concentration used). In all cases the absorption spectrum (over the 300–450-mμ range) of the reaction mixture after several half-lives corresponded within 2% to the "mock" infinity prepared by the appropriate N-nitrophenylamine. To achieve this result it was necessary to exercise extreme care in the purification of the reacting amines. This was essential in the reactions of fluoro-2-nitrobenzene or fluoro-2,4-dinitrobenzene with excess of the more bulky amines. Thus, if less hindered amines were present as impurities, the experimental infinity was substantially higher than the "mock" one. This is because the less hindered amines are more reactive (Table II) and give final products with higher molar absorbance (Figure 1).

In the case of slow reactions, samples of the reaction mixture were sealed under nitrogen into Pyrex tubes which were then placed at the desired temperature and cooled at room temperature; the content was diluted (50- to 2500-fold) with benzene and immediately transferred into a stoppered cuvette for the spectral analysis (the absorbance was determined against that of benzene–DMSO solutions of the same composition; 10-mm matched quartz cuvettes were used). The combined processes of cooling and diluting the sample with benzene practically stopped the reaction. In the case of more rapid reactions, carried out at 25°, the solutions of the two reagents were mixed and then samples of the reaction mixture were withdrawn at time intervals by means of a pipet in an atmosphere of dry N_2 and diluted with benzene as above. In the case of very rapid reactions, 100–300 μl of the appropriate amine solution was added to 3 ml of the solution of the appropriate fluoronitro compound contained in a 10-mm stoppered quartz cuvette in the spectrophotometer cell compartment. In this instance mixing was ensured by stirring the solution while adding the amine and, when possible, by vigorously shaking the cuvette after the process of mixing the reagents. The reverse process of adding 100–300 μl of the solution of fluoronitro compound to 3 ml of the amine solution gave the same rate values.

Rate coefficients were calculated by first-order plots when a large excess of amine was used, and by second-order plots in other cases. The stoichiometry used in the calculations was, in all cases, that shown by the equation below for the reaction of fluoro-2,4-dinitrobenzene with piperidine.

$$(O_2N)_2C_6H_3F + 2C_5H_{10}NH = (O_2N)_2C_6H_3NC_5H_{10} + C_5H_{10}NH_2{}^+F^-$$

Ultraviolet Spectra.—Ultraviolet spectra over the range 300–450 mμ were determined in benzene solutions (Figure 1) using a Beckman DU spectrophotometer with matched 10-mm, stoppered quartz cuvettes. Concentration never exceeded 4×10^{-4} *M* (Beer's law was obeyed in benzene as well).

Registry No.—I, 15822-69-2; II, 15822-70-5; III, 15822-71-6; IV, 6574-15-8; V, 839-93-0; VI, 15822-74-9; VII, 15889-61-9; VIII, 15822-76-1; IX, 15822-77-2; X, 15822-78-3; XI, 15822-79-4.

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Homolytic Decompositions of Hydroperoxides. I.[1] Summary and Implications for Autoxidation

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This paper summarizes and integrates the conclusions of the four succeeding papers which present experimental details on decompositions of hydroperoxides. Purely thermal decompositions by homolysis to alkoxy and hydroxy radicals have been experimentally approached but never fully attained. All decompositions of hydroperoxides are induced to a greater or lesser degree by metals or other sources of free radicals. The induced reactions are simple in principle; they depend mostly on competitions between nonterminating and terminating interactions of peroxy radicals (eq 3 and 4 below), competitions among two hydrogen abstractions by alkoxy radicals (from hydroperoxides or from reactive solvents in eq 2 and 9), and cleavage of alkoxy radicals by eq 7. These competitions depend on the hydroperoxide, solvent, and temperature. Decompositions induced by catalytic quantities of several metal salts are similar except for the participation of both metal and hydroperoxide in radical production. The complex kinetics of metal-catalyzed decompositions are ascribed to extensive association of metal salts and soaps in organic solvents and the constantly changing coordination of oxygen-containing compounds with the metals as the decompositions progress.

