[Contribution from the George Herbert Jones Laboratory of the University of Chicago]

# THE CHEMISTRY OF HYDROPEROXIDES. II. THE PREPARATION AND PROPERTIES OF α,α-DIMETHYLBENZYL (α-CUMYL) PEROXIDE[1]

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*Received December 7, 1949*

α-Cumyl peroxide cannot be conveniently prepared by any of the methods ordinarily used for the preparation of tertiary aliphatic peroxides. *tert*-Butyl and *tert*-amyl peroxides, for example, are readily obtained by treating the corresponding hydroperoxides with the corresponding alcohols in the presence of a strong acid (1) (*e.g.*, 60–70% sulfuric). But for α-cumyl peroxide, because of the great sensitivity of α-cumyl hydroperoxide to acids (see preceding paper in this series), this method is not suitable. If α-cumyl hydroperoxide is treated with a strong acid, the reaction products, depending on experimental conditions, are either phenol and acetone, or the dimer of α-methylstyrene, or all three of these compounds.

α-Cumyl peroxide has now been prepared by four different thermal reactions.

1. $C_6H_5(CH_3)_2C{-}OOH \xrightarrow[95^\circ]{\text{Norit}} [C_6H_5(CH_3)_2CO{-}]_2$ (40%) + $CH_3COC_6H_5$ (10%) + $C_6H_5(CH_3)_2COH$ (16%) + $C_6H_5OH$ (trace) + oil (unidentified) (30%) + $O_2$ (7%)
2. $C_6H_5(CH_3)_2C{-}OOH \xrightarrow[105^\circ]{CH_3COOH} [C_6H_5(CH_3)_2CO{-}]_2$ (20–35%) + $CH_3COC_6H_5 + CH_3OH + (CH_3)_2CO + C_6H_5OH$

The rate of decomposition of the hydroperoxide and the amount of α-cumyl peroxide formed vary in case 1 with the carbon used, and in case 2 with the dilution, temperature, and origin of the acetic acid. Thus, when the decomposition was conducted at 105° in "C.P." acetic acid (General Chemical Company) or in other acetic acid purified by crystallization, about 20% of α-cumyl peroxide was obtained. On the other hand, when the reaction was conducted in unpurified acetic acid purchased from the Niacet Chemical Company the yield of α-cumyl peroxide was consistently higher (often 35%, almost double the amount formed when recrystallized acetic acid was used). Many of the obvious impurities (water, anhydride, metallic salts) which might account for differences between acetic acids from various sources have been found to have little effect on the yield of the peroxide. The cause of the observed discrepancies is still unknown.

When equal weights of α-cumyl hydroperoxide and benzoic acid are heated to 105° for two hours, the yield of α-cumyl peroxide is 40%. The other principal

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[1] The authors wish to express their appreciation to the Research Corporation for support which made this work possible.

products of the reaction are acetophenone (6%), phenol (30%), and α,α-dimethylbenzyl alcohol (12%).

$$3.\ C_6H_5(CH_3)_2C\text{—}OOH \xrightarrow[95^\circ]{C_6H_5(CH_3)_2COH} [C_6H_5(CH_3)_2CO\text{—}]_2$$

This method is by far the best for preparing α-cumyl peroxide. The yield of the peroxide, on the basis of the hydroperoxide used (two moles of the hydroperoxide are converted into one mole of the peroxide), is almost quantitative. The extent of solvent participation is indicated by formation of 25% of acetophenone, about 7% of oxygen, and a small amount of methane.

When α-cumyl hydroperoxide was heated in tertiary aliphatic alcohols containing no aromatic group, traces of α-cumyl peroxide and mixed peroxide could be isolated. For example, the hydroperoxide decomposed when heated to 95° in *tert*-amyl alcohol, to give a small amount of methane, about 15% of oxygen, 26% of acetophenone, 39% of α,α-dimethylbenzyl alcohol, and 30% of an unidentified high-boiling material.

When α-cumyl hydroperoxide was heated to 95° in 1-phenylethanol, the reaction products were methane (about 2%), oxygen (15%), α,α-dimethylbenzyl alcohol (55%), and acetophenone (70%).

