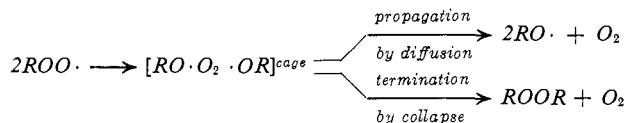# Bimolecular Combination Reactions of Oxy Radicals

A. Factor,[1] Carol A. Russell, and T. G. Traylor

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The chain decomposition of t-butyl hydroperoxide in chlorobenzene, initiated by $^{14}CH_3$-labeled di-t-butyl peroxyoxalate (DBPO), produces 1 mole of di-t-butyl peroxide and 20 moles of t-butyl alcohol per mole of DPBO and obeys the kinetic equation $d(O_2)/dt = k(DBPO)$, in agreement with the results of Hiatt. A comparison of the radioactivity in the product di-t-butyl peroxide obtained in this reaction with that resulting from cage reaction in DBPO decompositions indicates that the reaction $2RO \cdot \rightarrow ROOR$ is unimportant in solution. Similarly, the failure to find radioactivity in the remaining t-butyl hydroperoxide is presented as evidence against the occurrence of the reaction $RO \cdot + ROO \cdot \rightleftharpoons ROOOR$. Because the chain length of the subject decomposition is sensitive to viscosity changes we propose that the propagation and termination steps occur as follows.

$$2ROO \cdot \longrightarrow [RO \cdot O_2 \cdot OR]^{cage} \begin{cases} \xrightarrow[\text{by diffusion}]{\text{propagation}} 2RO \cdot + O_2 \\ \xrightarrow[\text{by collapse}]{\text{termination}} ROOR + O_2 \end{cases}$$

Introduction

Bimolecular reactions of alkoxy radicals (eq. 1)

$$RO \cdot + RO \cdot \longrightarrow ROOR \qquad (1)$$

and of alkylperoxy radicals (eq. 2) have often been

$$ROO \cdot + ROO \cdot \longrightarrow ROOR + O_2 \qquad (2)$$

proposed as terminating steps in autoxidation reactions[2,3] and peroxide decompositions.[2b] In a mixture of these two types of radicals, a usual situation, two further processes are possible[4] (eq. 3 and 4).

$$2ROO \cdot \longrightarrow 2RO \cdot + O_2 \qquad (3)$$

$$RO \cdot + ROO \cdot \rightleftharpoons ROOOR \qquad (4)$$
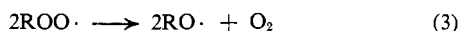
Definitive evidence is available[3,5a,6] for reaction 3, and reaction 2 is suggested by the kinetics of *t*-butyl hydroperoxide decomposition.[6] However, it has been suggested that neither reaction 1 nor 2 constitutes the termination step in autoxidation.[5a,7]

In order to understand the behavior of these two important intermediates RO· and ROO·, we have

studied the occurrence and nature of reactions 1, 2, 3, and 4. For this study we have used a simple chain reaction, previously studied by Bartlett, Moye, and Van Swett[8] and by Hiatt, Clipsham, and Visser[6] shown in eq. 5.[9] The only intermediates in this re-

$$(CH_3)_3COO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOC(CH_3)_3 + n(CH_3)_3COOH \longrightarrow 2CO_2 +$$
$$n(CH_3)_3COH + (n/2)O_2 + [(CH_3)_3CO]_2 \quad (5)$$

action are *t*-butoxy and *t*-butylperoxy radicals. In dilute solution, di-*t*-butyl peroxyoxalate (DPBO) is known to decompose cleanly to give high yields of *t*-butoxy radicals.[10] However, in viscous solutions, cage combination of *t*-butoxy radicals can be important.[11,12] Thus reaction 5 may be written

$$DBPO^* \xrightarrow{k_1} [t\text{-}\overset{*}{B}uO \cdot \overset{CO_2}{\underset{CO_2}{}} \cdot O t\text{-}\overset{*}{B}u] \xrightarrow[\text{collapse}]{\text{cage}} (t\text{-}\overset{*}{B}uO)_2 + 2CO_2 \quad (6a)$$

$$\xrightarrow{\text{diffusion}} 2t\text{-}\overset{*}{B}uO \cdot + 2CO_2 \quad (6b)$$

$$t\text{-}\overset{*}{B}uO \cdot + t\text{-}BuOOH \xrightarrow{k_2} t\text{-}BuOO \cdot + t\text{-}\overset{*}{B}uOH \quad (7)$$

$$2t\text{-}BuOO \cdot \xrightarrow{k_3} 2t\text{-}BuO \cdot + O_2 \quad (8)$$

$$2t\text{-}BuOO \cdot \xrightarrow{k_4} (t\text{-}BuO)_2 + O_2 \quad (9)$$

$$t\text{-}\overset{*}{B}uO \cdot + t\text{-}BuO \cdot \xrightarrow{k_5} (t\text{-}\overset{*}{B}uO)_2 \quad (10)$$

Using the usual steady-state assumptions, Hiatt[6] derived the rate expression

$$\frac{d(O_2)}{dt} = k(DBPO) \qquad (11)$$

for reactions 6b, 7, 8, and 9 and

$$\frac{d(O_2)}{dt} = k(DBPO)^{1/2}(t\text{-}BuOOH) \qquad (12)$$

for equations 6b, 7, 8, 10. Because eq. 11 described the observed kinetics, it was concluded that 10 did not occur.[6]