Traditionally, thermal decompositions of hydroperoxides, metal ion catalyzed decompositions, and decompositions by free-radical initiators have been treated as separate phenomena; yet all of these involve hydroperoxides in the presence of free radicals and are subject, to some extent,[3–5] to a concomitant radical-induced chain decomposition. The nature of this induced chain has been elucidated previously for simple cases.[6–8] This series of papers explains more complex aspects of this chain decomposition and shows how it operates as a unifying factor for all homolytic decompositions of hydroperoxides.

This report summarizes conclusions based on our own investigations and those of previous workers, and suggests some of their applications for autoxidations of hydrocarbons.

Free-Radical-Induced Decompositions

Background.—Hydroperoxides of all types are particularly labile toward attack by free radicals. An understanding of this destructive process, which is basic to our investigation, is facilitated if the initiating radicals are not generated by the hydroperoxides themselves. Decompositions of t-BuO_2H in benzene or chlorobenzene at 20–60°, initiated by di-*t*-butylperoxy oxalate (DBPO),[4,6] 2,2′-azobis(2-methylpropionitrile) (ABN),[9] and photolysis of hypochlorites[5] have elucidated a general mechanism. In the simplest instance,

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[1] Parts II–V: R. Hiatt, *et al.*, *J. Org. Chem.*, **33**, 1421, 1428, 1430, 1436 (1968). Equations are numbered consecutively in papers I–V.

[2] To whom all correspondence should be addressed at Brock University, St. Catherines, Ontario, Canada.

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

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

[5] W. H. Richardson, *J. Amer. Chem. Soc.*, **87**, 1096 (1965).

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

[7] D. B. Denny and J. D. Rosen, *Tetrahedron*, **20**, 1137 (1962).

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

[9] J. R. Thomas, *ibid.*, **87**, 3935 (1965).

where initiator generates an alkoxy radical directly (R is often, but not necessarily, *t*-Bu·), eq 1–5 apply.

$$\text{DBPO} \longrightarrow 2\text{RO}\cdot + 2\text{CO}_2$$
$$R_i = \text{rate of initiation} = 2k_1[\text{DBPO}] \quad (1)$$

$$\text{RO}\cdot + \text{RO}_2\text{H} \longrightarrow \text{ROH} + \text{RO}_2\cdot \quad (2)$$

$$2\text{RO}_2\cdot \longrightarrow 2\text{RO}\cdot + \text{O}_2 \quad (3)$$

$$2\text{RO}_2\cdot \longrightarrow \text{RO}_2\text{R} + \text{O}_2 \quad (4)$$

$$-\text{d}[\text{RO}_2\text{H}]/\text{d}t = 2k_1[\text{DBPO}](1 + k_3/k_4) = R_i(1 + k_3/k_4) \quad (5)$$

Under the conditions specified above, the chain length (equal to $1 + k_3/k_4$) is about 11. However, in other solvents or with other tertiary hydroperoxides, the reaction appears to be much more complex.[10] For nontertiary hydroperoxides, a quite different mechanism has been proposed[11] (eq 6) analogous to the base-

$$\text{R}_1\text{R}_2\text{HCO}_2\text{H} + \cdot\text{OH} \longrightarrow \text{H}_2\text{O} + \text{R}_1\text{R}_2\text{CO}_2\text{H} \longrightarrow \text{R}_1\text{R}_2\text{C}{=}\text{O} + \cdot\text{OH} + \text{H}_2\text{O} \quad (6)$$

catalyzed decomposition.[12] Our own investigations are reported in parts II and III.[1]

t-Butyl hydroperoxide was decomposed at 100° in the gas phase or in benzene by radicals generated from *t*-Bu_2O_2 or *sec*-Bu_2O_2. Decompositions initiated by DBPO were carried out in acetic acid, *t*-butyl alcohol, and Nujol at 35–45° and also in refluxing *n*-heptane, cyclohexane, and *n*-pentane. Decompositions of primary and secondary hydroperoxides by DBPO were carried out at 45° in benzene.