These products are well accounted for by assuming the following over-all reactions:

$$C_6H_5(CH_3)_2C\text{—}OOH$$

$$\left\{\begin{array}{l} \xrightarrow{\quad A \quad} C_6H_5(CH_3)_2COH(30\%) + O_2(15\%) \\ \xrightarrow{\quad B \quad} CH_3COC_6H_5(45\%) + CH_3OH \\ \xrightarrow[CH_3(C_6H_5)CHOH]{C} CH_3COC_6H_5(25\%) + C_6H_5(CH_3)_2COH(25\%) \end{array}\right.$$

Reactions *A* and *B* are thermal decompositions of α-cumyl hydroperoxide in 1-phenylethanol. Reaction *C*, however, involves the oxidation of 1-phenylethanol to acetophenone, and the reduction of the hydroperoxide to α,α-dimethylbenzyl alcohol. It is noteworthy that α-cumyl hydroperoxide by itself, or in solution in inert solvents (*e.g.*, cumene or benzene) is stable at 100°. Studies on the effect of solvents on the thermal stability of the hydroperoxide will be reported in another paper.

$$4.\ C_6H_5(CH_3)C\text{—}OOH\ (1.3\ \text{mole}) + (CH_3COO)_2\ (1\ \text{mole}) \xrightarrow[100^\circ]{C_6H_5(CH_3)_2CH}$$
$$[C_6H_5(CH_3)_2CO\text{—}]_2\ (0.44\ \text{mole}) + CH_4\ (1.3\ \text{mole}) + CO_2\ (1.64\ \text{mole}) +$$
$$C_6H_5(CH_3)_2COH\ (1.3\ \text{mole})$$

This rather bizarre reaction was attempted in the hope of elucidating the mechanism of formation of α-cumyl peroxide from α-cumyl hydroperoxide. It has been fairly well established that a tertiary aliphatic peroxide, when prepared from an aliphatic hydroperoxide and a tertiary aliphatic alcohol, is formed by a polar mechanism: that is, it is never necessary to assume that the peroxide is formed by a combination of two free radicals, 2 RO· → RO:OR. α-Cumyl peroxide cannot be formed from the hyperperoxide and the alcohol in the presence of strong acids, but this fact does not preclude the possibility that, under carefully adjusted conditions, the peroxide might be formed from the hydroperoxide by a polar mechanism. The methods (1, 2, and 3) already mentioned involve thermal reactions, and, hence, do not furnish unequivocal proof in favor of either a polar or a free-radical mechanism. It was, therefore, desirable to demonstrate whether or not the free radical $C_6H_5(CH_3)_2CO\cdot$ is stable enough to dimerize to α-cumyl peroxide. The formation of α-cumyl peroxide (along with other reaction products) when acetyl peroxide (dissolved in cumene) is slowly added to a hot (100°) solution of α-cumyl hydroperoxide in cumene, may be accounted for by assuming the dimerization of free $C_6H_5(CH_3)_2CO\cdot$ radicals, formed from α-cumyl hydroperoxide. The reaction may be assumed to proceed as indicated in (*a*) and (*b*).

TABLE I

REACTION OF α-CUMYL HYDROPEROXIDE WITH ACETYL PEROXIDE (1 EQUIV.) IN THE PRESENCE OF SOLVENTS

| REAGENTS (MOLES) | CUMENE | | ETHYLBENZENE | | 1-PHENYL-ETHANOL |
|---|---|---|---|---|---|
| | 75° | 100° | 75° | 100° | 85° |
| α-Cumyl hydroperoxide (initial) | 1.5 | 1.9 | 1.12 | 1.68 | 2.5 |
| α-Cumyl hydroperoxide (consumed) | 0.84 | 1.29 | 0.68 | 0.9 | None |
| PRODUCTS (MOLES) | | | | | |
| Methane[a] | 1.07 | 1.32 | 1.4 | 1.2 | 1.0 |
| Carbon dioxide | 1.5 | 1.64 | 1.67 | 1.7 | 1.0 |
| Acetophenone | 0.03 | Trace | 0.11 | 0.7 | 1.0[b] |
| α,α-Dimethylbenzyl alcohol | .27 | 1.3 | .15 | .9 | — |
| α-Cumyl peroxide | .44 | 0.44 | — | — | — |
| High-boiling oil[c] | .17 | .2 | — | — | None |
| α-Phenethyl α-cumyl peroxide | — | — | 0.55 | None | — |
| 1-Phenylethanol | — | — | None | None | — |

[a] In all cases the gas was pure methane. [b] Acetic acid (0.7 mole) was also isolated. [c] Molecular weight, 300.

