Homolytic Decompositions of Hydroperoxides. II.[1a]   Radical-Induced Decompositions of *t*-Butyl Hydroperoxide

R. HIATT,[1b] T. MILL, K. C. IRWIN, AND J. K. CASTLEMAN

Stanford Research Institute, Menlo Park, California

Three factors account for deviations from the simplest pattern for the radical-induced decomposition of *t*-BuO₂H (reactions 1–4 in part I): (1) variation in the ratio of terminating to nonterminating interactions of 2*t*-BuO₂· with the viscosity of the medium; (2) competition between the propagation and cleavage reactions of *t*-BuO· radicals; and (3) competition between hydroperoxide and solvent for *t*-BuO· radicals. Reactions in the gas phase illustrate all three factors. In solution cleavage is important at high temperatures and low concentrations of *t*-butyl hydroperoxide (as in 0.1 *M* *t*-BuO₂H in benzene or CCl₄ at 100°) or in hydroxylic solvents (AcOH or *t*-BuOH) at moderate temperatures. Attack on alkane solvents increases with increasing temperature. Chain lengths of 1 to 50 are observed. Both cleavage and solvent participation result in shorter chains and complex kinetics.

In benzene or chlorobenzene at 25–50°, *t*-BuO₂H is cleanly decomposed by alkoxy radicals to 90% *t*-BuOH, 10% *t*-Bu₂O₂, and 100% O₂. The rate of decomposition is about ten times the rate of initiation and is independent of the concentration of *t*-BuO₂H.[2] After considering the free-radical-generating efficiencies of the initiators used and the stability of *t*-BuO₂H in the absence of initiators, this paper deals with induced decompositions in several solvents at 45–100° and in the gas phase at 100°. We show that chain lengths and products vary and that kinetics may be complex, but that the results can be rationalized in terms of a few competing reactions.

Experimental Section

Materials.—*t*-BuO₂H (90%) obtained from Lucidol Corp. was vacuum distilled to 99+% purity (by iodometric titration). *sec*-Bu₂O₂ and *t*-BuO₂C₆H₁₁ (C₆H₁₁ = cyclohexyl) were prepared by the methods of Mosher and coworkers.[3] *sec*-Bu₂O₂ was shown to be pure by iodometric titration and by glpc. The *t*-BuO₂C₆H₁₁ contained about 5% of an unidentified contaminant. *t*-Bu₂O₂ obtained from the Matheson Co. was shown to be pure by glpc. Di-*t*-butyl peroxyoxalate (DBPO) was prepared by the method of Bartlett and coworkers.[4]

The solvents used were Matheson Chromatograde, refluxed and distilled from CaH₂ before use. Isobutane, *n*-butane, cyclopentane, and cyclopentene were Phillips research grade, used without further purification.

Analytical Procedures.   Iodometric Titrations.—*t*-BuO₂H, *sec*-Bu₂O₂, and DBPO were titrated iodometrically. In the basic technique the sample is added to a mixture of ~20 ml of 90:10 *i*-PrOH–HOAc; about 1 g of NaI is added; and the mixture is refluxed to hasten reaction and exclude air. For hydroperoxides, refluxing the mixture for 2–3 min gave quantitative liberation of I₂. DBPO liberated only 60% of the theoretical amount of I₂, but did so consistently when the amount to be analyzed was kept below 0.05 mmol. Dialkyl peroxides gave no titer under these conditions.

Di-*sec*-alkyl peroxides could be titrated quantitatively if a small amount of metal ion was added. Thus, *sec*-Bu₂O₂ liberated 100 ± 2% of the theoretical iodine when the 20 ml of NaI–HOAc–*i*-PrOH mixture contained 2 μl of a Nuodex solution of iron octoate and reflux time was extended to at least 5 min. Similarly, FeSO₄, FeCl₃, and Nuodex copper octoate were equally effective catalysts, while use of Nuodex solutions of cobalt or manganese octoate gave no I₂. *t*-Bu₂O₂ liberated no iodine even with higher concentrations of iron octoate and reflux times up to

20 min. *t*-Butyl cyclohexyl peroxide gave a maximum of 43% of the theoretical amount of iodine under these conditions.

Gas Chromatography.—Most analyses of reacted solutions were made using the Wilkens Model 90 or 350 gas chromatographs with thermal conductivity detectors and 10-ft columns of either 20% Carbowax 20M or 20% diisodecyl phthalate on Chromosorb P. *t*-Bu₂O₂ was eluted without decomposition, but other peroxides and hydroperoxides were decomposed in the injector cavity or on the column. Solutions containing hydroperoxides were usually reduced to alcohols with triphenylphosphine[5] (Ph₃P) before glpc analysis.

sec-Bu₂O₂ and *t*-BuO₂C₆H₁₁ were analyzed on a Wilkens gas chromatograph with a flame ionization detector ("Hi-Fi") where they were eluted without decomposition from a 5-ft column of 2% diisodecyl phthalate on Chromosorb P. The low-loaded column permitted use of a low temperature (70°), thereby minimizing decomposition. In one instance a solution of *t*-BuOH, *t*-Bu₂O₂, and *t*-BuO₂C₆H₁₁ in cyclohexane was analyzed by a combination of fractional distillation, quantitative ir analysis, and glpc.

Procedures for Reactions.—Most reactions in solution were carried out in a series of eight or nine sealed Pyrex ampoules, initially degassed, or with an air atmosphere as indicated in text. Ampoules were immersed in a constant-temperature bath and withdrawn at suitable intervals for iodometric and glpc analysis. Some ampoules were fitted with break-seals and opened on a vacuum line so that the amount of evolved gases could be estimated and samples analyzed by mass spectrometry. For solution reactions carried out under reflux, a cell consisting of a 50-ml bulb sealed to a condenser was immersed in a bath 10–15° warmer than the reflux temperature of the solvent. The solution of hydroperoxide was brought to reflux and reaction was started by addition of the initiator.

Gas phase experiments were carried out in 100-ml Pyrex bulbs with break-seals and capillary inlet tubes. Peroxide and hydroperoxide were added to the evacuated bulbs from a tared syringe. Hydrocarbons were added to some runs by vacuum distillation from a calibrated bulb. Formaldehyde was added in the form of paraformaldehyde. After being heated for appropriate time intervals, the bulbs were connected to the vacuum line and opened, and the contents were distilled into small liquid nitrogen-cooled traps which were then cut out of the line. Less volatile hydrocarbons were distilled with the hydroperoxide. Evolved gases were transferred to a gas buret with a Toepler pump, then analyzed using a Cu–CuO combustion furnace.

Where large amounts of butanes were present, the bulb contents were fractionally distilled under high vacuum at −80°. Blank experiments showed no significant loss of hydroperoxide under these conditions.

Thermal Decompositions of Initiators and of *t*-BuO₂H

It was necessary to measure rates and efficiencies of radical production by some of our initiators before chain lengths of induced decompositions could be evaluated. The possibility of some thermal decompo-

(1) (a) Part I: R. Hiatt, T. Mill, and F. R. Mayo, *J. Org. Chem.*, **33**, 1416 (1968). Equations 1–16 appear in part I. (b) To whom all correspondence should be addressed at Brock University, St. Catherines, Ontario, Canada.

