XXV, **81**, 5824 (1959).

[7] N. A. Milas and I. Belič, *ibid.*, paper XXIII, **81**, 3358 (1959).

pared against hydrogen peroxide. The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$; the intensity of each band is given in parenthesis: 3400 (8), 2990 (4), 2980 (3.5), 2800 (2.5), 1610 (2.5), 1460 (4.5), 1365 (8.5), 1340 (5.5), 1255 (5.5), 1195 (5.5), 1160 (8.5), 1035 (2.5), 940 (3), 875 (4), 830 (7.5).

Anal. Calcd. for $C_3H_8O_4$: (O), 29.60; mol. wt., 108.1. Found: (O), 29.10 (KI + CH_3COOH method); mol. wt., 115 (in exaltone).

Using the procedure of Brewster and Cotte[8] the bis-*p*-nitrobenzoate was prepared, m.p. 129–130° dec., from methyl alcohol.

Anal. Calcd. for $C_{17}H_{14}O_{10}N_2$: C, 50.25; H, 3.47; N, 6.89. Found: C, 50.33; H, 3.46; N, 6.68.

When the reaction between acetone and hydrogen peroxide was carried out at room temperature for 24 hr., the product contained over 95% of peroxide I and traces of peroxide III. Paper chromatograms taken daily of this reaction mixture showed a consistent increase of peroxide III in the mixture. After seven days the chromatogram began to show, in addition to peroxides I and III, traces of two new peroxides the R_f's of which were 0.110 and 0.168, respectively. Since the amounts of these peroxides were too small and their R_f's too close to the R_f of peroxide III, it was difficult to separate and identify them.

Decomposition of Peroxide I at 30–32°.—In a tube attached to a closed system similar to that used for the decomposition of 3,3-dihydroperoxypentane was placed 0.1264 g. of pure 2,2-dihydroperoxypropane (I) and the tube covered with aluminum foil and kept in an oil-bath at 30–32° for 500 hr. A small amount of gas which proved to be oxygen was evolved, but the loss of weight of the sample was negligible. A paper chromatogram of the residue showed four spots: one, the most intense, was attributed to the original peroxide I; another of lower intensity with an R_f of 0.052 due to peroxide III; and two others of slightly higher R'_fs present in traces. These results show that the main decomposition product is peroxide III.

2,2'-Dihydroperoxy-2,2'-diisopropylperoxide (III).—When the hydrogen peroxide–acetone mixture described above was allowed to stand at room temperature for ten days, it had produced about 20% of peroxide III estimated by means of paper chromatography. An equal volume of water was then added to the mixture and the solution extracted with pentane, dried and the pentane concentrated in vacuum to one fourth of its original volume. This was cooled in Dry Ice and the crystals separated and recrystallized several times at low temperatures from pentane; m.p. 35°, lit.[5b] 34–35°. A paper chromatogram showed a single spot with an R_f of 0.052. The infrared spectrum was identical with that reported by Criegee and Metz.[5b]

1,1,4,4,7,7-Hexamethyl-1,4,7-cyclononatriperoxane (II).—To 11.3 cc. (0.2 mole) of 50% hydrogen peroxide cooled to 0° was added with stirring 2.6 cc. (0.05 mole) of concd. sulfuric acid. To this solution was added dropwise at 0° with stirring 14.7 cc. (0.2 mole) of acetone in the course of one hr. Stirring was continued at 0° for three additional hr., then the mixture was extracted with 200 cc. of pentane, the extract washed 2 × 50 cc. of saturated ammonium sulfate solution followed by 3 × 50 cc. of water and dried over magnesium sulfate. The solution was filtered and analyzed by means of paper chromatography. When the chromatogram was sprayed with the hydrogen iodide–acetic acid reagent four spots appeared with R_f's at 0.052, 0.110, 0.168 and 0.918 with the last spot being very intense representing more than 90% of the total mixture. All of peroxide I went into the aqueous layer since it is insoluble in pentane; it was extracted from the aqueous layer with ether and when tested on paper it gave a single spot with an R_f of 0.01 and was identical with peroxide I.

The pentane layer was cooled to −10° and the colorless crystals which separated were recrystallized several times at −10° from pentane; m.p. 96°, lit.[5b] 98°. A paper chromatogram showed a single spot with an R_f of 0.918 when sprayed with the hydrogen iodide–acetic reagent. It does not react with potassium iodide–acetic acid mixture. This peroxide is unusually volatile and sublimes readily at room temperature. In fact, it is difficult to detect it on a paper chromatogram unless the spraying is done immediately after development. The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$: 2990 (3), 2900 (3), 1460 (3.5), 1370 (6.5), 1360 (7.5), 1270 (3.5), 1225 (4), 1175 (9), 1000 (2), 940 (6), 885 (6.5), 840 (3).

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[8] J. H. Brewster and C. J. Cotte, Jr., THIS JOURNAL, **77**, 6214 (1955).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

The Stereochemistry of the Hydrogenolysis of 1,2-Diphenyl-1,2-propanediol

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Optically active 1,2-diphenyl-1,2-propanediol (methylhydrobenzoin) has been hydrogenolyzed over copper chromium oxide at 200° to yield optically active 1,2-diphenylpropane. This reaction takes place with about 20% retention of configuration, which is less than in previously studied hydrogenolyses.

The reductive cleavage of a benzyl group linked to an oxygen, nitrogen or sulfur atom is a rather general reaction that can be effected by hydrogen in the presence of catalysts or by several chemical reducing agents. Previous work on atrolactic acid[2] and 2-phenyl-2-butanol[3] using a Raney nickel catalyst showed that replacement of the hydroxyl group by hydrogen proceeded predominately with retention of configuration.

The observation that *meso*-3,4-di-(*p*-hydroxyphenyl)-3,4-hexanediol reacted with hydrogen in the presence of copper–chromium oxide catalyst at 200° to yield *meso*-3,4-di-(*p*-hydroxyphenyl)-hexane (hexesterol)[4] suggested that a stereospecific process might be involved. Either retention or inversion of configuration at both centers could explain this result. Although retention would be expected by analogy with the previous results,[2,3] the differences in the structure of the molecule undergoing hydrogenolysis and the reaction condi-

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[1] Abstracted from a thesis presented to the Graduate School by B. R. Juliano for the Ph.D. degree, February, 1956.

[2] W. A. Bonner, J. A. Zderic and G. A. Casaletto, THIS JOURNAL, **74**, 5086 (1952).

[3] D. J. Cram and N. L. Allinger, *ibid.*, **76**, 4516 (1954).

[4] The details of this reaction and related hydrogenolyses will be reported in a future communication.