(0.19 g., 3.6 mmoles) was dissolved in 100 ml. of DEG[34] under nitrogen and 1,1-diphenyl-2-benzenesulfonylhydrazine (1.0 g., 3 mmoles) was added. The resulting suspension was stirred until all of the sulfonylhydrazine was in solution as its sodium salt. The reaction mixture was boiled under reflux (238–240°) for 3 hr., still under a nitrogen atmosphere, and then poured into 300 ml. of dilute aqueous base. Extraction with several portions of ether followed; the combined extract was washed repeatedly with water and dried over magnesium sulfate. Removal of the ether yielded a dark residue which was chromatographed on Fisher alumina. The column was eluted successively with petroleum ether, petroleum ether–carbon tetrachloride, carbon tetrachloride–benzene, benzene; 0.43 g. of solid, m.p. 40.5–49°, was obtained from the carbon tetrachloride–benzene fraction. Purification by recrystallization from methanol–water raised the melting point to 53–54°. The compound was identified as diphenylamine (crude yield 83%) by infrared spectral and mixture melting point comparison with an authentic sample.

A similar pyrolysis was carried out in refluxing triglyme[34] (225°); again diphenylamine was the major product. The yield

after purification by chromatography and repeated recrystallization was 40% (m.p. 53–54°).

When hot sulfolane (240–250°) was employed as the reaction medium, diphenylamine was isolated in 70% yield (m.p. 50–54°) by chromatography. Another crystalline substance was eluted prior to the amine. Sublimation or g.l.c. of this material gave colorless crystals which were shown to differ from diphenyl in g.l.c. retention time, but which were not further investigated.

No azobenzene was isolated in any of the above runs, despite the fact that the azo compound was recovered in substantial yield after being heated 3 hr. at about 240° in DEG.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

Induced Decompositions of Di-*t*-butyl Peroxide in Primary and Secondary Alcohols[1]

BY EARL S. HUYSER AND CORWIN J. BREDEWEG[2]

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Di-*t*-butyl peroxide undergoes an induced decomposition when heated at 125° in primary and secondary alcohols. The rate of decomposition of the peroxide in such alcohols is approximately first order in peroxide. Product analysis of the reaction of the peroxide in 2-butanol indicates that the attack of the alcohol-derived radical is exclusively at the oxygen–oxygen linkage of the peroxide. A mechanism involving the transfer of a hydrogen atom from an α-hydroxyalkyl derived from primary and secondary alcohols is suggested to account for both the induced decomposition and the major products of the reactions.

The kinetics of the decomposition of di-*t*-butyl peroxide have been studied both in the gas and liquid phases. In the gas phase, the rate of decomposition was found to be a reaction that was first order in peroxide, the rate-determining process being the homolytic rupture of the peroxide linkage yielding two *t*-butoxyl radicals.[3] The *t*-butoxyl radicals can decompose to

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \quad (1)$$
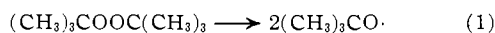
form methyl radicals and acetone and the products of such reactions depend on the subsequent reactions of the methyl radical. In solution, hydrogen abstrac-

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

tion from the solvent by the *t*-butoxyl radical producing *t*-butyl alcohol and a solvent-derived radical (reaction 3) competes with the fragmentation shown in reaction 2

$$(CH_3)_3CO\cdot + SH \longrightarrow (CH_3)_3COH + S\cdot \quad (3)$$
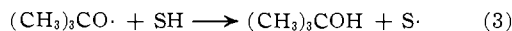
and the distribution of peroxide fragmentation products is solvent dependent.[4] Raley, Rust, and Vaughan

have shown that the rate of decomposition of the peroxide in cumene, tri-*n*-butylamine, and *t*-butylbenzene is a first-order reaction with essentially the same reaction rate observed for the gas phase reactions and concluded that in these solvents the decomposition of the peroxide is uncomplicated by any induced chain processes involving the solvent-derived radical.[4a]