This conclusion can be checked by employing radioactive DBPO, as indicated by the asterisks in eq. 6–10, by considering two more unlabeled reactions (eq. 7' and 10') and counting the activity in the propagation,

$$t\text{-}BuO \cdot + t\text{-}BuOOH \longrightarrow t\text{-}BuOH + t\text{-}BuOO \cdot \quad (7')$$

$$2t\text{-}BuO \cdot \longrightarrow (t\text{-}BuO)_2 \quad (10')$$

(1) National Institutes of Health Postdoctoral Fellow, 1963–1964.
(2) (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 9; (b) *ibid.*, p. 505.
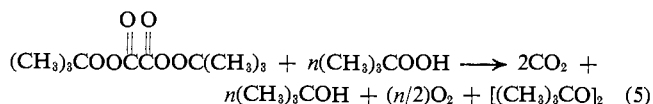(3) H. S. Blanchard, *J. Am. Chem. Soc.*, 81, 4845 (1959).
(4) Alkylperoxy and alkoxy radicals having an α-hydrogen may readily disproportionate (*e.g.*, $2R_2CHO \cdot \rightarrow R_2CHOH + R_2CO$). Thus, we have confined this study and its implications to *t*-alkylperoxy and *t*-alkoxy radicals.
(5) (a) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, 85, 2407 (1963); (b) P. D. Bartlett and T. G. Traylor, unpublished data.
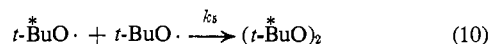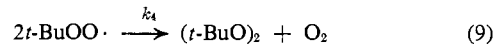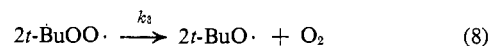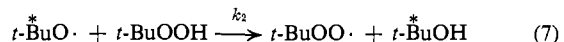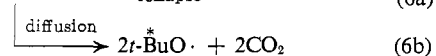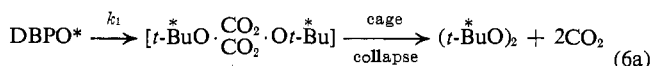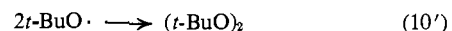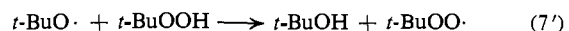(6) R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem.*, 42, 2754 (1964).
(7) See the following paper in this series for verification of this statement: T. G. Traylor and C. A. Russell, *J. Am. Chem. Soc.*, 87, 3698 (1965).

(8) P. D. Bartlett, A. J. Moye, and H. Van Swett, unpublished results.
(9) Although Hiatt, *et al.*, report only 60% yield of di-*t*-butyl peroxide based on DBPO, we observed 90–100%.
(10) (a) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, 82, 1762 (1960); (b) P. D. Bartlett and T. Funahashi, *ibid.*, 84, 2596 (1962).
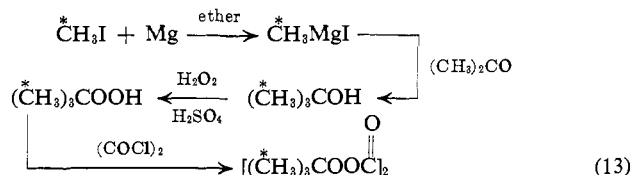(11) We are indebted to Dr. Richard Hiatt for suggesting this interpretation of our results and for collaborating with us in demonstrating cage reactions of *t*-butoxy radicals.[12] This finding, combined with the present data, allows us to draw several conclusions that were not previously apparent.
(12) R. Hiatt and T. G. Traylor, *J. Am. Chem. Soc.*, in press.

termination, and cage products. Because all *t*-butoxy radicals are chemically equivalent and because *t*-BuOH comes only from such radicals, the radioactivity in the product, *t*-BuOH, gives an accurate measure of the radioactivity in *t*-BuO·. By comparing the activity in the product di-*t*-butyl peroxide with that in *t*-BuOH we may ascertain how much of the peroxide arises through reaction 9 and how much arises through the sum of eq. 6a and 10. The amount of peroxide coming exclusively from cage reaction 6a has been separately established by carrying out the decomposition of DBPO in the presence of *t*-butoxy radical traps but in the absence of *t*-butyl hydroperoxide.[12]

Results

Radiochemistry. We have prepared radioactive di-*t*-butyl peroxyoxalate (DBPO)[10] by the following sequence of reactions.

$$\overset{*}{C}H_3I + Mg \xrightarrow{\text{ether}} \overset{*}{C}H_3MgI \longrightarrow$$

$$(CH_3)_2CO$$

$$(\overset{*}{C}H_3)_3COOH \xleftarrow[H_2SO_4]{H_2O_2} (\overset{*}{C}H_3)_3COH \longleftarrow$$

$$\xrightarrow[]{(COCl)_2} [(\overset{*}{C}H_3)_3COO\overset{O}{\overset{\|}{C}}]_2 \tag{13}$$

This product was then used to initiate the chain decomposition of unlabeled *t*-butyl hydroperoxide under two sets of conditions, as shown in Table I.

Table I. Decomposition of *t*-Butyl Hydroperoxide at 45.0° Initiated by Radioactive Di-*t*-butyl Peroxyoxalate

	Run I	Run II[a]
DBPO (*M*)	1.0	0.20
t-BuOOH (*M*)	10	4.0
Solvent	None	C_6H_5Cl
% DBPO decomposed	100	77
Yield *t*-BuOH[b]	69	77
Yield (*t*-BuO)₂[b]	9.0	3.7
Yield *t*-BuOOH[b]	22	19
Initial chain length[c]	9	10
Average chain length[d]	3.8	10.5
Radioactivity (c.p.m./mmole)		
In initial DBPO	1.15×10^6	1.15×10^6
In final DBPO	...	1.09×10^6
In product *t*-BuOH[e]	128,000	54,000
In product (*t*-BuO)₂[e]	153,000	56,060
In final *t*-BuOOH[e]	<500	<500

[a] Run 9 in the following kinetic discussion. [b] Mole % of the total *t*-butyl-containing product. [c] Determined kinetically, [(d(O₂)/d*t*)/(d(DBPO)/d*t*)]. [d] From product balance, [*t*-BuOH/2(*t*-BuO)₂]. [e] This radioactivity was calculated from counts of cold-diluted samples and therefore depends on the accuracy of product analysis.

