TABLE III

PRODUCTS OF PHOTOLYSIS OF PURE DI-*t*-BUTYL PEROXIDE IN LIQUID PHASE

Time, 212 hours; temp., *ca.* 17°; illumination, type AH-5 lamp, "stripped," *ca.* 10 cm. distant; peroxide charged, 86.5 g.; recovered, 66.9 g.

Product	Moles per 100 moles peroxide decomposed	Moles per 100 moles *t*-butoxy units
t-Butyl alcohol	109.0	54.5
Acetone[a]	7.2	3.6
Isobutylene oxide	41.0	20.5
Polymer[b]	36.6	18.3
Total	193.8	96.9

[a] 2.8 moles of methane and 0.1 mole of ethane were found. [b] "Moles of polymer" is given as moles of isobutylene oxide units since a combustion indicated the empirical formula of the polymer to be $C_{4.8}H_{7.7}O$.

Acknowledgment.—The authors are indebted to the Analytical and Spectroscopic Departments of this Company for the analytical data contained herein.

Summary

1. When pure di-*t*-butyl peroxide is decomposed by gentle refluxing at *ca.* 110°, isobutylene oxide is formed as a major product.

2. Isobutylene oxide is also formed when the pure liquid peroxide is photochemically decomposed at *ca.* 17°.

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[CONTRIBUTION FROM THE EMERYVILLE LABORATORIES OF SHELL DEVELOPMENT COMPANY]

Decompositions of Di-*t*-alkyl Peroxides. V. Relative Stabilities of Alkoxy Radicals Derived from Unsymmetrical Dialkyl Peroxides

BY FREDERICK F. RUST, FRANK H. SEUBOLD, JR., AND WILLIAM E. VAUGHAN*

Studies in these Laboratories[1] have shown that when di-*t*-alkyl peroxides are decomposed in the presence of organic solvents, the primary products, *t*-alkoxy radicals, may undergo either of two reactions to varying extents: (1) decomposition to an alkyl radical and a ketone, or, (2) abstraction of a hydrogen atom from the solvent to yield an alcohol. In reaction (1) the largest group attached to the tertiary carbon atom is preferentially lost as a radical. These two competing reactions—structure loss *vs.* structure retention—afford a ready method for comparing the relative stabilities of a series of alkoxy radicals in which primary, secondary and tertiary alkyl groups are involved. This paper describes the results obtained by decomposing a series of unsymmetrical alkyl *t*-butyl peroxides under uniform conditions in the presence of cyclohexene. The data indicate that under the experimental conditions the following order of stability obtains

$$CH_3O\cdot > CH_3{-}CH_2O\cdot > CH_3CH_2CH_2{-}CH_2O\cdot > CH_3{-}CH(CH_3)O\cdot > (CH_3)_2CH{-}CH_2O\cdot \approx CH_3{-}C(CH_3)_2O\cdot$$

Experimental

Materials.—Cyclohexene was chosen as the hydrogen atom donor because it possesses a suitable vapor pressure and is sufficiently reactive to give an adequate yield of alcohol with even the least stable alkoxy radical, $(CH_3)_3CO$. The samples used were peroxide-free and freshly distilled (b. p. 83.3°, lit. 83.19°; n^{20}_{D} 1.4465, lit. 1.4467).

The peroxides for which data are given in Table I were prepared as follows:

Methyl *t*-Butyl Peroxide.—One mole of dimethyl sulfate was added over a period of three hours with vigorous stirring at 25° to an aqueous suspension containing 1.0 mole of potassium *t*-butyl peroxide. After standing overnight, the mixture was diluted with water and the organic phase separated, dried with potassium carbonate, and vacuum distilled. This compound is rather hazardous; it can be exploded by impact and is highly inflammable. If dropped on a hot plate, it bursts into flame, evaporates, and the vapors re-ignite at a distance of *ca.* 50 cm. above the plate. The other peroxides are considerably more stable.

Ethyl *t*-Butyl Peroxide.—One-half mole of diethyl sulfate was shaken for two hours at 25° with an aqueous suspension of 1.0 mole of potassium *t*-butyl peroxide. Water was added to separate the organic phase which was water washed, dried with potassium carbonate, and vacuum distilled.

