Homolytic Decompositions of Hydroperoxides. V.[1a-d] Thermal Decompositions

R. HIATT[1e] AND K. C. IRWIN

Stanford Research Institute, Menlo Park, California

Received June 28, 1967

Solutions of 0.01–0.26 *M* *t*-butyl hydroperoxide in toluene have been thermally decomposed at 100–215°. Products included *t*-butyl alcohol, acetone, methane, CO, CO_2, bibenzyl, benzaldehyde, and benzyl alcohol in yields varying with temperature and peroxide concentration. At initial concentrations below 0.02 *M*, decompositions of hydroperoxide were first order; nevertheless, even at 0.001 *M* peroxide, at least 30% of the total decomposition at 180° was induced decomposition. Acetone is a mild catalyst of thermal decomposition. The rate constant *for homolytic cleavage of the O–O bond at 170–215° is about* $10^{15.8}e^{-43,000}/RT$. At 100°, *extraneous unexplained* factors caused a thermal decomposition 20 times as fast as expected from this relation. The absence of methanol in the products excludes a previously postulated rearrangement of *t*-butylperoxy radicals at 180°. Less detailed studies in benzene, cumene, *n*-heptane, and cyclohexane showed that these decompositions are largely radical induced in the nonaromatic solvents and are mostly homolytic in aromatic ones. Some decompositions of dilute solutions of *n*-BuO_2H, *sec*-BuO_2H, and α-cumyl hydroperoxide in toluene at 170–180° gave rates two to three times as fast as those found for *t*-BuO_2H. From the products of decomposition, 21% of the *n*-BuO· and 60% of the α-cumyl-O· radicals are estimated to cleave in toluene at 182°. About 50% of the *t*-BuO· radicals cleave under these conditions. The absence of cumene in the products from decompositions of 1.4 *M* α-cumyl hydroperoxide in toluene at 125 and 139° shows that a previously proposed reaction, $PhCH_2\cdot$ + α-cumyl O_2H → cumene + $PhCH_2O_2H$, does not occur. This research probably pushes to its limits the technique of increased dilution as a means for measuring the uncomplicated homolytic decomposition of *t*-BuO_2H. There are methods for monitoring hydroperoxide concentration at much higher dilution, but they, like the iodometric method of analysis, do not distinguish between the hydroperoxide originally present and that possibly produced from the solvent. Analyses for products, on which a postulated mechanism must ultimately rest, become exceedingly tenuous at 0.001 *M* hydroperoxide.

The thermal decomposition of hydroperoxides, unlike that of dialkyl peroxides or peroxy esters, is complex. Rate constants for decomposition in solution depend strongly on concentration, on the nature of the hydroperoxide, and on the character of the solvent, even in the absence of known catalysts such as acids, bases, certain metal ions, and olefins.[2] Even for *t*-BuO_2H, the best-behaved of the class, attempts to measure rates for thermal homolysis of the O–O bond, have given activation energies well below[3] that calculated for the reaction[4]

$$RO_2H \longrightarrow RO\cdot + \cdot OH \qquad (15)$$

and have shown unexplained rate effects in the presence of oxygen[5] and of presumably innocuous solvents.[6] Probably the most serious complication is the induced decomposition, in which radicals arising from spontaneous homolysis[7] of the O–O bond or from other sources attack the hydroperoxide (see eq 2 and 3). Thus, in

$$RO\cdot(HO\cdot) + RO_2H \longrightarrow ROH\ (HOH) + RO_2\cdot \qquad (2)$$

$$2RO_2\cdot \longrightarrow 2RO\cdot + O_2 \qquad (3)$$

chlorobenzene solution at 140°,[3] or undiluted at 100°,[8] *t*-BuO_2H decomposes almost quantitatively to *t*-BuOH and oxygen. Below 100°, where the hydroperoxide is thermally stable, induced decomposition has received intensive study and is now well understood (part II[1b]).[9,10]

We reinvestigated thermal homolysis in the hope of (1) establishing some reliable rates and activation energies, (2) determining effects of solvents on these, and (3) exploring effects of structure on thermal homolysis of some structurally simple hydroperoxides and on cleavage of alkoxy radicals at elevated temperatures. Previous work showed that induced decomposition is minimized at very low initial concentrations of hydroperoxide.[11] We have extended this work to even lower initial concentrations and to a variety of solvents, paying careful attention to both rates and products of decomposition.

Experimental Section

Analyses.—Hydroperoxides were titrated iodometrically, usually by the method described in part II,[1b] which gave consistent blank titers of 0.0008 mequiv. For concentrations of RO_2H below 0.002 *M*, 1 ml of a freshly prepared saturated aqueous solution of KI was substituted for the solid NaI. Blanks were then less than 0.0001 mequiv.

Products of decomposition were analyzed by glpc on a Carbowax 20M column after reduction of any residual hydroperoxide to alcohol with Ph_3P. Gaseous products were analyzed by mass spectroscopy.