(*a*) $(CH_3COO—)_2 \rightarrow CH_3\cdot + CO_2 + CH_3COO\cdot$

(*b*) $C_6H_5(CH_3)_2CH + CH_3\cdot \rightarrow C_6H_5(CH_3)_2C\cdot + CH_4$

In the absence of α-cumyl hydroperoxide, the free radical thus formed would dimerize (quantitatively) to bi-α-cumyl (2,3-dimethyl-2,3-diphenylbutane). However, since no bi-α-cumyl is formed under these conditions, reactions (*c*) and (*d*) suggest themselves.

(*c*) $C_6H_5(CH_3)_2C\cdot + C_6H_5(CH_3)_2C—OOH \rightarrow C_6H_5(CH_3)_2COH + C_6H_5(CH_3)_2CO\cdot$

(*d*) $2\ C_6H_5(CH_3)_2CO\cdot \rightarrow [C_6H_5(CH_3)_2CO—]_2$

The quantitative relationships of the various reaction products (transformation of over 75% of the α-cumyl hydroperoxide to the peroxide; formation of two moles α,α-dimethylbenzyl alcohol per mole of α-cumyl peroxide, etc.), are consistent with this scheme.

However, a more thorough study of the reactions of acetyl peroxide and α-cumyl hydroperoxide in different solvents, and at various temperatures (Table I), completely rules out reaction (*d*) as the source of the $(RO—)_2$ compounds. It is also doubtful to what extent reaction (*c*) contributes to the formation of the α,α-dimethylbenzyl carbinol. Actually, reactions (*c*) and (*d*) cannot be reconciled with the following phenomena recorded in Table I: (a) the variation in yield of α,α-dimethylbenzyl alcohol with temperature when cumene is the solvent, (b) the formation of a mixed peroxide (α-phenethyl α-cumyl peroxide) when ethylbenzene is the solvent and the reaction is conducted at 75°, and (c) the preferential attack upon the 1-phenylethanol when the latter material and α-cumyl hydroperoxide are heated with acetyl peroxide.

Whereas all the evidence thus far available indicates that free RO· radicals do not dimerize (and this point is of importance in kinetic studies, for no such reaction should be assumed as a chain-terminating step), another explanation of the results cited must be sought. Provisionally, reactions (*e*) to (*j*) are suggested.

(*e*)[2] $C_6H_5(CH_3)_2CH + CH_3\cdot \rightarrow C_6H_5(CH_3)_2C\cdot + CH_4$

(*f*) $C_6H_5(CH_3)_2C\cdot + C_6H_5(CH_3)_2C{—}OOH \rightarrow [C_6H_5(CH_3)_2C{—}OOH\cdot C(CH_3)_2C_6H_5]$ complex $\{A\}$

(*g*)[3] $\{A\} + C_6H_5(CH_3)_2C{—}OOH \rightarrow [C_6H_5(CH_3)_2CO{—}]_2 + C_6H_5(CH_3)_2CO\cdot + H_2O$

(*h*) $\{A\} + (CH_3COO{—})_2 \rightarrow [C_6H_5(CH_3)_2CO{—}]_2 + CH_4 + CO_2 + CH_3COO\cdot$

(*i*) $\{A\} + C_6H_5(CH_3)_2CH \rightarrow 2\ C_6H_5(CH_3)_2COH + C_6H_5(CH_3)_2C\cdot$

(*j*) $C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2CH \rightarrow C_6H_5(CH_3)_2COH + C_6H_5(CH_3)_2C\cdot$

The formation (when cumene is the solvent) of larger amounts of α,α-dimethylbenzyl alcohol at 100° than at 75°, may be explained in either or both of the following ways. At the lower temperature (75°), the decomposition of acetyl peroxide is slow; and therefore the concentration of acetyl peroxide in the solution is high, and reaction (*h*), which is wasteful of the initiating material, is favored. At the higher temperature (100°), the concentration of the acetyl peroxide in solution is low (for it is introduced very slowly and is rapidly decomposed); therefore reaction (*g*) predominates. Since reaction (*i*) takes place readily at 100°, but less readily at 75°, somewhat longer reaction chains are possible under the latter conditions; hence more α-cumyl hydroperoxide is consumed (Table I), and the yield of α,α-dimethylbenzyl alcohol is larger. These con-

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[2] The gas formed in these reactions is pure methane.

