Organic Peroxides. Part V. Isotopic Tracer Studies on the Formation and Decomposition of Organic Peroxides.*

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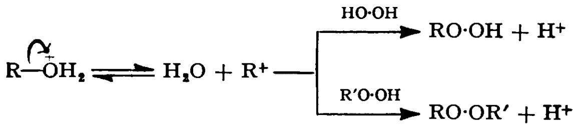
The formation of organic peroxides by the reaction of secondary and tertiary alcohols with hydrogen peroxide and with *tert.*-butyl hydroperoxide has been examined with the alcohols labelled with ^{18}O. Fission of the alkyl–oxygen bond of the alcohol is observed in all the reactions studied (cf. Davies *et al.*, Parts I and III *).

No ^{18}O exchange could be detected between $H_2{}^{18}O$ and hydrogen peroxide or 1-phenylethyl hydroperoxide under acid conditions, indicating again that an O–O bond was not formed by co-ordination of nucleophilic and electrophilic oxygen atoms. It is concluded that a synartetic mechanism may be involved in the O–O heterolysis of some organic peroxides.

In earlier papers * it was suggested that acid-catalysed reactions between secondary and tertiary alcohols, and hydrogen peroxide or alkyl hydroperoxides, are of S_N1 type, *i.e.*:



$$R{-}\overset{+}{O}H_2 \rightleftharpoons H_2O + R^+ \begin{cases} \xrightarrow{HO\cdot OH} RO\cdot OH + H^+ \\ \xrightarrow{R'O\cdot OH} RO\cdot OR' + H^+ \end{cases}$$

This conclusion was based on the following observations: (i) The reactivity of the alcohols (and their esters) could be correlated with their known or predicted readiness to undergo unimolecular alkyl–oxygen heterolysis. (ii) Optically active 1 : 2 : 3 : 4-tetrahydro-1-naphthol and 1-phenylethanol yielded the corresponding hydroperoxides with, respectively, racemisation, and racemisation accompanied by inversion, which is compatible with the formation of intermediate carbonium ions. (iii) Olefins could be caused to react with hydrogen peroxide and with *tert.*-butyl hydroperoxide in the presence of acid; in these reactions the intermediate carbonium ions are formed by protonation of the olefin (Davies and White, *Nature*, 1952, **170**, 668; Davies, Foster, and White, Parts I and III; Davies, Feld, and White, *Chem. and Ind.*, 1954, 1322).

This mechanism requires that both oxygen atoms in the peroxidic products should be derived from the hydrogen peroxide or alkyl hydroperoxide, and that the eliminated water should derive its oxygen from the alcohol. This has now been confirmed by the use of alcohols enriched in the ^{18}O isotope.

The ^{18}O was introduced into *tert.*-butanol, 1-phenylethanol, diphenylmethanol, 2-phenylpropan-2-ol, and triphenylmethanol, either by hydrolysis of the corresponding halide, or by acid-catalysed hydroxyl-exchange of the alcohol, with enriched water. These alcohols were then treated with acidified concentrated hydrogen peroxide, and the corresponding hydroperoxides were isolated by modifications of methods which we have described (Parts I and III); from the reaction of *tert.*-butanol with an equivalent amount of hydrogen peroxide, the water which was formed was also isolated. Similarly the reaction between triphenylmethanol and *tert.*-butyl hydroperoxide was carried out by the established method. The reactants and products were pyrolysed *in vacuo* and the abundance of the ^{18}O isotope was determined mass-spectrometrically.

Experimental

Materials.—Water enriched in ^{18}O was obtained by fractional distillation (Dostrovsky, Llewellyn, and Vromen, *J.*, 1952, 3509) and was chemically purified by distillation from alkaline permanganate.

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* Parts I, II, III, IV, *J.*, 1953, 1541, 1808; 1954, 2200, 2204.

Hydrogen peroxide (99·5% and 87%) was supplied by Laporte Chemicals Limited, Luton.

2-Phenylpropan-2-ol (b. p. 93—94°/14 mm.) was prepared by the Grignard reaction between phenylmagnesium bromide and acetone.

Pyrolysis of Organic Compounds.—In preliminary experiments the decomposition of *tert.*-butanol and *tert.*-butyl hydroperoxide was carried out in sealed tubes at *ca.* 450° and 200° respectively. The water obtained from the alcohol was purified by static distillation and equilibrated with carbon dioxide; the carbon monoxide and dioxide obtained from the peroxide were analysed directly in the mass spectrometer.