There are, however, reported instances of induced decompositions of di-*t*-butyl peroxide. The neat liquid was found to decompose at a rate faster than that observed for decompositions in solution or in the gas phase.[5] The explanation given for this induced decomposition, based largely on the appearance of isobutylene oxide as a reaction product, involves attack of a hydrogen of the peroxide by a radical fragment producing the radical A· which decomposes into isobutylene oxide and the chain-carrying *t*-butoxyl radical. An induced decomposition of di-*t*-butyl peroxide, again involving the alkyl hydrogens of the

$$(CH_3)_3CO\cdot + CH_3C(CH_3)_2OOC(CH_3)_3 \longrightarrow$$
$$(CH_3)_3COH + \cdot CH_2C(CH_3)_2OOC(CH_3)_3 \quad (4)$$
$$A\cdot$$

$$A\cdot \longrightarrow CH_2{-}{-}C(CH_3)_2 + (CH_3)_3CO\cdot \quad (5)$$
$$\underset{O}{\diagdown\diagup}$$

peroxide, was noted in styrene polymerizations in which the peroxide was present.[6]

This paper is concerned with the decomposition of di-*t*-butyl peroxide in primary and secondary alcohols. Rate studies show that in such alcohols the peroxide

(1) This work was supported in part by a grant (A-5620) from the National Institutes of Health.
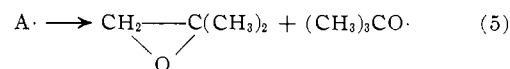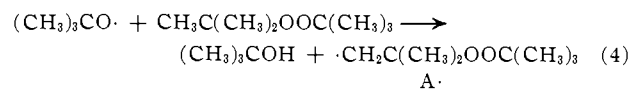
(2) National Science Foundation Cooperative Fellow, 1961–1963. This paper is taken from the thesis submitted by C. J. B. in partial fulfillment of the requirements for the Ph.D. Degree from the University of Kansas, 1963.

(3) (a) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 88 (1948); (b) M. Szwarc and J. S. Roberts, *J. Chem. Phys.*, **18**, 561 (1950); **19**, 683 (1951); (c) R. K. Brinton and D. H. Valman, *ibid.*, **20**, 25 (1952); (d) F. Lossing and A. W. Tichner, *ibid.*, **20**, 907 (1952); (e) M. T. Jaquiss, J. S. Roberts, and M. Szwarc, *J. Am. Chem. Soc.*, **74**, 6005 (1952); (f) G. O. Pritchard, H. O. Pritchard, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1425 (1954).

(4) (a) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948); (b) A. L. Williams, E. A. Oberright, and J. W. Brooks, *ibid.*, **78**, 1190 (1956); (c) F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, *ibid.*, **70**, 3258 (1948); (d) K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1168, 1446 (1960); (e) E. L. Patmore and R. J. Gritter, *J. Org. Chem.*, **27**, 4196 (1962).

(5) E. R. Bell, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **72**, 337 (1950).

(6) W. A. Pryor, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, p. 34M.
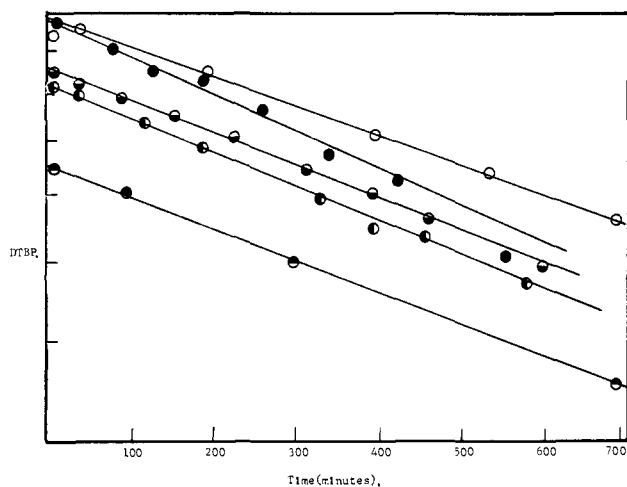
Fig. 1.—First-order plots for the decomposition of di-t-butyl peroxide (DTBP) in inert solvents at 125°. Initial peroxide to solvent ratios are: O, 8.98 mmoles of DTBP in 81 mmoles of cyclohexane; ●, 10.02 mmoles of DTBP in 90 mmoles of benzene; ◒, 8.39 mmoles of DTBP in 80 mmoles of tetrahydropyran; ◐, 8.12 mmoles of DTBP in 77 mmoles of toluene; ◓, 6.47 mmoles of DTBP in 63 mmoles of n-butyl mercaptan.

undergoes an induced decomposition presumably due to the interaction of an α-hydroxylalkyl radical derived from the alcohol with the peroxide. Product studies indicate that the reaction of this solvent-derived radical with the peroxide very likely occurs at the oxygen–oxygen linkage of the peroxide.