Tertiary Hydroperoxides. The Viscosity of the Medium.—The chain length for radical-induced decomposition, according to eq 3–6, depends on the ratio of nonterminating to terminating interactions of peroxy radicals (k_3/k_4). If the initial result of interaction of two peroxy radicals is a pair of alkoxy radicals (+ oxygen) in a solvent cage, the ratio k_3/k_4 is controlled by the rate of diffusion out of the cage, and should be inversely proportional to the viscosity of the solvent. The expected relationship was observed for chain lengths of *t*-BuO_2H decompositions in benzene at 25–100°, a 2.5-fold change in solvent viscosity corresponding to an apparent activation energy of 2.3 kcal/mol for diffusion. Chain lengths as high as 50 (in the gas phase at 100°) and as low as 1 (in Nujol at 35°) were found. However, other factors also affect chain lengths.

Cleavage of Alkoxy Radicals.—Decomposition of *t*-BuO_2H at 100° in benzene, carbon tetrachloride, or gas phase, or at 45° in *t*-butyl alcohol or acetic acid did not obey the simple rate expression of eq 5 when the initial concentration of *t*-BuO_2H was less than 0.2 *M* (as it was for most measurements). Over-all chain lengths (here dependent on [*t*-BuO_2H]) as low as 1.5 were found and products included up to 27% acetone. Yields of oxygen, where measured, were as low as 25% of theory.

These differences between theory and experiment are due to cleavage of *t*-butoxy radicals (eq 7). As

$$t\text{-BuO}\cdot \longrightarrow \text{CH}_3\text{COCH}_3 + \text{CH}_3\cdot \quad (7)$$

Walling and Wagner[13] have shown, cleavage is favored in protic solvents over H abstractions such as reaction 2. Cleavage of *t*-BuO· becomes competitive at low [*t*-BuO_2H], even in benzene at higher temperatures, and then oxygen is partly scavenged by methyl radicals. Participation of $\text{CH}_3\cdot$ or $\text{CH}_3\text{O}_2\cdot$ in rapid termination reactions reduces chain lengths. When cleavage is the rate-determining step for termination, eq 8 applies. Experimentally determined rate laws

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

for less than 0.2 *M* *t*-BuO_2H at 100° (excepting those in the gas phase) closely approximate eq 8.

Protection of Hydroperoxides from Radical Attack.—Decompositions in alkanes, refluxed to expel oxygen, had chain lengths lower than corresponding runs in benzene, although alkoxy cleavage and yields of acetone were minimal. The maximum effect occurred in refluxing *n*-heptane where *t*-BuO_2H appeared to be untouched by initiating radicals. Similar effects were observed in the gas phase on addition of cyclopentene or isobutane vapor. The results are readily explained as increasing competition for RO· by solvent (SH) (eq 9) and the rapid terminations available to S·

$$\text{RO}\cdot + \text{SH} \longrightarrow \text{ROH} + \text{S}\cdot \quad (9)$$

(eq 10). Substantial quantities of the mixed peroxide

$$\text{S}\cdot + \text{RO}_2\cdot \longrightarrow \text{SO}_2\text{R} \quad (10)$$

SO_2R were isolated from products of decomposition in refluxing cyclohexane. Alkanes did not exert a protective effect at 170° probably because the mixed peroxides thermally decompose at that temperature.

Decompositions in the Gas Phase.—In the absence of added free-radical initiators, 3–27% *t*-BuO_2H decomposed in the gas phase at 100° in 15 hr, the time ordinarily used for induced decompositions. The lowest values were obtained using new or base-washed vessels. This surface-catalyzed reaction was thought to contribute about 10% to the total decomposition in ordinary vessels with added radical initiators, but was too erratic for meaningful corrections to be made. The rate expression for homogeneous induced decompositions is given in eq. 11. This relation cor-

$$-\text{d}[t\text{-BuO}_2\text{H}]/\text{d}t = k(R_i)^{1/2}[t\text{-BuO}_2\text{H}]^{1/2-1} \quad (11)$$

responds for unit order in [*t*-BuO_2H] to the expression expected for the chain decomposition if termination results only from random combination of alkoxy radicals. When decomposition was induced by *sec*-Bu_2O_2, no significant amount of *t*-Bu_2O_2 was found in the products, suggesting that MeO· or $\text{MeO}_2\cdot$ was involved in most terminations. Other products included 1–10% acetone, 90–95% *t*-BuOH, and 30–50% of the theoretical amount of O_2.

