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The Vapor Phase Decomposition of *t*-Butyl Hydroperoxide and Reactions of the *t*-Butylperoxy Radical

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Introduction

Although the importance of peroxides, peroxy radicals and oxy radicals in free radical processes such as oxidation, polymerization, inhibition of certain chain reactions, and thermal decompositions is well-known, the relationships between these radicals are not completely understood. The formation of alkyl hydroperoxides, demonstrated in the interaction of many reactive hydrocarbons with oxygen, is an example of the abstraction of a hydrogen atom by an alkylperoxy radical.[1] Equally well-known are the cleavage of dialkyl peroxides[2] and the reactions of the alkoxy radicals produced.[3] The formation of alkylperoxy radicals by the reaction of alkyl radicals with oxygen has been advanced not only as a mode of inhibition of polymerization and chlorination processes but also as the initial step in hydrocarbon oxidations.[4] The formation of alkylperoxy radicals by free radical attack on alkyl hydroperoxides has now been demonstrated. Conversion of peroxy radicals to alkoxy radicals in the presence and absence of oxygen has been proved, and an intermediate dialkyl peroxide has been isolated in the latter case but not in the former. A mechanism for the decomposition of *t*-butyl hydroperoxide has been formulated to include the processes described.

Results and Discussion

Although pure *t*-butyl hydroperoxide is relatively stable in the gas phase at 195°—only 10% decomposition in a two-minute residence time—the addition of di-*t*-butyl peroxide accelerates the chain decomposition which consumes over 90% of the hydroperoxide when the mole fraction of dialkyl peroxide exceeds 0.34 (Table I). The existence of a chain reaction (in which, as would be expected, the chain length is greater at the lower concentrations of di-*t*-butyl peroxide) necessitates free radical attack on the hydroperoxide. Further requirements for the reaction may be deduced from the product distribution for the experiments reported in Table I. The fact that a substantial yield of formaldehyde is produced at the lower radical concentrations, even though more than enough alkyl radicals are formed to convert it all to carbon monoxide, indicates that some species present can compete successfully with formaldehyde as a hydrogen atom donor. The absence of ethane, the product of methyl radical association, in the experiments at low radical concentration recalls the failure of alkyl radicals to combine in the presence of oxygen,[5] and suggests that some highly reactive intermediate is present which is readily attacked by alkyl free radicals. These requirements would be met if the hydrogen–oxygen bond strength in *t*-butyl hydroperoxide is of the order of 80 kcal. mole,[6] so that the peroxide would be easily attacked. The resultant peroxy radical, resembling oxygen, should be capable of reacting rapidly with alkyl radicals.

TABLE I

DECOMPOSITION OF *t*-BUTYL HYDROPEROXIDE–DI-*t*-BUTYL PEROXIDE MIXTURES AT 195°

Residence time, *ca.* 2 min.

DTBP (mole per cent.)	5	22	34	42	50
TBHP reacted (per cent.)	27	65	90	94	96
$\frac{\text{Moles TBHP reacted}}{\text{Moles DTBP decomposed}}$	5.2	2.8	2.2	1.6	1.1
Product	Yield in moles/100 moles of input CH_3[a]				
CH_3OH	29.6	[b]	[b]	[b]	27.1
CH_2O	12.4	[b]	[b]	[b]	1.1
CO	1.7	1.8	6.0	7.2	6.4
CH_4	10.4	9.0	23.4	31.6	21.2
C_2H_6	0	0	16.3	27.6	38.9

[a] Input CH_3 taken as sum of moles of hydroperoxide reacted plus twice the moles of dialkyl peroxide reacted. [b] Not determined.

Removal of the peroxide hydrogen atom by radical attack and the accompanying formation of a *t*-butylperoxy radical was readily demonstrated by mass spectrometric identification of methane-*d* in the product of the reaction of di-*t*-butyl peroxide with an equimolar amount of *t*-butyl deuteroperoxide (containing 63 mole per cent deuterium attached to oxygen) in the gas phase at 195° (Table II).

$$CH_3\cdot + (CH_3)_3COOD \longrightarrow CH_3D + (CH_3)_3COO\cdot \quad (1)$$

The presence of methanol-*d* in the product tends to confirm this hypothesis, but is not in itself definitive since the possibility of vapor phase exchange between the deuteroperoxide and methanol is not to be excluded, although it is considered unlikely. Additional proof for the abstraction of hydrogen from the HO—O— group was the identification of ethane-*d* in the product of the reaction at 195° of the deuteroperoxide with di-*t*-amyl peroxide, a source of ethyl radicals.[2b]

Repetition of the experiment on a larger scale with hydro- rather than deuteroperoxide provided evidence for the mechanism of disappearance of peroxy radicals by the isolation of a 6% yield of ethyl *t*-butyl peroxide as well as appreciable amounts of products typical of ethoxy radical reactions, such as ethanol and acetaldehyde.