It is possible that pyrolysis in a sealed tube at *ca.* 200° does not give accurate sampling of both the oxygen atoms of peroxides (*e.g.*, by formation of phenol as a primary decomposition product). This objection is eliminated in the following more general method which was applied to all the compounds which were studied. The organic compound was completely pyrolysed *in vacuo* to carbon monoxide, either on hot Monel gauze coated with carbon, or in a carbon tube heated by an induction furnace. The mass-spectrometric analysis was carried out directly on the carbon monoxide. The possible presence of atmospheric nitrogen (giving mass 28) was excluded by examining the samples for argon (mass 40).

Mass Spectrometric Analyses.—Mass-spectrometric analyses were carried out in a 180° mass spectrometer of conventional design. If R is the ratio $^{12}C^{16}O^{16}O : {}^{12}C^{16}O^{18}O$ for carbon dioxide and $^{12}C^{16}O : {}^{12}C^{18}O$ for carbon monoxide, the atoms % of ^{18}O (α') is given by: CO, $\alpha' = 100/(R + 1)$; CO_2, $\alpha' = 100/(2R + 1)$; H_2O, $\alpha' = 100/(2{\cdot}076R + 1)$ (Cohn and Urey, *J. Amer. Chem. Soc.*, 1938, **60**, 679; Dostrovsky and Klein, *Analyt. Chem.*, 1952, **24**, 414). The contributions of $^{13}C^{17}O$ and of $^{13}C^{16}O^{17}O$ to masses 30 and 46, respectively, were ignored. The atoms % excess (α) quoted in this paper are the excess abundances above those of the normal compounds.

The Reaction of ^{18}*O-Labelled Alcohols with Hydrogen Peroxide.*—(i) tert.-*Butyl alcohol. tert.*-Butyl chloride (20 c.c., 16·9 g.) was heated under reflux for 6 hr. with water (40 c.c.), α = *ca.* 0·5. Distillation yielded an azeotrope of the chloride, alcohol, and water. The aqueous layer was saturated with sodium chloride, and the upper layer separated, dried (K_2CO_3), and distilled, yielding *tert.*-butanol, b. p. 80—81°, which solidified on cooling.

A mixture of the above alcohol (3 c.c.), 87% hydrogen peroxide (3 c.c.), and sulphuric acid (0·03 c.c.) after 30 hr. at room temperature was extracted with light petroleum (3 c.c.), and the extract washed and dried (Na_2SO_4). Distillation yielded *tert.*-butyl hydroperoxide (1·39 g.), b. p. 37°/19 mm., which was redistilled, a middle fraction of 1·12 g. being collected at 32°/15 mm.

Both the water and *tert.*-butyl hydroperoxide were isolated from the reaction, in the following manner. After 15 days a mixture of 87% hydrogen peroxide (0·73 g.), concentrated sulphuric acid (0·010 g.), and *tert.*-butanol (1·3 g., 1 mol.), was still homogeneous but smelled strongly of *tert.*-butyl hydroperoxide. On the addition of light petroleum (5 c.c.) a lower layer of water was formed, which was separated and washed three times with light petroleum. The combined petroleum extracts were distilled, yielding *tert.*-butyl hydroperoxide (0·53 g.), b. p. 40—41°/13 mm.

(ii) 1-*Phenylethanol.*—A mixture of 1-phenylethyl chloride (10 c.c., b. p. 88°/25 mm.) was shaken with ^{18}O-enriched water (100 c.c.) at 50° for 12 hr. The organic layer was separated, washed with aqueous sodium carbonate, and dried (Na_2SO_4). Distillation yielded 1-phenylethanol (4 c.c.), b. p. 102—104°/18 mm., n_D^{25} 1·5246.

A mixture of this alcohol (3 c.c.), hydrogen peroxide (8 c.c.), and concentrated sulphuric acid (0·05 c.c.) was shaken for 2 hr. at 0° and 4 hr. at room temperature. Water (20 c.c.) was added and the product extracted with ether, washed with aqueous sodium hydrogen carbonate and with water, and dried (Na_2SO_4). Distillation yielded 1-phenylethyl hydroperoxide, b. p. 46°/0·2 mm., n_D^{25} 1·5230.