Primary and Secondary Hydroperoxides.—Decompositions of *sec*-butyl hydroperoxide by DBPO in benzene had a chain length of 1.0 at 45° and yielded about 50% each of *sec*-butyl alcohol and methyl ethyl ketone. At 100°, some acetaldehyde and acetic acid also appeared. Where measured at 45°, oxygen yields were 75–80% of theory. We interpret these results to mean that induced decompositions of nontertiary

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[10] In neat *t*-BuO_2H, decomposition by DBPO had a gradually decreasing chain length, nearing 1 at 50% conversion: P. D. Bartlett, private communication, 1964.

[11] A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1578 (1948).

[12] A. G. Davies, "Organic Peroxides," Butterworth and Co. Ltd., London, 1961, p 183.

[13] C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, **86**, 3368 (1964).

hydroperoxides at 45° differ from those of t-BuO_2H only in that the interaction of two primary or secondary peroxy radicals almost always terminates the chain.

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

We do not know what happens in the solvent cage, but believe that free alkoxy radicals are not formed there (part III[1]). Results from metal-catalyzed decompositions of *sec*-BuO_2H at 45° indicate that two *sec*-$BuO_2\cdot$ radicals yield *sec*-Bu_2O_2 about 3% of the time.

DBPO-induced decompositions of *n*-butyl, tetralyl, and cyclopentenyl hydroperoxides at 45° had over-all chain lengths of 0.6–0.7. For *n*-BuO_2H this probably resulted from some radical attack on the PrCHO produced from hydroperoxide decomposition. For the others, abstraction of allylic, rather than hydroperoxidic, H may have constituted terminating, chain-shortening reactions.

In benzene at 100° *sec*-butyl hydroperoxide was decomposed by *t*-butoxy radicals, producing variable amounts of ketone and alcohol and very little oxygen. This reaction probably involved attack at both the indicated bonds in $H(Me)CO_2(Et)H$ by alkylperoxy or alkoxy radicals as well as induced oxidations. Studies of this reaction are continuing. Much of the difference between the 45 and 100° results seems to be due to differences in rate of production of initiating t-$BuO\cdot$ radicals (part III[1]). Above 100°, primary and secondary hydroperoxides seem to have undergone radical-induced decompositions[4] with longer chain lengths (part V[1]).

Results of induced decompositions of *sec*-BuO_2H in the gas phase at 100° were complicated by surface-catalyzed decompositions of the hydroperoxide (part III[1]).

Implications for Autoxidations.—This section considers the implications of parts II and III[1] for the oxidation of hydrocarbons, first with respect to making and keeping hydroperoxides as primary oxidation products and then with respect to rates of oxidation as a function of structure. The generalizations below apply to alkanes and alkylbenzenes. They are tentative and subject to later revision. Our experience with allylic hydroperoxides is too limited to include alkenes in this discussion.

The preparation of hydroperoxides by autoxidation depends on a balance between closely related chain reactions. High concentrations of alkanes not only assist synthesis but retard decomposition. With alkanes the maximum protective effect is found at about 100°; with alkylbenzenes it is found at lower temperatures. Kinetic chain lengths for both synthesis and decomposition are greatest for *t*-alkyl hydroperoxides under conditions where little cleavage of alkoxy radicals occurs. Chain lengths are shortest with primary and secondary hydroperoxides because of the high activity of the corresponding peroxy radicals in chain termination.

In oxidations of hydrocarbons, reactions of peroxy radicals with substrate are desirable and chain terminations should be minimized. Three sets of competing reactions are therefore crucial. The first competition is between the reaction of peroxy radicals with hydrocarbon (to give hydroperoxide) and their reactions with each other (to give alkoxy radicals or cleavage products or chain termination). This choice can be controlled by the concentration of hydrocarbon and the rate of chain initiation, but usually the rate of initiation has to be higher than otherwise desirable to obtain a useful rate of reaction.