Rate Measurements.—For kinetic runs, seven to nine Pyrex ampoules (10 mm) containing 2–3 ml of a dilute solution of hydroperoxide were degassed, sealed under vacuum, and immersed in a constant temperature bath for appropriate lengths of time; then residual hydroperoxide was titrated iodometrically. For some product studies, 20 ml of hydroperoxide solution was degassed and sealed under vacuum in a 100-ml bulb provided with a break-seal. Despite the differences in available vapor space between these runs and those in ampoules, no difference in percentages of products was observed. Thus, gas phase decomposition did not contribute significantly to the reaction.

Decompositions of *t*-BuO_2H

Solvent Purity.—Even reagent or chromatograde solvents contain impurities which affect peroxide

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[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) Part II: R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *ibid*, **33**, 1421 (1968). Equations 17–24 appear on part II. (c) Part III: R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *ibid.*, **33**, 1428 (1968). Equation 12a and b appear in part III. (d) Part IV: R. Hiatt, K. C. Irwin, and C. W. Gould, *ibid.*, **33**, 1430 (1968). Equations 25–37 appear on part IV. (e) To whom all correspondence should be addressed at Brock University, St. Catharines, Ontario, Canada.

[2] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 504.

[3] E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discussions Faraday Soc.*, **10**, 242 (1951).

[4] S. W. Benson, *J. Chem. Phys.*, **40**, 1007 (1964).

[5] B. K. Morse, *J. Amer. Chem. Soc.*, **79**, 3375 (1957).

[6] C. Walling and L. Heaton, *ibid.*, **87**, 38 (1965).

[7] We realize that "homolysis" is ambiguous in the sense that *all* of their reactions under discussion are homolytic (free radical) in character. By "homolysis" we mean spontaneous homolytic cleavage of the O–O bond, and "induced" refers to any other form of decomposition.

[8] N. A. Milas and D. M. Surgenor, *ibid.*, **68**, 205 (1946).

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

[10] A. Factor, C. A. Russell, and T. G. Traylor, *J. Amer. Chem. Soc.*, **87**, 3692 (1965).

[11] R. Hiatt and W. M. J. Strachan, *J. Org. Chem.*, **28**, 1893 (1963).

TABLE I

THERMAL DECOMPOSITION OF t-BuO$_2$H IN AROMATIC SOLVENTS

Temp, °C	[t-BuO$_2$H]$_0$, mol/l.	$k_1 \times 10_5$, sec^{-1}	Yields based on RO$_2$H decomposed, % AcMe	 t-BuOH	 S—S[a]	 S—OH[b]	 S=O[c]
			In Toluene				
100.0	0.0161	0.0057	~1	87	31	29	46
172.5	0.0012	0.92			48		
181.5	0.025	2.69	46	47	41	26	7.3[d]
192.6	0.021	8.3	52	48	30		
204.5	0.010	15.2			45	8	<0.5
204.5	0.027	18.0	62	36	43	21	4
214.9	0.011	32.4	70	28	51	6	<0.5
			In Benzene				
172.5	0.022	4.64[e]	62	22	3		
172.3	0.022	1.09					
182.6	0.021	3.1					
			In Cumene				
182.6	0.021	8.1	50	50	50	28	5.8[f]
182.6	0.040	9.6					
182.6	0.090	14.3	36	64		47	8.3
			In Toluene with Added Material				
181.2	0.025	2.81				0.026 M t-BuOH added	
181.2	0.025	3.30				0.026 M AcMe added	
181.5	0.022	3.40			34	g	
181.5	0.025	4.36			37	h	

[a] Products from solvent were bibenzyl from toluene, biphenyl from benzene, and bicumyl from cumene. [b] Products from solvent were benzyl alcohol from toluene and α-cumyl alcohol from cumene. [c] Products from solvent were benzaldehyde from toluene and acetophenone from cumene. [d] Also 32% CH$_4$, 0.5% CO, 0.04% CO$_2$, 41% H$_2$O, *no* O$_2$. [e] Solvent not treated with CaH$_2$. [f] Also 13% α-methylstyrene. [g] Fresh t-BuO$_2$H added to a decomposed mixture of 0.25 M t-BuO$_2$H in toluene. [h] Ampoules packed with broken Pyrex tubing to increase surface area sevenfold.

decomposition. Walling and Heaton[6] found excessively rapid decomposition of t-BuO$_2$H in chlorinated aromatic hydrocarbons. We found that aliphatic hydrocarbons were particularly bad, the half-life of t-BuO$_2$H in n-heptane at 100° being less than 3 hr. Fractional distillation with or without thermal decomposition of 2,2′-azobis(2-methylpropionitrile) (ABN) in the solvent was ineffective. By accident it was discovered that refluxing the solvent over CaH$_2$ before distillation removed the catalytic agent, although the solvent composition as determined by glpc was unchanged. With this treatment the half-life of t-BuO$_2$H in n-heptane at 100° was about 1000 hr. In benzene at 180° the half-life was increased fourfold. The saturation of solvents with water had no deleterious effect. Without understanding the results of this treatment, we are convinced of its efficacy.[12]

Thermal Decomposition of t-BuO$_2$H in Aromatic Solvents. Results.—Table I shows the rates and products of the thermal decomposition of t-BuO$_2$H in toluene, benzene, and cumene at 100–215°. At 170 and 180°, rates of decomposition were first order in hydroperoxide to at least 90% decomposition; they were the same in benzene and toluene and slightly higher in cumene.