(iii) *Diphenylmethanol.* A 6% solution of diphenylmethanol in dioxan–$H_2{}^{18}O$ (70 : 30 v/v) which was 0·06N with respect to hydrogen chloride, was kept at 100° for 2 hr. The solvent was removed in a high vacuum, giving diphenylmethanol, m. p. 67—68° after recrystallisation from light petroleum. We are indebted to Mr. R. H. Flowers for carrying out this reaction.

The alcohol (1·0 g.), in the minimum of ether, was stirred with 87% hydrogen peroxide (10 c.c.) and concentrated sulphuric acid (0·02 c.c.) at 0° for 5 hr. By the usual procedure, diphenylmethyl hydroperoxide was isolated (from light petroleum; 0·43 g.), m. p. and mixed m. p. 50—52·5°, liquid when ground with benzophenone.

(iv) 2-*Phenylpropan*-2-*ol.* 2-Phenylpropan-2-ol (10 c.c.; b. p. 94—95°/13 mm.) was shaken with ^{18}O-enriched water (9·5 c.c.; α = *ca.* 2·8%) and sulphuric acid (0·5 c.c.) for 48 hr. at room temperature. The alcohol was recovered (b. p. 93—94°/13 mm.).

The alcohol (2·7 c.c.) was shaken with 87% hydrogen peroxide (8 c.c.) containing sulphuric acid (0·05 c.c.) at 0° for 2 hr. and at room temperature for 4 hr. Isolation of the product in the usual manner yielded 1-methyl-1-phenylethyl hydroperoxide; on distillation at 70°/0·4 mm. some decomposition occurred, the odour of phenol being present in the product which had a high refractive index, n_D^{20} 1·5319 (literature, n_D^{20} 1·5242). This partial decomposition, however, should not invalidate the result of the mass-spectrometric measurement.

(v) *Triphenylmethanol.* A sample of triphenylmethanol (m. p. 160—161°) enriched in ^{18}O was kindly provided by Dr. J. R. Quayle.

The finely powdered alcohol (2·0 g.) was added to 83% hydrogen peroxide (5 c.c.) containing concentrated sulphuric acid (0·05 c.c.). Sufficient ether was added from time to time to dissolve the triphenylmethanol. After 9 hours' stirring, and 18 hours' storage, the ether was allowed to evaporate, yielding a solid (2·0 g.; m. p. 79—80°) which was filtered off. Recrystallisation from ether–light petroleum gave triphenylmethyl hydroperoxide (0·99 g.), m. p. 83—86° (Found: C, 82·7; H, 6·2. Calc. for $C_{19}H_{16}O_2$: C, 82·6; H, 5·8%).

The Reaction of ^{18}*O-labelled Triphenylmethanol with* tert.*-Butyl Hydroperoxide.*—*tert.*-Butyl hydroperoxide (0·5 g.) was added to a solution of the above triphenylmethanol (1·3 g.) in glacial acetic acid (29 c.c.); on the addition of sulphuric acid (0·06 c.c.) a yellow colour developed. After 4 hr. the pale yellow solution was poured on ice, and the precipitated solid was twice recrystallised from methanol, yielding *tert.*-butyl triphenylmethyl peroxide (0·91 g.), m. p. 72·5—73°.

Mass-spectrometric analyses of alcohols and peroxides.

Alcohol	α	Peroxide	α
$Me_3C{\cdot}OH$	0·501, 0·510	$Me_3C{\cdot}O{\cdot}OH$ [b]	0·007, 0·005,[a] 0·010[a]
$Ph{\cdot}CHMe{\cdot}OH$	0·765	$Ph{\cdot}CHMe{\cdot}O{\cdot}OH$	0·007
$Ph_2CH{\cdot}OH$	0·354	$Ph_2CH{\cdot}O{\cdot}OH$	0·001
$Ph{\cdot}CMe_2{\cdot}OH$	1·87	$Ph{\cdot}CMe_2{\cdot}O{\cdot}OH$	0·019
$Ph_3C{\cdot}OH$	0·407	$Ph_3C{\cdot}O{\cdot}OH$	0·000
,, ...	,,	$Ph_3C{\cdot}O{\cdot}O{\cdot}CMe_3$	0·002, 0·002[a]