The other two sets of competing reactions correspond to the two competitions discussed above. Interaction of peroxy radicals may be terminating or nonterminating (eq 3 and 4) and the alkoxy radicals may cleave or react with hydrocarbon (eq 7 and 9). *t*-Butoxy radicals are the most stable *t*-alkoxy radicals toward cleavage[14–16] and so all other branched hydrocarbons will give more cleavage effects than isobutane.

These considerations indicate that in oxidations of hydrocarbons to hydroperoxides the longest kinetic chains will be obtained when attack on the tertiary hydrogen atoms is maximized and cleavage of any tertiary hydrogen atoms is maximized and cleavage of any tertiary alkoxy radicals is minimized. When secondary (or primary) hydrogen atoms are involved in oxidation in solution, long chains can be obtained only with very reactive C–H bonds (fast propagation) or low rates of chain initiation (minimum chain termination). Our results admit the possibility that the last restriction may not apply in gas phase oxidations if the terminating efficiency in interactions of secondary alkylperoxy radicals proves to be low.

Except where these restrictions can be avoided, most commercial oxidations must be short-chain processes in which fairly high proportions of chain-initiation and chain-termination products contaminate the chain-propagation products. Use of acetic acid, water, or other hydroxylic (even polar) solvents will favor cleavage of alkoxy radicals. These considerations suggest that additional data on competitive reactions of other tertiary and a few secondary peroxy and alkoxy radicals in oxidations would be useful in supplementing the few data available.

The decreasing protective effect of alkanes on hydroperoxides (RO_2H) at high temperatures is ascribed to formation of dialkyl peroxides (RO_2S) from the solvent (S–H) and reinitiation of chains by the RO_2S. Formation of RO_2S should also occur in oxidations as the temperature increases and the oxygen pressure decreases enough to permit combination of $RO_2\cdot$ with $R\cdot$ radicals. When the hydrocarbon serves as solvent, immediate or delayed initiation by R_2O_2 corresponds to chain propagation by alkoxy radicals to produce alcohols as primary products. Boric acid has been most useful in stabilizing alcohols in oxidations at low oxygen pressures.[17] Its function may therefore be the simple esterification and stabilization of alcohols, possibly unrelated to any special effect of boric acid on hydroperoxides.

Metal-Catalyzed Decompositions

Background.—The literature on metal ion catalyzed decompositions is immense and diverse both in experimental conditions and opinions about the operative

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(14) F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholz, and W. N. Smith, *J. Amer. Chem. Soc.*, **83**, 2196 (1961).

(15) J. K. Kochi, *ibid.*, **84**, 1193 (1962).

(16) C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963).

(17) F. Broick and H. Groseman, *Erdoel Kohle*, **18**, 360 (1965).

mechanisms. Among the reactions which appear to involve free radicals are those (which we call stoichiometric) in which each metal ion decomposes only one or two molecules of hydroperoxide and others (catalytic) in which many hydroperoxide molecules are decomposed.

To determine the mechanisms of catalytic decompositions and the possibilities for controlling their products, we carried out experiments, detailed in part IV[1], on decompositions of *n*-butyl, *sec*-butyl, *t*-butyl, and α-cumyl hydroperoxides in chlorobenzene, mixtures of chlorobenzene with acetic acid or alcohols, and refluxing alkanes, at 0–99°. Cobalt carboxylates were the most frequently used catalysts, but iron phthalocyanine, acetylacetonates of CO^{II}, CO^{III}, Fe^{II}, Fe^{III}, Mn^{II}, V^{III}, and Ce^{IV}, and Nuodex solutions (octoates) of lead, copper, vanadium, and manganese were also tested.