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[1] Hock and Lang, *Ber.*, **77**, 257 (1944), provide a typical example of this type of reaction in the oxidations of cumene and tetralin.

[2] (a) Milas and Surgenor, THIS JOURNAL, **68**, 205 (1946); (b) Raley, Rust and Vaughan, *ibid.*, **70**, 88 (1948); (c) Rust, Seubold and Vaughan, *ibid.*, **70**, 95 (1948).

[3] Rust, Seubold and Vaughan, *ibid.*, **72**, 338 (1950).

[4] Bates and Spence, *ibid.*, **53**, 1689 (1931); Jones and Bates, *ibid.*, **56**, 2285 (1934); Blaedel, Ogg and Leighton, *ibid.*, **64**, 2500 (1942).

[5] Raley, Porter, Rust and Vaughan, *ibid.*, **73**, 15 (1951).

[6] Gorin, *J. Chem. Phys.*, **7**, 256 (1939), has proposed a maximum value of 78 kcal./mole for the dissociation $H_2CO \longrightarrow H + HCO$ from consideration of formaldehyde photolysis in the presence of iodine vapor.

TABLE II

REACTION OF *t*-BUTYL DEUTEROPEROXIDE (63%) WITH DI-*t*-BUTYL PEROXIDE AT 195°

Residence time, 2 min.; mole ratio of reactants, 1

Product	Yield in moles/100 moles of available *t*-BuO[a]	CH₃[b]	O[c]	D[d]
$(CH_3)_2CO$	89.0		66.7	
$(CH_3)_3COH$	2.5		1.9	
$(CH_3)_3COD$	4.0		3.0	19.1
CH_3OH		8.3	5.6	
CH_3OD		13.1	8.8	55.6
CH_3CH_3[e]		44.9		
CH_3H		20.2		
CH_3D		3.7		15.7
C_2H_4		1.8		
CH_2O		0.9	0.7	
CO		7.0	4.8	
H_2O[f]			2.6	?
Total	95.5	99.9	94.1	90.4 + ?

[a] Available *t*-butoxy radicals taken as sum of moles of decomposed *t*-butyl hydroperoxide and twice the moles of decomposed di-*t*-butyl peroxide. [b] Available methyl radicals taken equal to moles of acetone produced. [c] Available moles of oxygen taken equal to total moles of peroxide decomposed. [d] Moles/100 moles of deuterium atoms introduced. [e] Contains <0.1% deuterium. [f] Insufficient water was formed for isolation and analysis of its deuterium content.

The dialkyl peroxide was identified by its refractive index and by the congruence of its infrared spectrum with that of an authentic sample prepared from potassium *t*-butyl peroxide and ethyl sulfate.[3] It is evident that ethyl radicals were converted to ethoxy radicals by reaction with alkylperoxy radicals, possibly through an intermediate dialkyl peroxide.

$$(CH_3)_3COO\cdot + C_2H_5\cdot \longrightarrow (CH_3)_3COOC_2H_5 \longrightarrow (CH_3)_3CO\cdot + C_2H_5O\cdot \tag{2}$$

The importance of dialkyl peroxide formation was tested by lowering the reaction temperature to 180° at which point only 65% of the di-*t*-amyl peroxide decomposed. On the assumptions that every successful collision of an ethyl- and a *t*-butyl peroxy radical yielded ethyl *t*-butyl peroxide, and that the half-life of that peroxide is approximately the same as that of di-*t*-amyl peroxide,[2b] the maximum yield of the ethyl derivative must be greater than 23% of the input di-*t*-amyl peroxide. The minimum value of 23% would be achieved if all the ethyl *t*-butyl peroxide were formed at the reactor inlet. Since in reality it is formed throughout the length of the reactor, its residence time will be less than that of the di-*t*-amyl peroxide and the yield will be greater. The actual yield was 30%, indicating that the most important mechanism for the formation of alkoxy radicals from alkyl and alkylperoxy radicals is

$$R\cdot + R'OO\cdot \longrightarrow ROOR' \longrightarrow RO\cdot + R'O\cdot \tag{3}$$

The information derived from the preceding experiments makes possible the formulation of a mechanism which accounts for the characteristics of the reaction as well as for all the products.