[3] Reaction (*g*) could also be written so as to make it yield the peroxide, α,α-dimethylbenzyl alcohol, and a free hydroxyl radical. The data now at hand do not justify an unequivocal choice.

clusions are strikingly supported by consideration of the reaction products at 75° and 100° with ethylbenzene as a solvent.[4]

Additional evidence for the formation of the peroxide by reactions (*e*), (*f*), (*g*), and (*h*) is the formation of *tert*-butyl $\alpha$-cumyl peroxide when acetyl peroxide is decomposed in a mixture of cumene and *tert*-butyl hydroperoxide.

$$(CH_3)_3C\text{—}OOH + C_6H_5(CH_3)_2CH + (CH_3COO\text{—})_2 \xrightarrow{85\text{–}100^\circ} C_6H_5(CH_3)_2C\text{—}OO\text{—}C(CH_3)_3 + CH_4 + CO_2$$

It is of interest that no *tert*-butyl peroxide nor $\alpha$-cumyl peroxide is formed under these conditions.

Two other points invite comment. First, the oxygen-to-oxygen bond in $\alpha$-cumyl peroxide is remarkably stable in the presence of free radicals, as evidenced by the fact that when the peroxide, dissolved in ethylbenzene, is treated with acetyl peroxide at 85–100°, practically all of it is recovered unchanged, and the reaction product is a mixture of the *meso* and racemic forms of 2,3-diphenylbutane (2). Second, the hydrogen atoms of tertiary alcohols are highly resistant to an attack by alkyl free radicals as evidenced by the data of Table II, which show that the products of decomposition of acetyl peroxide in $\alpha,\alpha$-dimethylbenzyl alcohol are approximately those of a simple thermal decomposition.

TABLE II

DECOMPOSITION OF ACETYL PEROXIDE (1 MOLE) IN $\alpha,\alpha$-DIMETHYLBENZYL ALCOHOL (5 MOLES)

| | MOLES |
|---|---|
| $\alpha,\alpha$-Dimethylbenzyl alcohol (consumed) | 0.23 |
| $CO_2$ | 1.0 |
| $CH_4$ | 0.27 |
| $C_2H_6$ | .27 |
| Acetic acid | .65 |
| Methyl acetate | .10 |
| Polymer (average mol. wt., 617) | .04 |

### PROPERTIES OF $\alpha$-CUMYL PEROXIDE

$\alpha$-Cumyl peroxide melts at 39°, and can be sublimed, without decomposition, at 100°/0.2 mm. Thermally it is less stable than $\alpha$-cumyl hydroperoxide. It does not oxidize hydrogen iodide under the conditions ordinarily used for the deter-

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[4] The somewhat shorter chain where ethylbenzene, instead of cumene, is the solvent (Table I) may be explained as follows: the free radical complex {A} first formed, namely $\{C_6H_5(CH_3)_2C\text{—}OOH\cdot C_6H_5(CH_3)(H)C\cdot\}$ disproportionates preferentially at the higher temperatures $2\,\mathbf{A}' \rightarrow 2\,C_6H_5(CH_3)_2OH + C_6H_5COCH_3 + C_6H_5CHOHCH_3$, and therefore reactions (*g*), (*h*), and (*i*) are suppressed. The fact that no 1-phenylethanol can be isolated is readily understood, since it reacts faster with acetyl peroxide than any of the other substances present in solution.

mination of peroxides (3). Sodium powder, in ether, reduces the peroxide quantitatively to α,α-dimethylbenzyl alcohol. A solution of the peroxide in glacial acetic acid is transformed by small amounts of perchloric acid, into acetone, phenol, and the dimer of α-methylstyrene.

## EXPERIMENTAL PART

*Preparation of α-cumyl peroxide in the presence of charcoal.* To 10 g. of α-cumyl hydroperoxide (purified as specified in the preceding paper) was added 0.6 g. of Norit A, (Pfanstiehl Chemical Company). The reaction mixture was kept at 95° for 36 hours. Gas (15 mole-%) was evolved at the beginning of the reaction. The reaction mixture was separated from the Norit by filtration, and the residual liquid was removed from the Norit by washing with ether. The Norit recovered corresponded in weight to the amount used originally. Only a small amount (0.1 g.) of the reaction product was soluble in alkali. The low-boiling fractions (acetophenone and α,α-dimethylbenzyl alcohol) were removed from the filtrate by distillation at 1 mm. The products obtained were: α-cumyl peroxide, 24%; high-boiling residue, 16%; acetophenone, 12%; α,α-dimethylbenzyl alcohol, 48%. Use of another sample of Norit (of unknown origin) resulted in the formation of α-cumyl peroxide, 43%; high-boiling oil, 31%; acetophenone, 10%; α,α-dimethylbenzyl alcohol, 16%. Decolorizing charcoal (of unknown origin) led to a reaction product (73%) containing high-boiling oils from which no α-cumyl peroxide could be recovered.