(2) R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem.*, **42**, 2754 (1964).

(3) F. Welch, H. R. Williams, and H. S. Mosher, *J. Amer. Chem. Soc.*, **77**, 551 (1955).

(4) P. D. Bartlett, E. Benzing, and R. E. Pincock, *ibid.*, **82**, 1762 (1960).

(5) L. Horner and W. Jurgleit, *Ann. Chem.*, **591**, 139 (1955).

TABLE I
RATES AND PRODUCTS OF DECOMPOSITIONS OF INITIATORS

Temp, °C	Solvent	[R$_2$O$_2$]$_0$, M	Decomposition^a		Yields on peroxides decomposed, %			
			$10^5 k_1$, sec^{-1}	%	AcMe	t-BuOH	t-Bu$_2$O$_2$	S—S^{b-e}
			t-Bu$_2$O$_2$					
100	C$_6$H$_6$	0.0066	0.0875	62	96	1.6		
100	C$_6$H$_6$	0.245	0.102	70	29	68		20^b
100	PhMe	0.264	0.0682	22				100^c
			sec-Bu$_2$O$_2$					
100	PhMe	0.10	0.27	83				23^c
100	PhMe	0.027	0.27	75				25^c
100	Gas phase	0.0008	0.15^f	7–82^f				
			Di-*t*-butyl Peroxyoxalate (DBPO)					
25.0	*t*-BuOH	0.08	1.83	70			10^g	
37.8	*n*-C$_5$H$_{12}$	0.008	10.1	39	0	77	5.4	29^d
81.5	C$_6$H$_{12}$	0.006				92		62^e

^{a} Apparent first-order rate constant and extent of decomposition over which it was measured. $^{b-e}$ Products of radical coupling: toluene,^{b} bibenzyl,^{c} C$_{10}$H$_{22}$,^{d} (C$_6$H$_{11}$)$_2$.^{e} ^{f} Average of seven runs. ^{g} See ref 7.

sition of *t*-BuO$_2$H under the experimental conditions also had to be checked.

Decompositions of Initiators in the Absence of Hydroperoxides. *t*-Bu$_2$O$_2$.—At and above 100°, *t*-Bu$_2$O$_2$ gave convenient rates of initiation. In toluene at 100°, the first-order rate constant for decomposition of *t*-Bu$_2$O$_2$ was found[6] to be 6.8 ×10^{-7}/sec, and the efficiency of radical production was 100% (measured by the yield of bibenzyl). This rate constant was used for calculation of chain lengths for induced decompositions in both gas phase and solution, although in some of the induced runs the disappearance of *t*-Bu$_2$O$_2$, as measured by glpc, was faster (see below). Typical results are shown in Table I.

Di-*t*-Butyl Peroxyoxalate.—DBPO was used to initiate runs at 80° and below. Rate constants for the thermal decompositions of DBPO at several temperatures in benzene and cumene have been given by Bartlett and coworkers.[4] We found the same rates in *n*-pentane and in *t*-BuOH. DBPO has been shown to give about 5% *t*-Bu$_2$O$_2$ by a cage reaction in solvents of moderate viscosity (pentane, benzene, HOAc) at 35–45°.[7] In *t*-BuOH and in Nujol, cage recombination accounted for 10 and 76%, respectively, of the radicals formed. For this work we assumed an initiator efficiency of 100% minus the per cent yield of *t*-Bu$_2$O$_2$ for the particular solvent.

sec-**Bu$_2$O$_2$.**—Some runs at 100° were initiated by *sec*-Bu$_2$O$_2$. Pryor, *et al.*,[8] have shown that this peroxide initiates the polymerization of styrene at 80° about as rapidly as *t*-Bu$_2$O$_2$ does. We have measured rates of decomposition at 100° in toluene and in the gas phase (Table I) using both glpc and a modified iodometric titration for peroxide analysis. Rates were first order in peroxide, and about four times as fast in solution as for the decomposition of *t*-Bu$_2$O$_2$, but the efficiency of radical production in solution, as measured by the yield of bibenzyl, was only 25%. Analysis of the other products of decomposition (Table I) gave an unexpected 25–30% hydrogen gas, which might be explained by a concerted decomposition of the

kind discovered by Mosher and Durham[9] for primary hydroperoxy hemiacetals.
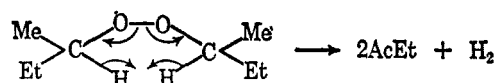
The gas phase decomposition of *sec*-Bu$_2$O$_2$ was first order, but only 2.7 times as fast as decomposition of *t*-Bu$_2$O$_2$: k_d = 1.8 × 10^{-6}/sec. The faster rate in solution suggests more chain decomposition due to the higher concentrations used.

Decomposition of *t*-BuO$_2$H in the Absence of Initiators.—Thermal decompositions of *t*-BuO$_2$H in solution are treated extensively in part V. At 100° or below, 0.1 *M* *t*-BuO$_2$H decomposed less than 1% in 2 days, a negligible contribution to the induced decompositions which usually lasted no longer than 15 hr.

Early experiments showed low but erratic rates of decomposition, 4–12% in 15 hr, in the gas phase at 100°. In subsequent work with a second batch of purified hydroperoxide, rates were considerably higher, 6–27% in 15 hr. Using new vessels or vessels which had been treated with NaOH[10] narrowed the range to 4.4–10.2%. (An average rate of decomposition for 0.007 *M* *t*-BuO$_2$H was 3.6–7.9 × 10^{-7} mole/l. min.$^{-1}$). Addition of cyclopentene (which should have quenched any radical chain decomposition) had no effect. This higher rate is apparently connected with surfaces and with otherwise indistinguishable differences between batches of hydroperoxide. It was not caused by the presence of *t*-Bu$_2$O$_2$ as an impurity; as will be shown, about 10% *t*-Bu$_2$O$_2$ would be required to give the average rates above.

Induced Decompositions of *t*-BuO$_2$H in Solution

Decompositions at >0.2 *M* in Benzene at 100°.—At concentrations of *t*-BuO$_2$H above 0.2 *M* *t*-Bu$_2$O$_2$-induced decompositions gave *t*-BuOH, O$_2$, and, presumably, *t*-Bu$_2$O$_2$;[11] yields of acetone were negligible. The rate of decomposition was independent of [*t*-BuO$_2$H] to at least 50% decomposition. The rather

(6) This value is close to the value (5.0 ± 2.5) × 10^{-7}/sec obtained by extrapolation from the 130–150° gas phase data of L. Batt and S. W. Benson [*J. Chem. Phys.*, **36**, 895 (1962)].

(7) R. Hiatt and T. G. Traylor, *J. Amer. Chem. Soc.*, **87**, 3766 (1965).

(8) W. A. Pryor, D. M. Huston, T. R. Fiske, T. L. Pickering, and E. Ciuffarin, *ibid.*, **86**, 4237 (1964).

(9) H. S. Mosher and L. J. Durham, *ibid.*, **82**, 4537 (1960), and preceding papers.