The Role of the Metal Ion.—The products of decomposition of hydroperoxides by catalytic amounts of metal ions are so similar to those from radical-induced reactions over a wide range of solvents and temperatures and so little affected by the choice of metal catalyst, that the mechanistic similarity seems unquestionable. We conclude that the metal ion acts primarily as an initiator *via* one-electron transfer with hydroperoxides. Equation 13 and 14 (where M is

$$\left.\begin{array}{ll} M^n + RO_2H \longrightarrow & \\ M^{n+1} + RO\cdot + OH^- & (13) \\ M^{n+1} + RO_2H \longrightarrow & \\ M^n + RO_2\cdot + H^+ & (14) \end{array}\right\} 2RO_2H \longrightarrow RO\cdot + RO_2\cdot + H_2O$$

metal ion and where OH^- and H^+ may not be formed as free ions, but as part of the metal–ligand complex) provide the cycle whereby one metal ion may destroy much more hydroperoxide.[18]

The radicals formed in eq 13 and 14 initiate the induced chains discussed above. For nontertiary hydroperoxides or for *t*-BuO_2H in protic solvents, the chains may be very short, but the products are the same as in the absence of metal ions. Metal ions may be involved in the chain-terminating steps but radical–radical reactions seem to be the most important route.

Rates of Decomposition.—Rates of decomposition of *n*-BuO_2H, α-cumyl O_2H, and *t*-BuO_2H by cobalt carboxylates in chlorobenzene were proportional to their chain lengths in DBPO-induced decompositions. Rates were first order in $[RO_2H]$ and [Co]; with 10^{-4} *M* cobaltous 2-ethyl hexanoate ($CoOct_2$) at 45°, the half-life of *t*-BuO_2H was 1.3 min. Retardation by millimolar quantities of materials which strongly complex metal ions (carboxylic acids, 1,10-phenanthroline, acetylacetone, or trimethylenetetramine) suggested that complexing of hydroperoxide with the metal ion preceded eq 13 or 14. Small amounts of H_2O or *t*-BuOH did not affect the rate, but, in 2:3 *t*-BuOH–PhCl or 2:3 *i*-PrOH–PhCl, reactions were only $^1/_{500}$th as fast as in chlorobenzene alone, as if the overwhelming concentrations of alcohol were competing with hydroperoxide molecules for bonding sites on the metal ion. In 1:1 AcOH–PhCl, decompositions were very slow. Rates in alkanes were about the same as in chlorobenzene.

Kinetics for reactions in alkanes or mixtures of protic solvents with PhCl were complex as might be expected.

Solubility of Metal Catalysts and Autoretardation.—In addition to the foregoing major reactions of metal-catalyzed decompositions, autoretardation always appeared sooner or later. There was more in alcohol mixtures and alkanes; in refluxing *n*-pentane it occurred so smoothly that the reaction falsely appeared to be third order in hydroperoxide. Clearly the catalyst becomes deactivated as materials are formed which complex and eventually precipitate it. These materials are volatile and are formed in sufficient quantity to instantly deactivate added catalyst. We suspect that formic acid or formaldehyde is the chief offender.

Peroxide decompositions which are first order in metal ion are rare. Depending on solvent, catalyst concentration, and temperature the apparent order ranges from 0.05 to 3. This feature has led other investigators[5,19,20] to propose intricate schemes for metal-catalyzed decompositions. A simple explanation, documented in part IV,[1] is that most metal catalysts are associated to various degrees in organic solvents.

Decompositions by Lead and Magnesium.—We found that lead naphthenate (a Nuodex solution, presumed to be Pb^{II}) catalyzed slow decomposition of *t*-BuO_2H, yielding products indistinguishable from those obtained with more active catalysts. Van Leeuwen and coworkers[21] reported a catalytic effect of Mg^{II} on decompositions of tetralin hydroperoxide at 120°. Their argument that Mg^{II} does not initiate chains is based on the dubious assumption that the hydroperoxide was undergoing thermal homolytic scission at that temperature (part V[1]). Since the participation of Pb^{II} or Mg^{II} in eq 13 and 14 seems most unlikely, we suggest that these results arise from nonradical reactions or, like those of some base-catalyzed decompositions,[7] from trace impurities in the catalysts.

