[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1]]

Preparation and Properties of Some Allylic Peroxides

BY TOD W. CAMPBELL AND GALVIN M. COPPINGER

Allyl-*t*-butylperoxide and cyclohexenyl-*t*-butylperoxide have been synthesized and their properties described. It has been shown that their thermal decomposition yields *t*-butanol and the appropriate unsaturated carbonyl compound in good over-all yield. Attempts to prepare benzyl-*t*-butylperoxides resulted in the production of aromatic aldehydes in fair yield.

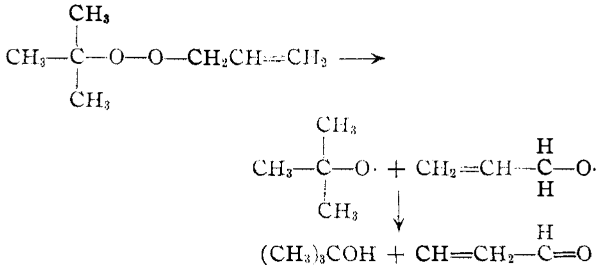
The important and complex problem of the autoxidation of naturally occurring olefinic substances, such as carotene, unsaturated fatty acids, etc., has been the subject of considerable work.[2-5] The experimental difficulties involved in working with most naturally occurring olefins are great, and a number of efforts have been made to avoid these problems by working with model compounds.[6]

In connection with a program on the chemistry of model organic peroxides derived from olefins structurally related to carotene, allyl-*t*-butylperoxide and cyclohexenyl-*t*-butylperoxide have been synthesized and some of their properties studied.

These peroxides, prepared by allowing an organic halide to react with the potassium salt of *t*-butylhydroperoxide[7,8]

$$[t\text{-}C_4H_9OO]^- + RBr \longrightarrow Br^- + t\text{-}C_4H_9OOR$$

are relatively stable and may be distilled at reduced pressure, but decompose slowly at room temperature or more rapidly at elevated temperatures, into *t*-butyl alcohol and an unsaturated carbonyl compound. It is assumed that the decomposition involves intermediate alkoxy radicals[9] which then "disproportionate" by transfer of a hydrogen atom from the allyloxy radical to the *t*-butoxy radical. This may be represented formally by the equation



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-CH_2CH{=}CH_2 \longrightarrow$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O\cdot + CH_2{=}CH-\underset{H}{\overset{H}{C}}-O\cdot$$

$$\downarrow$$

$$(CH_3)_3COH + CH{=}CH_2-\overset{H}{C}{=}O$$

although the hydrogen transfer probably does not require collision of two radicals, as indicated, since the radical, once formed, may remove hydrogen from the α-methylene group of the unreacted peroxide.[10]

Attempts to prepare and isolate benzyl *t*-butylperoxides by the same method were unsuccessful. The intermediate peroxides decomposed spontaneously to give aromatic aldehydes in fair yield.

$$[ArCH_2OOC_4H_9\text{-}t] \longrightarrow t\text{-}C_4H_9OH + ArCHO$$

Experimental

***t*-Butylhydroperoxide.**—Commercial *t*-butylhydroperoxide, obtained from the Lucidol Corporation,[11] was distilled and the fraction boiling at 46° (30 mm.) was used in the experiments.

Halides.—Allyl bromide and certain substituted benzyl halides were obtained from Eastman Kodak Co.[11] and redistilled. The 3-bromocyclohexene-1 was prepared by the method of Ziegler.[12] Mesitylene and tetralin were chloromethylated according to standard methods.[13]

Potassium *t*-Butylperoxide.[7,8]—The solid potassium salt of *t*-butylhydroperoxide was made by mixing a slight excess of *t*-butylhydroperoxide with an aliquot of 5–6 *M* methyl alcoholic potassium hydroxide, followed by evaporation *in vacuo*. The solid analyzed iodometrically for better than 90% of the required compound. In most of the experiments described, isolation of the solid salt was not carried out; the solution described above, about 5–6 *M* in potassium salt, was used directly in reaction with the halides.

The potassium salt appears to be of somewhat dubious stability, especially in concentrated solutions. The following experiences indicate that due caution should be exercised at all times when working with this substance.