(10) Heated with 10% NaOH for 30 min at 100°, rinsed repeatedly with water, and oven dried.

(11) The concentration of the initiator, within the accuracy of the glpc analyses, remained constant, as if all terminations gave *t*-Bu$_2$O$_2$.

wide variation in chain length, 23–32 in Table II, was probably due to some "thermal" decomposition at these high concentrations of hydroperoxide.

TABLE II

t-Bu$_2$O$_2$-INDUCED DECOMPOSITIONS OF t-BuO$_2$H
IN BENZENE AT 100°

[t-Bu$_2$O$_2$]$_0$, M	[t-BuO$_2$H]$_0$, M	Chain length^a	Yields on t-BuO$_2$H decomposed, %		
			AcMe	t-BuOH	O$_2$
0.246	0.878	30.0			
0.251	0.554	32.0			100
0.247 (*sec*-Bu$_2$O$_2$)	0.199	23.3	4	82	
0.248	0.506	12^b			

^{a} Moles of t-BuO$_2$H destroyed/mole of initiating radicals. ^{b} Average for first 2 hr, corrected to 25% efficiency of *sec*-Bu$_2$O$_2$.

The principal difference between these results and those previously reported[2] for decompositions initiated by DBPO in benzene or chlorobenzene at 25 to 45° is the longer chain length, paralleled by the lower viscosity of benzene at 100°:

$$\frac{\text{specific viscosity at } 35°}{\text{specific viscosity at } 100°} = 2.5$$

$$\frac{\text{chain length at } 100°}{\text{chain length at } 35°} = 2.7$$

The factor 2.7 corresponds to an activation energy for escape of alkoxy radical pairs from the cage to continue the chain (eq 3[1a]) which is 3.5 kcal/mol higher than for their cage reaction with each other to give t-Bu$_2$O$_2$ (eq 4[1a]).

A more striking example of viscosity control is thermal decomposition at 35° of 0.03 M DBPO in Nujol containing 0.1 M t-BuO$_2$H. The result, *no* hydroperoxide decomposed, is due partly to competition by the Nujol for alkoxy radicals but mostly to a viscosity effect. (DBPO itself is no more than 24% efficient in producing free radicals in this very viscous medium,[7] and we infer that few, if any, alkoxy radical pairs, if produced by interactions of 2t-BuO$_2$·, would escape from the solvent cage.)

sec-Bu$_2$O$_2$ was used to initiate one decomposition in benzene at 100° (Table II). Products were not analyzed, but the results prove that some pairs of *sec*-BuO· radicals are able to escape from the solvent cage. The indicated initial chain length, 12, depends too much on the uncertain efficiency of the initiator (*vide supra*) to permit comparison with runs initiated with t-Bu$_2$O$_2$.

Decompositions with Cleavage of t-BuO · Radicals.— Decompositions of 0.1 M t-BuO$_2$H at low concentrations (0.1 M) in solvents without reactive hydrogen gave up to 30% yields of acetone as cleavage products. Reaction chains were short and the kinetics complex. These results and their implications are discussed below.

Low Concentrations of t-BuO$_2$H in Benzene at 100°. —The results of t-Bu$_2$O$_2$-initiated decompositions of 0.02–0.1 M t-BuO$_2$H in benzene are shown in Table III. Runs were generally carried to 50–100% decomposition of t-BuO$_2$H and 2.5–5% decomposition of t-Bu$_2$O$_2$. The products included acetone (but no methanol), t-BuOH, CO, CO$_2$, and a small amount of O$_2$. Relative yields of acetone and t-BuOH were dependent on the

TABLE III

INDUCED DECOMPOSITIONS OF t-BUTYL HYDROPEROXIDE
WITH HIGH CLEAVAGE OF t-BUTOXY RADICALS^a

[I]$_0$,^{a} M	$k_d{}^b$ × 10^7, sec^{-1}	[t-BuO$_2$H]$_0$, M	Chain length^c	Yields on t-BuO$_2$H decomposed, %		
				AcMe	t-BuOH	t-Bu$_2$O$_2$
In Benzene at 100°, Initiation by t-Bu$_2$O$_2$						
0.246^d		0.096	15.9			
0.245^d	7.16	0.091	13.3	20	79	
0.241^d	6.86	0.081		27	75	
0.245		0.021	5.14			
0.0510^d		0.098	20.1			
0.0196^d		0.100	15.8			
0.0103^d		0.120	7.0			
0.247^e	11.2	0.093	12.8			
0.247^e		0.026	4.7			
0.048^e		0.094	9.3			
0.0071^e		0.0083	0			
In CCl$_4$ at 100°, Initiation by t-Bu$_2$O$_2$						
0.210^e		0.0868	11.2			
0.0498^e		0.0818	11.6			
0.0425^e	21.7	0.0733	11.2	12		
0.0466^e	19.2	0.0182	4.1	13		
0.0133^e		0.0389	9.7			
In Acetic Acid at 45°, Initiation by DBPO						
0.0164^e		0.137	1.57^f	25	68	7
In t-BuOH at 45°, Initiation by DBPO						
0.0232^e		0.202	1.11^f	17		14
0.0409^e		0.117	0.54^f			

^{a} Initial concentration of initiator. ^{b} Apparent average rate constant for disappearance of initiator. ^{c} Initial chain length calculated using $R_i = 2 \times 6.86 \times 10^{-7}$ [t-Bu$_2$O$_2$]$_0$ from third experiment unless otherwise indicated. ^{d} In sealed tubes in absence of air. ^{e} In sealed tubes in presence of air. ^{f} Average chain length for complete decomposition of initiator.

concentration of t-BuO$_2$H, since t-BuO· could either cleave or abstract hydrogen from the hydroperoxide. Some t-BuOH appears to be formed by reaction of t-BuO· radicals with a radical–benzene adduct, but this reaction becomes important only at very low concentrations of t-BuO$_2$H.

For individual runs, plots of long [t-BuO$_2$H] *vs.* time were linear to at least 80% decomposition. For the several runs, eq 17[1a] applies. Chain lengths thus

$$-\text{d}[t\text{-BuO}_2\text{H}]/\text{d}t = k[t\text{-Bu}_2\text{O}_2]^{\sim 1}[t\text{-BuO}_2\text{H}]^{\sim 1} \qquad (17)$$

were proportional to [t-BuO$_2$H] and those in Table III were calculated from initial rates determined graphically. The concentration of t-Bu$_2$O$_2$, determined by glpc, also decreased (Table III), showing that interaction of t-butylperoxy radicals was not the sole termination reaction.[12]

To see how much termination, if any, resulted in formation of t-Bu$_2$O$_2$, some decompositions at 100° in benzene were initiated by ABN (Table IV). The fast decomposition of ABN at 100° (half-life about 7 min)[13] precluded rate measurements but products were determined. Ampoules were heated for 100 min and analyzed by titration for residual t-BuO$_2$H and by glpc after the hydroperoxide had been reduced with Ph$_3$P. Over-all chain lengths and yields of acetone varied with [t-BuO$_2$H], as in runs initiated by t-

(12) This decrease was only a few per cent of the total concentration of t-Bu$_2$O$_2$ and had negligible effect on the rate of initiation during a run, but it was significantly different from runs at high concentrations of t-BuO$_2$H where [t-Bu$_2$O$_2$] remained constant within the accuracy of the analysis.
(13) J. P. Van Hook and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **80**, 780 (1958).