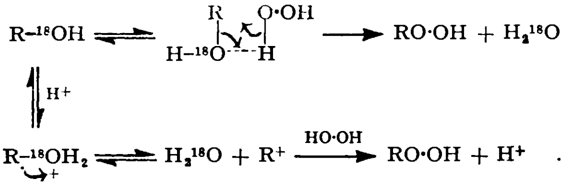
By pyrolysis in a sealed tube. [b] The water which was isolated from the reaction between equivalents of *tert.*-butanol and 87% hydrogen peroxide had $\alpha = 0{\cdot}389$. If allowance is made for dilution by the 13% of normal water initially present in the hydrogen peroxide, the water liberated by the alcohol should have $\alpha = 0{\cdot}392$.

The Absence of Oxygen Exchange between Hydrogen Peroxide and Water.—99·5% Hydrogen peroxide (18·015 g.) was mixed with water (2·620 g.) enriched in ^{18}O (α 9·1), giving 87·4% aqueous hydrogen peroxide. Part of this mixture (0·620 g.) was acidified with 0·02 g. of sulphuric acid. After 14 hr. at room temperature, half the reaction mixture (sample *a*) was separated and stored at −80°; the second half was similarly treated after 7 days (sample *b*). Two drops of each sample were then decomposed with an excess of acidified potassium permanganate in a Y-tube, and the oxygen which was evolved was analysed mass-spectrometrically and compared with that from an 87% solution of hydrogen peroxide in normal water: (*a*) $\alpha = 0{\cdot}001$; (*b*) $\alpha = 0{\cdot}001$. It has been shown (Bunton and Llewellyn, *Research*, 1952, **5**, 142; Cahill and Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 2312; Dole, Rudd, Muchow, and Comte, *J. Chem. Phys.*, 1952, **20**, 961) that the oxygen evolved in this reaction is derived wholly from the hydrogen peroxide.

The Absence of Oxygen Exchange between 1*-Phenylethyl Hydroperoxide and Water.*—A mixture of 1-phenylethyl hydroperoxide (1·0 c.c.), ^{18}O-enriched water (9·0 c.c.) (α 2·8), and sulphuric acid (1·0 c.c.) was shaken for 3 hr. After 3 days, the discoloured upper layer was extracted with ether, washed with aqueous sodium hydrogen carbonate and with water, and dried (Na_2SO_4). The ether was removed at the pump and the majority of the phenol by sublimation on to a cold finger. By the usual procedure (Part III) the 1-phenylethyl hydroperoxide was isolated from residual phenol by the formation of 1-phenylethyl triphenylmethyl peroxide, m. p. 84°, α 0·006. The results recorded earlier in this paper, and work on the triphenylmethylation of optically active 1-phenylethyl hydroperoxide (Davies, Feld, and White, *loc. cit.*), demonstrate that the peroxide bond remains intact during the alkylation.

DISCUSSION

The results recorded in the Table demonstrate unequivocally that the oxidation of the alcohols proceeds by alkyl–oxygen fission, and to that limit confirm our conclusion that alkyl–oxygen heterolysis occurs, principally by a unimolecular mechanism. Recent results which we have obtained on the reactions of optically active alcohols (Davies and Feld, unpublished work) indicate that the S_N1 mechanism may sometimes be accompanied by an S_Ni component, *i.e.* :



$$R{-}^{18}OH \rightleftharpoons \begin{matrix} R \quad O{\cdot}OH \\ H{-}^{18}O{\cdots}H \end{matrix} \longrightarrow RO{\cdot}OH + H_2{}^{18}O \quad . \quad . \quad . \quad . \quad (S_Ni)$$

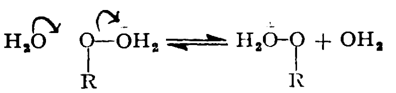
$$R{-}^{18}OH_2 \rightleftharpoons H_2{}^{18}O + R^+ \xrightarrow{HO{\cdot}OH} RO{\cdot}OH + H^+ \quad . \quad . \quad . \quad . \quad . \quad (S_N1)$$

The possibility of any major portion of the reaction proceeding by electrophilic attack of $H_2\overset{+}{O}{-}OH$ or of $\overset{+}{O}H$ on the oxygen atom of the alcohol (or by attack of $H_2\overset{+}{O}{-}OBu^t$ or of $\overset{+}{O}{-}Bu^t$ in the reaction of *tert.*-butyl hydroperoxide with triphenylmethanol) is excluded.