A plot of first-order rate constants and products at 180° as a function of [t-BuO$_2$H]$_0$ (Figure 1) clearly shows a change in mechanism of decomposition at 0.02–0.03 M. The relative insensitivity of k_{15} to [t-BuO$_2$H]$_0$ below this concentration suggests that here the reaction is largely a true homolysis.[13] The rate constants are about half as large as previously reported rates[11] in benzene at 180°. An Arrhenius plot for runs at 170–190° gives an E_a of 43 ± 1 kcal/mol, in good agreement with the value calculated by Benson.[4] The A factor, $10^{16.1}$, is reasonable for a first-order reaction.

Results above and below this optimum temperature range were less conclusive. In toluene at 100° the rate, measured over 3 months (about one half-life), was cleanly first order, but k_1 was 20 times that extrapolated from the decompositions at 170–190°. At 190–215° first-order rate constants were more sensitive to initial concentration (Table I). Also, plots of log [RO$_2$H] *vs.* time became slightly curved after one half-life. For 0.01 M t-BuO$_2$H in toluene at 205–215° (from k_1 for the first half-life), E_a was only 34.5 kcal/mol.

Closer scrutiny of the 180° reaction brought out some complications. First, there appeared to be some decomposition on the Pyrex walls. Increasing the surface to volume ratio sevenfold by filling the ampoules with crushed Pyrex tubing increased the first-order rate constant by 60% (Table I). A very small amount of added acetone in 0.02 M t-BuO$_2$H in toluene increased k_{15} significantly (Table I). Decomposing 0.02 M t-BuO$_2$H in the total reacted solution from a previous run caused a similar increase[14] in k_{15}. Thus, decompo-

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(12) Possible catalysts include trace amounts of thiols, acids, and metal ions. Since extraction of benzene with aqueous NaOH before use was about half as effective as treatment with CaH$_2$, acids or thiols are good possibilities. Autocatalysis in the thermal decomposition of silyl peroxides in chlorobenzene results from generation of HCl by reaction of radicals with the solvent: R. Hiatt, *Can. J. Chem.*, **42**, 985 (1964).

(13) Added 0.003 M t-Bu$_2$O$_2$ to 0.025 M t-BuO$_2$H in benzene at 170° decomposed an average of only 1.2 molecules of hydroperoxide per molecule of dialkyl peroxide decomposed, a chain length of 0.6.

(14) Addition of small amounts of t-BuOH did not affect the thermal decomposition. Attempts to decompose 0.02 M t-BuO$_2$H in t-BuOH as solvent resulted in explosion of the ampoule minutes after it was put in an 180° oil bath. An ampoule of 0.02 M t-BuO$_2$H in 20% t-BuOH-80% benzene exploded after 2 hr in a 170° bath.

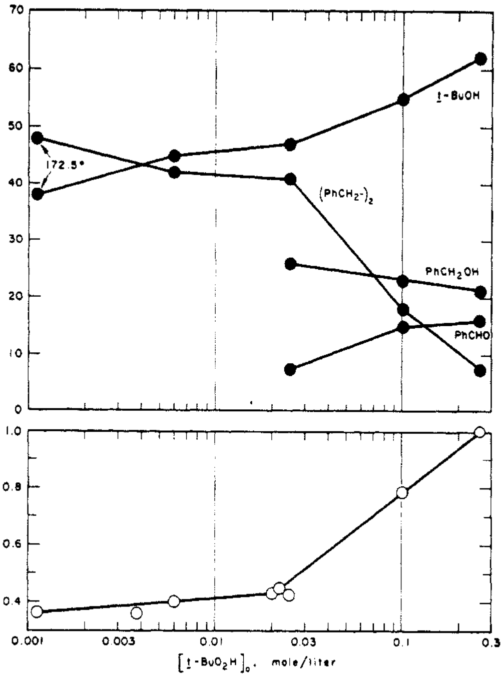


Figure 1.—Rate constants and products of decomposition of t-BuO_2H in toluene at 182°.

sitions at 180° (at least at 0.02 M) are slightly autocatalytic, and the straight line plots of log [RO_2H] *vs.* time result from a compensatory effect of autocatalysis and decomposition greater than first order.

Discussion.—Our analysis of these complex results (assuming that they are valid)[15] is based on the products, how these change with [t-BuO_2H]$_0$, and how they compare with products of t-Bu_2O_2 decomposed in similar circumstances (Table II). The argument is based mostly on the results in toluene, since these are the most comprehensive, but findings in other solvents are used where appropriate. The results below suggest the following. (1) At 180° for [t-BuO_2H]$_0$ > 0.03 M, decomposition proceeds mainly by a t-BuO·-induced reaction of the usual type. (2) At 180° for [t-BuO_2H]$_0$ ≥ 0.025 M, homolysis accounts for 40–70% of the reaction, so that the true k_1 at 182.6° is approximately 1×10^{-5} sec^{-1}. The rest of the reaction is mainly short chain induced decomposition involving benzyl radical attack on the *oxygen* of t-BuO_2H. (3) At 215°, for [t-BuO_2H]$_0$ = 0.01 M, decomposition is nearly all by spontaneous homolysis. (4) The reaction at 100° is partly induced but at least 30% is a bimolecular homolysis in which hydroperoxide reacts with the walls, with solvent, with itself, or with some other species to produce radicals.