(1) Occasionally a preparation of the salt in an alcohol at room temperature began to boil spontaneously, with evolution of gas (oxygen?). The residue contained no peroxide. (2) The solid salt, when dry, appeared to be perfectly stable at the boiling point of toluene; however, in one experiment the toluene was boiled off gradually until the amount was insufficient to prevent superheating. A mild explosion occurred with excessive carbonization. The toluene remaining was partially oxidized to benzoic acid. (3) A dilute aqueous solution of potassium *t*-butylperoxide on dropwise addition of bromine, effervesced. Shortly after, a sharp explosion and a flash of light occurred at the mouth of the flask. (4) Methanolic solutions of potassium *t*-butylperoxide lose all of their active (peroxidic) oxygen content on boiling for 30 minutes.

Allyl-*t*-butylperoxide.—To potassium *t*-butylperoxide (0.48 mole) in 100 ml. methyl alcohol and 400 ml. acetone was added in one portion 60 g. of allyl bromide, with efficient cooling of the flask. After the vigorous reaction had subsided, 1.5 l. of water was added and the mixture extracted with four 100-cc. portions of benzene. The extract was dried with magnesium sulfate and distilled. Allyl-*t*-butylperoxide is a liquid, b.p. 55° (75 mm.), yield 28.5 g. (46%); $n^{25}D$ 1.4015; $d^{25}{}_4$ 0.8262; $MR^{25}D$ 38.3. Calcd. $MR^{25}D$ 37.9.[14]

Anal.[15] Calcd. for $C_7H_{14}O_2$: C, 64.6; H, 10.8. Found: C,[16] 63.9; H, 11.1.

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[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] D. Swern, J. T. Scanlan and H. B. Knight, *J. Am. Oil Chem. Soc.*, **25**, 193 (1948).

[3] C. E. Frank, *Chem. Revs.*, **46**, 155 (1950).

[4] R. I. Hunter and M. R. Krakenberger, *J. Chem. Soc.*, 1 (1947).

[5] Faraday Society Discussion, "Labile Molecules," 1946.

[6] (a) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1574 (1948). (b) C. H. Farmer, A. Sundralingam and D. Sutton, *ibid.*, 121 (1942). (c) H. Hock, S. Lang, *et al.*, *Ber.*, **71**, 1430 (1938); **72**, 1562 (1939); **75**, 300, 1051 (1942); **76**, 169, 1130 (1943); **77**, 257 (1944); **83**, 227, 238 (1950).

[7] F. H. Dickey and E. R. Bell, U. S. Patent 2,403,709, July 9, (1946).

[8] N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 206 (1946).

[9] J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 88 (1949).

[10] Compare F. F. Rust, F. H. Seubold and W. R. Vaughan, *ibid.*, **72**, 338 (1950).

[11] Mention of this product does not imply that it is endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

[12] K. Ziegler, *et al.*, *Ann.*, **551**, 120 (1942).

[13] R. C. Fuson and C. H. McKeever, *Org. Reactions*, **1**, 63 (1942).

[14] N. A. Milas, D. M. Surgenor and L. H. Perry, THIS JOURNAL, **68**, 1617 (1946).

[15] Carbon is low because of unavoidable explosive decomposition in tube.

Thermal Decomposition of Allyl-*t*-butylperoxide.—Allyl-*t*-butylperoxide (7.0 g.) was heated for 72 hours at 60°, then the products distilled. The distillate, which all distilled below 85° at 760 mm., weighed 4.60 g. and reeked of acrolein. A polymeric residue (2.15 g.) remained in the distilling flask; this residue may be principally acrolein polymer. A sample of the distillate was hydrogenated over Adams catalyst; from the data, it was calculated that the distillate was about 25% acrolein and 75% *t*-butyl alcohol. From 1.0 g. of distillate, hydrogenated in ethanol, was obtained 0.8 g. of propionaldehyde 2,4-dinitrophenylhydrazone (about 90%). Final confirmation of the composition of the distillate was made by comparing its infrared spectrum with that of a synthetic sample of 25% acrolein and 75% *t*-butyl alcohol. From these data it appears that the decomposition of allyl-*t*-butylperoxide to acrolein and *t*-butyl alcohol is smooth and nearly quantitative. Formaldehyde was looked for carefully and could not be found among the decomposition products.

Cyclohexenyl-*t*-butylperoxide.—This compound was made as above, with the substitution of 92 g. of 3-bromocyclohexene for the allyl bromide. The product, obtained in 45% yield, was a pleasant-smelling oil, b.p. 63° (6 mm.).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.6. Found: C, 70.4; H, 10.7.