Acetophenone was estimated as the dinitrophenylhydrazone. The carbinol was estimated by a quantitative adaptation of Holmberg's (4) method of converting α,α-dimethylbenzyl alcohol into its thioglycolic acid derivative. To the mixture suspected to contain 0.5–1.0 g. of carbinol, 1.0 g. of thioglycolic acid and 10 cc. of 2 *N* hydrochloric acid was added. The resulting mixture was agitated at reflux temperature for 2.5 hours, cooled, washed with water, and then extracted with alkali. The alkaline extract was acidified, and the resulting thioglycolic acid derivative was allowed to crystallize. The α,α-dimethylbenzyl alcohol derivative may be separated from the corresponding 1-phenylethanol derivative by making use of the greater solubility of the latter in petroleum ether. Thus, by merely shaking an aqueous suspension of a mixture of the two derivatives with petroleum ether the α,α-dimethylbenzyl alcohol-thioglycolic acid compound may be made to crystallize. It should be mentioned that in this determination no distinction is made between α-methylstyrene and α,α-dimethylbenzyl alcohol.

To the higher-boiling residue remaining after removal of the acetophenone and carbinol was added 95% ethanol. When the ethanol solution was cooled to −70°, α-cumyl peroxide crystallized. The crystals were collected from the cold solution.

*Preparation of α-cumyl peroxide in acetic acid.* α-Cumyl hydroperoxide (15.2 g. of 99% titre) dissolved in 18 g. of glacial acetic acid (Niacet) was held at 94° for 2 hours. By this time the peroxide titre had fallen to zero. Practically all the acetic acid was removed by distillation at reduced pressure (15 mm.). From the residue phenol was extracted with alkali, and isolated as crystalline phenol (27%). Acetone was estimated in the acetic acid distillate; it corresponded in amount to the amount of phenol. From the residue remaining after alkaline extraction, acetophenone was distilled; traces of α,α-dimethylbenzyl alcohol were found. The oil remaining after removal of the acetophenone, was heated to 70°/0.01 mm., and the α-cumyl peroxide which sublimed was collected (35%). A small amount (0.2 g.) of oily residue remained. Samples of glacial acetic purified by crystallization gave decreased amounts (15–20%) of α-cumyl peroxide, along with a correspondingly increased amount of phenol.

Lowering the reaction temperature, addition of small amounts of water to the acetic acid, or higher dilution of the α-cumyl hydroperoxide decreased the yield of the peroxide. Increased amounts (52%) of peroxide were formed when α,α-dimethylbenzyl alcohol was added (in amount equivalent to the hydroperoxide present) to the acetic acid solution.

*α-Cumyl peroxide formation in benzoic acid.*—α-Cumyl hydroperoxide (15.2 g.) and benzoic acid (15 g.) were heated at 105° for 20 hours. From the reaction mixture were obtained: phenol, 30%; acetophenone, 6%; α,α-dimethylbenzyl alcohol, 12%; α-cumyl peroxide, 40%; high-boiling residue, 0.3 g.

When 1-phenylethanol (0.15 mole) and α-cumyl hydroperoxide (0.1 mole) in benzoic acid (0.5 mole) were heated at 105° for 48 hours a gas was evolved. This gas (12 mole-%) contained 5–10 mole-% of methane. From the reaction product the following substances were isolated: phenol 20%; high-boiling residue, 30%. From this residue only small amounts of α-cumyl peroxide could be separated. The small yield of α-cumyl peroxide is not surprising in view of the extended duration of the heating.

*Preparation of α-cumyl peroxide in α,α-dimethylbenzyl alcohol.*[5] A mixture of α-cumyl hydroperoxide (15.2 g.) and dimethylbenzyl alcohol (22 g.) was heated at 95° for 48 hours. During this time 6.7 mole-% of gas was evolved. The unchanged carbinol, the α-methylstyrene, and the acetophenone were removed at reduced pressure. The amount of acetophenone formed in this reaction (estimated from the weight of the 2,4-dinitrophenylhydrazone derivative) was 25 mole-%. From the oily residue 50 mole-% of α-cumyl peroxide was obtained by crystallization from ethanol. The oil remaining after the crystallization was heated to 70°/0.01 mm., and the material that sublimed was collected. The additional amount of α-cumyl peroxide thus obtained was 50 mole-% on the basis of the hydroperoxide used (total yield, 13.5 g., *ca* 100 mole %). A very small amount of oily residue still remained.