Table II

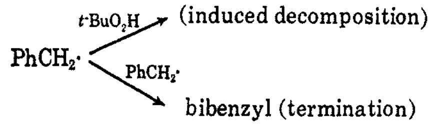
Products of Thermal Decomposition of t-Bu_2O_2 in Toluene[a]

Temp, °C	[t-Bu_2O_2]$_0$, mol/l.	Yields based on t-Bu_2O_2 decomposed, % Acetone	t-BuOH	$(PhCH_2)_2$
100	0.294			100
171.5	0.0244	52	47	80
181.5	0.0348	58	39	67
181.5[a]	0.0373	57	39	60

[a] All runs were carried to more than eight half-lives except the first, for which decomposition was 18% in 71 hr. The ampoules in the last run were filled with crushed Pyrex tubing.

Decompositions at 180°.—Above 0.02 M, increases in [t-BuO_2H]$_0$ result in lower yields of bibenzyl and higher [t-BuOH]/[acetone] ratios (Figure 1). The higher concentration of t-BuO_2H thus favors t-BuO· + t-BuO_2H → t-BuO_2· + t-BuOH (eq 2) over other fates for the t-butoxy radical. Decomposition probably occurs largely by an induced chain of the usual type, O_2 being produced by interaction of 2t-BuO_2· radicals and scavenged by benzyl (or methyl) radicals. (Yields of benzaldehyde should be a good index to this kind of reaction.) Chain lengths must be at least 4–5, since decomposition[4] is $^3/_2$ (or $^4/_3$) order in [t-BuO_2H].

At [t-BuO_2H]$_0$ ≤ 0.02 M, most t-BuO· radicals abstract from toluene or cleave, since t-BuOH/acetone ratios are relatively insensitive to [t-BuO_2H]$_0$ (Figure 1) and are in good agreement with those from t-Bu_2O_2 decompositions (Table II). Thus the relevant competition at these concentrations of t-BuO_2H is



(38)

(39)

The substantial yields of bibenzyl show that a large fraction of the hydroperoxide decomposes *via* homolysis. The questions are (1) how much, if any, disappears by a benzyl radical-induced decomposition, and (2) what is its mechanism. The discussion below shows that there is no simple answer for either question.

If *all* hydroxyl radicals (which can only be formed by homolysis) abstract hydrogen, then the yield of water (41% at [t-BuO_2H]$_0$ = 0.02 M, Table I) is identical with the amount of homolysis. This supposition seems sound in view of the activity of ·OH, the availability of the solvent, and the low steady-state concentration of other radicals with which it might couple, but the actual yield of H_2O is subject to considerable experimental uncertainty.

A better criterion for homolysis is the yield of identifiable products of radical–radical termination. For [t-BuO_2H]$_0$ ≤ 0.2 M we could find only about 50% [40–45% $(PhCH_2)_2$ and 7% PhCHO[17]].[18] This would be acceptable evidence for 50% homolysis except for the results of the t-Bu_2O_2 pyrolyses. At 180° in toluene this presumably well-behaved material gave only 60–70% of identifiable radical termination products (all bibenzyl). We do not understand why the yield of bibenzyl from t-Bu_2O_2 decreased with increasing temperature (Table II) but are reluctant to ascribe the decrease to induced decomposition. Possibly it is due to some as yet un-

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[15] Possibly surface catalysis is responsible for the faster than expected results at 100°. The experiments with packed vessels indicate that surface effects, though present, are small at 180°. The slower than expected rates above 200° could mean simply that temperatures in the reaction vessels did not attain bath temperature during the relatively short reaction times. However, the log plots for individual runs showed no evidence of any "warm up" period. Moreover, the rate constants for decompositions of α-cumyl hydroperoxide[16] in cumene or in benzene show the same S-shaped Arrhenius plot at somewhat lower temperatures.

[16] G. H. Twigg, G. W. Godin, H. C. Bailey, and J. Holden, *Erdoel Kohle*, **15**, 74 (1962).

[17] Though PhCHO is a product of induced decomposition, it must also be a product of a termination reaction between $PhCH_2O$· and some other radical (X·), *e.g.*, $PhCH_2O$· + X· → XH + PhCHO.

[18] Other possible termination products looked for *but not found* included ethane, ethylbenzene, xylenes, t-$BuOCH_3$, CH_3OH, and tarry residues. We could not be sure about the absence of other t-butyl ethers, but, since ~97% of t-BuO groups was accounted for in other products, their yield could not be significant. It seems most unlikely that any of the benzyl alcohol results from coupling of ·OH and $PhCH_2$·.

discovered products of $CH_3\cdot$ radicals; the yield of these parallels the termination-products gap, and our material balance for them was not good.