Decomposition of Cyclohexenyl-*t*-butylperoxide.—The peroxide (4.0 g.) was heated slowly at 760 mm. to boiling and held there 30 minutes. Decomposition was smooth. The product was distilled up to 160°. The residue, a black tar, weighed 1.1 g. The distillate consisted of 1.5 g. of *t*-butyl alcohol and about 1.3 g. of cyclohexenone, which was hydrogenated to cyclohexanone and identified in this form as its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 155°.

Reaction of Potassium *t*-Butylperoxide with Benzyl Halides.—The reaction of the salt and benzyl halides according to the technique described above does not give an isolable intermediate peroxide. Instead, the corresponding aromatic aldehyde is obtained in moderate yield, along with *t*-butyl alcohol. Also obtained are traces of the aromatic acid, though no substituted benzyl alcohol could be isolated. The data for several substituted halides are listed in Table I.

TABLE I

PREPARATION OF ALDEHYDES FROM SUBSTITUTED BENZYL HALIDES

Substd. benzyl halide	Temp., °C.	Time, hr.	Yield of corresponding aldehyde,[a] %	B.p. or m.p., °C., of aldehyde
Benzyl chloride	Reflux	8	23	B. 179
p-Nitrobenzyl chloride	Reflux	3	32	M. 104–5
2-Chloromethyltetralin	Reflux	5	56	B. 126 (10 (mm.)[b]
o-Chlorobenzyl chloride	40	1	74	B. 209
Chloromethylmesitylene	Reflux	5	58	B. 109 (24 mm.)

[a] The aldehydes were characterized as their known 2,4-dinitrophenylhydrazones. [b] 2,4-Dinitrophenylhydrazone, m. p. 199–200°. *Anal.* Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.9; H, 4.69. Found: C, 60.1; H, 4.84.

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Kinetics of the Reaction between Potassium *t*-Butylperoxide and Organic Halides

BY GALVIN M. COPPINGER AND TOD W. CAMPBELL

The kinetics of the reaction between three organic halides and potassium *t*-butyl peroxide has been studied at 30 and 50° in methanol solution. The reaction was found to be second-order, with an energy of activation of 21–23 kcal./mole.

In view of the relatively facile production of organic peroxides by a typical displacement reaction[2] it appeared reasonable to suspect that the reaction of the potassium salt of *t*-butyl hydroperoxide and substituted benzyl halides[2a] to give aromatic aldehydes and *t*-butyl alcohol progressed *via* bimolecular mechanism to form an unstable intermediate peroxide. This then decomposed to an aromatic aldehyde and *t*-butyl alcohol

$$ArCH_2Cl + {}^-OOC_4H_9\text{-}t \longrightarrow ArCH_2OOC_4H_9\text{-}t + Cl^-$$

$$ArCH_2OOC_4H_9\text{-}t \longrightarrow t\text{-}C_4H_9OH + ArCHO$$

This reaction has been investigated to confirm the order of the first reaction and to determine the velocity constants and the energy of activation for the reaction of *o*-chlorobenzyl chloride[2a] and potassium *t*-butyl peroxide. In addition, the kinetics of the reaction between the peroxide salt and certain other halides were investigated for comparative purposes.

The data collected are summarized in Table I. Since the data indicate that the reaction is clearly second-order, a bimolecular displacement of halogen from the halide is indicated, implying that an intermediate peroxide must exist.

Calculation of the energies of activation for the various reactions (Table I) shows that they are of the same order of magnitude as for the corresponding displacement of halogen by an alkoxide ion (Table II) to give an ether.[3–6]

Experimental

Materials.—Standard solutions of potassium *t*-butyl peroxide (PBP) were prepared by addition of *t*-butyl hydroperoxide (b.p. 46°, 30 mm.) in 15% excess to a standard methyl alcoholic solution of potassium hydroxide. The halides were redistilled commercial products; methanol was reagent grade.

Procedure A.—Freshly prepared solutions of PBP in methanol were allowed to reach the experimental temperature in a thermostated bath and added to a weighed sample of the halide in a volumetric flask. The initial concentration of PBP was checked by titration of a blank at the reaction temperature and corrected for the volume of halide used. The course of the reaction was followed by removing aliquots and titrating the remaining PBP with standard acid, using phenolphthalein indicator. The aliquots were pipetted into 100 ml. of ice-water to which had been added an approximate acid titer, in order to quench the reaction.

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(1) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) (a) T. W. Campbell and G. M. Coppinger, THIS JOURNAL, **73**, 1849 (1951); (b) F. H. Dickey and E. P. Bell, U. S. Patent 2,403,709 (July 9, 1946).

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