Product Composition. The composition of products in run I was determined by n.m.r. analyses using the relative areas of the methyl hydrogen absorptions of *t*-BuOH, *t*-BuOOH, and (*t*-BuO)₂. A more accurate analysis was obtained by gas–liquid chromatography in run II. Within the accuracy of either method it appears that 1 molecule of di-*t*-butyl peroxide is produced per molecule of DBPO consumed. Thus, the ratio of di-*t*-butyl peroxide plus DBPO to total *t*-butyl groups at the end of both experiments is the same as the ratio of DBPO to total *t*-butyl groups initially. Yields of products are shown in Table I.

The average chain length, calculated from the ratio of *t*-butyl alcohol to di-*t*-butyl peroxide (*t*-BuOH/2(*t*-

$BuO)_2 = C.L.$), is 3.8 in neat hydroperoxide and 10.5 in chlorobenzene. This apparent discrepancy prompted us to make further kinetic studies discussed below.

Radiochemical Results. In order to simplify product isolation for counting, aliquots of unlabeled alcohol, peroxide, and hydroperoxide were added to known quantities of product mixtures whose compositions were known. The alcohol was first distilled and then converted to a phenylurethan. The latter was recrystallized to constant activity and the activity was corrected for dilution. Alternatively, the diluted alcohol was separated by gas–liquid chromatography and counted. The activity (which was identical by these two procedures) is entered in Table I as activity of undiluted product. Di-*t*-butyl peroxide was isolated by cold dilution followed either by distillation and redistillation from LiAlH₄ or separation by g.l.c., and counted. Activities in Table I similarly represent those of undiluted product.

The hydroperoxide which remained in each run was separated roughly by low-temperature distillation, then either extracted with base or converted to a 3,5-dinitrobenzoate which was then repeatedly recrystallized. Although quenching of scintillation counting was observed with this derivative, it was still possible to show that the hydroperoxide contained negligible activity. To further ensure that no exchange of hydroperoxide with perester (*e.g.*, transesterification), had occurred, the second run was stopped after 77% calculated decomposition and all volatiles were removed, leaving as a residue pure DBPO. After recrystallization, this DBPO had an activity (line 12, column 2) approximating that of the original DBPO. $(1.09 \times 10^6$ c.p.m./mole compared to 1.15×10^6 c.p.m./mmole).

In order to check the possibility of predecomposition of solid DBPO to di-*t*-butyl peroxide, 2.0 ml. of peroxide was added to 70 mg. of radioactive DBPO, distilled off at 25°, and purified by g.l.c. The distillate contained no radioactivity.

In summary, the data indicate no exchange between *t*-BuOOH or DBPO and any other species. The peroxide activity must therefore arise from *t*-butoxy radicals or directly from DBPO. The ratios of peroxide and alcohol activities show 60 and 52% as much activity per *t*-butyl group in the peroxide as in the alcohol in runs I and II, respectively. This would correspond to 13 and 4.8% yield of di-*t*-butyl peroxide directly from DBPO in these two runs.

Kinetics. Because there seemed to be a large difference between the kinetic behavior in pure *t*-butyl hydroperoxide, where the chain length decreased rapidly, and that observed here and by Hiatt[6] in benzene or chlorobenzene solution, we have investigated the kinetics further. For this purpose an automatic recording gasometer was developed which allowed us to take a sufficient number of points over the time of DBPO decomposition so that the record could be treated as a series of zero-order plots.[7] The instantaneous slope thus obtained (d(O₂)/d*t* + d(CO₂)/d*t*) was corrected for CO₂ evolution by calculating the concentration and instantaneous decomposition rate of DBPO from the data of Bartlett, Benzing, and Pincock.[10] The corrected d(O₂)/d*t* × 2 is divided by d(CO₂)/d*t* to give an instantaneous chain length.

Table II. Summary of Kinetics of Di-*t*-butyl Peroxyoxalate Induced Decomposition of *t*-Butyl Hydroperoxide

Run	Concn. of DBPO, mole l.$^{-1}$	Concn. of *t*-BuOOH,[a] mole l.$^{-1}$	Vol. % *t*-BuOH[b]	Temp., °C.	Chain length[c]	Vol. % C_6H_5Cl[b]
1	0.200	6.00	0	45.00	7.5	40
2	0.200	4.00	0	45.00	8.6	60
3	0.200	2.00	0	45.00	9	80
4	0.100	4.00	0	45.00	7.0	60
5	0.0434	4.56	46	45.00	5.1	8.7
6	0.172	4.00	60	45.00	5.6	0
7	0.200	1.00	20	45.00	10	70
8	0.200	10.00	0	45.00	7.4–4.2	0
9	0.200	4.00	0	45.00	10	60
10	0.147	0.93	0	25.00	9.3	91
11[d]	(0.147)	(0.93)	0	35.00	9.8	91
14	0.101	2.00	0	45.00	10.2	80
15	0.083	1.67	83	45.00	3.8	0
26	0.053	2.79[e]	0	45.00	7.8	60

[a] Because *t*-butyl hydroperoxide has 0.100 ml./mequiv., the numbers in this column represent roughly (volume per cent in the solvent)/10. [b] The volume per cent of component *i* is $100(V_i/\Sigma V_i)$. [c] These chain lengths are not corrected for cage recombination of *t*-BuO· which occurs to the extent of 5–10%. The tabulated chain lengths represent averages over the run but do not include data after about 90% of the *t*-butyl hydroperoxide is consumed. All runs displayed constant chain lengths except those discussed in the text. [d] Run 11 is a continuation of run 10 warmed quickly to 35.00°. The warm-up period represents negligible reaction time. [e] Cumene hydroperoxide.

A summary of the kinetic data appears in Table II. The chain lengths which are listed are average chain lengths over the run up to 90% consumption of *t*-butyl hydroperoxide. It is clear from the table that above 1.0 *M* concentration *t*-butyl hydroperoxide decreases the chain length. (Compare runs 1 and 8 with runs 3 and 11.) In addition, *t*-butyl alcohol above 20 vol. % decreases the chain length even more.