Since t-BuO_2H can give only half as many methyl radicals as t-Bu_2O_2, we might accept 15–20% as the amount of undiscovered termination products, thus setting 30% as the lower limit for induced decomposition of the hydroperoxide.

The mechanism of the induced decomposition depends on whether benzyl radicals abstract *hydrogen* from t-BuO_2H as Benson[4] asserted, or attack at oxygen to form benzyl alcohol directly, as Twigg, *et al.*,[16] suggested.[19] The yield of $PhCH_2OH$, though curiously insensitive to $[t\text{-}BuO_2H]_0$ (Figure 1), is less informative than the yield of α-cumyl alcohol (or the α-cumyl alcohol/acetophenone ratio) when t-BuO_2H is decomposed in cumene[20] (Table I). Cleavage of cumyloxy radicals to acetophenone and methyl is known to proceed more readily than the cleavage of t-$BuO\cdot$;[21] yet, while yields of acetone and t-BuOH were about equal, five to six *times as much cumyl alcohol* as acetophenone was formed. Thus the bulk of the cumyl alcohol cannot be formed from cumyloxy radicals.

Translated to the results in toluene, this suggests that, while *some* of the benzyl alcohol is undoubtedly formed from benzyloxy radicals (since some benzaldehyde is also produced), *most* of it is not. The alternatives are that it is formed by coupling of benzyl and hydroxyl (which has already been ruled out) or that it is formed directly by attack of benzyl· on t-BuO_2H (eq 40).

$$PhCH_2\cdot + t\text{-}BuO_2H \longrightarrow PhCH_2OH + t\text{-}BuO\cdot \qquad (40)$$

In accepting the reaction in eq 40 as the mechanism, we are not suggesting that the benzyl radical is unable to abstract hydrogen from t-BuO_2H. Most probably it *does*, but owing to the low steady-state concentrations of radicals, the reverse reaction (eq 41) occurs more

$$t\text{-}BuO_2\cdot + PhCH_3 \longrightarrow t\text{-}BuO_2H + PhCH_2\cdot \qquad (41)$$

frequently than any other reactions of t-$BuO_2\cdot$ radicals, leading to an induced chain.[22]

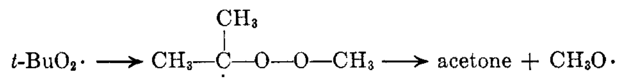
The rate expression for the induced part of the decomposition, according to the proposed mechanism in eq 42 is $^3/_2$ order in hydroperoxide, but, since the induced reaction accounts for less than half of the decomposition, the observed deviation from first-order kinetics is small.

$$-d[t\text{-}BuO_2H]/dt = k_{15}[t\text{-}BuO_2H] + k_{16}(k_{15}/k_3)^{1/2}\,[t\text{-}BuO_2H]^{3/2} \qquad (42)$$

Decompositions at 205–215° and at 100°.—The low yields of oxidized solvent show that induced decomposition was minimal at 205–215° when $[t\text{-}BuO_2H]_0 = 0.01\ M$. At 215° the yield of bibenzyl was only 51%, but by extrapolation from Table II, bibenzyl yields expected from t-Bu_2O_2 would be no higher. An assumed E_a of 43 kcal and a k_1 at 180° of 1×10^{-5} sec^{-1} gives 31×10^{-5} sec^{-1} for k_1 at 215°, in excellent agreement with the experimental value.

At 100° the rate (much faster than predicted) and the high yields of benzaldehyde and benzyl alcohol imply an induced decomposition. However, there is a 31% yield of bibenzyl. Less than $^1/_{20}$th of this can arise from unimolecular homolysis if the Arrhenius parameters obtained at higher temperatures are correct. Instead it must come from an externally assisted homolysis, perhaps catalyzed by the walls. The results on surface effects at 180° (Table VI) show that a wall-catalyzed reaction can yield almost as much bibenzyl as the unimolecular homolysis. However, low temperature homolyses of hydroperoxides are too confused and complex to allow any definite answers at this time. Hydroperoxides may react bimolecularly with another hydroperoxide,[23–25] with a ketone,[26,27] with an olefin,[6,28] perhaps even with solvent,[16,29] to produce radicals. Our own results are paradoxical if the formation of *benzaldehyde* as well as of bibenzyl is counted as chain termination. Further work is indicated.

Rearrangements of Peroxy Radicals.—The rearrangement of t-$BuO_2\cdot$ has been proposed to explain the formation of CH_3OH and acetone in gas phase oxidations of isobutylene,[30] rather than the alternate



$$t\text{-}BuO_2\cdot \longrightarrow CH_3\text{—}\overset{CH_3}{\overset{|}{C}}\text{—}O\text{—}O\text{—}CH_3 \longrightarrow \text{acetone} + CH_3O\cdot$$

interaction of $2t$-$BuO_2\cdot$ radicals to give $2t$-$BuO\cdot$ radicals (which cleave to $CH_3\cdot$ and acetone) and O_2. The absence of methanol in the products of our decompositions shows that this rearrangement does not occur in solution at 180°. However, this may not be significant, since in the gas phase concentration factors favor intramolecular reactions over their intermolecular alternatives.[31]