TABLE IV

DECOMPOSITIONS OF t-BuO$_2$H BY ABN IN BENZENE[a] AT 100°

[ABN]$_0$	$10^5[R_i]_0$, mol/l. sec^{-1}	[t-BuO$_2$H]$_0$, M	$-\Delta[t$-BuO$_2$H] 1.2[ABN]$_0$	Yields on t-BuO$_2$H decomposed, %[b]	
				[Acetone]$_t$	[t-Bu$_2$O$_2$]$_t$
0.00828	3.0	0.263	14.1	7.1	5.0
0.00828	3.0	0.132	8.5	12	4.4
0.00166	0.6	0.134	14.4	18	4.4

[a] In O$_2$-saturated sealed tubes for 100 min, 14 half-lives for ABN. [b] Remainder of t-BuO· was in t-BuOH. Analyses of these three products accounted for 99% of original t-BuO$_2$H in each run.

Bu$_2$O$_2$, but in each run the yield of t-Bu$_2$O$_2$ accounted for 4.4–5% of the t-BuO· groups from decomposed hydroperoxide. This number provides another measure of the ratio of nonterminating to terminating interactions of $2t$-BuO$_2$· radicals (k_3/k_4) in benzene at 100°, since all hydroperoxide decomposes through t-BuO$_2$·radicals; 100/4.4 = 22, in fair agreement with the chain lengths (23 to 32) found at high concentrations of t-BuO$_2$H.

Some unexpected effects of oxygen were found in reactions initiated by ABN and t-Bu$_2$O$_2$. A solution of 0.1 M t-BuO$_2$H and 0.01 M ABN in benzene, refluxed to remove any O$_2$ that might be formed during decomposition, underwent no change in peroxide titer over many hours. For the decompositions in Table IV, ampoules were sealed in an atmosphere of O$_2$. Apparently the Me$_2$CCN radical does not attack hydroperoxides efficiently, but the corresponding peroxy or alkoxy radical does.
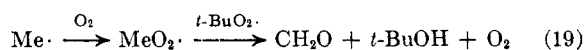
On the other hand, oxygen retarded the t-Bu$_2$O$_2$-initiated runs in benzene, the effect being most pronounced at the lowest initial concentrations of t-BuO$_2$H (Table III). Initially degassed runs with 0.02 M [t-BuO$_2$H]$_0$ showed marked autoretardation as the reaction proceeded, and O$_2$ was produced by the decomposition. This effect was not found in any other solvent, or in the gas phase, and may be due to formation of phenols. We found that ampoules of 0.27 M t-Bu$_2$O$_2$ in benzene sealed in an air atmosphere and heated for 15–20 hr at 100° developed a small hydroperoxide titer. Apparently some of the methylperoxy radicals which are formed abstract H· from benzene (or from t-BuOC$_6$H$_6$·) to form MeO$_2$H. Production of small quantities of methyl hydroperoxide would lead to artificially high titers for [t-BuO$_2$H] in runs of low [t-BuO$_2$H]$_0$. The MeO$_2$H might retard the induced decomposition as well.

In CCl$_4$ at 100°.—Because the complex results reported above seemed related to the formation of methyl radicals, and because Walling and Wagner[14] reported less cleavage of t-BuO· radicals in CCl$_4$ than in benzene, we carried out some t-Bu$_2$O$_2$-initiated decompositions of t-BuO$_2$H in CCl$_4$. With 0.08 M t-BuO$_2$H, the yield of acetone was about half that in benzene (Table III) (confirming Walling and Wagner's results), and so our work was not carried very far. Chain lengths and kinetics for decomposition were similar to those found in benzene.

In Acetic Acid and in t-BuOH at 25–45°.—In addition to a reported retardation of DBPO-induced decomposition by t-BuOH,[15] we observed (part IV) similar retardations of the (Co^{II})-catalyzed decomposition of t-BuO$_2$H in alcohols and in acetic acid at 25–45°.

The decompositions in t-BuOH and in AcOH, summarized in Table I, were carried out to check these results and determine the products. Decomposition of DBPO, a convenient initiator at these temperatures, was carried to completion and only products and over-all chain lengths of decomposition were determined. In both solvents yields of acetone were comparable with those in benzene at 100° but chain lengths were shorter, 1.5 or less.

Discussion.—All the reactions discussed in the preceding section have large yields of acetone, low yields of oxygen where measured, and complex rate expressions. All of these features are associated with the generation of methyl radicals, their scavenging of oxygen, and their participation in termination reactions such as[16] those in eq 18 and 19 which are apparently

$$\text{Me·} + t\text{-BuO}_2\text{·} \longrightarrow \text{MeO}_2\,t\text{-Bu} \qquad (18)$$

$$\text{Me·} \xrightarrow{\text{O}_2} \text{MeO}_2\text{·} \xrightarrow{t\text{-BuO}_2\text{·}} \text{CH}_2\text{O} + t\text{-BuOH} + \text{O}_2 \qquad (19)$$

much faster than attack by Me· on t-BuO$_2$H. To the extent that each Me· radical produced takes part in one of these termination reactions, the cleavage of t-BuO· to Me· radicals becomes rate-controlling for termination and, as pointed out in part I[1a] (eq 8),

$$-\text{d}[t\text{-BuO}_2\text{H}]/\text{d}t = R_i k_2[t\text{-BuO}_2\text{H}]/2k_7 \qquad (8)$$

close to that determined experimentally in benzene and in CCl$_4$.[17]

That basic features of the induced decomposition mechanism[18] are retained even in these more complex situations is shown by the results with ABN in benzene at 100°. Here the kinetics are complex, but the yield of t-Bu$_2$O$_2$ is nearly constant, independent of chain length and initiator efficiency. The ratio of nonterminating to terminating interactions of 2RO_2·, k_3/k_4, though no longer the same as the chain length (to which other terminations contribute), can be measured by the yield of t-Bu$_2$O$_2$.

The low chain lengths in t-BuOH may be due partly to its high viscosity relative to benzene or acetic acid, which would increase the proportion of terminating to nonterminating interactions of $2t$-BuO$_2$· radicals. However, we have a measure of this effect in the relative proportions of t-BuO· radicals which escape when produced by thermal decomposition of DBPO (95% in benzene or acetic acid, 90% in t-BuOH at 45°[7]) and it is slight.

(14) C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, **86**, 3368 (1964).
(15) T. G. Traylor, personal communication, 1965.

(16) F. H. Seubold, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **73**, 18 (1951).
(17) Since reaction orders in initiator and hydroperoxide were always slightly less than one, eq 7 is probably the major, but not the only, termination. When eq 4 controls termination, the order in [t-BuO$_2$H] approaches zero (eq 5). When Me· radicals do not terminate but abstract hydrogen from t-BuO$_2$H, then reaction order approaches $^1/_2$ in R_i. A complete solution of the steady-state equation is too complex to be useful.
(18) S. W. Benson, *J. Chem. Phys.*, **40**, 1007 (1964).

