

THE CHEMISTRY OF HYDROPEROXIDES. XII. THE GENERATION AND PROPERTIES OF FREE RO₂• RADICALS

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It has been established (1) that *tert*-hydroperoxides react with ferrous salts to give free alkoxy radicals (RO•). These add to conjugated olefins (butadiene, isoprene, chloroprene) to form free radicals which then dimerize. It has also been suggested (2) that the decomposition of *tert*-hydroperoxides by traces of cobalt salts (acetate or naphthenate) proceeds by a chain mechanism, schematically represented by the following equations.

1. ROOH + Co⁺⁺ → RO• + Co⁺⁺⁺ + (OH)⁻
2. ROOH + Co⁺⁺⁺ → RO₂• + Co⁺⁺ + H⁺
3. RO• + Co⁺⁺ → (RO)⁻ + Co⁺⁺⁺
4. RO• + ROOH → Induced decomposition of hydroperoxide
(ketone + alcohol + RO•)
5. RO₂• + Co⁺⁺⁺ → (R)⁺ + Co⁺⁺ + O₂

It appeared reasonable, therefore, that the evolution of oxygen from the hydroperoxides would be suppressed if acceptors of free RO₂• radicals (*e.g.* olefins) were present. Experiments confirmed this prediction. The reaction products formed when *tert*-butyl hydroperoxide is decomposed by traces of cobalt salts (acetate or naphthenate) in the presence of olefins (cyclohexene, octene-1, butadiene) were carefully investigated.

The reaction products formed from cyclohexene and octene-1 are well accounted for by the following scheme.

1. RCH₂CH=CH₂ + R'O₂• → RCH₂- $\dot{\text{C}}\text{HCH}_2\text{OOR}'$
2. RCH₂ $\dot{\text{C}}\text{HCH}_2\text{OOR}'$ + Ox → RCH=CHCH₂OOR' (A) + H⁺ + (Ox + e)

The oxidants may be (a) Co⁺⁺⁺ (or a complex of this ion), or (b) free RO• radicals. An alternative mechanism whereby these products might be formed, namely

3. RCH₂CH=CH₂ + Ox → RCHCH=CH₂ + (Ox + e) + H⁺
 $\begin{array}{c} \uparrow \\ \text{RCH}=\dot{\text{C}}\text{HCH}_2\cdot \end{array}$
4. RCHCH=CH₂ + R'O₂• → RCHCH=CH₂ (B) + RCH=CH₂CH₂O₂R' (C)
 $\begin{array}{c} \uparrow \\ \text{RCH}=\dot{\text{C}}\text{HCH}_2\cdot \end{array} \quad \begin{array}{c} | \\ \text{O}_2\text{R}' \end{array}$

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ence of these substances at one stage of the reaction. Under the experimental conditions here used the compounds (if present) would have been converted into polymers. However, since the high-boiling residues found did not exceed 10% of the total reaction products, this figure represents the maximum yield of these dialdehydes or keto-aldehyde.

Both **D** and **E** when allowed to stand form carbonyl compounds. This fact was established by examining the infrared spectra of freshly distilled and aged materials. Both **D** and **E** when freshly distilled showed weak carbonyl absorption; after two or three days standing, their carbonyl absorption was very strong. The other chief feature of their infrared spectra were bands characteristic of the $(\text{CH}_3)_3\text{C}$ group. The infrared spectra of compounds **A**, **F**, **D**, and **C** also show that the first three compounds have non-terminal double bonds whereas the latter has a terminal double bond.

Compound **D** when allowed to stand in air decomposed to fumaric acid. Furthermore, when compound **D** is treated with phenylhydrazine it is converted into the bis-phenylhydrazone of fumaric (or maleic) dialdehyde. The analyses and melting point of this product correspond to those given in the literature (3).

The structure of the compounds **D** and **E** was established by treating them with lithium aluminum hydride. The unsaturated glycols thus obtained were then hydrogenated to the corresponding saturated compounds and the latter converted to well-known derivatives. In all cases, these derivatives did not depress the melting points of authentic samples of the respective compounds prepared by well established methods.

EXPERIMENTAL

Reaction of tert-butyl hydroperoxide with cyclohexene. To a mixture of cyclohexene (120 g.) and *tert*-butyl hydroperoxide (36 g.), cobalt naphthenate (8 drops of Uversol Drier which contains 6% of cobalt) was added. The air in the apparatus was displaced by nitrogen. Heat was evolved and the reaction mixture was maintained at 40–45° for 2 hours. Additional catalyst (10 drops) was then added and the whole maintained at 45° for 2 hours longer. At the end of that time, the mixture gave only a faint test for hydroperoxide. No oxygen gas was evolved during the reaction.