Decompositions of t-BuO_2H in Aliphatic Hydrocarbons.—Thermal decompositions of 0.01–0.02 M t-BuO_2H in cyclohexane and in n-heptane at 170° gave substantially the same first-order rate constants as reported by Bell, *et al.*[3] (Table III). Even at those low concentrations, rate constants were dependent on

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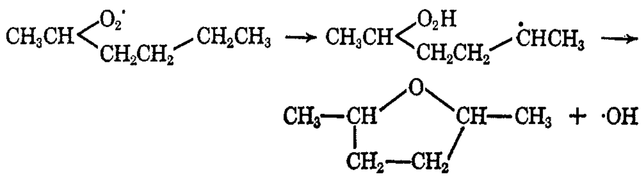
[19] The work of W. A. Pryor, A. Lee, and C. E. Witt [*J. Amer. Chem. Soc.*, **86**, 4229 (1964)] suggests that below 100° radical displacements on O–O bonds are infrequent. However, at 170–190° the situation appears to be different.

[20] This argument assumes that mechanisms in cumene and toluene are similar, as is indicated by our results and those of Twigg and coworkers.[16]

[21] See ref 2, pp 503–505. To make sure of this point, we decomposed 0.02 M α-cumyl hydroperoxide in toluene at 182° and found 1.6 times as much acetophenone as α-cumyl alcohol in the products (see below).

[22] The formation of heterocycles in the gas phase oxidation of hexane [C. F. Cullis, A. Fisk, A. Saeed, D. L. Trimm, *Proc. Roy. Soc.* **A289**, 402 (1966)] at 275° is analogous. Reabstraction of H· undoubtedly occurs, but the only reaction to effect an irreversible change is the radical displacement on oxygen.



[23] D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Amer. Chem. Soc.*, **87**, 4832 (1965).

[24] J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950).

[25] E. T. Denisov, *Fiz. Khim.*, **38**, 2085 (1964).

[26] E. T. Denisov, V. V. Kharatonov, and E. N. Raspupova, *Kinet. Katal.*, **5**, 981 (1964); *Chem. Abstr.*, **62**, 11657 (1965).

[27] Von K. Uberreiter and W. Rabel, *Makromol. Chem.*, **68**, 12 (1963).

[28] E. T. Denisov and L. N. Denisova, *Dokl. Akad. Nauk SSSR*, **157**, 907 (1964).

[29] V. L. Antonovskii, E. T. Denisov, and L. V. Solntseva, *Kinet. Katal.*, **6**, 815 (1965); *Chem. Abstr.*, **64**, 1923 (1966).

[30] (a) V. Ya. Shtern, "The Gas-Phase Oxidation and Hydrocarbons," translated by M. F. Mullins, The Macmillan Co., New York, N. Y., 1964, p 463–466. (b) A. P. Zeelenberg and A. F. Bickel, *J. Chem. Soc.*, 4014 (1961).

[31] A. Fish, *Quart. Rev.*, **18**, 243 (1964).

Table III

Decomposition of t-BuO$_2$H in Aliphatic Hydrocarbons

Solvent	Temp, °C	$[t\text{-BuO}_2\text{H}]_0$, mol/l.	$k_i \times 10^5$, sec^{-1}	Yields based on RO$_2$H decomposed, %: AcMe	t-BuOH	S—S[a]	S—OH[b]	S=O[c]
Cyclohexane	100.0	0.021	0.012	1.5[d]	80	0	59	9
	172.0	0.010	10.8					
	172.0	0.025	9.6					
	182	0.019		Some[d]	85	0	66	3.3
	172.0	0.024	7.3					
n-Heptane	172.0	0.022	4.3[e]					
	172.0	0.046	14.1					
Octane	169.0	0.05	7.0[f]					

[a] The product from solvent was bicyclohexyl. [b] The product from solvent was cyclohexanol. [c] The product from solvent was cyclohexanone. [d] Acetone largely obscured by cyclohexane on glpc; quantitative estimation not attempted. [e] With 0.0037 M t-Bu$_2$O$_2$ added; initial rate from part II.[1b] [f] Taken from Bell, *et al.*[3]

Table IV

Decompositions of α-Cumyl O$_2$H, n-BuO$_2$H, and sec-BuO$_2$H in Toluene

Temp, °C	$[\text{RO}_2\text{H}]_0$, mol/l.	$k_1 \times 10^5$, sec^{-1}	Yields based on RO$_2$H decomposed, %: R=O[a]	ROH[b]	PhCHO	PhCH$_2$OH	(PhCH$_2$)$_2$
			α-Cumyl O$_2$H				
182.3	0.0214	6.45	51	32	5.2	21	17
139	1.4	3[c]	28	65	7.6	7.1	0[c]
125	1.0	0.9[c]	25	56	5.6	11	0[c]
			n-BuO$_2$H				
172.0	0.0116	2.2[d]					
172.0	0.0300	4.2[d]					
172.0	0.0638	6.4[d]					
182.3	0.0060	3.2[d]					
182.3	0.0112	4.8[d]	16	63[e]	3	9	30
182.3	0.0193		16	62			
			sec-BuO$_2$H				
172.0	0.027	2.65					
182.3	0.0127	4.9	12	20			40
182.3	0.0186		22	33[f]			

[a] Ketone or aldehyde[a] from hydroperoxide radical. [b] Alcohol from hydroperoxide radical. [c] Estimated from times for 90% decomposition. [d] $(-2[\text{RO}_2\text{H}]/dt)_0/[\text{RO}_2\text{H}]_0$. [e] No carboxylic acid. [f] Also 19% CH$_3$CHO.