TABLE V

INDUCED DECOMPOSITIONS OF t-BuO$_2$H IN REFLUXING ALKANES

Temp, °C	Solvent	[DBPO]$_0$, M	[t-BuO$_2$H]$_0$, M	Chain length[a]	S—OH, %[b,c]	S=O, %[b,d]
98.6	n-Heptane[e]	0.254	0.0797	$\sim$0		
81.5	Cyclohexane	0.0169	0.104	0.97	70 (55[f])	17 (32[f])
81.5	Cyclohexane	0.061	0.098	0.84		
81.5	Cyclohexane	0.0120	0.091	0.83	99	11
81.5	Cyclohexane	0.0081	0.0419	0.47		
81.5	Cyclohexane	0.0205	0.0285	0.38	69 (69[f])	29 (29[f])
37.8	n-Pentane	0.0112	0.196	5.9[g]		
37.8	n-Pentane	0.0076	0.118	2.9[h]	Present	40

[a] [t-BuO$_2$H decomposed]/2[DBPO]. Reactions were carried out to complete decomposition of DBPO, 30 hr at 37.8°, 0.5 hr at 81.5°. [b] Products by glpc in % of t-BuO$_2$H decomposed; many are secondary products (see text). [c] Alcohol derived from solvent. [d] Ketone derived from solvent. [e] Initiated by t-Bu$_2$O$_2$. [f] By glpc before reduction of product mixture with Ph$_3$P. [g] Initial chain length; average chain length for complete decomposition of DBPO = 2.9. [h] Initial *and* average chain length: 2.7% AcMe, 89% t-BuOH, and 8.5% t-Bu$_2$O$_2$.[b]

Walling and Wagner[14] have observed that solvents influence the propensity of t-BuO· to cleave rather than abstract hydrogen from a substrate. We find also that, at least in benzene, cleavage is more temperature-dependent than abstraction. More novel is the large effect of a few methyl radicals on the induced decomposition of t-BuO$_2$H.

Solvents with Reactive Hydrogen. Refluxing Alkanes.—In gas phase oxidations at 100°, induced decomposition of t-BuO$_2$H is retarded by some hydrocarbons. We suspected that alkyl radicals, resulting from hydrogen abstraction by t-BuO·, might act like methyl radicals resulting from cleavage of t-BuO· radicals. We have tested this hypothesis by investigating decomposition products of t-BuO$_2$H in alkane solvents at several temperatures. These solvents were refluxed in an effort to expel oxygen and prevent autoxidation during the reaction.

t-BuO$_2$H (0.1 M) was stable almost indefinitely in the presence of 0.28 M t-Bu$_2$O$_2$ in refluxing n-heptane (98.6°), although chain lengths in benzene at 100° (Table I) were about 15. In DBPO-initiated decompositions in cyclohexane (81.5°) and in n-pentane (37.8°), protection by the solvent was less complete. Chain lengths in Table V are based on initial and final hydroperoxide titers after complete decomposition of DBPO.[19] The formation of alkyl hydroperoxides in some runs (see below) complicates the interpretation of these numbers, but it is clear that chains are longer at lower temperatures and higher initial concentrations of t-BuO$_2$H.

The products included t-BuOH and significant yields of t-BuO$_2$S (where SH is solvent). Yields of acetone were small; O$_2$ was not measured. *No* solvent dimers were produced, though these were found when DBPO was decomposed in the absence of t-BuO$_2$H (Table I).
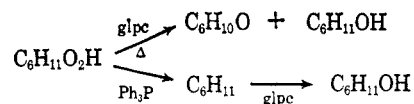
Products determined by glpc analysis are shown in Table VI. Most of the alcohols and ketones shown are not the primary products but the pyrolysis products, during gas chromatography, of solvent peroxides,[20]

t-BuO$_2$S and SO$_2$H (S is solvent). For example, combination of quantitative ir with glpc data showed that the true products of the last run with cyclohexane were 75% t-BuO$_2$H$_{11}$, 10% t-Bu$_2$O$_2$, and 11% cyclohexene; yields are on DBPO decomposed to show that 96% of radical termination products are accounted for. Refinement of our glpc techniques gave for the second cyclohexane run, carried to 100% decomposition of hydroperoxide *via* successive additions of DBPO, 60% t-BuO$_2$C$_6$H$_{11}$, 13% cyclohexanol, and 6.5% cyclohexanone.

Some solvent hydroperoxide was also formed. This claim rests on finding *some* cyclohexanone and cyclohexanol when reaction was carried to completion, and, in runs not carried to completion, on a shift in cyclohexanone–cyclohexanol ratio depending on whether the solutions had, or had not, been reduced with Ph$_3$P prior to glpc analysis under pyrolytic conditions.

$$C_6H_{11}O_2H \xrightarrow[\text{Ph}_3\text{P}]{\overset{\text{glpc}}{\Delta}} \begin{array}{c} C_6H_{10}O + C_6H_{11}OH \\ C_6H_{11} \xrightarrow{\text{glpc}} C_6H_{11}OH \end{array}$$

n-Heptane at 170°.—Although n-heptane completely protected 0.1 M t-BuO$_2$H from induced decomposition at 100° (Table V), it did not prevent decomposition at 170°. Figure 1 shows that added t-Bu$_2$O$_2$ enhanced the rate of disappearance of titratable hydroperoxide over that for the normal thermal decomposition and that this action persisted long after the initial t-Bu$_2$O$_2$ should have been completely decomposed (half-life[6] about 8 min at 170°). A chain length of 6 was calculated by comparison of initial thermal and induced rates. In benzene at 170°, the thermal decomposition of t-BuO$_2$H had been only slightly affected by added t-Bu$_2$O$_2$ (part V). The products from the heptane runs were not analyzed.

Discussion.—Although a thorough understanding of induced decompositions of hydroperoxides in alkanes would require more product studies (including a method for distinguishing between different kinds of hydroperoxides in reacted solutions), the results above permit us to define the important features. Most interesting is the maximum stabilizing effect of alkanes near 100°. This effect probably results from the preferential re-

(19) For two of the runs in n-pentane, the reaction mixture was sampled at several points and residual RO$_2$H was determined by titration and by subtracting a calculated titer for undecomposed DBPO. In one of these the chain length was constant throughout the reaction. In the other, the initial chain length was higher than this but decreased drastically as the run proceeded, so that the over-all chain length was the same. We do not understand these results.