The unreacted cyclohexene and the *tert*-butanol, formed in the reaction, were removed at reduced pressure. The *tert*-butanol (15 g.) was separated from this distillate as the azeotrope with cyclohexene (b.p. 73.2°). The residue was distilled at reduced pressure (50°/0.3 mm.) in order to separate it from the catalyst, and the distillate (28 g.) distilled at 12 mm. pressure. The following fractions were collected: Fraction 1, below 60° (1.3 g.); Fraction 2, 60–69° (1.6 g.); Fraction 3, 69–73° (6.7 g.); Fraction 4, 73–77° (18.3 g.). On refractionation of Fractions 1 and 2, a fraction was obtained which boiled at 60–62.5° ($n_D^{21.5}$ 1.4720) which was largely cyclohexenone. The 2,4-dinitrophenylhydrazone of this material melted at 165–167° and the melting point was not depressed by admixture of an authentic sample of the 2,4-dinitrophenylhydrazone of cyclohexenone.

The *phenylsemicarbazone* of this material melted at 194°.

Anal. Calc'd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}$: C, 68.0; H, 6.6; N, 18.3.

Found: C, 68.1; H, 6.5; N, 18.3.

Fractionation of Fraction 4 at reduced pressure (35°/0.7 mm.) gave a material which was essentially pure cyclohexenyl-*tert*-butyl peroxide² (n_D^{20} 1.4522).

² This compound was prepared by Campbell and Coppinger, *J. Am. Chem. Soc.*, **73**, 1788 (1951) by the interaction of 3-bromocyclohexene and *tert*-butyl hydroperoxide in the presence of a base (b.p. 63°/6 mm.). They do not record the index of refraction of this material.

Anal. Calc'd for $C_{10}H_{18}O_2$: C, 70.6; H, 10.6; Mol. wt., 170.

Found: C, 70.9; H, 10.5; Mol. wt., 165.

Reaction of tert-butyl hydroperoxide with octene-1. To a mixture of octene-1 (135 g.) and *tert*-butyl hydroperoxide (30 g.), 20 drops of cobalt naphthenate (10 + 5 + 5) (Uversol Drier) were added over a period of one hour. The temperature of the reaction mixture rose to 40–45°. It was maintained at that temperature for 2 hours longer. At the end of that time 10 more drops of catalyst were added and the heating continued for 2 hours.

The unreacted octene-1 and the *tert*-butanol, formed in the reaction, were removed at reduced pressure (20°/3 mm.). Upon distillation of this distillate *tert*-butanol (18 g.) came over first, followed by a mixture of *tert*-butyl hydroperoxide and octene-1, and finally pure octene-1. The residue (16 g.) was removed from the catalyst at reduced pressure (20°/0.05 mm.), and fractionated. The following fractions were collected: Fraction 1, up to 75°/12 mm. (2.2 g.); Fraction 2, 75–81°/12 mm. (2.2 g.); Fraction 3, 80–86°/12 mm. (2.8 g.); Fraction 4, 86–93°/12 mm. (4.0 g.); Fraction 5, 50–60°/1 mm. (1.0 g.); Fraction 6, 60–65°/mm. (3.0 g.).

Fractions 1 and 2 were largely 2-octenal. They reacted at once with 2,4-dinitrophenyl hydrazine to give a hydrazone. The hydrazone crystallized from ethanol in orange-red prisms. The compound melted at 121–123°.

Anal. Calc'd for $C_{14}H_{18}N_4O_4$: C, 54.9; H, 5.9.

Found: C, 55.0; H, 6.1.

The 2-octenal from fractions 1 and 2 was further identified by conversion to octaldehyde (hydrogenation). Both the 2,4-dinitrophenylhydrazone (m.p. 103–104°) and the phenylsemicarbazone (m.p. 127–128°) of the octaldehyde did not depress the melting point of corresponding derivatives prepared from a known sample of octaldehyde.

Fractions 3, 4, 5, and 6 consisted largely of *tert*-butyl 2-octenyl peroxide. Fractions 4, 5, and 6 were combined and distilled at reduced pressure. The main fraction boiled at 74–75.5°/2.3 mm. The index of refraction of this material was n_D^{20} 1.4309.

Anal. Calc'd for $C_{12}H_{24}O_2$: C, 71.9; H, 12.1; Mol. wt., 200.

Found: C, 71.7, 71.4, 72.2; H, 12.05, 12.1, 11.9; Mol. wt., 192.

