Two examples illustrate the application (really the foundation) of these generalizations. In experiments at about the same t-BuO_2H–t-Bu_2O_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_2O_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_2H 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°.

Registry No.—t-BuO_2H, 75-91-2; *sec*-Bu_2O_2, 4715-28-0; t-$BuO_2C_6H_{11}$, 15619-54-2.

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

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

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Received June 28, 1967

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_2O_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_2O_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_2H (92%) and *sec*-BuO_2H (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_2H 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.*, $-\Delta[RO_2H]/-\Delta2[\text{initiator}]$, 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_2H. 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_2H	$[RO_2H]_0$, M	$[DBPO]_0$, M	Chain length[b]	Products, %: 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_2H. [d] Aldehyde or ketone from R, based on decomposed RO_2H. [e] Also butyric acid, not determined quantitatively.

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[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).

TABLE II

t-Bu_2O_2-INDUCED DECOMPOSITION OF *sec*-BuO_2H IN BENZENE AT 100°

	Reactants, mol/l.		% RO_2H	Chain	Products,[b] %		
Time, min	[*sec*-BuO_2H]$_0$	[t-Bu_2O_2]$_0$	decomposed	length[a]	*sec*-BuOH	AcEt	O_2
4025	0.187	0	4				
2671	0.183	0.186	39	0.98	65	35	
2838	0.184	0.180	39	1.5[c]	0	35	0.1
2890	0.180	0.177	45	1.4	44	48	2
7202	0.180	0.177	71	1.1	35	41[d]	

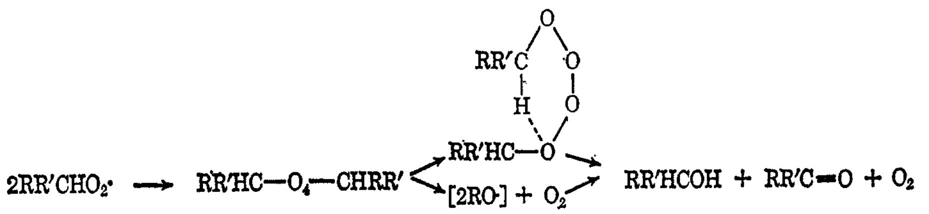
[a] Calculated from measured changes in concentrations of both peroxides. [b] As percentage of hydroperoxide decomposed. [c] Calculated from $\Delta RO_2H/\Delta t$-BuOH. [d] Also 4% acetaldehyde and 13% acetic acid.

eq 12 plus some oxidation by the oxygen evolved of the alcohol and aldehyde formed.

Although about 5% t-Bu_2O_2 based on decomposed DBPO originates by cage recombination of t-BuO· radicals from DBPO, no *sec*-Bu_2O_2 could be detected when the decomposition products from *sec*-BuO_2H were examined by combined fractional distillation and infrared techniques. *sec*-Bu_2O_2 (2.5%) *was* found when 0.3 *M* *sec*-BuO_2H in benzene was completely decomposed by cobaltous octoate and the products were analyzed by flame ionization gas chromatography. balances on *sec*-butyl groups were generally low by 25%, and, where measured, only 27 and 0% oxygen were found.

Discussion

One of the major objectives of this work was to gain some detailed knowledge about the extent to which interactions of primary and secondary peroxy radicals lead to termination *via* a concerted Russell-type mechanism[5] (eq 12a) or by disproportionation of caged alkoxy radicals (eq 12b).



$$2RR'CHO_2\cdot \longrightarrow RR'HC{-}O_4{-}CHRR' \rightarrow RR'HCOH + RR'C{=}O + O_2$$

(12a)

(12b)

If our interpretation of metal-catalyzed decompositions is correct (part IV), the yield from radical-induced decompositions should be about 3%.

Of greater interest was the behavior of a primary or secondary hydroperoxide at 100° where several corresponding hydrocarbons have been oxidized. *sec*-Butyl hydroperoxide was chosen for this purpose, and some results of rate measurements and product analyses are presented in Table II.

These experiments at 100° are characterized by erratic ketone–alcohol ratios and chain lengths and essentially no oxygen production. Since the products found in Table II exclude the possibility of reaction of much of the expected oxygen, some of the analyses must be faulty; *e.g.*, some other hydroperoxide may have replaced *sec*-BuO_2H in the titration.