Results

Rate Studies.—The earlier decomposition rate studies of di-t-butyl peroxide in solution were accomplished by infrared analysis of reaction mixtures.[4a] Our rate studies were made by gas chromatographic analyses of the reaction mixtures (see Experimental). The reliability of our method is shown by the agreement of the values of the rate constants for the decomposition of di-t-butyl peroxide in toluene, cyclohexane, n-butyl mercaptan, and tetrahydropyran at 125° shown in Table I with those reported previously for the de-

TABLE I

FIRST-ORDER RATE CONSTANTS FOR DECOMPOSITION OF
DI-t-BUTYL PEROXIDE IN INERT SOLVENTS AT 125°

Solvent	Molar ratio of solvent:peroxide	$k \times 10^5$, sec.$^{-1}$	Half-life $\times$ 10^{-5}, sec.
Cyclohexane	9.02	1.4	4.9
Tetrahydropyran	9.65	1.5	4.7
n-Butyl mercaptan	8.72	1.5	4.7
Toluene	9.07	1.6	4.3
Benzene	8.99	1.7	4.0
Cumene[a]	..	1.6 ± 0.1	(4.3)
t-Butylbenzene[a]	..	$1.5 \pm .2$	(4.7)
Tri-n-butylamine[a]	..	$1.7 \pm .3$	(4.0)

[a] Data of Raley, Rust, and Vaughan, found in ref. 4a.

composition of the peroxide in cumene, tri-n-butylamine, and t-butylbenzene at the same temperature. Figure 1 shows the first-order plots of our data for the decomposition of di-t-butyl peroxide in these solvents. It can be assumed that the rate of decomposition is very likely independent of the solvent in these cases since the rate is essentially the same as that found in the gas phase reactions.[4a] The rate of decomposition of the peroxide in cyclohexanol, 1-propanol, 2-butanol, 2-octanol, and benzhydrol is still, for the most part,
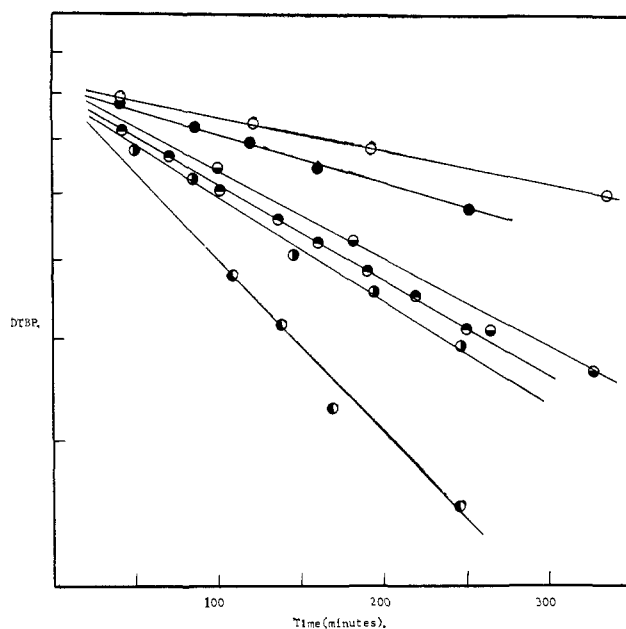

Fig. 2.—First-order plots for the decomposition of di-t-butyl peroxide (DTBP) in alcohols at 125°. Peroxide content corrected to the same initial amount in each case: O, 8.12 mmoles of DTBP in 77 mmoles of toluene; ●, 8.06 mmoles of DTBP in 72 mmoles of cyclohexanol; ◒, 8.30 mmoles of DTBP in 73 mmoles of 2-butanol; ◓, 7.88 mmoles of DTBP in 70 mmoles of exo-norborneol; ◑, 7.64 mmoles of DTBP in 72 mmoles of 2-octanol; ◐, 8.77 mmoles of DTBP in 38 mmoles of benzhydrol.

apparently a first-order reaction in peroxide through the first half-life of the peroxide but appreciably faster as can be seen in the first-order plots of the decomposition of the peroxide in these solvents compared with that of toluene (Fig. 2). Furthermore, the rate of decomposition of the peroxide is dependent on the alcohol used (as can be seen from Fig. 2) and the rate constants calculated for these reactions of the peroxide in the alcohols shown in Table II.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR DECOMPOSITION OF
DI-t-BUTYL PEROXIDE IN ALCOHOLS AT 125°

Alcohol	Molar ratio of solvent:peroxide	$k' \times 10^5$, sec.$^{-1}$[a]	Half-life $\times$ 10^{-5}, sec.
Cyclohexanol	8.95	2.4	2.8
1-Propanol	10.88	2.8	2.4
Norborneol	8.94	4.4	1.6
2-Butanol	8.87	4.8 ± 0.2[b]	1.4
2-Octanol	8.88	5.5 ± 0.0[c]	1.3
Benzhydrol	4.36	8.7	0.8

[a] The significance of this first-order reaction rate constant is found in the Discussion. [b] Average deviation of three separate kinetic runs. [c] Average deviation of two separate kinetic runs.