For purposes of identification the *tert*-butyl 2-octenyl peroxide was hydrogenated (using palladium on charcoal as the catalyst). About 1.7 moles of hydrogen gas was absorbed. A sample of this solution, when treated with 2,4-dinitrophenyl hydrazine, gave the hydrazone of octaldehyde (m.p. 103°). As indicated from the hydrogen absorption part of the aldehyde was further hydrogenated. For this reason, the entire product obtained from the hydrogenation, after removal of the solvent, was subjected to reduction with the aid of lithium aluminum hydride (in the usual way). The reaction product thus produced was octanol-1. The α -naphthylurethane prepared from this alcohol did not depress the melting point of the α -naphthylurethane prepared from an authentic sample of octanol-1.

Careful fractionation of Fractions 1 and 2 (from two experiments), after removal of the 2-octenal with bisulfite solution, gave a small amount of a material which boiled at 74–75°/10 mm. (n_D^{20} 1.4225). The infrared spectrum of this material indicates that it contains a terminal double bond. The material is probably $CH_3(CH_2)_4CH(OOC(CH_2)_3)CH=CH_2$.

Anal. Calc'd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.1.

Found: C, 72.3; H, 12.1.

The yield of this material was too small for full characterization.

Reaction of tert-butyl hydroperoxide with butadiene. To a mixture of butadiene (200 g.) and *tert*-butyl hydroperoxide (40 g.), cooled to –15°, cobalt naphthenate (0.5 cc.) was added. Additional cobalt naphthenate (2 cc.) was added, in equal portions, at three 2-hour intervals. The mixture was then maintained at –7° for 48 hours longer, and the unreacted butadiene was removed at room temperature. The *tert*-butanol (15 g.) formed in the reaction, and some unchanged *tert*-butyl hydroperoxide were removed at reduced pressure (20°/0.5 mm.). The reaction products were separated from the catalyst by distillation at reduced pressure in a molecular still. The material thus obtained was then fractionated (Vigreux column) at reduced pressure and the following fractions were collected: Fraction 1, 43–

45°/0.2 mm. (7.5 g.); Fraction 2, 38–52°/0.05 mm. (10 g.); Fraction 3, 53–56°/0.05 mm. (7 g.). Upon fractionation of Fraction 2 additional 3 grams of Fractions 1 and 3 were obtained.

Fraction 1. This material was distilled at reduced pressure (35°/0.05 mm.; n_D^{19} 1.4220). It was identified as 3,4-di(*tert*-butylperoxy)butene-1.

Anal. Calc'd for $C_{12}H_{24}O_4$: C, 62.1; H, 10.3; Mol. wt., 232.

Found: C, 62.2; H, 10.4; Mol. wt., 221.

The infrared spectrum of this material indicated the presence of a terminal double bond. The carbonyl absorption was very weak, but increased with time. Because it was not possible to identify this compound conveniently as the 1-butenediol-3,4 (see later), the following procedure was used to transform the 3,4-di(*tert*-butylperoxy)butene-1 to butanediol-1,2. The diperoxide was first hydrogenated in ethanol using palladium on charcoal as the catalyst. This resulted in the uptake of 1.7 moles of hydrogen.⁵ The catalyst was then collected and the solvent from the filtrate was removed at reduced pressure. The residue was dissolved in ether and treated with lithium aluminum hydride. The excess of the hydride was then destroyed with ethyl acetate and the mixture poured into dilute hydrochloric acid. The whole was then saturated with sodium chloride and extracted with ether in a continuous extractor. Upon evaporation of the ether butanediol-1,2 was obtained. For identification the bis-*p*-nitrobenzoate of this glycol was prepared. This compound did not depress the melting point of the bis-*p*-nitrobenzoate prepared from an authentic sample of butanediol-1,2.

For analyses Fraction 3 was distilled at reduced pressure (55°/0.05 mm.; n_D^{20} 1.4290). It was shown to be 1,4-di-*tert*-butylperoxybutene-2.

Anal. Calc'd for $C_{12}H_{24}O_4$: C, 62.1; H, 10.3; Mol. wt., 232.

Found: C, 62.0; H, 10.4; Mol. wt., 217.

The infrared spectrum of this material indicated the presence of a non-terminal double bond and only very slight carbonyl absorption. However, the carbonyl absorption became appreciable after 1–2 days standing in air. Upon prolonged standing in air fumaric acid separated from the material. The melting point of the fumaric acid thus obtained was not depressed by admixture with an authentic sample of fumaric acid.