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \tag{4}$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot \tag{5}$$

$$R\cdot + (CH_3)_3COOH \longrightarrow RH + (CH_3)_3COO\cdot \tag{6}$$

$$CH_3\cdot + (CH_3)_3COO\cdot \longrightarrow (CH_3)_3COOCH_3 \tag{7}$$

$$(CH_3)_3COOCH_3 \longrightarrow (CH_3)_3CO\cdot + CH_3O\cdot \tag{8}$$

$$(R = (CH_3)_3CO\cdot,\ CH_3\cdot,\ CH_3O\cdot)$$

Further reactions of the alkoxy radicals have been discussed in a previous publication.[3]

Unimolecular decomposition of the hydroperoxide

$$(CH_3)_3COOH \longrightarrow (CH_3)_3CO\cdot + HO\cdot \tag{9}$$

must occur only to a limited extent, since so small a fraction of the peroxide decomposes under these conditions without added initiator. Abstraction of hydrogen from copresent molecules or radicals by hydroxyl is probably responsible for the small amount of water found. Methanol formation by combination of a hydroxyl with a methyl radical is improbable according to the data of Table I, which shows that the yield of methanol is appreciable under conditions in which radical combination, as judged by ethane formation, is negligible. The association of a methyl with a hydroxyl radical seems no more probable than combination with another methyl radical, so that abstraction of a hydrogen atom from some donor molecule or radical by a methoxy radical is the most plausible mechanism in this system. This over-all mechanism (5 to 9) will apply equally well for the decomposition of pure *t*-butyl hydroperoxide, which would thus be a composite of unimolecular and chain processes.

Although the conversion of an alkyl and an alkylperoxy radical to two alkoxy radicals has been shown to involve an intermediate dialkyl peroxide, there is no evidence that such an intermediate is present in low temperature hydrocarbon oxidations, in which it seems certain that all alkyl radicals combine immediately with oxygen.[5] Thus, in such systems alkylperoxy radicals must be converted to alkoxy radicals by some means other than reaction with an alkyl radical. When sufficient oxygen was added to the *t*-butyl hydroperoxide–di-*t*-amyl peroxide system at 180° to react with all the alkyl radicals which could be formed, the products of reaction of ethoxy and methoxy radicals were present, but neither ethyl *t*-butyl nor diethyl peroxides could be detected. Thus, from 0.112 mole of *t*-butyl hydroperoxide, 0.180 mole of di-*t*-amyl peroxide and 0.349 mole of oxygen, there resulted 0.374 mole of acetone, 0.025 mole of methyl ethyl ketone, 0.024 mole of *t*-butyl alcohol, 0.190 mole of ethanol, 0.043 mole of methanol, and lesser amounts of acetic and formic acids, carbon dioxide and carbon monoxide. The amounts of hydrocarbons, methane through butane, formed by reaction of alkyl radicals with one another or with hydrogen atom donors were so small as to make even qualitative detection uncertain, in agreement with the conclusion that alkyl radical reactions other than combination with oxygen can be neglected. It is apparent that alkyl radicals were converted to alkylperoxy and then to alkoxy radicals, but not through an intermediate dialkyl peroxide as is the case in the absence of oxygen.

$$(CH_3)_3COO\cdot + C_2H_5OO\cdot \longrightarrow (CH_3)_3CO\cdot + C_2H_5O\cdot + O_2 \tag{10}$$

The exact details of this transformation cannot be specified at present.

Experimental

Materials.—*t*-Butyl hydroperoxide was distilled through a four-foot helices-packed column from a commercial product (Lucidol Corp.); b. p. 13° (3 mm.), f. p. 5.5°, n^{20}D 1.4010.

t-Butyl deuteroperoxide was prepared by equilibrating 99.8% *t*-butyl hydroperoxide with an equimolar amount of 99.8% deuterium oxide for one week. The water was removed *in vacuo* as its azeotrope with benzene and the peroxide was fractionated to yield a product (b. p. 22° (8 mm.), n^{20}D 1.4013) which was shown to be 99.6% pure by iodometric titration. Infrared absorption analysis showed the purified peroxide to contain 63 ± 1 mole per cent. O–D bonds. The di-*t*-butyl peroxide was a commercial product (Shell Chemical Corporation). Di-*t*-amyl peroxide was prepared from *t*-amyl alcohol and hydrogen peroxide[2a]; b. p. 38–39° (9 mm.), n^{20}D 1.4085.