Therefore the change in chain length during the radiochemical run I is clearly a solvent phenomenon in which the hydroperoxide is replaced by *t*-butyl alcohol as solvent. A plot of chain length *vs.* time for the reaction run in pure *t*-butyl hydroperoxide (run 8, Figure 1) indicates that the chain length decreases with time to approach the chain length obtained in *t*-BuOH. This plot along with the plots of runs 1, 2, and 15 show the effect of alcohol and hydroperoxide on chain length.

Two runs (3 and 7) were designed to consume all hydroperoxide under conditions where large solvent changes do not occur. In Figure 1 it can be seen that the chain length remains around 9–10 until about 90% hydroperoxide is consumed and then decreases abruptly. These data and the fact that no oxygen evolution occurs until the DBPO is added attest to the radical nature of the process, which was proposed by Hiatt, *et al.*,[6] and by Bartlett, *et al.*[8]

Discussion

We have confirmed the finding of Hiatt, Clipsham, and Visser[6] that the reaction under study can be represented accurately by eq. 5, in which *n* is about 20, and that in dilute chlorobenzene or benzene solution the kinetics are accurately described by eq. 11. However, both the rate and *n*, the chain length, decrease with increasing concentration of the solvents *t*-butyl alcohol or *t*-butyl hydroperoxide, the alcohol being more effective. This could be due to complexing of peroxy or alkoxy radical with solvents[13,14] or to

(13) F. F. Rust and E. A. Youngman, *J. Org. Chem.*, **27**, 3778 (1962).
(14) (a) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964); (b) D. G. Henry and G. A. Russell, *ibid.*, 2368 (1964).

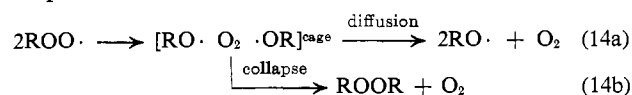hydrogen bonding between *t*-butyl hydroperoxide and solvent.

However, the recent discovery of viscosity-dependent cage recombination of *t*-butoxy radicals[12] suggests a more attractive explanation for this solvent effect. Table III presents a summary of the effect of solvent on "chain lengths" of DBPO and ROOH decompositions.

Table III. Effect of Solvent Viscosity on Chain Length of Hydroperoxide Decomposition and on DBPO Cage Reaction[a]

Solvent	Viscosity, mp.[b]	Chain Lengths — DBPO decompn.[c]	ROOH decompn.[d]
Benzene	5.6	17	10.5
Chlorobenzene	7	..	10.5
Chlorobenzene–cumene hydroperoxide	16	14	7.8[e]
t-Butyl hydroperoxide	33	..	7.5
t-BuOOH + *t*-BuOH	41	..	5.6
t-Butyl alcohol	46	10	3.8

[a] Data on the cage reaction from ref. 12. [b] At 25.0°. See ref. 12. [c] This column is the ratio of reactions 6b to 6a. [d] k_3/k_4 from Table II. [e] Cumene hydroperoxide decomposition. All other entries are for *t*-butyl hydroperoxide.

It is apparent from Table III that the interaction of peroxy radicals [reactions 8 and 9] shows the same kind of dependence on solvent viscosity which characterizes the decomposition of DBPO in reactions 6a and 6b.[12] We therefore suggest that the interaction of peroxy radicals leads to a caged pair of *t*-butoxy radicals which then either diffuse apart to continue the chain or collapse and terminate.

$$2ROO\cdot \xrightarrow{} [RO\cdot \; O_2 \; \cdot OR]^{cage} \xrightarrow{\text{diffusion}} 2RO\cdot + O_2 \quad (14a)$$
$$\xrightarrow{\text{collapse}} ROOR + O_2 \quad (14b)$$

The effect of temperature on the chain length of this reaction is much smaller than that observed for cage recombinations of methyl radicals.[15] We therefore

(15) S. Kodama, *Bull. Chem. Soc. Japan*, **35**, 827 (1962).

tentatively conclude that the activation energy for combination of t-butoxy radicals is greater than that for combination of methyl radicals.

External Combination of Alkoxy Radicals. Radioactivity may be introduced into product di-t-butyl peroxide through either the cage reaction (eq. 6a) or external combination (eq. 10). We have previously established[12] that, under the same conditions of viscosity and temperature used in the radiochemical experiment, run II, at least 5% of DBPO decomposition results in the cage reaction 6a. In run II, if all of the radioactivity in isolated di-t-butyl peroxide is assumed to come directly from DBPO, a value of 4.8% is obtained for this cage reaction. Thus the cage combination of t-butoxy radicals (eq. 6a) can entirely account for the observed radiochemical result, and we conclude that the external combination reaction 10 does not occur under these conditions.

In run I, where the concentration of initiator DBPO was unusually high (1 M), the radioactivity in the isolated di-t-butyl peroxide corresponds to about 13% cage reaction of DBPO, 3% higher than the yield of cage product actually observed in solvents of similar viscosities.[12] Thus about one-fourth of the observed activity (12% of total termination) might have arisen from reaction 10 in this experiment. Since autoxidation and other radical reactions are almost never conducted at such high initiation rates, we conclude that reaction 10 is unimportant in usual free-radical reactions.

Absence of Dialkyl Trioxide Formation. Finally, these experiments bear on the possible occurrence of trioxide in the cross reaction (eq. 4). If a trioxide ROOOR formed reversibly, this would introduce radioactivity into t-butylperoxy radicals (eq. 15)

$$R*OOOR \rightleftharpoons R*OO\cdot + RO\cdot \qquad (15)$$
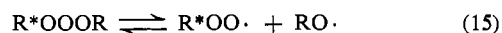
which, by rapid abstraction from t-butyl hydroperoxide (eq. 16),[16] would form radioactive t-butyl hydro-

$$R*OO\cdot + ROOH \longrightarrow ROO\cdot + R*OOH \qquad (16)$$

peroxide. Analysis of the remaining t-butyl hydroperoxide for radioactivity showed it to be virtually inactive. Since radioactivity to the extent of 1% that found in t-butyl alcohol would have been detectable, we can conclude that in these experiments less than 1% of t-butoxy radicals formed trioxide by reaction 4.