*Decomposition of α-cumyl hydroperoxide in tert-amyl alcohol.* α-Cumyl hydroperoxide (10 g.) in *tert*-amyl alcohol (14 g.) was refluxed for 3 days. During this time 430 cc. of gas was evolved. Analysis showed that 50% of this gas was not condensible in liquid nitrogen; it was therefore assumed to be oxygen. The remainder of the gas was fractionated on a vacuum line. It consisted of 5-10% of methane (identified by its vapor pressure at liquid nitrogen temperature, 11 mm.), and a mixture of 2-methyl-1-butene and 2-methyl-2-butene (mol. wt., 68; calc'd mol. wt., 70; vapor pressure at −10°, 122 mm.).

The liquid reaction product was distilled at reduced pressure to remove the more volatile fractions. The distillate was analyzed for acetophenone (26%) and α,α-dimethylbenzyl alcohol (39%) in the manner previously described. A high-boiling oil remained; from this only traces (1%) of α-cumyl peroxide could be isolated. The remainder of the oil (mol. wt., 297 in benzene) was not further investigated.

*Decomposition of α-cumyl hydroperoxide in 1-phenylethanol.* 1-Phenylethanol (free of acetophenone) was prepared as follows. To a stirred solution of lithium aluminum hydride (12 g.) in 250 cc. of ether, 120 g. of acetophenone was added dropwise. After the reaction was completed, water was added slowly; the ether layer was separated and dried, and the ether was distilled. 1-Phenylethanol was distilled at reduced pressure (yield 95%). It gave a negative test for acetophenone.

α-Cumyl hydroperoxide (15.2 g.) in 1-phenylethanol (24 g.) was heated at 90° for 96 hours. During this time 340 cc. of gas was evolved, and all the α-cumyl hydroperoxide was consumed. The gas consisted of a mixture of methane and oxygen. Calculated on the basis of α-cumyl hydroperoxide used, there was 2% methane and 15% oxygen. The reaction mixture was analyzed for acetophenone (75%) and α,α-dimethylbenzyl alcohol (55%) as previously described.

*The acetyl peroxide-induced decomposition of α-cumyl hydroperoxide in the presence of cumene.* To a mixture of 0.188 mole of α-cumyl hydroperoxide and 0.45 mole of cumene at 100° a solution of 0.10 mole of acetyl peroxide in 0.50 mole of cumene was added dropwise over a period of two hours. Provision was made for absorbing carbon dioxide and collecting the methane evolved in the decomposition. The products formed are recorded in Table I. The reaction was considered complete when there was no further evolution of gas. Titration of the reaction mixture indicated the presence of 0.056 mole of unchanged α-cumyl hydroperoxide. There was no significant change in titre after two-hours additional heating at

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[5] It is noteworthy that the presence of some impurities, particularly traces of alkali, prevents the formation of α-cumyl peroxide by the method here described.

100°. The reaction mixture was distilled at reduced pressure. α,α-Dimethylbenzyl alcohol and cumene were collected between 60–80° at 12 mm. The carbinol was determined as the thioglycolic acid derivative as previously described. The amount of acetophenone found was less than 3%. Unused α-cumyl hydroperoxide was removed by distillation at 0.1 mm.; an oily residue remained. Under conditions suitable for crystallizing bi-α-cumyl in the presence of α-cumyl peroxide, namely in methanol solution cooled to 0°, no bi-α-cumyl was found. Crystalline α-cumyl peroxide, however, was isolated when an ethanolic solution of the oil was cooled to −80°. The product thus obtained melted sharply at 39°; recrystallizations indicated that no bi-α-cumyl was present. The oil remaining from the first crystallization of the α-cumyl peroxide could not be crystallized. This oil in benzene had a molecular weight of 300.

When the decomposition was carried out at 75°, the rate of gas evolution was slow, and consequently the acetyl peroxide was added at a slower rate to prevent, insofar as possible, an accumulation of the peroxide. Thus 30 hours elapsed before addition of all the acetyl peroxide solution. The reaction products, which were isolated as usual, are recorded in Table I.

*Properties of α-cumyl peroxide.* α-Cumyl peroxide is a white crystalline compound, m.p. 39°.