$[t\text{-BuO}_2\text{H}]_0$ and their 10–15-fold increase over those in benzene or toluene suggests strongly that homolytic decomposition accounts for little of the hydroperoxide disappearance. No oxygen or other gas was produced, but large quantities of oxygenated solvent molecules were found. Decomposition in cyclohexane gave cyclohexanone and cyclohexanol, but *no* bicyclohexyl. Cyclohexene may have been produced in *small* quantities,[32] but was not a major product.

In radical-induced decompositions of t-BuO$_2$H, (part II[1b]), we found that small amounts of t-Bu$_2$O$_2$ had a pronounced effect (Table III). In contrast to the effect of added t-Bu$_2$O$_2$ in benzene, the rate enhancement was large and persisted long after most of the t-Bu$_2$O$_2$ should have decomposed.

The prevalence of complexing between hydroperoxides and aromatic solvents has recently been documented.[33] We have expected to ascertain what effect this would have on the rate of homolytic cleavage of the O-O bond by comparing thermal rates in toluene with those in nonaromatic hydrocarbons. However, because of the complexity of the thermal decomposition in alkanes at 170–180° it is unlikely that a homolytic rate can be measured under these conditions. The controlling factor appears to be formation of thermally unstable peroxides which decompose to give degenerate chain branching (part II[1b]). At 100° these

$$t\text{-BuO}_2\cdot + \text{S}\cdot \longrightarrow t\text{-BuO}_2\text{S} \longrightarrow t\text{-BuO}\cdot + \text{SO}\cdot \quad (43)$$

peroxides are relatively stable and contribute little to radical-induced decomposition.

Decomposition of α-Cumyl Hydroperoxide in Toluene

The results of decomposition of 0.02 M α-cumyl hydroperoxide in toluene at 182° (Table IV) were needed to substantiate the conclusions of the preceding section. The decompositions at high concentrations and low temperatures were done in order to investigate claims by Shushunov and coworkers,[34] who postulated the reaction in eq 44 because they re-

$$\text{PhCMe}_2{}^*\cdot + \text{PhCMe}_2\text{O}_2\text{H} \longrightarrow \text{PhCMe}_2{}^*\text{O}_2\text{H} + \text{PhCMe}_2\cdot \quad (44)$$

covered ^{14}C-labeled cumene from decomposition of ^{14}C-labeled α-cumyl hydroperoxide in unlabeled cumene. We reasoned that decomposition of the same concentration of α-cumyl O$_2$H in toluene should yield cumene if such a mechanism were operative. We found *no* cumene on the most scrupulous examination of the products. Examination of these authors'

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[32] We were unable to effect a practicable glpc separation of trace amounts of cyclohexene from cyclohexane. As little as 0.1% bicyclohexyl could have been observed. We have found bicyclohexyl when other free radical initiators have been decomposed in cyclohexane, but never when t-BuO$_2$H has also been present in the solution (part II[1b]).

[33] C. Walling and L. Heaton, *J. Amer. Chem. Soc.*, **87**, 38 (1965).

[34] M. R. Leonov, B. A. Redoshkin, and V. A. Shushunov, *Zh. Obhsch. Khim.*, **32**, 3959 (1962).

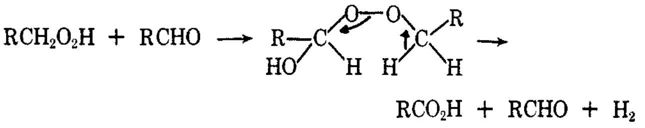
experimental techniques convinces us that they were misled by incomplete separation of decomposition products from the solvent.

Decompositions of *n*-BuO_2H and *sec*-BuO_2H in Toluene at 170–180°

Thermal decompositions of dilute solutions of *n*-BuO_2H and *sec*-BuO_2H in toluene were carried out to determine the extent of homolysis and to gain some information on cleavage reactions of primary and secondary alkoxy radicals under these conditions. Although both hydroperoxides were slightly contaminated with their parent alcohols, this was not expected to invalidate the results. Rate constants and products are shown in Table IV.

Decompositions of *n*-BuO_2H were autocatalytic, even at 0.01 *M* in toluene. Plots of per cent of RO_2H *vs.* time were linear, and the first-order rate constants in Table IV are calculated from the initial rates of hydroperoxide decomposition determined from such plots. Values of k_1 so determined were approximately proportional to $[n\text{-BuO}_2\text{H}]^{1/2}$ and suggested induced decomposition, although the rates of lowest initial concentration and the yields of bibenzyl were not much different from those for *t*-BuO_2H under similar circumstances.