The absence of reaction 4 is inconsistent with the recent thermochemical calculations of Benson[17] which indicated that the stability of RO_nR decreases with increasing n. While we do not agree that all the assumptions used by Benson are justified (especially that ΔH^* for RO· combination is zero), we do agree that RO_3R should be somewhat more stable than RO_4R because the nonbonded repulsions between oxygen atoms should be cumulative.

We are therefore led to the tentative explanation that some special mechanism is available for the combination of two peroxy radicals. One possible mechanism is the direct production of caged alkoxy radicals through a transition state having some double-bond character in the center oxygens (eq. 17). Such a

(16) J. R. Thomas and C. A. Tolman, *J. Am. Chem. Soc.*, **84**, 2079 (1962).
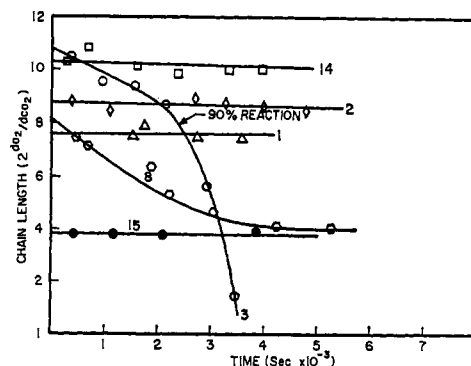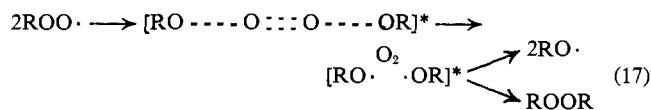(17) S. W. Benson, *ibid.*, **86**, 3922 (1964).

Figure 1. Chain length as a function of time in the DBPO-induced decomposition of t-butyl hydroperoxide at 45.0°. The conditions of the various runs indicated by the numbers are shown in Table II.

$$2ROO\cdot \longrightarrow [RO\text{---}O:::O\text{---}OR]* \longrightarrow$$

$$[RO\cdot \ \ \cdot OR]* \underset{\nwarrow}{\overset{O_2 \quad \nearrow 2RO\cdot}{\longrightarrow}} ROOR \qquad (17)$$

mechanism would seem to deny the existence of RO_4R as an intermediate, for which there seems to be some evidence.[18] This problem, which has been discussed by Benson,[17] is being investigated.

Experimental

Materials. All chemicals except those described below were reagent grade.

t-Butyl alcohol, Eastman Kodak White Label, was distilled from calcium hydride.

Chlorobenzene was shaken with portions of sulfuric acid until a colorless acid phase was obtained, washed with water, dried over sodium sulfate and distilled through a 10-plate column under nitrogen.

t-Butyl hydroperoxide from Lucidol Corp. was distilled at reduced pressure. To check this material for di-t-butyl peroxide, 2 ml. was treated with 16 ml. of 10% sodium hydroxide and the resulting solution was extracted with 1 ml. of carbon tetrachloride. The carbon tetrachloride solution, after drying, showed no trace of a di-t-butyl peroxide peak at 11.4 μ but did show the spectrum of t-butyl hydroperoxide. The amount of t-butyl peroxide in 2 ml. was therefore less than the detectable limit of about 10^{-6} mole, or less than 0.1%.

Radioactive methyl iodide containing 1 mcurie of ^{14}C was purchased from New England Nuclear Corp.

t-Butyl Alcohol-methyl-[14]C. The labeled methyl iodide was diluted with unlabeled methyl iodide, converted to the Grignard reagent, and then to the alcohol by adding acetone. The resulting solution was treated with saturated ammonium chloride solution, and the ether layer was separated, dried over potassium carbonate, and distilled. The activity was 76,400 c.p.m./μl.

t-Butyl Hydroperoxide-methyl-[14]C. One milliliter of the labeled t-butyl alcohol was added to 4 ml. of unlabeled alcohol and this was treated with hydrogen peroxide by the method of Davies.[19] Two layers were obtained. The upper layer was removed and later combined with three 4-ml. portions of t-butyl hydro-

(18) N. A. Milas and S. M. Djokic, *Chem. Ind.* (London), 405 (1962).
(19) A. G. Davies and R. V. Foster, *J. Chem. Soc.*, 1541 (1953).

peroxide which had been used to extract the lower layer. The lower layer was additionally extracted with four 10-ml. portions of petroleum ether (b.p. 30–60°), and these extracts were added to the combined *t*-butyl hydroperoxide extracts. The total extract solution was then washed twice with 4 ml. of water, dried with sodium sulfate, and distilled at reduced pressure. A flat cut at 41° of 9.5 ml. was obtained.

Di-t-butyl Peroxyoxalate-methyl-^{14}C. This was prepared from 3.05 ml. of the above hydroperoxide by the method of Bartlett, Benzing, and Pincock[10a] except that the crude product mixture was filtered through anhydrous magnesium sulfate directly into a nitrogen-filled recrystallization apparatus and cooled slowly to −10° to produce 2.0 g. of large crystals. The activity of this product was 4900 c.p.m./mg.

Instruments. Radioactivity measurements were made in a Nuclear Chicago Scintillation Counter using reagent grade toluene containing 4 g. of 2,5-diphenyloxazole (PPO) and 50 mg. of 1,4-di[2-(5-phenyloxazolyl)]benzene (POPOP) (both Calbiochem scintillator grade) per liter. N.m.r. measurements were made on a Varian HR-60 spectrometer. Infrared spectra were taken on a Perkin-Elmer Model 137B spectrophotometer. Vapor phase chromatography, both analytical and preparative, was done on a Wilkins Instrument Co. autoprep.