Figure 3 shows plots of the rate of decomposition of di-t-butyl peroxide in 2-butanol in the presence of 1-octene, a radical scavenger, and in the presence of toluene, a solvent reactive toward t-butoxyl radicals. In the presence of an appreciable quantity of 1-octene, there apparently is no appreciable amount of induced decomposition of the peroxide, whereas the presence of toluene does decrease the amount of induced decomposition but only slightly compared to the effect of 1-octene. In a smaller amount of 1-octene, the induced decomposition is not great initially but becomes appreciable when the 1-octene has been consumed in the reaction.

Product Analysis.—In order to determine the nature of the interaction of alcohols with the di-t-butyl peroxide, we made a careful analysis of the products obtained from the reaction of 2-butanol with the peroxide. The data shown in Table III were obtained by gas chromatographic analysis of a reaction mixture obtained from the reaction of the peroxide in 2-butanol at 125° for a period of several half-lifes of the peroxide.
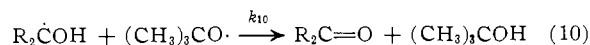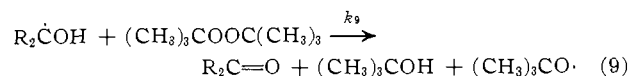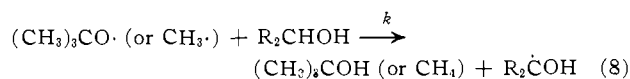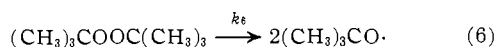
TABLE III

MATERIAL BALANCE FOR THE DECOMPOSITION OF DI-t-BUTYL PEROXIDE IN 2-BUTANOL AT 125°

Reactants	Wt., g. (mmoles)	Products	Wt., g. (mmoles)
Di-t-butyl peroxide	4.63 (31.68)	Acetone	0.38 (6.6)
2-Butanol	18.19 (245.8)	t-Butyl alcohol	4.06 (54.9)
		2-Butanone	1.66 (23.1)
		Residue[a]	0.45 (1.92)
		Unreacted 2-butanol	16.07 (217.2)
Total wt.	22.82		22.62

[a] Av. mol. wt., 235; infrared spectrum of residue showed the presence of both hydroxy groups and carbonyl groups.

Examination of these data shows that (1) the peroxide is converted quantitatively to t-butyl alcohol and acetone, (2) the major reaction product of 2-butanol is 2-butanone, and (3) a considerably smaller amount of a higher boiling complex residue is formed.

Discussion

The results of our kinetic experiments indicate that the mechanism of the reaction of di-t-butyl peroxide with primary and secondary alcohols necessitates a path that requires the participation of the peroxide in some reaction other than the unimolecular, homolytic fission of the oxygen–oxygen linkage. Further, this reaction almost undoubtedly involves an attack at the oxygen–oxygen linkage of the peroxide since only acetone and t-butyl alcohol are observed as fragmentation products of the peroxide. A mechanism which satisfactorily accounts for the major products of the reaction and involves the peroxide in a free radical chain sequence is

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{k_6} 2(CH_3)_3CO\cdot \quad (6)$$

$$(CH_3)_3CO\cdot \xrightarrow{k_7} CH_3COCH_3 + CH_3\cdot \quad (7)$$

$$(CH_3)_3CO\cdot \text{ (or } CH_3\cdot) + R_2CHOH \xrightarrow{k}$$
$$(CH_3)_3COH \text{ (or } CH_4) + R_2\dot{C}OH \quad (8)$$

$$R_2\dot{C}OH + (CH_3)_3COOC(CH_3)_3 \xrightarrow{k_9}$$
$$R_2C{=}O + (CH_3)_3COH + (CH_3)_3CO\cdot \quad (9)$$

$$R_2\dot{C}OH + (CH_3)_3CO\cdot \xrightarrow{k_{10}} R_2C{=}O + (CH_3)_3COH \quad (10)$$