*Anal.* Calc'd for $C_{18}H_{22}O_2$: C, 80.00; H, 8.13; Mol. wt., 270.
Found: C, 79.64; H, 8.10; Mol. wt., 274.

A supercooled solution had $n_D^{21}$ 1.5360. It may be purified by crystallization from ethanol or by sublimation at reduced pressure. The material is stable at room temperature, but on prolonged standing in the light it gradually turns slightly yellow. The peroxide does not oxidize hydriodic acid under the usual conditions. It reduces neutral permanganate in acetone, and reacts violently with concentrated sulfuric acid; the product thus formed gives a qualitative test for tertiary alcohols (probably α,α-dimethylbenzyl alcohol). The peroxide does not react with concentrated nitric acid or hydrochloric acid. In contrast to α-cumyl hydroperoxide, which is stable up to 140°, α-cumyl peroxide decomposes rapidly at 120°, and slowly, but appreciably, above 100° to form compounds of higher molecular weight.

*Proof of structure of α-cumyl peroxide.* α-Cumyl peroxide (3.0 g.) and 1.2 g. of sodium powder (prepared under ligroin in absence of air) were added to absolute ether. The mixture was allowed to stand at room temperature for five hours. The excess sodium was decomposed with ethanol, the reaction mixture was poured on ice, and the ether layer was separated and dried over sodium sulfate. After removal of the ether, the residue was distilled, and the fraction boiling at 48–50°/0.5 mm. was collected (2.9 g.). This substance melted at 36°, and when supercooled had $n_D^{21}$ 1.5223. The thioglycolic acid derivative had m.p. 67°. There was no depression of the melting point upon admixture with the authentic thioglycolic acid derivative of α,α-dimethylbenzyl alcohol. It is noteworthy that the values in the literature for the refractive index of the alcohol are usually higher than that here reported. This difference is undoubtedly due to the presence of α-methylstyrene or acetophenone in the materials reported as pure α,α-dimethylbenzyl alcohol. After several crystallizations, α,α-dimethylbenzyl alcohol of a constant refractive index ($n_D^{21}$ 1.5221) was obtained.

*Acidic decomposition of α-cumyl peroxide.* α-Cumyl peroxide (7.2 g.) in 50 cc. of glacial acetic acid was treated with 0.2 cc. of 5% perchloric acid solution in acetic acid. The temperature of the reaction mixture was maintained below 30°. After 24 hours it was poured into water, and the mixture was extracted with ether. The ether solution was extracted, first with sodium bicarbonate solution to remove acetic acid, and then with 5% sodium hydroxide to remove phenolic materials. From the alkaline extract, phenol (40%) was obtained by acidification and subsequent extraction with ether. The neutral residue was distilled at 62°/0.001 mm. The distillate was identified by refractive index, molecular weight, and elementary analysis as the dimer of α-methylstyrene.

When the decomposition was carried out in acetic acid (50 cc.) containing 10 g. of α,α-dimethylbenzyl alcohol less than 2% of phenol was obtained. The major part of the peroxide was converted to the dimer of α-methylstyrene.

*The acetyl peroxide-induced decomposition of α-cumyl hydroperoxide in the presence of ethylbenzene.* The reactions were carried out in a fashion similar to that when cumene was used as the solvent. The products found are shown in Table I.

1-Phenylethanol was estimated by oxidation of the reaction mixture with chromic oxide in acetic acid; the oxidation mixture was extracted with petroleum ether, and the extract was examined for the presence of acetophenone.

*α-Phenethyl α-cumyl peroxide.* This mixed peroxide has the following properties: b.p. 110–116°/0.3–0.5 mm.; $n_D^{20}$ 1.5397.

*Anal.* Calc'd for $C_{17}H_{20}O_2$: Mol. wt., 256; C, 79.7; H, 7.8.

Found: Mol. wt., 250; C, 79.6; H, 7.7.

The peroxide was reduced with sodium powder in ether in the same manner as α-cumyl peroxide. The α,α-dimethylbenzyl alcohol formed was determined by conversion to the thioglycolic acid derivative. It amounted to 50 mole-%. The 1-phenylethanol formed was determined by oxidation with chromic acid to acetophenone, and by comparing the conversion thus obtained with that obtained from known mixtures of the two carbinols. Thus 30 mole-% of 1-phenylethanol was found in the reduction products.