Kinetic Measurements. All oxygen evolution rates were measured in an automatic, recording, constant-pressure gasometer which is described elsewhere.[7b] Solutions of *t*-butyl hydroperoxide and solvent were placed in a 50-ml., round-bottom flask which was immersed in an accurately thermostated oil bath, stirred magnetically, and attached to the recording gasometer. The DBPO was placed in an ampoule in the neck of the flask (not in the bath) and added after it was established that no oxygen was evolved without catalyst. Evolution began immediately after the solid DBPO was added. See ref. 7b for a complete description of the method.

In a typical DBPO-induced *t*-butyl hydroperoxide decomposition, e.g., run 9 (the second radiochemical experiment), the hydroperoxide (4.0 ml.) and solvent (6.0 ml. of chlorobenzene) were equilibrated with the 45.0 ± 0.03° bath, and then 0.4680 g. (2 mmoles) of DBPO-^{14}C was added in the capsule.

The data, displayed as a series of approximately zero-order plots on the chart paper by repeatedly refilling the buret, are actually first-order rate plots consisting of several thousand points. About 50 such points constitute an accurate instantaneous slope. Instantaneous slopes, $d(O_2)/dt$, are taken at various times and the remaining (DBPO) calculated at such times from the rate constant of Bartlett, Benzing, and Pincock.[10a] The instantaneous rate of CO_2 evolution was calculated from the same rate expression and this was subtracted from $(d(gas)/dt)$ to give $d(O_2)/dt$. The chain length, $(d(ROOH)/dt)/(2d(DBPO)/dt) = (d(O_2)/dt)/(d(DBPO)/dt)$, is shown in the last column in Table IV. It should be noted that the average of such chain lengths is very close to chain lengths determined in other ways.

Products of Radio-DBPO Induced Decomposition of t-Butyl Hydroperoxide. Two experiments were carried

Table IV. DBPO-C^{14} Induced Decomposition of *t*-Butyl Hydroperoxide (Run 9)[a]

Time, sec.	Gas rate,[b] ml. sec.$^{-1}$	Concn. of DBPO, mM	CO_2 evolution[b] × 10^2, ml. sec.$^{-1}$	$d(O_2)$[b]/dt, ml. sec.$^{-1}$	Chain[c] length
336	0.158	1.832	2.16	0.136	12
576	0.146	1.720	2.01	0.126	12
936	0.125	1.567	1.85	0.106	11.5
1296	0.108	1.423	1.67	0.091	10.9
2016	0.0822	1.18	1.38	0.0684	9.9
2646	0.0693	1.003	1.16	0.0577	9.9
3246	0.0591	0.858	1.02	0.0489	9.5
3996	0.0485	0.704	8.15	0.0483	9.9
4896	0.0376	0.557	5.90	0.0317	10.8
5615	Quenched	0.463			

[a] Temperature, 45.0°; concentration of DBPO, 0.20 M; concentration of *t*-BuOOH, 4.0 M; solvent, chlorobenzene; volume, 10.0 ml. [b] The gas was measured at 25°. Thus these rates may be converted to mole l.$^{-1}$ sec.$^{-1}$ by multiplying by 1/22.4 × volume. The other kinetic runs, which were treated in the same way, are presented and discussed in the Results section. [c] This high initial chain length is due to an experimental error. The solution was mistakenly saturated with CO_2 prior to addition of catalyst. Other runs in this solvent, which were air saturated, displayed constant chain lengths of 10.

out at 45°. Because these experiments differed widely in kinetic behavior and in methods of isolation and yet yielded similar results, both will be described.

Experiment 1. A 10-ml. flask containing a magnetic stirring bar was attached to a simple leveling bulb gasometer. To this flask was added 1.1583 g. (4.95 mmoles) of radio-DBPO and 5.00 ml. (50.0 mmoles) of purified *t*-butyl hydroperoxide. About 2 mmoles of oxygen evolution was measured at 25°, 2 mmoles at 35°, and the remainder at 45°. The chain length was about 9 at 25 and 35°, and at 45° it rapidly decreased to a value of about 2. After 6 hr. at 45°, the solution was analyzed for products. The n.m.r. spectrum of a mixture of *t*-butyl alcohol, *t*-butyl peroxide, and *t*-butyl hydroperoxide in a molar ratio 2:1:3 indicates the respective methyl absorptions to be 65.6, 62.45, and 64.0 c.p.s. downfield from tetramethylsilane. Such a mixture can be analyzed quantitatively to about ±5% in each of these components by estimating the area under these peaks. Applying this technique to our reaction mixture (density 0.804), we find 69 mole % (60 wt. %) *t*-butyl alcohol, 22 mole % (24 wt. %) *t*-butyl hydroperoxide, and 9 mole % (15.7 wt. %) *t*-butyl peroxide. This indicates an average chain length of 3.8 for the entire decomposition of DBPO and a yield of 1 mole of *t*-butyl peroxide per mole of DBPO. Two milliliters of this solution was diluted with 3.0 ml. of *t*-butyl peroxide, dissolved in 10 ml. pentane, and extracted with four 5-ml. portions of 30% sodium hydroxide (A). This extract, after adding 2.0 ml. of *t*-butyl hydroperoxide, was washed with three 10-ml. portions of pentane, then with three 10-ml. portions of methylene chloride, and neutralized with 10% sulfuric acid at 0°. It was extracted with 10 ml. of pentane and the pentane solution was dried over magnesium sulfate and evaporated at 20 mm. The 71 mg. of product which was obtained gave 250 c.p.m. or a maximum activity of about 5 c.p.m./mg. in the original product *t*-butyl hydroperoxide. A 3,5-dinitrobenzoate of the *t*-butyl hydroperoxide was ob-

tained by adding 0.995 g. of *t*-butyl hydroperoxide to 0.2505 g. of the crude product, distilling off about 0.1 g. at 100 mm., and preparing the ester from the residue. It did not show greater than background count in 25- to 50-mg. samples for any of five successive recrystallizations. This perester was identified by its infrared spectrum and a mixture melting point with an authentic sample (m.p. 93.5–94°). The pentane solution from the point labeled A above was dried over magnesium sulfate and distilled at atmospheric pressure. Three middle cuts were taken: (1) 0.81 g., having 3410 c.p.m./0.05 ml.; (2) 0.46 g., having 4160 c.p.m./0.05 ml.; and (3) 0.6 g., having 4740 c.p.m./0.05 ml. Based on the n.m.r. yields and the dilutions this indicates about 1000 c.p.m./mg. in the product di-*t*-butyl peroxide. To be sure that the other products were removed, 0.554 g. of the third cut was diluted with 3.341 g. of unlabeled di-*t*-butyl peroxide and this was distilled from lithium aluminum hydride at reduced pressure at 70° after being heated for 15 min. at 80°. Two cuts of about 1.5 ml. were taken. These cuts gave 6800 c.p.m. for 0.515 g. and 5970 c.p.m. for 0.407 g., respectively, indicating an average of 1030 c.p.m./mg. in the original di-*t*-butyl peroxide product.