Identification of the material as 1,4-di(*tert*-butylperoxy)butene-2 was performed as follows: The diperoxide, dissolved in acetic acid, was hydrogenated with the aid of palladium on charcoal. Two moles of hydrogen gas were taken up. The solution was then separated from the catalyst. When treated with 2,4-dinitrophenylhydrazine it gave a hydrazone which was submitted to chromatography on silica gel. The hydrazone thus purified when crystallized from benzene separated in the form of yellow needles which melted at 123°. This hydrazone did not depress the melting point of the hydrazone of an authentic sample of γ -hydroxybutyraldehyde (2-hydroxytetrahydrofuran).

Anal. Calc'd for $C_{16}H_{12}N_4O_8$: C, 44.8; H, 4.5; N, 20.9.

Found: C, 45.0; H, 4.7; N, 20.9.

Reaction of 1,4-di(tert-butylperoxy)butene-2 with phenylhydrazine. To a mixture of 1,4-di(*tert*-butylperoxy)butene-2 (0.7 g.) and phenylhydrazine (4 cc.), acetic acid (5 drops) was added, and the whole was heated on the water-bath. Air was excluded during the heating. The evolution of a gas was noted. At the end of 4 hours, the mixture was diluted with acetic acid (5 cc.) and ethanol (5 cc.). The whole was then heated and water added until the appearance of a slight turbidity. Upon cooling a yellow crystalline material separated. Upon crystallization from alcohol, it separated in shiny yellow flakes which decomposed at 172°.

⁵ The mixture at this point contains carbonyl material and when treated with *p*-nitrophenylhydrazine gives deep red-colored compound which decomposes above 270°. It crystallizes in deep red prisms from ethyl acetate. *Anal.* Calc'd for $C_{16}H_{16}N_2O_4$: C, 53.9; H, 4.5. Found: C, 53.8; H, 4.7. This substance may be the osazone $CH_3CH_2C(:NNHC_6H_4NO_2)-CH=NNHC_6H_4NO_2$. The earlier literature claims the compound decomposes at 225–227° but Reiter (U. S. Patent 2,428,270) states that the compound decomposes at 267°.

when heated rapidly in a sealed tube. The compound decomposed at 160° when heated slowly. This substance was the bis-phenylhydrazone of maleic or fumaric dialdehyde (3).

Anal. Calc'd for $C_{16}H_{16}N_4$: C, 72.7; H, 6.1.

Found: C, 72.8; H, 6.5.

Reaction of 1-butenediol-3,4 with p-nitrobenzoyl chloride. It was previously mentioned that the reaction of 1-butenediol-3,4 with *p*-nitrobenzoyl chloride is not a suitable method of identification of this diol. The proof of this assertion is provided by the following experiment.

An excess of *p*-nitrobenzoyl chloride was added to a solution of 1-butenediol-3,4 in pyridine. The mixture was warmed on the water bath for 30 minutes, cooled, and diluted with 2 *N* hydrochloric acid. The precipitate which separated was collected, washed with a solution of sodium carbonate, then with water, and dried. The material was only partly soluble in ether. It was crystallized from acetone. The solid which separated upon cooling was identical with the bis-*p*-nitrobenzoate prepared from 2-butenediol-1,4. It melted at 177-178° and the melting point was not depressed by admixture with the bis-*p*-nitrobenzoate of an authentic sample of 2-butenediol-1,4.

Anal. Calc'd for $C_{18}H_{14}N_2O_8$: C, 56.0; H, 3.7; N, 7.3.

Found: C, 55.8; H, 3.6; N, 7.4.

The washings from the various crystallizations were combined and evaporated to dryness. The solid material thus obtained was crystallized from a mixture of ether and benzene. It melted at 84-86.5°. It is believed to be a somewhat impure mixture of the bis-*p*-nitrobenzoates of the 2-butenediol-1,4 and 1-butenediol-3,4.

Anal. Calc'd for $C_{18}H_{14}N_2O_8$: C, 56.0; H, 3.7.

Found: C, 55.8; H, 4.4.

SUMMARY

1. It has been demonstrated that *tert*-butyl hydroperoxide is decomposed by cobalt salts (acetate or naphthenate) to give free $RO_2\cdot$ radicals.

2. The free $RO_2\cdot$ radicals add to olefins. With octene-1, octenal and *tert*-butyl 2-octenyl peroxide are formed; with cyclohexene, cyclohexenone and cyclohexenyl-*tert*-butyl peroxide are formed, and with butadiene 1,4-di(*tert*-butylperoxy)butene-2 and 3,4-di(*tert*-butylperoxy)butene-1 are the major products.

CHICAGO 37, ILLINOIS

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- (3) Cf. HUFFORD, TARBELL, AND KOSZALKA, *J. Am. Chem. Soc.*, **74**, 3014 (1952).