Support for the suggestion that the α-hydroxyalkyl radical is involved in the reaction with the peroxide comes from the kinetic experiments performed in the presence of 1-octene and toluene (Fig. 3). Previous work has shown that α-hydroxyalkyl radicals add readily to terminal olefins forming the adduct radical shown in 11.[7] Thus, if the rate of this addition

$$R_2\dot{C}{-}OH + n{-}C_6H_{13}CH{=}CH_2 \xrightarrow{k_{11}} n{-}C_6H_{13}\dot{C}HCH_2CR_2OH \quad (11)$$
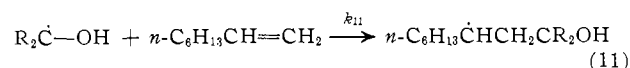
(7) W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *J. Am. Chem. Soc.*, **76**, 450 (1954).
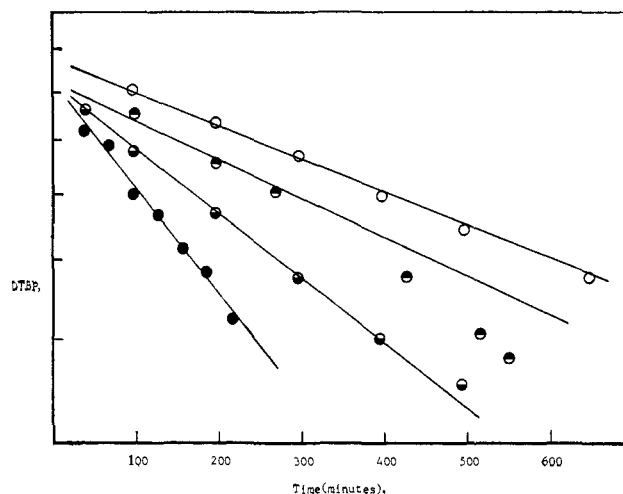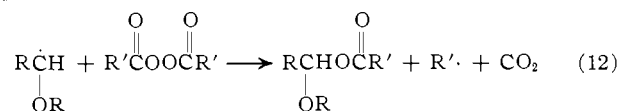

Fig. 3.—First-order plots of the decomposition of di-t-butyl peroxide (DTBP) in 2-butanol in the presence of 1-octene and toluene: O, 8.51 mmoles of DTBP in 30 mmoles of 2-butanol and 32 mmoles of 1-octene; ◓, 8.48 mmoles of DTBP in 71 mmoles of 2-butanol and 16 mmoles of 1-octene; ◔, 8.52 mmoles of DTBP in 30 mmoles of 2-butanol and 39 mmoles of toluene; ●, 8.10 mmoles of DTBP in 74 mmoles of 2-butanol.

of the α-hydroxyalkyl radical to the alkene is fast compared to its rate of attack on the peroxide, the peroxide will not be consumed to any significant extent in reaction 9 until the alkene is consumed. Decreasing the amount of alkene initially present apparently makes the rates of reactions 9 and 11 competitive and some induced decomposition is observed. In this experiment with a smaller amount of 1-octene, two other observations were made that support this hypothesis: (1) As soon as the 1-octene was completely consumed, the rate of decomposition of the peroxide increased. (2) The formation of 2-butanone was insignificant until the 1-octene was consumed.

The interpretation of these experiments with 1-octene is valid if it can be shown that the alkoxyl radicals obtained from the peroxide are indeed reacting with the alcohol and not solely with the olefin. The fact that a marked induced decomposition of the peroxide in 2-butanol is observed when 1-octene is replaced with toluene, a material that might be expected to be as reactive as 1-octene toward attack by the t-butoxyl radicals, indicates that α-hydroxyalkyl radicals are formed from the alcohol and are available for reaction with the peroxide in this case.