A 0.500-ml. sample of the original product was diluted with 10.0 ml. of *t*-butyl alcohol, distilled at 97 mm. and 40°, and converted to the phenylurethan. Successive recrystallization crops were counted. The urethan gave 19,400, 19,900 and 20,900 c.p.m./g. on successive recrystallizations. This indicates 1728 c.p.m./mg. of *t*-butyl alcohol product. Before preparation of the urethan the *t*-butyl alcohol indicated 1950 c.p.m./mg. A 0.0109-g. sample of the original radio-DBPO gave 53,276 c.p.m. or 4900 c.p.m./mg. Thus, based on the n.m.r. analyses, the products contain: *t*-butyl hydroperoxide, <5 c.p.m./mg.; di-*t*-butyl peroxide, 1030 c.p.m./mg.; and *t*-butyl alcohol, 1728 c.p.m./mg.

Experiment 2. A solution of 4.00 ml. (40.0 mmoles) of *t*-butyl hydroperoxide in 6.00 ml. of chlorobenzene was equilibrated with the 45.0° bath in the kinetic apparatus.[7] This solution was saturated with carbon dioxide gas at 1 atm., and when no oxygen evolution had been observed for several minutes, 0.4680 g. (2 mmoles) of radio-DBPO was added from the side arm. Oxygen evolution began immediately, was recorded, and appears as run 9 in Tables II and III. After 5616 sec., the reaction was stopped by cooling to −20°. At this point a total of 1.537 mmoles of DBPO had been consumed (calculated), leaving 0.463 mmole. A 435-ml. volume (19.4 mmoles) of gas was evolved, corresponding to 16 mmoles of oxygen. The average chain length is thus $16/1.537 = 10.5$. After 0.3 ml. was removed for g.l.c. and n.m.r analyses, the remainder was warmed to 25° on a vacuum line and quickly distilled into a nitrogen trap and the reactor pumped another 10 min. at 0.1 mm. The trap following this nitrogen trap was found to contain negligible radioactivity. There remained behind in the reactor 0.0938 g. of crystalline material identified as pure DBPO by infrared spectra. This corresponds to 0.40 mmole of DBPO compared to the above calculated residue of 0.46 mmole based on the rate constant for DBPO decomposition reported by Bartlett, Benzing, and Pincock.[10a]

DBPO Activity. The residue was dissolved in 1 ml. of dry pentane and cooled to 0° to afford large crystals of DBPO. A 0.0081-g. sample of these crystals gave a net count of 37,440 c.p.m. This corresponds to 1.09×10^6 c.p.m./mmole or 4600 c.p.m./mg., compared to 4900 c.p.m./mg. for starting DBPO. Thus at most 6% exchange could have occurred.

Product Separation. To the distillate, which weighed 9.13 g., was added 5.00 ml. each of *t*-butyl alcohol, di-*t*-butyl peroxide, and *t*-butyl hydroperoxide. The resulting mixture was distilled at reduced pressure. Cuts C (3 ml., b.p. 32–36° at 78 mm.), E (1 ml., b.p. 30° at 65 mm.), F (5 ml., b.p. 40° at 45 mm.), and G (2 ml., b.p. 40° at 30–35 mm.) were obtained.

t-Butyl Alcohol Activity. A phenylurethan was prepared from cut C above and was recrystallized from heptane in two crops. The first crop melted at 138–139.5 and had 19,480 c.p.m./mmole. The second crop, m.p. 132–133°, had 17,900 c.p.m./mmole. The second crop was recrystallized to yield material having 19,470 c.p.m./mmole. The mixture in distillation cuts E and F, which was shown by infrared to consist mostly of *t*-butyl alcohol and di-*t*-butyl peroxide, was easily separable on an 8 ft. × ³/₈ in. column packed with firebrick containing 20% diethylene glycol succinate. By operating at an injection temperature of 150° and column temperature of 70° with 60 ml./min. flow rate the peroxide and alcohol could be eluted in about 4 and 6 min., respectively, with a clean separation and were collected in ice-bath traps. The peroxide thus obtained contained less than 1 part of alcohol in 800 by analysis on the same type column. The *t*-butyl alcohol so obtained gave 18,650 c.p.m./mmole, consistent with that of the urethan.

Di-t-butyl Peroxide Activity. The peroxide, obtained by chromatography above, showed 1311 c.p.m. for 68.8 mg. or 2803 c.p.m./mmole of diluted peroxide.

t-Butyl Hydroperoxide Activity. Cut G above, which appeared by infrared to be mostly hydroperoxide, was converted to the 3,5-dinitrobenzoate (identified by infrared spectrum) as previously described. Several fractions obtained by recrystallizing this compound from ether all showed less than background activity but varied widely in quenching. One fraction, however (m.p. 93.5–94°, infrared identical with an authentic sample), which weighed 38.5 mg., showed exactly one-half background, and when a sample of ^{14}C-toluene (giving 2100 c.p.m. without the perester) was added, 1028 c.p.m. was obtained. Thus the perester quenched 50% and did not contain measurable activity itself in 38.5 mg. (0.135 or 0.02 mmole of product hydroperoxide. If we set 10 c.p.m. as detection limit this gives a maximum of 500 c.p.m./mmole for *t*-butyl hydroperoxide, compared to 10^6 c.p.m./mmole in DBPO or 45,000 c.p.m./mmole for product *t*-butyl alcohol.