Decompositions of *sec*-BuO_2H at 100° in the Gas Phase

In the gas phase at 100°, 9–19% of 0.009 *M* *sec*-BuO_2H decomposed in 15 hr in Pyrex *in the absence of free-radical initiators.* This erratic thermal decomposition, about twice as fast as for t-BuO_2H in similar circumstances,[2] was reduced to about one-fifth that rate (9–16% in 70 hr) by adding 5 atm of ethane, which is practically inert to alkoxy radical attack at 100°.

With 0.006 *M* added t-Bu_2O_2, the rates of disappearance of 0.004 *M* *sec*-BuO_2H (in 5 atm of ethane) were considerably faster than in the absence of initiator (80–90% in 70 hr) and chain lengths estimated from $\Delta RO_2H/\Delta t$-BuOH were 2.7–3 for four replicate runs. Ketone–alcohol ratios were 1.6 : 3; material

The short chain lengths at 45° (0.7–1.0) establish only that no measurable proportion of *free* radicals is produced in eq 12 at this temperature. The good oxygen yield and close to 50% yields of alcohol from primary and secondary hydroperoxides in benzene at 45° are also consistent with eq 12 (without distinguishing between 12a and 12b) but not with any important contribution from eq 6. Thus, the DBPO-induced decomposition at 45° occurs (as for tertiary hydroperoxides) by abstraction of the peroxy hydrogen atom,[6] and nearly every interaction of the resulting primary or secondary peroxy radicals leads to termination, in marked contrast to interactions of tertiary peroxy radicals which terminate only once in eight to ten interactions at 45°.[7]

In the 100° decompositions, particularly in the gas phase, the chain lengths exceed unity and the ketone–alcohol ratios are higher than at 45°. All the material balances at 100° are unsatisfactory. At 45°, the DBPO decomposes rapidly and the relatively high concentration of *sec*-BuO_2 · radicals favors their interaction (eq 12). At 100°, the t-Bu_2O_2 decomposes very slowly, apparently favoring reactions which are first order in *sec*-BuO_2· [induced oxidation of peroxide decomposition products or attack of the α C–H bond in *sec*-BuO_2H

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(5) G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 3871 (1957).

(6) The chain lengths of less than one found for *n*-butyl cyclopentenyl, and tetralyl hydroperoxides probably arise from attack of some RO· radicals on allylic hydrogens in the latter two cases and on product *n*-PrCHO from *n*-BuO_2H. The radicals thus produced may terminate without destroying hydroperoxide and lead to waste of initiator.

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

(with formation of ketone as in eq 6)]. Because of the apparent intrusion of a reaction such as eq 6, we do not yet know whether to attribute any of the increased chain length at 100° to escape of free RO· radicals from eq 12b. Clarifying experiments are in progress.

Registry No.—*n*-BuO_2H, 4813-50-7; *sec*-BuO_2H, 13020-06-9; α-tetralyl hydroperoxide, 771-29-9.

Homolytic Decompositions of Hydroperoxides. IV.[1a–c] Metal-Catalyzed Decompositions

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Received June 28, 1967

t-Butyl hydroperoxide has been decomposed by a variety of cobalt salts and compounds of other metals (Fe, V, Mn, Ce, and Pb). In chlorobenzene or alkanes at 25–45° half-lives for decomposition of 0.1 *M* *t*-BuO_2H by 10^{-4} *M* catalyst ranged from 1 to 10 min. Products included approximately 88% *t*-BuOH, 11% *t*-Bu_2O_2, 1% acetone, and 93% O_2. Decompositions in alcohol–chlorobenzene mixtures yielded more acetone but were only *ca.* one-hundredth as fast as in pure chlorobenzene. Reactions in all solvents were subject to autoretardation owing partly to formation of aldehydes and carboxylic acids and partly to changes in the catalyst which caused its eventual precipitation. Decompositions of α-cumyl, *n*-butyl, and *sec*-butyl hydroperoxides were normally one-fourth to one-tenth as fast as those of *t*-BuO_2H. *n*-BuO_2H and *sec*-BuO_2H yielded 70% O_2 and the corresponding alcohol and aldehyde or ketone in a ratio of about 2. The results suggest that these reactions are essentially the same as free-radical-induced decompositions but are initiated by metal ion–hydroperoxide interactions. Generally speaking the choice of metal ion, as long as it can undergo a facile one-electron redox reaction, has little influence on either products or rates of decomposition except in the presence of olefins.

Metal ion catalyzed decompositions of hydroperoxides are important in metal ion catalyzed autoxidations of hydrocarbons. While it is generally agreed that these autoxidations are initiated by radicals generated from ion hydroperoxide interactions,[2,3] the interactions themselves and the mechanisms by which useful products arise from the hydroperoxides are poorly understood despite numerous investigations.[4] This report shows how metal-catalyzed decompositions are related to free-radical-induced decompositions (parts II[1b] and III[1c]). Only about a third of our experiments are reported.