(20) These did not arise from air. Decomposition of DBPO in refluxing alkanes in the absence of t-BuO$_2$H gave only olefins and solvent dimers (Table I). In only one case was more oxygen found in solvent products than

would have come from decomposed t-BuO$_2$H; here the DBPO was introduced into the refluxing solution of t-BuO$_2$H and cyclohexane in 1 ml of air-saturated solvent. In all other runs it was added as a solid to the refluxing mixture.
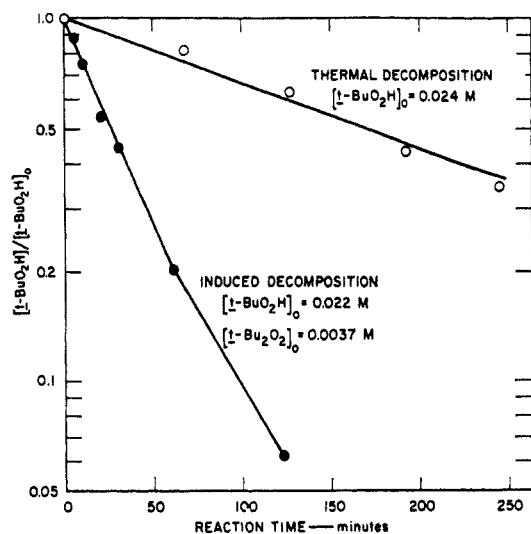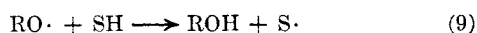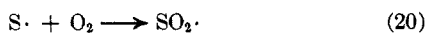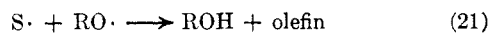
Figure 1.—Decompositions of 0.02 M t-BuO$_2$H in n-heptane at 170°

action of RO· radicals with solvent instead of with hydroperoxide, and is of course dependent on [RO$_2$H].

At lower temperatures, more RO· radicals attack hydroperoxide because of the higher activation energy for solvent attack.[21] Much above 100°, termination products such as RO$_2$S and olefin accelerate decomposition of hydroperoxide, offsetting the retarding effect of the solvent. The situation is further confused by the formation of alkyl hydroperoxides, probably from solvent radicals and oxygen formed from interaction of $2t$-BuO$_2$· radicals (eq 20 and 9) followed by chain

$$S· + O_2 \longrightarrow SO_2· \tag{20}$$

$$RO· + SH \longrightarrow ROH + S· \tag{9}$$

termination (eq 21 or 10). The high yields of SO$_2$R

$$S· + RO· \longrightarrow ROH + \text{olefin} \tag{21}$$

$$S· + RO_2 \longrightarrow SO_2R \text{ (or } RO_2H + \text{olefin)} \tag{10}$$

show that t-BuO$_2$· radicals are the predominating radicals in these systems and effectively scavenge S· radicals. This conclusion agrees with our own unpublished esr results and those of Thomas.[22]

Gas Phase Decompositions of t-BuO$_2$H by Free-Radical Initiators

Decompositions Initiated by t-Bu$_2$O$_2$ at 100° Rates.— In a typical gas phase mixture of 0.004 M t-BuO$_2$H and 0.001 M t-Bu$_2$O$_2$, t-BuO$_2$H decomposes to the extent of 25–30% in 15 hr at 100°. Table VI summarizes the effects of initial concentrations of t-Bu$_2$O$_2$ on rates of decomposition of t-BuO$_2$H. In these runs conversions of t-BuO$_2$H varied from 11 to 62% and of t-Bu$_2$O$_2$, from 2 to 4%.

Although both the radical-induced and thermal decompositions contribute to the measured rates of disappearance of t-BuO$_2$H, no corrections for the thermal rate have been applied here because of the erratic nature of these reactions and our lack of a firm

(21) Shorter chain lengths in cyclohexane than in pentane may result partly from much more rapid initiation by DBPO at 81.5° than at 37.8°. However, the very short chains with slow initiation by t-Bu$_2$O$_2$ in n-heptane at 98.6° show that the rate of initiation is less important than temperature in controlling chain lengths.

(22) J. R. Thomas, *J. Amer. Chem. Soc.*, **87**, 3935 (1965).

TABLE VI

EFFECTS OF t- AND sec-Bu$_2$O$_2$ ON RATES OF GAS PHASE DECOMPOSITIONS (R_{HP}) OF t-BUTYL HYDROPEROXIDE AT 100°[a]

Run no.	Time, min	[Bu$_2$O$_2$]$_0$, initial	[t-BuO$_2$H]$_0$, mM	% conversion of t-BuO$_2$H	R_i,[a] mol/l. min × 10^7	R_{HP}, mol/l. min × 10^7	Chain length, R_{HP}/R_i
			t-Bu$_2$O$_2$				
69A	495	0.918	0.622	37	0.75	4.6	6.1
69B	495	0.952	0.663	41	0.78	5.5	7.0
65A	900	0.862	0.79	51	0.70	4.0	5.7
65B	900	0.925	1.58	62	0.75	6.6	8.8
65C	900	0.926	2.58	35	0.76	10.0	13
69C	495	0.986	3.17	18	0.80	12.0	15
67A	1120	0.466	4.25	22	0.380	8.4	26
67B	1120	1.10	4.39	33	0.90	13	15
67C	1120	1.74	4.31	43	1.4	16	12
67D	1120	3.11	4.53	52	2.5	21	8.4
67E	1120	4.36	4.20	67	3.6	25	6.7
65D	900	0.938	4.82	24	0.77	13.0	17
69D	495	0.964	8.84	11	0.79	19.0	24
65E	900	0.921	11.0	21	0.75	25.0	33
69F	495	0.958	14.86	13	0.78	38.0	49
			sec-Bu$_2$O$_2$				
86M	929	0.960	8.91	39	2.1	37.0	18
86O	944	0.927	8.99	29	2.0	28.0	14

[a] Calcd from data in Table I: $R_i = 2k_d[Bu_2O_2]_0$, where $k_d = 6.8 \times 10^{-7}$ sec^{-1}($t^{1/2} = 283$ hr) for t-Bu$_2$O$_2$ and $k_d = 18 \times 10^{-7}$ sec^{-1}($t^{1/2} = 107$ hr) for sec-Bu$_2$O$_2$.

basis for such corrections. For most experiments in Table VI we used a single sample of t-BuO$_2$H which gave thermal rates that are generally about 10% of the induced rates in experiments having comparable amounts of hydroperoxide.

A log–log plot of the rate of hydroperoxide decomposition *vs.* [t-Bu$_2$O$_2$]$_0$ (runs 67A–E, Table VI) gave a good straight line with a slope of 0.5. The plot of change in rate with average concentration of t-BuO$_2$H (runs 69A–F and 65B–E) showed marked deviation from linearity (too fast) at the highest concentrations. These data could be fitted about equally well to lines with slopes of 0.5 and 1. Thus the over-all rate law for the induced decomposition takes the form of eq 11

$$R_{HP} = k(R_i)^{1/2}[ROOH]^{1/x-1} \tag{11}$$

and

$$\text{chain length} = R_{HP}/R_i = k[t\text{-BuO}_2\text{H}]^{1/x-1}/2k_d[t\text{-Bu}_2\text{O}_2]^{1/2} \tag{22}$$

At the highest concentration of hydroperoxide used (almost 0.015 M in 69F), each t-BuO· radical decomposes 40–45 hydroperoxide molecules, wall catalysis accounting for the other 5–10.