Isopropyl *t*-Butyl Peroxide.[2]—One mole of potassium *t*-butyl peroxide was added to 1.5 moles of isopropyl bromide in 150 cc. of isopropyl alcohol at 25°, and the mixture was allowed to stand for a week with occasional shaking. The solution was washed with 4 l. of water and then steam distilled to obtain isopropyl *t*-butyl peroxide (0.33 mole) as distillate at 81-82° (33% yield). An improved yield of 38% was obtained by stirring an aqueous slurry of 0.54 mole of potassium *t*-butyl peroxide with 0.54 mole of diisopropyl sulfate (prepared from sulfuryl chloride and sodium isopropoxide) for twenty-four hours. The product was thoroughly water washed, steam distilled, and finally vacuum distilled.

Isobutyl *t*-Butyl Peroxide.—One mole of sodium *t*-butyl peroxide was heated at 60° for forty-six hours with an isopropyl alcohol solution containing 1.0 mole of isobutyl bromide, and the product recovered as above.

***n*-Butyl *t*-Butyl Peroxide.**—One mole of *n*-butyl bromide was stirred for forty-eight hours with an aqueous slurry of 1.0 mole of potassium *t*-butyl peroxide and the product recovered as above.

Di-*t*-butyl Peroxide.—Method of Vaughan and Rust.[3]

Method.—Cyclohexene solutions of each peroxide in *ca.* 33 mole per cent. concentration were metered by a microrotameter through a steam-jacketed vaporizer into a 50-mm. i. d. Pyrex tube (1000-cc. volume) held at 195° by a refluxing vapor-bath. Residence times in the reactor were approximately two minutes (based on gaseous input volume) and in all cases virtually all of the peroxide was decomposed. The effluent was passed successively through traps held at *ca.* 25, 0 and −78°. The non-condensable gas was collected over salt water and analyzed both by

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(1) Raley, Rust and Vaughan, THIS JOURNAL, **70**, 1336 (1948).

(2) Dickey and Bell, U. S. Patent 2,403,709 (July 9, 1946).

(3) Vaughan and Rust, U. S. Patent 2,403,771 (July 9, 1946).

TABLE I

PROPERTIES OF ALKYL *t*-BUTYL PEROXIDES, R—OO-*t*-C_4H_9

		Analyses, %w.										
	Yield,	C		H		Mol. wt.[a]		B. p.,		F. p.,		
R	%	Found	Theory	Found	Theory	Found	Theory	°C.	Mm.	°C.	n^{20}_D	d^{20}_4
CH_3	80+	57.8	57.7	11.7	11.5	113	104	23	119	−102.1	1.3761	0.811
CH_3CH_2	80–85	61.1	61.0	12.1	11.9	128	118	35	84	−83.1	1.3840	.809
$(CH_3)_2CH$	38	63.4	63.6	12.2	12.1	140	132	52	125	Glass	1.3864	.801
$CH_3(CH_2)_3$	29	65.4 65.5	65.8	12.4 12.4	12.3	157	146	52	30	Glass	1.4001	.819
$(CH_3)_2CHCH_2$	30	66.1 65.9	65.8	12.7 12.7	12.3	148	146	53	50	−67.7	1.3959	.809
$(CH_3)_3C$	100	65.0 65.0	65.8	12.3	12.3	147	146	70	197	−40.0	1.3890	.794
								111	760			

[a] Cryoscopic (benzene).

Orsat and mass spectrometric methods. The contents of the traps were carefully fractionated through an efficient analytical column packed with glass helices. The composition of these fractions was in agreement with the gross analysis of the crude liquid product for primary or secondary and tertiary alcohol, total carbonyl and aldehyde by conventional methods. The accuracy of these determinations was found to be satisfactory by analysis of synthetic samples.

Results and Discussion

The results of a single run, the decomposition of isopropyl *t*-butyl peroxide, are given in Table II to illustrate the precision of the experiments.

TABLE II

ISOPROPYL *t*-BUTYL PEROXIDE–CYCLOHEXENE AT 195° MATERIAL BALANCE

Peroxide reacted = 0.349 − 0.033 = 0.316 mole

Component	Mole	*t*-Butoxy[a]	Isopropoxy[a]	Methyl[b]
$(CH_3)_2CO$	0.294	82.0[c]	11.1[c]	
$(CH_3)_3COH$	.019	6.1		
$(CH_3)_2CHOH$	.059		18.7	
CH_3CHO	.112		35.4	
CO	.072		22.8	
CH_4	.330			64.1
C_2H_6	.058			22.5
Total		88.1	88.0	86.6

