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Decompositions of Di-*t*-alkyl Peroxides. IV. Decomposition of Pure Liquid Peroxide

BY E. R. BELL, FREDERICK F. RUST AND WILLIAM E. VAUGHAN*

The decomposition of di-*t*-butyl peroxide in various solvents has been shown[1] to proceed by a first order process in which scission of the oxygen-oxygen bond is apparently unimolecular and rate-determining. The principal products are *t*-butyl alcohol, acetone and methane.

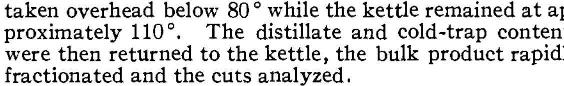
When pure di-*t*-butyl peroxide in the liquid phase undergoes decomposition—either thermal or photochemical—isobutylene oxide is a major reaction product and the rate of peroxide breakdown is accelerated. This alteration in the reaction is attributed to attack on the peroxide by its own decomposition fragments when solvent is removed as a hydrogen donating source. Thus the half-life of di-*t*-butyl peroxide in *t*-butylbenzene at 110° is computed from the equation $t_{1/2} = 1.7(10^{-20})e^{38,000/RT}$[1] to be seventy-six hours, whereas 70% of the pure peroxide decomposed at 110° in thirty and one-half hours. The steps proposed for this thermal or photochemical reaction are analogous in certain important respects to the changes postulated to occur when di-*t*-butyl peroxide is decomposed in the vapor phase in the presence of hydrogen chloride[2]

$$(1)\quad (CH_3)_3COOC(CH_3)_3 \xrightarrow[h\nu]{\Delta\ \text{or}} 2(CH_3)_3CO—$$

$$(CH_3)_3CO— \longrightarrow CH_3COCH_3 + CH_3— \quad (2)$$

$$(CH_3)_3CO— + (CH_3)_3COOC(CH_3)_3 \longrightarrow (CH_3)_3COH + (CH_3)_3COOC(CH_3)_2CH_2— \quad (3)$$

$$CH_3— + (CH_3)_3COOC(CH_3)_3 \longrightarrow CH_4 + (CH_3)_3COOC(CH_3)_2CH_2— \quad (4)$$



$$(CH_3)_3COOC(CH_3)_2CH_2— \longrightarrow (CH_3)_3CO— + (CH_3)_2\underset{\diagdown\,O\,\diagup}{C\text{———}CH_2} \quad (5)$$

Experimental

Thermal Decomposition.—The peroxide was refluxed behind a barricade in a decomposition still packed with glass helices, the stillhead of which was fitted with a graduated receiver and connected through a carbon dioxide-cooled trap to an aspirator bottle. By the end of thirty and one-half hours, approximately half the charge had been taken overhead below 80° while the kettle remained at approximately 110°. The distillate and cold-trap contents were then returned to the kettle, the bulk product rapidly fractionated and the cuts analyzed.

Acetone was determined by reaction with hydroxylamine hydrochloride and titration of the liberated acid[3]; *t*-butyl alcohol, by converting it to its nitrite ester, distilling and hydrolyzing the ester, and subsequent determination of the nitrous acid[4]; isobutylene oxide, by a modified hydrochlorination method to be described in a forthcoming publication by the analytical department of this Company; methane and ethane, by mass spectrometry.

The isobutylene oxide was identified by comparison of its infrared spectrum with that of a known pure sample, together with its boiling point (micro) 53.1°, and refractive index, $n^{20}D$ 1.3730 (lit. 53.0° and 1.3732, respectively).

The balance of the products from a typical experiment is given in Table I.

TABLE I

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

Time, 30.5 hr.; temp., *ca.* 110°; peroxide charged, 100 g.; recovered, 30.4 g.

Product	Moles per 100 moles peroxide decomposed	Moles per 100 moles *t*-butoxy units
t-Butyl alcohol	49.6	24.8
Acetone	65.5	32.8
Isobutylene oxide	69.8	34.9
Polymer	Trace	Trace
Total	184.9	92.5
Methane	62.5	31.3
Ethane	1.9	1.0

Photochemical Decomposition.—The optical density of di-*t*-butyl peroxide, when plotted as a function of wave length, follows a smooth curve which shows no structural absorption down to 2200 Å. Selected values of the optical density are given in Table II.

TABLE II

ULTRAVIOLET ABSORPTION OF DI-*t*-BUTYL PEROXIDE[a]

1-cm. cell, Beckman spectrophotometer, 10 g./l. solution in isoöctane

Å.	Optical density[b]
3400	0.017
3000	.137
2800	.285
2600	.469
2400	.603
2200	.815

[a] Measurements by Donald D. Tunnicliff of the Spectroscopic Department, these Laboratories. [b] Optical density = $\log_{10}$ (1/transmission).

In the photochemical decomposition experiments, the peroxide was contained in a clear quartz vessel (36 mm. i. d. × 19 cm.) which, since a previous experiment had shown a cold trap to be superfluous, was connected directly to an aspirator bottle. The reaction vessel, which was cooled and screened from infrared radiation by a continuous stream of water, was illuminated by a "stripped" 250-watt type AH-5 General Electric ultraviolet lamp at a distance of ten centimeters.

After two hundred and twelve hours of illumination the products were separated, and identified as before; the balance is given in Table III.

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* Harvard University, National Research Fellow, 1931-1932; Private Assistant, 1933-1937.

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

[2] Raley, Rust and Vaughan, *ibid.*, **70**, 2767 (1948).

[3] This procedure is a modification of the method of Marasco (*Ind. Eng. Chem.*, **18**, 701 (1926)), and is described in "Methyl Ethyl Ketone, its Uses and Data on its Properties," Shell Chemical Co., San Francisco, Calif., 1938, p. 45.

[4] W. M. Fischer and A. Schmidt, *Ber.*, **57**, 693 (1924); Skrabal, *Z. anal. Chem.* **119**, 222 (1940).

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°.

EMERYVILLE 8, CALIF. RECEIVED SEPTEMBER 6, 1949

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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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* Harvard University, National Research Fellow, 1931-1932; Private Assistant, 1933-1937.

[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).