Further attempts to detect this acid-catalysed formation of an O–O bond by the co-ordination of electrophilic and nucleophilic oxygen were made in the following two experiments using more highly ^{18}O-enriched water.

87·4% Hydrogen peroxide containing water with 9·1% excess of ^{18}O was acidified with sulphuric acid ; no exchange of oxygen between the hydrogen peroxide and water could be detected after 7 days. The equilibria (1) and (2) (R = H), which involve respectively S_N1 and S_N2 reaction at an oxygen atom, do not therefore exist under these conditions. This result confirms and extends those obtained earlier on dilute aqueous acidic solutions of hydrogen peroxide (Bunton and Llewellyn, *loc. cit.*).

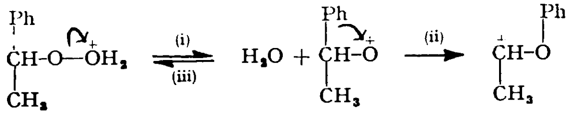
$$RO{-}\overset{+}{O}H_2 \rightleftharpoons R\overset{+}{O} + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$



$$H_2O \quad \underset{R}{O}{-}\overset{+}{O}H_2 \rightleftharpoons H_2\overset{+}{O}{-}\underset{R}{O} + OH_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

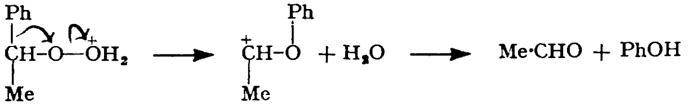
A similar experiment was conducted with 1-phenylethyl hydroperoxide in which heterolysis of the O–O bond might again proceed by an S_N1 or S_N2 mechanism [equations (1) and (2), R = Ph·CHMe–], both of which would involve oxygen exchange with added water. The hydroperoxide was treated with ^{18}O-enriched water and sulphuric acid so that partial decomposition to phenol occurred. The undecomposed hydroperoxide, which was isolated as its triphenylmethyl derivative, contained oxygen of approximately normal isotopic constitution. Again, therefore, under these experimental conditions, there is no evidence for the formation of a peroxide link by the co-ordination of electrophilic and nucleophilic oxygen.

This result also provides evidence of the mechanism of the ready acid-catalysed rearrangement of the hydroperoxide to form phenol and acetaldehyde (Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, 1951, **16**, 128). The two processes involved—removal of water (i) and migration of a phenyl group (ii)—may occur stepwise (equation 3) or by a synchronous mechanism.



$$\overset{Ph}{\underset{CH_3}{CH}}{-}O{-}\overset{+}{O}H_2 \underset{(iii)}{\overset{(i)}{\rightleftharpoons}} H_2O + \overset{Ph}{\underset{CH_3}{CH}}{-}\overset{+}{O} \xrightarrow{(ii)} \overset{+}{\overset{Ph}{\underset{CH_3}{CH}}}{-}O \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The absence of ^{18}O-exchange in 1-phenylethyl hydroperoxide during decomposition shows either that the rate of migration of the phenyl group (ii) is very much greater than the rate of reaction of the alkoxy-cation with water (iii), or that steps (i) and (ii) are not distinct but combine to form a single step. The latter mechanism implies synartetic acceleration of the rearrangement, and it would be difficult to account for the high rate of acid-catalysed decomposition of 1-phenylethyl hydroperoxide compared with that of *tert.*-butyl hydroperoxide except on this assumption. It appears that the migrating phenyl group assists in the heterolysis of the O–O bond (equation 4), the reaction being analogous to the ready unimolecular solvolysis with rearrangement of 2 : 2 : 2-triphenylethyl chloride (Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 514).



$$\overset{\text{Ph}}{\underset{\text{Me}}{\text{C}}}\text{H-O—}\overset{+}{\text{O}}\text{H}_2 \longrightarrow \overset{+}{\underset{\text{Me}}{\text{C}}}\text{H-}\overset{\text{Ph}}{\text{O}} + \text{H}_2\text{O} \longrightarrow \text{Me·CHO} + \text{PhOH} \quad . \quad . \quad . \quad (4)$$

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