[a] Moles of product/100 moles of peroxide reacted. [b] Eq. of product/100 moles of available methyl radicals; the available methyl radicals are taken as the sum of the acetone derived from *t*-butoxy radicals plus the acetaldehyde plus twice the carbon monoxide. [c] The acetone distribution was calculated as follows: Let x = acetone derived from the isopropoxy radical; $0.294 - x$ = acetone derived from the *t*-butoxy radical. $(CH_3)_3COH + 0.294 - x = (CH_3)_2CHOH + CH_3CHO + CO + x$. Thus $0.019 + 0.294 - x = 0.059 + 0.112 + 0.072 + x$, and $x = 0.035$. Because of uncertainty in the determination of *t*-butyl alcohol, the value of x may vary by ± 25%. This variation will not, however, affect the placement of the isopropoxy radical in the stability series.

The cyclohexene was recovered quantitatively (103%), 28% appearing as the "dimer" and higher polymers. The products are probably formed as follows, once the peroxide has cleaved into the two alkoxy radicals

(A) from *t*-butoxy and its products

$$(CH_3)_3CO\cdot + C_6H_{10} \longrightarrow (CH_3)_3COH + C_6H_9\cdot \quad (1)$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot \quad (2)$$

$$CH_3\cdot + C_6H_{10} \longrightarrow CH_4 + C_6H_9\cdot \quad (3)$$

$$2C_6H_9\cdot \longrightarrow (C_6H_9)_2 \quad (4)$$

$$2CH_3\cdot \longrightarrow C_2H_6 \quad (5)$$

(B) from isopropoxy and its products

$$(CH_3)_2CHO\cdot + C_6H_{10} \longrightarrow (CH_3)_2CHOH + C_6H_9\cdot \quad (6)$$

$$(CH_3)_2CHO\cdot \longrightarrow CH_3CHO + CH_3\cdot \quad (7)$$

$$CH_3CHO + R\cdot \longrightarrow RH + CH_3CO\cdot \quad (8)$$

$$CH_3CO\cdot \longrightarrow CO + CH_3\cdot \quad (9)$$

$$(CH_3)_2CHO\cdot + R\cdot \longrightarrow (CH_3)_2CO + RH \quad (10)$$

Reactions (2), (7) and (9) depict C–C bond rupture. Equation (8) shows the attack of any radical R on acetaldehyde. (4) and (5) are termination steps involving the association of two radicals. Evidence for (4) is the isolation of dicyclohexenyl by distillation. It was not obtained pure, but was converted by hydrogenation to dicyclohexyl; b. p. 238–240°, n^{20}_D 1.4977 (lit., b. p. 238–239°, n^{20}_D 1.4975). Infrared examination of the product boiling in the range 80–130° at atmospheric pressure gave no evidence for methylcyclohexene, methylcyclohexane or dimethylcyclohexane. Most of the reacted cyclohexene remained as high boiling, semisolid bottoms, indicating a considerable degree of polymerization as a result of repeated attack.

The results of the decompositions of the several peroxides are summarized in Table III, which shows the yields of products of reaction of the radicals RO· by hydrogen atom abstraction, hydrogen atom loss or decomposition by C–C bond rupture.

We define the relative stability of an alkoxy radical as the ratio of the number of moles of alcohol produced by hydrogen atom abstraction by the radical (Table III, column 2) to the sum of that quantity and the number of moles of products of decomposition of the radical (Table III, column 4). The order of stability of the alkoxy radicals so calculated is qualitatively in accord with predictions based on known bond strengths in straight and branched chain hydrocarbons as shown in Table IV.

The possibility of intramolecular decomposition of the *n*- and isobutyl *t*-butyl peroxides to yield the appropriate butyraldehyde and *t*-butyl alcohol without the formation of the corresponding free butoxy radical was suggested by the large amount of *t*-butyl alcohol isolated. The high yield of this alcohol is not due to attack of a free alkoxy radical on the peroxide itself, since isopropyl *t*-butyl peroxide should be more reactive in this respect but still gives only a 6% yield of the tertiary

TABLE III

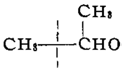
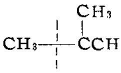
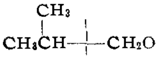
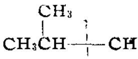
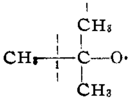
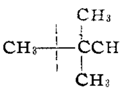
REACTIONS OF $(CH_3)_3COOR$ WITH CYCLOHEXENE AT 195°