The interaction of a solvent-derived radical with di-t-butyl peroxide appears to be peculiar to α-hydroxyalkyl radicals. Isolation of acylals[8] and isotopic labeling experiments[9] indicate that α-alkoxyalkyl radicals attack the oxygen–oxygen linkage of diacyl peroxides in the manner shown in eq. 12. A similar

$$R\underset{\underset{OR}{|}}{\dot{C}}H + R'\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}R' \longrightarrow R\underset{\underset{OR}{|}}{C}HO\overset{\overset{O}{\|}}{C}R' + R'\cdot + CO_2 \quad (12)$$
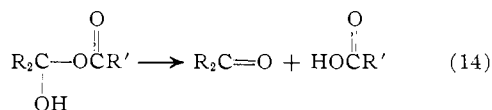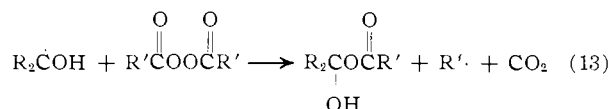
mode of interaction for the reaction of α-hydroxyalkyl radicals might well be inferred for the observed induced decomposition of diacyl peroxides in alcohols.[10]

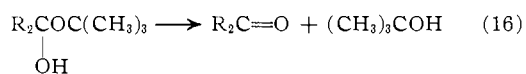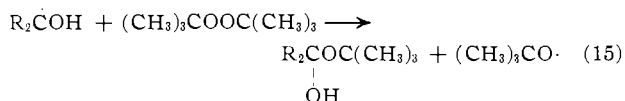(8) W. E. Cass, *ibid.*, **69**, 500 (1947).

(9) D. B. Denney and G. Feig, *ibid.*, **81**, 5322 (1959); E. H. Drew and J. C. Martin, *Chem. Ind.* (London), 925 (1959).

(10) M. S. Kharasch, H. N. Friedlander, and W. H. Urry, *J. Org. Chem.*, **14**, 91 (1949); M. S. Kharasch, J. L. Rowe, and W. H. Urry, *ibid.*, **16**, 905 (1951); P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **69**, 2299 (1947).

In these reactions the radical would attack the peroxide linkage yielding a hemiacylal and a peroxide fragmentation product (eq. 13). The hemiacylal formed in this

$$R_2\overset{\cdot}{C}OH + R'\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R' \longrightarrow R_2\underset{\underset{OH}{|}}{\overset{O}{\overset{\|}{C}}}OCR' + R'\cdot + CO_2 \quad (13)$$
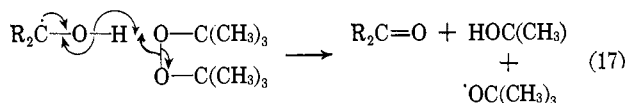
process would undergo spontaneous decomposition yielding the observed ketone and carboxylic acid. A similar mechanism might be proposed for the interaction of α-hydroxyalkyl radicals with the dialkyl peroxide. In this case, the hemiketal which would be formed could decompose to the observed ketone and t-butyl alcohol as shown in eq. 15 and 16. If this were

$$R_2\underset{\underset{OH}{|}}{\overset{O}{\overset{\|}{C}}}O\overset{\|}{C}R' \longrightarrow R_2C{=}O + HO\overset{O}{\overset{\|}{C}}R' \quad (14)$$

$$R_2\overset{\cdot}{C}OH + (CH_3)_3COOC(CH_3)_3 \longrightarrow$$
$$R_2\underset{\underset{OH}{|}}{\overset{}{C}}OC(CH_3)_3 + (CH_3)_3CO\cdot \quad (15)$$

$$R_2\underset{\underset{OH}{|}}{\overset{}{C}}OC(CH_3)_3 \longrightarrow R_2C{=}O + (CH_3)_3COH \quad (16)$$

indeed the mechanism for the reaction for α-hydroxyalkyl radicals with di-t-butyl peroxide, a similar process might be expected for α-alkoxyalkyl radicals derived from ethers. Our experiments indicate that this apparently is not the case since there is no observable increase in the rate of decomposition of di-t-butyl peroxide in tetrahydropyran over that of the simple first-order decomposition. Further, if such a reaction did occur, a stable ketal, namely α-t-butoxytetrahydropyran, would be formed and no detectable amounts of this material were observed among the reaction products obtained from the decomposition of di-t-butyl peroxide in tetrahydropyran.