TABLE III

REACTION OF *tert*-BUTYL HYDROPEROXIDE (1.6 MOLE) WITH ACETYL PEROXIDE (1 mole) IN THE PRESENCE OF CUMENE (4.8 moles)

| | MOLES |
|---|---|
| *tert*-Butyl hydroperoxide (consumed) | 0.85 |
| Methane | *ca* 1.1 |
| Carbon dioxide | *ca* 1.7 |
| *tert*-Butyl α-cumyl peroxide | 0.62 |
| α,α-Dimethylbenzyl alcohol | *ca* .1 |
| *tert*-Butyl alcohol | .22[a] |

[a] Calculated from the difference of the *tert*-butyl hydroperoxide consumed and the peroxide formed.

*The acetyl peroxide-induced decomposition of tert-butyl hydroperoxide in cumene.* The reaction was carried out as with the induced decomposition of α-cumyl hydroperoxide. The products isolated are shown in Table III.

The *tert*-butyl α-cumyl peroxide ($n_D^{20}$ 1.4831) thus formed was identical with the compound formed by the acid-catalyzed reaction of *tert*-butyl hydroperoxide with α,α-dimethylbenzyl alcohol (see paper IV in this series).

*Anal.* Calc'd for $C_{13}H_{20}O_2$: C, 75.0; H, 9.68; Mol. wt., 208.

Found: C, 75.9; H, 9.2; Mol. wt., 195.

The refractive index of this material indicates that it contains a small amount of an impurity with a higher refractive index. In harmony with this we find that, when the peroxide (2.5 g.) is dissolved in acetic acid and perchloric acid is added to it, the yield of phenol (0.5 g.) is somewhat less than the amount obtained when the pure peroxide is used (paper IV in this series).

*Decomposition of acetyl peroxide in the presence of α-cumyl peroxide in ethylbenzene.* This decomposition was carried out in the usual fashion at 85°. After gas evolution ceased the reaction products were isolated. There was thus obtained by fractional crystallization from ethanol: *meso*-2,3-diphenylbutane (0.132 mole per mole of acetyl peroxide); α-cumyl peroxide (80% of the starting material).

*Decomposition of acetyl peroxide in the presence of α-cumyl hydroperoxide in 1-phenyl-*

*ethanol.* This decomposition was carried out at 85° in the manner described previously. The results obtained are tabulated below.

| REAGENTS | MOLES | PRODUCTS | MOLES |
|---|---|---|---|
| Acetyl peroxide | 1.0 | α-Cumyl hydroperoxide (consumed) | none |
| α-Cumyl hydroperoxide | 2.5 | Carbon dioxide | 1.0 |
| 1-Phenylethanol | 9.5 | Methane | 1.0 |
| | | Acetophenone | 1.0 |
| | | Acetic acid | 0.7 |

*Decomposition of acetyl peroxide in α,α-dimethylbenzyl alcohol.* Acetyl peroxide (1.0 mole) in α,α-dimethylbenzyl alcohol was added dropwise to α,α-dimethylbenzyl alcohol at 95–100°. After cessation of gas evolution, the carbinol was removed by distillation; a glassy resin remained. This residue had a molecular weight (cryoscopic in benzene) of 617, or (Rast method in camphor) of 580. The other products obtained are shown in Table II.

## SUMMARY

1. α-Cumyl peroxide is formed from α-cumyl hydroperoxide under the following conditions: (a) heating the hydroperoxide in the presence of Norit at 100°; (b) heating the hydroperoxide in acetic acid at 100°; (c) heating the hydroperoxide in the presence of dimethylbenzyl alcohol at 100° (in the presence of *tert*-amyl alcohol and 1-phenylethanol at 100° no α-cumyl peroxide was formed); (d) decomposition of acetyl peroxide in a solution of α-cumyl hydroperoxide and cumene.

2. α-Phenethyl α-cumyl peroxide was prepared by decomposing acetyl peroxide in a solution of α-cumyl hydroperoxide and ethylbenzene at 75°.

(3) *tert*-Butyl α-cumyl peroxide was formed by the decomposition of acetyl peroxide in a solution of *tert*-butyl hydroperoxide and cumene.

4. The formation of the various reaction products, the relative amounts of these formed, and the short chain-reaction encountered, are best explained by assuming the formation of an intermediate complex. This complex is formed by the addition of the solvent free radical to the hydroperoxide. The experiments with acetyl peroxide indicate that peroxide formation in free-radical reactions is not necessarily a chain-terminating event.

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