Products.—Because so little material was available from each run, analyses for products and for remaining hydroperoxide were done on duplicate runs. In a typical experiment, 1.26 mmol of t-BuO$_2$H was 55.6% decomposed in 950 min (by t-Bu$_2$O$_2$ initially 0.888 mM), giving 84.6% t-BuOH, 4.5% acetone, and 32% O$_2$. In general, yields of acetone were 5–10%. More than 90% of the t-butoxy radicals formed was accounted for in analyses as AcMe or t-BuOH, but only a third to a half of the theoretical amount of oxygen was liberated. The remainder might be accounted for by reaction with methyl radicals to give CO$_2$.

The yield of t-Bu$_2$O$_2$ (the only termination product when t-BuO$_2$H is decomposed by DBPO at 45°)[2]

was estimated using sec-Bu$_2$O$_2$ as the initiator. In a close duplicate of run 69D (Table VI), 0.93 mM sec-Bu$_2$O$_2$ and 8.86 mM t-BuO$_2$H were heated for several half-lives of the initiator. All the t-BuO$_2$H decomposed with an estimated average chain length of 10. Although 0.45 mM yield of t-Bu$_2$O$_2$ is expected from the amount of chain initiation (see below), glpc analysis showed only 0.05 mM t-Bu$_2$O$_2$ to be formed.[23] Thus for these short chains, few terminations result from interactions of 2t-BuO$_2$· radicals. The significant yield of acetone (and methyl radicals) suggests an alternate route. A low termination tendency of 2t-BuO$_2$· in the gas phase is consistent with the long chains found at high [t-BuO$_2$H] (Table VI).

Initiation Efficiency of sec-Bu$_2$O$_2$ in the Gas Phase.— The first experiments with sec-Bu$_2$O$_2$ and t-BuO$_2$H were done to establish that sec-BuO· could be generated satisfactorily in the gas phase and that it would initiate a chain with t-BuO$_2$H. The two runs (runs 86M and O in Table VI) gave rates of disappearance of hydroperoxide somewhat faster than comparable experiments using t-Bu$_2$O$_2$. With 65E as comparison (and correcting for a first-power dependence on hydroperoxide concentrations) we found that t-BuO$_2$H disappears 1.5 times as fast in 86M and 1.8 times as fast in 86O. In the gas phase, sec-Bu$_2$O$_2$ decomposes about 2.7 times as fast as t-Bu$_2$O$_2$ (Table I). If the two peroxides are equally efficient in radical production and self-destruction, we would expect $(2.7)^{1/2}$ or 1.6-fold greater rate for the reaction with secondary peroxide. This factor of 1.6 (perhaps only by coincidence) is remarkably close to the experimental value, and strongly suggests that the low efficiency of sec-Bu$_2$O$_2$ in toluene was due to disproportionation of pairs of sec-BuO·s in solvent cage and/or induced decomposition of the peroxide.

Retardation by Added Hydrocarbons.—Addition of hydrocarbons to the gas phase decompositions decreased the chain lengths of induced decompositions in proportion to the concentration of added material and its reactivity[24] toward alkoxy radicals. The chain length for 2.0 mM t-BuO$_2$H with 1.0 mM t-Bu$_2$O$_2$ (about 15 with no additive, Table VI) was about 1.0 when 29 mM cyclopentene was added. The same effect was achieved with about 250 mM or 270 mM isobutane.

Whereas results are in accord with reactions in solution, they are particularly interesting because they suggest that removal of a hydrogen atom from hydroperoxide (O$_2$H) by an alkoxy radical is very much faster than from hydrocarbons having hydrogens with bond strengths equal to or lower than that of t-butyl hydroperoxide [$H°_D$(O$_2$-H) = 90 kcal], cyclopentane or isobutane [$H°_D$(C-H) $\simeq$ 91], and cyclopentene [allylic $H°_D$(C-H) $\sim$ 78].[25] In these reactions, activation energies for abstraction are not a constant fraction of bond strength, being a much smaller fraction for RO$_2$-H than for C-H. Thus even at low concentrations (1%) in the gas phase, hydroperoxide can compete effectively for alkoxy radicals.
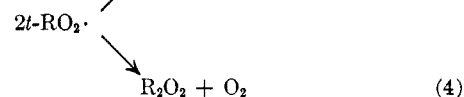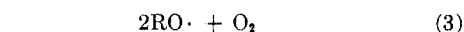
Comparison of Gas and Liquid Phase Decompositions

Our measurement of rates, chain lengths, and products of decompositions of hydroperoxides and the effects of alkanes on these show that the basic features of the gas phase and liquid phase reactions are the same. Both reactions involve the two pairs of competing reactions, terminating and nonterminating reactions of peroxy radicals (eq 3 and 4) and propagation

$$2RO· + O_2 \qquad (3)$$
$$2t\text{-RO}_2· $$
$$R_2O_2 + O_2 \qquad (4)$$

and cleavage of t-alkoxy radicals (eq 9 or 2 and 7).

$$RR'R''CO· + SH \text{ (or } RO_2H) \longrightarrow $$
$$RR'R''COH + S· \text{ (or } RO_2·) \quad (9 \text{ or } 2)$$

$$RR'R''CO· \longrightarrow R'COR'' + R· \qquad (7)$$

Interactions of t-BuO$_2$· radicals in the liquid phase produce more free t-BuO· radicals and less termination as the temperature increases. This effect may be due either to the decreasing viscosity of the solvent or to the higher activation energy[22] for eq 3 over eq 4 or to both. In the gas phase where there is no solvent cage, termination by 2t-BuO$_2$· radicals becomes negligible: the same kinetic order for termination as for generation of t-BuO· radicals must lead to rates dependent on the first power of initiator, but the rate is clearly dependent on [initiator]$^{1/2}$.

If termination is by two free t-BuO· radicals as in

$$2t\text{-BuO}· \longrightarrow t\text{-Bu}_2O_2 \qquad (23)$$
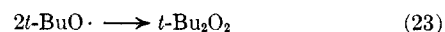
then eq 24 can be written as shown. This mechanism

$$-d[t\text{-BuO}_2H]/dt = k_2[t\text{-BuO}_2H](R_i/2k_{24})^{1/2} \qquad (24)$$

may apply at high concentrations of t-BuO$_2$H where cleavage of t-BuO· is suppressed, but it does not apply when chains are short. Using data from run 69F (Table VI) to solve eq 24 for k_2 gives ~400 l./mol sec, a reasonable value.[26]

The second set of competing reactions is given in eq 9, 7, and 2 of alkoxy radicals. The reaction in eq 2 tends to continue the decomposition chain but eq 9 and 7 tend to terminate the chains at or below 100° because they produce alkyl radicals. Whereas these alkyl radicals are capable of abstracting hydroperoxide hydrogen to continue decomposition chains, the relatively large steady-state concentration of t-BuO$_2$· radicals[27] provides a ready termination. The competition between propagation (eq 2) and cleavage (eq 7) depends on the concentration of hydroperoxide (essential for propagation) and the effect of reaction medium on cleavage. Cleavage is least favored in the gas phase[14] and most favored in polar hydroxylic solvents without reactive hydrogen atoms.[14,28]

(23) While during the time of reaction (about one half-life for t-Bu$_2$O$_2$) any t-Bu$_2$O$_2$ formed will also have partially decomposed, clearly the amount remaining will be *at least* half of the total produced.