The interaction of the α-hydroxyalkyl radical with the peroxide linkage apparently is peculiar to the hydroxy function. The transfer of a hydrogen atom from the hydroxy function of the radical in the manner shown in eq. 17 satisfies this requirement for the induced decomposition for the observed products.

$$R_2\overset{\frown}{C}{\overset{\frown}{O}}{\overset{\frown}{H}}\quad\underset{\underset{O{-}C(CH_3)_3}{|}}{O{-}C(CH_3)_3} \longrightarrow \begin{matrix} R_2C{=}O + HOC(CH_3) \\ + \\ \cdot OC(CH_3)_3 \end{matrix} \quad (17)$$

From the standpoint of energetics, a hydrogen atom transfer reaction such as shown in eq. 17 is exothermic. The breaking of one oxygen–hydrogen bond would be balanced out by the formation of a new one. The formation of the carbon–oxygen π-electron system, calculated from the $D_{C=O}$ estimated as $\sim$150 kcal./mole and D_{C-O} as 77 kcal./mole, will give about 73 kcal./mole at the expense of breaking the oxygen–oxygen linkage which is about 37 kcal./mole,[11] thus making the over-all process exothermic to the extent of about 36 kcal./mole. Both the exothermicity of this reaction and the favorable polar factor involving the transfer of a hydrogen atom[12] may cause this reaction to proceed readily.

(11) Bond dissociation energies taken from T. L. Cottrell, "The Strength of Chemical Bonds," Butterworth, London, 1954.

(12) E. S. Huyser and D. C. Neckers, J. Am. Chem. Soc., **85**, 3641 (1963).

The observation that the rate of decomposition of di-t-butyl peroxide is very nearly first order in peroxide in all cases where induced decomposition is observed is consistent with the cross-termination reaction 10.[13] The derived rate expression for the disappearance of peroxide based on a steady state approximation and involving only cross-termination is

$$\frac{-d[Per]}{dt} =$$
$$\left[k_9 + \left(\frac{k_9}{k_6} \pm \frac{k_6}{2k_9}\sqrt{\frac{1}{4} + \frac{2k_9k_8[R_2CHOH]}{k_6k_{10}}}\right)\right][Per]$$

This expression shows that the rate will not only be first order in peroxide, provided an excess of alcohol is present to maintain a constant value of $[R_2CHOH]$ throughout the reaction, but that the over-all rate of the reaction will be dependent on the particular alcohol involved since the reaction rate constants for reactions 8, 9, and 10 are involved in the constant term. If termination proceeded by coupling or disproportionation of two α-hydroxyalkyl radicals

$$2R_2\overset{\cdot}{C}OH \overset{k_{18}}{\longrightarrow}$$
$$R_2C{=}O + R_2CHOH \text{ (or } R_2C(OH)C(OH)R_2) \quad (18)$$
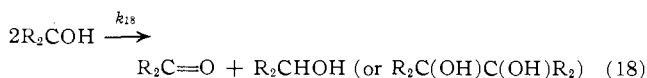
the rate expression for the disappearance of peroxide would be

$$\frac{-d[Per]}{dt} = k_6[Per] + k_9\left(\frac{k_6}{2k_{18}}\right)^{1/2}[Per]^{1/2}$$

The slight deviations observed in the first-order plots in Fig. 2 may be due to some termination by reaction of two α-hydroxyalkyl radicals. The appearance of a high molecular weight residue in the reaction mixture is certainly indicative of some termination by a coupling reaction. Most of this residue could have been formed near the end of the reaction when the peroxide concentration was very low causing the steady state concentration of the alkoxyl radicals to be small and thereby decreasing the possibility of the cross-termination reaction. The kinetic data, on the other hand, were obtained for the first half-life of the peroxide, and under such conditions the steady state concentration of alkoxyl radicals could always be sufficient for the cross-termination reaction.

The observation that ketone is the major product of the reaction of di-t-butyl peroxide with secondary alcohols in our experiments may itself be largely due to a concentration factor. Previous work[14] has shown that glycols, presumably formed by coupling of α-hydroxyalkyl radicals, are the major products formed when the initial ratio of peroxide to alcohol is 20:1. At low peroxide concentrations, the rate of interaction of the α-hydroxyalkyl radicals with the peroxide leading to ketone will be diminished as would the probability of the cross-termination reaction occurring to produce ketone. It might even be suggested that the ketone produced comes largely from these two sources and α-hydroxyalkyl radicals do not disproportionate to any significant extent to produce ketone.

(13) A. T. Blomquist and A. F. Ferris, ibid., **73**, 3412 (1951); J. E. Leffler, ibid., **72**, 67 (1950); P. D. Bartlett and K. Nozaki, ibid., **69**, 2299 (1947).

(14) K. Schwetlick, W. Geger, and H. Hartmann, Angew. Chem., **72**, 779 (1960).