RO	Yield in moles/100 moles of peroxide reacted: Products derived from RO: By H abstraction	By H loss	By decompn.	Products derived from *t*-BuO: By stabilization $(CH_3)_3COH$	By decompn. $(CH_3)_2CO$
CH_3O	76 CH_3OH	8 CH_2O 5 CO	........[a]	10	82
CH_3CH_2O	65 CH_3CH_2OH	8 CH_3CHO 8 CO[b]	10 CH_2O 1 CO[b]	12	80
$CH_3CH_2CH_2CH_2O$	30 $CH_3CH_2CH_2CH_2OH$	10 $CH_3CH_2CH_2CHO$ 16 CO[b]	26 CH_2O 3 CO[b]	20	69
$(CH_3)_2CHO$	19 $(CH_3)_2CHOH$	11 $(CH_3)_2CO$	35 CH_3CHO 23 CO[b]	6	82
$(CH_3)_2CHCH_2O$	6 $(CH_3)_2CHCH_2OH$	11 $(CH_3)_2CHCHO$ 14 CO[b]	61 CH_2O 6 CO[b]	22	67
$(CH_3)_3CO$	8 $(CH_3)_3COH$	....	94 $(CH_3)_2CO$	8	94

[a] Decomposition of $CH_3O\cdot$ according to $CH_3O\cdot \rightarrow CH_2O + H$ cannot exceed 0.2 mole/100 moles of peroxide reacted, the amount of hydrogen produced. [b] Carbon monoxide is formed by decomposition of aldehydes following free radical attack. The assumed distribution is based on the stability of formaldehyde as observed in the decomposition of ethyl *t*-butyl peroxide with no additive present.

TABLE IV

ESTIMATED BOND STRENGTHS AND OBSERVED STABILITIES OF ALKOXY RADICALS

RO radical	Reference hydrocarbon	C-C bond in reference hydrocarbon[a] (kcal./mole)	Relative stability
$H-\vert-CH_2O\cdot$	No C-C bond	..	..
$CH_3-\vert-CH_2O\cdot$	$CH_3-\vert-CH_2CH_3$	85.0	0.86
$CH_3CH_2CH_2-\vert-CH_2O\cdot$	$CH_3CH_2CH_2-\vert-CH_2CH_3$	80[b]	.51
 $CH_3-\vert-CH(CH_3)O\cdot$	 $CH_3-\vert-CH(CH_3)CH_3$	78.0	.25
 $(CH_3)_2CH-\vert-CH_2O\cdot$	 $(CH_3)_2CH-\vert-CH_2CH_3$	76[b]	.08
 $CH_3-\vert-C(CH_3)_2-O\cdot$	 $CH_3-\vert-C(CH_3)_2CH_3$	75.5	.08

[a] Butler and Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943). [b] Estimated on the assumption that the addition of a methyl group lowers the bond energy by *ca.* 2 kg. cal./mole from that observed in *n*-butane and isobutane, respectively.

alcohol. Neither is it due to the presence of a relatively high concentration of butyraldehyde, since decomposition of ethyl *t*-butyl peroxide in the presence of a molar excess of isobutyraldehyde at 195° gave only an 11.2% yield of *t*-butyl alcohol.

The importance of the cyclohexene is well demonstrated by the decomposition of ethyl *t*-butyl peroxide at 195° using nitrogen as an inert diluent. The ethoxy radical yielded (moles/100 moles of peroxide reacted): 72.5 formaldehyde, 10.2 carbon monoxide, 5.9 ethanol, 2.4 acetaldehyde and 0.9 methyl ether ether.[4] The yields of formaldehyde and ethanol, especially, should be compared with those given in Table III for the reaction in the presence of cyclohexene. In the same experiment 79.5% of the *t*-butoxy radicals appeared as acetone and 5.1% as *t*-butyl alcohol.

Acknowledgment.—The authors wish to express their appreciation to Mr. L. M. Porter and Dr. John H. Raley for carrying out the preparation and decomposition of methyl *t*-butyl peroxide and analyzing the data thereon.

Summary

1. A series of new alkyl *t*-butyl peroxides has been synthesized.

2. These peroxides have been decomposed in the vapor phase in the presence of cyclohexene to determine the relative stabilities of the alkoxy free radicals formed by thermal scission of the oxygen–oxygen linkage.

3. The relative stabilities in decreasing order are methoxy > ethoxy > *n*-butoxy > isopropoxy > isobutoxy ≈ *t*-butoxy.

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(4) Tentative identification from mass spectrometric analysis.