Procedure.—The mixture of peroxides was metered by a rotameter through a steam-jacketed preheater into a one-liter Pyrex vessel (70 mm. inside diameter) heated by a refluxing vapor-bath. A differential flowmeter was used to admit one and a half moles of diluent nitrogen per "mole" of the peroxide mixture to moderate the reaction. In the oxidation experiment, oxygen was substituted for part of the nitrogen, the total input flow remaining constant. The residence time in each experiment was approximately two minutes based on gaseous input volume. The products were passed successively through receivers held at 25, 0 and −78°. The non-condensable gas was collected over brine and analyzed both by Orsat and mass spectrometric methods. The liquid product was fractionated through an efficient helices-packed analytical column; the composition of the fractions agreed well with that of the crude product as determined by the following methods. The accuracy of these analyses is illustrated by the product balance presented in Table II which is typical of the results obtained in the other experiments. Total alcohol was determined by a modified procedure based on that described by Skrabal[7] and Schmidt.[8] *t*-Butyl alcohol was taken as the difference between that value and the methanol which was determined by a procedure similar to that of Elving and Warshowsky.[9] Total carbonyl was determined by the procedure of Mitchell, *et al.*[10] Acetone was taken as the difference between the total carbonyl and the formaldehyde which was determined polarographically.[11] Water was determined with the Karl Fischer reagent according to the procedure of Bryant, *et al.*[12]

The deuterium content of alcohols was determined by treatment of the appropriate distillation fractions with lithium aluminum hydride followed by mass spectrometric analysis of the evolved gas for hydrogen and deuterium.

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Summary

t-Butyl hydroperoxide readily loses a hydrogen atom upon free radical attack to yield a *t*-butylperoxy radical. In the absence of oxygen, these radicals combine with alkyl radicals to form dialkyl peroxides which decompose to yield alkoxy radicals. With these entities—alkylperoxy, alkoxy and alkyl radicals—as chain carriers, the hydroperoxide decomposes by a chain mechanism in the gas phase, the more rapidly when a less stable initiator such as di-*t*-butyl peroxide is present. Alkoxy radicals are still formed in the reaction when excess oxygen is added to the system, but no longer through an intermediate dialkyl peroxide. The exact mechanism of this transformation is unknown.

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[7] Skrabal, *Z. anal. Chem.*, **119**, 222 (1940).

[8] Fischer and Schmidt, *Ber.*, **59**, 679 (1926).

[9] Elving and Warshowsky, *Ind. Eng. Chem.*, *Anal. Ed.*, **19**, 1006 (1947).

[10] Mitchell, Smith and Bryant, THIS JOURNAL, **63**, 573 (1941).

[11] Whitnack and Moshier, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 496 (1944).

[12] Bryant, Mitchell and Smith, THIS JOURNAL, **62**, 3504 (1940).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

The Configuration of the Camphenilyl Amines*

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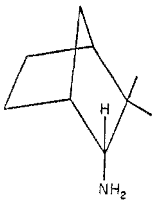
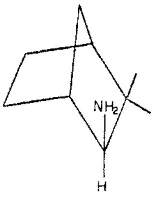
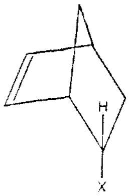
As part of a study of terpene derivatives, it became desirable to determine the configuration of the two camphenilyl amines (I and II) which have been reported by Hückel[1] with, however, no suggestion of relative configuration.



I



II

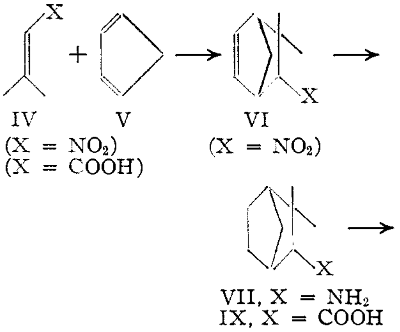


III

The methods most generally useful for the unambiguous determination of relative configuration, *e. g.*, ring closure, or *meso* character of suitable derivatives, were not applicable in this case. Hence the basis used in the present work was the fact that the Diels–Alder synthesis leads predominantly to compounds of the *endo* series (III) in all simple cases.[2]

The condensation of cyclopentadiene with two appropriately substituted dienophiles was therefore investigated. The scheme of these syntheses is shown in Chart I.

CHART I



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* Presented before the 118th meeting of the American Chemical Society, Chicago, Illinois, September 3-8, 1950.

[1] Hückel and Tappe, *Ber.*, **69**, 2769 (1936).

[2] Alder and Stein, *Angew. Chem.*, **50**, 510 (1937); for exception, see Woodward and Baer, THIS JOURNAL, **66**, 645 (1944), and Alder and Ruhrmann, *Ann.*, **566**, 1 (1950).