However, the chemical nature of the residue itself suggests that the termination process in reactions that are allowed to proceed to almost complete reaction of the peroxide are not quite so simple. The appearance of a carbonyl absorption in the infrared spectra of the residue indicates the involvement of the ketone produced during the course of the reaction in the termination reaction. Furthermore, the molecular weight of the residue is greater than that of a dimer of the alcohol or ketone which means that a residue-derived radical itself participates in the termination reaction. Since both the ketone and residue are present in comparatively small amounts, the fact that they are involved to any significant extent in the reaction is somewhat surprising. The problem of the formation of this carbonyl-containing residue as well as other aspects of induced decompositions of dialkyl peroxides are currently under further investigation.

Experimental

Materials.—Commercial materials were used throughout this work with the exception of benzhydrol (m.p. 67°), which was prepared by the reduction of benzophenone with zinc in sodium hydroxide. In each case, the material was redistilled (under vacuum when necessary) until it gave a single gas chromatographic peak. *exo*-Norborneol (m.p. 127–129°) was purified by recrystallization from petroleum ether.

Apparatus.—The gas chromatographic analyses were performed with an Aerograph A-90-P using a 15 ft. by 0.25 in. column packed with 15% of the polyethylene glycol E-600 (Dow Chemical Co.) on 30–60 mesh Chromosorb-P. The chromatograms were traced on a Sargent recorder (Model SR) fitted with a Disc integrator.

The infrared spectra were performed on a Beckman IR-5.

The molecular weight determination was made with a Mechrolab Model 301-A osmometer.

The kinetic experiments were performed in a reaction tube constructed in the following manner: a 2 cm. by 7 mm. Pyrex tube was sealed perpendicular to and about 1 cm. from the end of a 13.5 cm. by 12 mm. Pyrex tube which was sealed at both ends. The open end of the smaller tube was fitted with a syringe cap which could be clamped tightly in place. With this system, samples could be withdrawn without any loss from mixtures containing components that boiled well below 125°. This tube was mounted with the large tube horizontal in a constant temperature oil bath maintained at $125 \pm 0.2°$ and with the syringe cap above the level of the oil. Liquid samples were withdrawn from the tube with a 2-cc. syringe fitted with a No. 25 needle.

Kinetic Measurements.—An accurately weighed reaction mixture (usually amounting to about 5 ml.) consisting of di-*t*-butyl peroxide and the indicated reagent in the amounts indicated in Fig. 1, 2, and 3 was placed in the oil bath. At various intervals, samples (about 0.3 ml.) were withdrawn and placed in vials which had been cooled to 0°. The di-*t*-butyl peroxide content in the reaction mixture at the time the sample was removed was determined in the following manner: an accurately weighed portion of the removed sample was mixed with a known amount of ethyl acetate which served as an internal standard for the gas chromatographic analyses. This mixture was subjected to gas chromatographic analysis on the column indicated above which was maintained at about 65°. The amount of di-*t*-butyl peroxide in the weighed sample was determined from the peak areas of the peroxide and ethyl acetate using the correction factor determined from known samples relating the chromatographic peak area ratio to the mole ratio. With this information, the peroxide content in the reaction mixture at the time the sample was withdrawn could be calculated. Duplicate chromatograms were made in each case. The logarithm of the peroxide content was plotted against time and the reaction rate constant calculated from the "best fit" line drawn through these points.

Product Analysis.—A reaction mixture consisting of 4.63 g. (31.68 mmoles) of di-*t*-butyl peroxide and 18.19 g. (245.8 mmoles) of 2-butanol was sealed in a Pyrex tube and was heated in an oil bath at 125° for 5 days. After cooling, the tube was opened and the amounts of acetone, *t*-butyl alcohol, 2-butanone, and unreacted 2-butanol were determined by gas chromatographic nalysis using the E-600 column set at 72° and *sec*-butyl acetate as an internal gas chromatographic standard. Necessary correction factors relating the peak area ratios to mole ratios had been determined from known mixtures of each component with the internal standard. Gas chromatographic analysis of the reaction mixture on the same column at 125° showed a peak with retention time identical with that of 3,4-dimethyl-3,4-hexanediol, the coupling product of two of the α-hydroxyalkyl radicals derived from 2-butanol. The reaction mixture also gave a positive periodic acid test. The total content of the residue in the reaction mixture was determined by removing the volatile components of a weighed portion of the mixture under vacuum. The resulting residue was not, however, solely the glycol. It had a molecular weight of 235 which corresponds to an average of 3.2 alcohol units per molecule. The infrared spectra of the residue showed a strong absorption in the carbonyl absorption region $(5.8\,\mu)$ as well as an absorption due to hydroxy groups.