Autocatalysis for *n*-BuO_2H was not surprising in view of the Mosher[35] reaction for primary hydroperoxides, but the absence of butyric acid in the products



appeared to eliminate any large contribution from this reaction. The evolved gases were not analyzed.

sec-BuO_2H gave reasonably good first-order plots for decomposition and gave as much or more bibenzyl as *n*-BuO_2H did.

In product studies on completely decomposed solutions, only 79% of *n*-BuO residues and 74% of *sec*-BuO residues from the respective hydroperoxides were accounted for. Up to 21% *n*-BuO· radicals could have been lost through cleavage to Pr· + CH_2O·. *sec*-BuO· radicals can cleave in two ways. While the production of methane in the thermal decomposition of *sec*-Bu_2O_2 in toluene at 100° (part II[1b]) suggests that at 180° CH_3· radicals and EtCHO are being formed, we were unable to find the expected propionaldehyde or carboxylic acids in the products. Thus, there appear to be many opportunities for further experimental work on thermal decomposition of primary and secondary hydroperoxides, but little possibility of obtaining clean reactions and high yields of single products.

Registry No.—*t*-BuO_2H, 75-91-2; *t*-Bu_2O_2, 110-05-4; *α*-cumyl O_2H, 80-15-9; *n*-BuO_2H, 4813-50-7; *s*-BuO_2H, 13020-06-9.

Acknowledgment.—Mr. Brian Guilbert assisted with part of the experimental work.

[35] H. S. Mosher and L. J. Durham *J. Amer. Chem. Soc.* **82**, 4537 (1960).

Strained Organic Molecules. I. 1,5,6-Triphenyltricyclo[3.1.0.$0^{2,6}$]hexan-3-one[1-3]

AUDREY SMALL MONAHAN

Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268

Received July 11, 1967

The synthesis of 1,5,6-triphenyltricyclo[3.1.0.$0^{2,6}$]hexan-3-one (I) from 1-(1,2,3-triphenylcycloprop-2-enyl)-3-diazopropan-2-one (II) is described. Upon heating I rearranges quantitatively to 3,4,5-triphenylphenol. In base, I readily gives 4,5,6-triphenylbicyclo[3.1.0]hex-3-en-2-one (IV). Upon irradiation with ultraviolet light I rearranges almost exclusively to 2,4,5-triphenylphenol, whereas IV gives substantial amounts of both 3,4,5-triphenylphenol and 2,4,5-triphenylphenol. Compound I reacts with methylmagnesium iodide to give 3-methyl-1,5,6-triphenyltricyclo[3.1.0.$0^{2,6}$]-3-hexanol (V).

Since 1961 the intramolecular cyclization of "carbenes"[4] has been used to synthesize a number of strained ring compounds. We wish to report on such a synthesis of 1,5,6-triphenyltricyclo[3.1.0.$0^{2,6}$]hexan-3-one (I) and some of its reactions. Masamune and coworkers[5] have communicated the results of extensive studies on an analogous compound, 1,6-diphenyltricyclo[3.1.0.$0^{2,6}$]hexan-3-one, and the next lower homolog, 1,5-diphenyltricyclo[2.1.0.$0^{2,5}$]pentan-3-one.

Compound II, (1,2,3-triphenylcycloprop-2-enyl)acetic acid, was prepared in good yield by the hydrolysis of the crude reaction product from treatment of triphenylcyclopropenyl bromide with ethyl bromoacetate in the presence of zinc in refluxing benzene–ether. It had the typical uv spectrum of a diphenylcyclopropene double bond[6] and the infrared spectrum and analysis also supported the proposed structure (see Experimental Section).

Compound III, 1-(1,2,3-triphenylcycloprop-2-enyl)-3-diazopropan-2-one, was synthesized from the acid chloride of II and diazomethane in the usual manner. Its spectra and analysis supported its structure. When this diazo ketone was treated with copper in refluxing benzene, a good yield of compound I was obtained after chromatography. The structure of I was indicated by analysis and by spectral and chemical properties. The infrared spectrum showed a carbonyl

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[1] Preliminary communications of this work have been published: A. Small, *J. Amer. Chem. Soc.*, **86**, 2091 (1964); A. M. Small, *Chem. Commun.*, 243 (1965).

[2] This compound was previously named 4,5,6-triphenyltricyclo[2.1.1.$0^{5,6}$]hexan-2-one but renamed to follow the IUPAC rules as pointed out by Meinwald.[3]

[3] J. Meinwald and J. K. Crandall, *J. Amer. Chem. Soc.*, **88**, 1292 (1966).

[4] The first example of such a cyclization was reported by G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961).

[5] (a) S. Masamune, *ibid.*, **86**, 735 (1964); (b) S. Masamune, *Tetrahedron Lett.*, 945 (1965); (c) S. Masamune and N. T. Castellucci, *Proc. Chem. Soc.*, 298 (1964). (d) S. Masamune, *et al.*, *Tetrahedron Lett.*, 193 (1966).

[6] R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, **80**, 5991 (1958), and subsequent papers by R. Breslow and coworkers.