Experimental Section

Materials.—Hydroperoxides and chlorobenzene were obtained and purified by the methods described in parts II[1b] and III.[1c] *n*-Pentane, cyclohexane, *n*-heptane, and 2,2,4-trimethylpentane were Matheson Coleman and Bell "Chromatograde" reagents, refluxed for 6 hr over CaH_2 and distilled.

Cobaltous stearate ($CoSt_2$) and cobaltous 2-ethylhexanoate ($CoOct_2$) were prepared by the methods of Dyer[5] and of Vold.[6] An aqueous solution of the sulfate was added to a neutralized ethanol solution of the carboxylic acid and the precipitate was collected and dried at 90° in vacuum. Infrared absorptions of the compounds at 1708 cm^{-1} revealed that they contained 15–20% of the free carboxylic acid, as did the cobaltous stearate obtained from K & K Laboratories. Two reprecipitations of the salts with acetone from a hexane solution gave acid-free catalysts (less than 0.5%) of decreased solubility in chlorobenzene and a higher then theoretical amount of cobalt (Table I). Cobaltic stearate ($CoSt_3$), prepared by treatment of a solution of $CoSt_2$ in acetic and stearic acids with an excess of H_2O_2, also contained free acid which was removed as above.

TABLE I

ANALYSES OF REPRECIPITATED COBALT SALTS

Salt	% cobalt Experimental[a]	% cobalt Theory
Cobaltous laurate	15.05	12.88
Cobaltous stearate	10.59	9.42
Cobaltous 2-ethylhexanoate	20.50	17.06
Cobaltic stearate	14.04	6.89
$CoCO_3$[b]	49.08	49.55

[a] *Analyses were by West Coast Analytical Laboratory by both* polarography and reduction to metal. [b] Baker reagent grade.

The high percentage of cobalt in these compounds indicated their formula to be $[Co(RCO_2)_2]_x[Co(RCO_2)(OH)]_y$.[6] The analysis of the cobaltic stearate showed it to be nearer CoOSt than $CoSt_3$.

Cobaltous acetylacetonate (CoA_2) was obtained from K & K Laboratories and dried at 60° under vacuum. Cobaltic acetylacetonate (CoA_3) was prepared by oxidation of the cobaltous salt with H_2O_2 in the presence of excess acetylacetone and recrystallized. V^{III}, Fe^{III}, Ni^{II}, Mn^{II}, and Ce^{II} acetylacetonates, vanadous octoate, and cobalt salicylalethylenediimine were obtained from K & K Laboratories and used without further purification.

Iron phthalocyanine (FePCN) was obtained from the Pigment Colors Division of Du Pont.

Lead naphthenate ($PbNap_2$) manganous octoate, and cupric octoate were Nuodex solutions, 24, 8, and 8%, respectively, by weight in metal.

Procedures.—Reactions in mixtures of chlorobenzene with protic solvents were started by syringing 0.2–3 ml of neat hydroperoxide into 20 ml of the catalyst-containing solution immersed in a constant-temperature bath. Reactions in alkanes were refluxed to exclude oxygen from the air and expel that produced by the peroxide decomposition. Flasks were immersed in a bath 10–15° warmer than the reflux temperature of the solvent. Boiling chips were used to minimize superheating.

Rates of decomposition were measured by pipetting aliquots into a stop bath of 1:10 AcOH–*i*-PrOH and determining residual hydroperoxide by reflux iodometric titration (part II[1b]).

For most analyses of products a gas chromatograph with thermal conductivity sensing was used. Columns were packed with a 20% loading of Carbowax 20M or didecyl phthalate on Chromosorb P. Residual hydroperoxides were reduced to al-

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[1] 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 in part II. (c) Part III: R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *ibid.*, **33**, 1428 (1968). Equations 12a and b appear in part III. (d) To whom all correspondence should be addressed at Brock University, St. Catherines, Ontario, Canada.

[2] N. Uri, *Nature* **177**, 1177 (1956).

[3] E. T. Denisov and N. M. Emanuel, *Usp. Khim.*, **29**, 1409 (1960).

[4] Reference 3 contains a useful summary of work to 1960. This report considers some more recent investigations.

[5] E. Dyer, K. R. Carle, and D. E. Weiman, *J. Org. Chem.*, **23**, 1464 (1958).

[6] R. D. Vold and G. S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949).