Possible Contamination in Di-t-butyl Peroxide from DBPO. Because DBPO might slowly decompose in the solid state on storage at −20° to give di-*t*-butyl peroxide, a check was made. To 0.0639 g. of radio-DBPO was added 2.0 ml. of *t*-butyl peroxide. This (1.5 ml.) was distilled at 25° into a Dry Ice trap and the distillate was purified by the above-mentioned g.l.c. Counting 0.1459 g. of this product gave 115 c.p.m.

with a background of 40. This indicated that the DBPO contained less than 0.3% t-butyl peroxide.

Yields of Products. The absolute yield of t-butyl alcohol was estimated from total oxygen evolution. However, the ratio of alcohol to peroxide, which is important to our radiochemical results, is obtained by measuring the area under the g.l.c. curves obtained by injecting 2 μl. of either the original product containing unreacted DBPO or product which had been vacuum distilled away from the DBPO onto an 8 ft. $\times$ $^1/_8$ in. column as described above. By comparison with synthetic mixtures they gave weight ratios of 10.5:1 and 11.2:1, respectively. Added DBPO did not affect the results. This indicates about 21 moles of alcohol per mole of di-t-butyl peroxide, representing an average chain length of 10.5.

Thus t-BuOH/2(tBuO)$_2$ = 10.5, O$_2$/DBPO used = 10.5, and average 2d(O$_2$)/d(CO$_2$) = 10.5. The composition of products can therefore be calculated from the DBPO which was used. Alcohol = 21 $\times$ DBPO used = 32 mmoles, di-t-butyl peroxide = DBPO used = 1.54 mmoles, t-butyl hydroperoxide = (initial t-BuOOH) − (t-BuOH) = 8.0 mmoles.

Calculation of Activities. Of the 10.700 g. total weight used in run 9, 0.094 g. of DBPO remained behind, and 0.138 g. of CO$_2$ and 0.515 g. of O$_2$ were evolved, leaving 9.935 g. of volatile products of which 9.136 g. were used for dilution with alcohol, peroxide, and hydroperoxide. The activity in the alcohol product based on a chain length of 10.5 is therefore

$$\frac{(52.6 \text{ mmole} + 32.4)(0.92 \text{ mmole})}{(32.4)(0.92 \text{ mmole})} \times$$

18,800 c.p.m./mmole diluted = 52,000 c.p.m./mmole

The activity in the peroxide is

$$\frac{(32.4)(0.92/10.5 + 26.92 \text{ mmole})}{(32.4)(0.92/10.5)} \times$$

$$2803 = 56,050 \text{ c.p.m./mmole}$$

This represents

$$\frac{(56,050)(1)}{(56,050 + 21.0)(52,000)} \times$$

$$100 = 4.8\% \text{ of DBPO activity}$$

Decomposition of Cumene Hydroperoxide. A solution of 4.00 ml. of cumene hydroperoxide (2.79 M) purified by the method of Kharasch[20] in 6.00 ml. of chlorobenzene was decomposed at 45.0° in the kinetic apparatus described above. As initiator 0.125 g. (0.055 M) of radioactive DBPO was used. The DBPO gave a net count of 5230/mg. The average chain length was 7.8 by kinetic measurement and 8.0 over-all (see Table II). The final solution was cooled to −80° to condense any volatile materials, and 1.00 ml. (0.793 g.) of di-t-butyl peroxide was added. About 6 ml. of liquid was distilled at 25° under high vacuum and a small amount of lithium aluminum hydride was added to the distillate and then redistilled. The peroxide was separated by g.l.c. fractionation as described above, shown to contain negligible t-butyl alcohol, and counted. For 84.4 mg. the activity was 4765 c.p.m. This represents a 6.8% yield of di-t-butyl peroxide from DBPO.

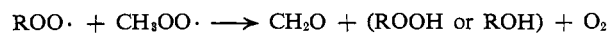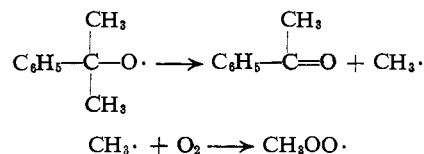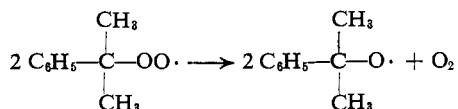(20) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **16**, 113 (1951).

Mechanisms of Autoxidation. Terminating Radicals in Cumene Autoxidation

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The effect of t-butyl hydroperoxide on the rate of cumene autoxidation has been studied. Although t-butyl hydroperoxide does not initiate cumene autoxidation, it accelerates the autoxidation initiated by α,α-azobisisobutyronitrile (AIBN). Furthermore, the rate of autoxidation depends directly on the ratio of cumene hydroperoxide to t-butyl hydroperoxide. These and other data, combined with previous studies, strongly indicate the following termination mechanism for autoxidation of cumene and other tertiary hydrocarbons. The CH_3

$$2 \text{ C}_6\text{H}_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OO\cdot \longrightarrow 2\,\text{C}_6\text{H}_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O\cdot + \text{O}_2$$

$$\text{C}_6\text{H}_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O\cdot \longrightarrow \text{C}_6\text{H}_5-\overset{\overset{\displaystyle CH_3}{|}}{C}=\text{O} + \text{CH}_3\cdot$$

$$\text{CH}_3\cdot + \text{O}_2 \longrightarrow \text{CH}_3\text{OO}\cdot$$

$$\text{ROO}\cdot + \text{CH}_3\text{OO}\cdot \longrightarrow \text{CH}_2\text{O} + (\text{ROOH or ROH}) + \text{O}_2$$

deuterium isotope effect found by Boozer, et al., is also explained by this scheme.

Introduction

The autoxidations of hydrocarbons at moderate temperatures and oxygen pressures display kinetic