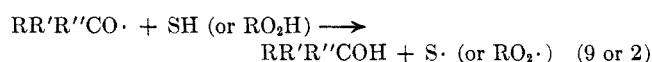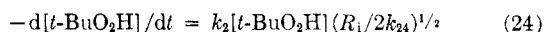(24) P. Gray and A. Williams, *Chem. Rev.*, **59**, 270 (1959).

(25) S. W. Benson, *J. Chem. Educ.*, **42**, 5021 (1965).

(26) Assuming $k_{24} = 10^7$ based on 2t-BuO· reacting $1/10$th as fast as they escape from the solvent cage.

(27) R. Hiatt and T. G. Traylor, unpublished work.

(28) J. D. Bacha and J. Kochi, *J. Org. Chem.*, **30**, 3272 (1965).

Two examples illustrate the application (really the foundation) of these generalizations. In experiments at about the same t-BuO$_2$H–t-Bu$_2$O$_2$ ratio, chain lengths in the decomposition of hydroperoxide are about the same at 100° in the gas phase (run 65D in Table VI) and in benzene solution (0.0196 M t-Bu$_2$O$_2$ experiment in Table III). Despite the 4-fold higher concentrations in solution, 10–30% of the t-BuO· radicals cleave compared to only 5–10% in the gas phase. At higher concentrations of t-BuO$_2$H cleavage of t-BuO· radicals becomes unimportant compared to propagation, and the kinetics and the products change and resemble the liquid phase reaction at 45°.

Homolytic Decompositions of Hydroperoxides. III.[1a,b] Radical-Induced Decompositions of Primary and Secondary Hydroperoxides

R. HIATT,[1c] T. MILL, K. C. IRWIN, AND J. K. CASTLEMAN

*Stanford Research Institute, Menlo Park, California*

Radical-induced decompositions of primary and secondary hydroperoxides at 45° in benzene have chain lengths of 0.7–1.4. However, at 100° in benzene solution or in the gas phase the reaction is more complex, involving both peroxy and carbon radicals, and gives little or no oxygen. At 45° alkoxy radicals preferentially attack the peroxy hydrogen atom instead of the hydrogen in these peroxides; at 100° attack must occur on both positions. Interactions of two nontertiary peroxy radicals are almost always terminating. They appear to react mostly by a concerted, nonradical decomposition of intermediate R$_2$O$_4$.

Primary or secondary hydroperoxides are intermediates in many important autoxidations such as those of toluene, tetralin, and cyclohexane. The routes by which these are decomposed to useful products are of more general interest than the reactions of tertiary hydroperoxides described in part II.[1b] We expected that free-radical-induced decompositions of primary and secondary hydroperoxides would differ from those of tertiary hydroperoxide for two reasons. (1) Terminating interactions by disproportionation of two primary or secondary peroxy radicals appear to be much faster[2,3] than interactions of two tertiary peroxy radicals. Therefore chain lengths of decompositions involving the former peroxy radicals should be short (eq 12). (2) To the extent that α-hydrogen atoms

$$2R_1R_2HCO_2\cdot \longrightarrow R_1R_2HCOH + R_1R_2C{=}O + O_2 \quad (12)$$

in primary and secondary hydroperoxides rather than the peroxy hydrogen atoms are abstracted, then hydroxyl radicals may become the chain carrier (eq 6). This report describes decompositions of n-butyl,

$$R_1R_2HCO_2H + \cdot OH \longrightarrow (H_2O +)R_1R_2\dot{C}O_2H \longrightarrow$$
$$R_1R_2C{=}O + OH \quad (6)$$
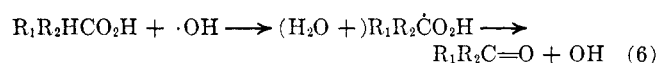
sec-butyl, 3-cyclopentenyl, and α-tetralyl hydroperoxides by DBPO in benzene at 45° and of sec-butyl hydroperoxide by t-Bu$_2$O$_2$ in benzene and in the gas phase at 100°.

Experimental Section

α-Tetralyl and cyclopentenyl hydroperoxides were prepared by air oxidation of the hydrocarbons and respectively recrystallized or vacuum distilled to 95+ % purity (by reflux iodometric titration, part II[1b]). n-BuO$_2$H (92%) and sec-BuO$_2$H (94+%) were prepared by the methods of Mosher and coworkers.[4] Other materials, analytical procedures, and procedures for decompositions were as described in part II.[1b]

t-BuO· -Induced Decompositions of p- and sec-Hydroperoxides in Benzene at 45 and 100°

The results with t-BuO$_2$H in part II[1b] raised the question of whether interaction of two primary or secondary solvent peroxy radicals would also produce alkoxy radicals (eq 3, part I[1a]) capable of continuing the chain. Radical-induced decompositions of primary and secondary hydroperoxides in benzene were therefore investigated.

Table I shows chain lengths, *i.e.*, $-\Delta[RO_2H]/-\Delta 2[\text{initiator}]$, and products of the DBPO-induced decompositions of one primary and three secondary hydroperoxides in benzene at 45°; oxygen evolution, where measured, was 75–80% of theory for sec-BuO$_2$H. For 3-cyclopentenyl and sec-butyl hydroperoxides, the only ones for which the kinetics were measured, $-d[RO_2H]/dt \propto [DBPO]$. The over-all result corresponds to

TABLE I

DBPO-INDUCED DECOMPOSITION OF PRIMARY AND SECONDARY HYDROPEROXIDES IN BENZENE[a] AT 45°

RO$_2$H	[RO$_2$H]$_0$, M	[DBPO]$_0$, M	Chain length[b]	ROH[c]	R=O[d]	O$_2$
n-Butyl	0.217	0.0862	0.70	53	14[e]	
sec-Butyl	0.272	0.098	1.0	50	46	
sec-Butyl	0.221	0.118	0.9			76
3-Cyclopentenyl	0.124	0.0100	0.72			
α-Tetralyl	0.092	0.055	0.72			

[a] Solutions were degassed, sealed in ampoules, and heated for 450 min or ten half-lives of the initiator. [b] Corrected for cage effect of DBPO; *cf.* part II.[1b] [c] Alcohol from R, based on decomposed RO$_2$H. [d] Aldehyde or ketone from R, based on decomposed RO$_2$H. [e] Also butyric acid, not determined quantitatively.

(1) (a) Part I: R. Hiatt, J. Mill, and F. R. Mayo, *J. Org. Chem.*, **33**, 1416 (1968). Equations 1–16 appear in part I. Part II: R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *ibid.*, **33**, 1421 (1968). Equations 17–24 appear in part II. (c) To whom all correspondence should be addressed at Brock University, St. Catherines, Ontario, Canada.
(2) G. A. Russell, *J. Amer. Chem. Soc.*, **77**, 4583 (1955).
(3) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **44**, 1119 (1966).

(4) F. Welch, H. R. Williams, and H. S. Mosher, *J. Amer. Chem. Soc.*, **77**, 551 (1955).