Metal-Catalyzed Autoxidations.—In metal ion catalyzed autoxidations, acetic acid is a good solvent for the metal catalysts and provides a desirable moderator for the metal–hydroperoxide reaction. When the objective is to initiate chains, rather than to decompose hydroperoxide, the rate of radical production in acetic acid leads to longer chains and more efficient use of initiator. On the other hand, a mixture of hydroperoxides and metal catalysts, added to neat styrene, do not give efficient polymerization, nor does it give a long lasting or efficient autoxidation, when added to chlorobenzene solutions of polyisoprene, though the combination is initially effective.[22]

The present work indicates that the chances for effecting chain decompositions of hydroperoxides to *single products* by catalytic amounts of metal ions seem

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[18] While other cycles are conceivable, they are inconsistent with the products found with other well-established reaction patterns. Metal ion–free-radical interactions are important in some stoichiometric decompositions (part IV[1]), but catalytic quantities of metals do not usually compete successfully with solvent, hydroperoxide, or other radicals.

[19] H. Berger and A. F. Bickel, *Trans. Faraday Soc.*, **57**, 1325 (1961).

[20] M. H. Dean and G. Skirrow, *ibid.*, **54**, 849 (1958).

[21] H. B. Van Leeuwen, J. P. Wibaut, A. F. Bickel, and E. C. Kooyman, *Rec. Trav. Chim.*, **78**, 667 (1959).

[22] Unpublished work in these laboratories.

small and that there would be little hope for control of products from autoxidation of hydrocarbon by choice of the right metal catalyst. However, vanadium and molybdenum salts catalyze nonradical reactions of hydroperoxides with alkenes to give epoxides,[23] and there are several examples of substantial proportions of boric acid altering the alcohol–ketone ratio in an autoxidation.

Thermal Decompositions

Background.—The difficulty of measuring true rates of thermal homolysis of hydroperoxides is attested by the many attempts which were later found to have failed.[4] Rates were too fast, activation energies too low. Previously we have had some success[24] in reducing the radical-induced decomposition that usually accompanies thermal decomposition by decomposing very dilute solutions of t-BuO$_2$H in benzene. This approach has been continued in part V.[1]

t-Butyl Hydroperoxide.—Solutions of 0.001 M to 0.26 M t-BuO$_2$H in toluene were decomposed at 100–215°; similar but less extensive studies were done with benzene, cumene, n-heptane, and cyclohexane. In toluene at 180° the measured first-order rate constant for decomposition at 0.001 to 0.02 M t-BuO$_2$H was about 2.2×10^{-5}/sec, and had an apparent activation energy of 43 kcal at 170 to 190°. A 40% yield of bibenzyl (based on t-BuO$_2$H decomposed) showed that at least 40% of the reaction was homolysis, and set a lower limit for k_{15} of 1×10^{-5}/sec. Decompositions

$$t\text{-BuO}_2\text{H} \longrightarrow t\text{-BuO}\cdot + \cdot\text{OH} \qquad (15)$$

yielded approximately 50% each of acetone and t-butyl alcohol, no O$_2$, but small amounts of CO and CO$_2$. Small amounts of acetone were a mild catalyst for the decomposition.

At initial concentrations above 0.02 M, first-order rate constants increased in proportion to $[t\text{-BuO}_2\text{H}]_0^{1/2}$ as is common for thermally induced decompositions. Yields of t-butyl alcohol were higher and of bibenzyl, lower. At 100° unexplained factors caused thermal decomposition 20 times as fast as expected from extrapolation of rates at 170–190°.

Decompositions of 0.02 M t-BuO$_2$H in benzene at 180° had rates similar to those in toluene; in cumene the rates were four times as fast, although a 50% yield of bicumyl showed that homolysis was occurring to the same extent as in toluene (and, therefore, four times as fast). Yields of 28% cumyl alcohol and only 5.8% acetophenone posed an interesting problem, since, if these had cumyloxy radicals as the common precursor, the yields should be in reverse ratio. Seemingly unlikely reactions such as coupling of cumyl and hydroxyl radicals or attack[25] by cumyl radicals on t-BuO$_2$H have to be reconsidered.

$$\text{PhMe}_2\text{C}\cdot + t\text{-BuO}_2\text{H} \longrightarrow t\text{-BuO}\cdot + \text{PhMe}_2\text{COH} \qquad (16)$$

Decompositions in alkanes at 170–180° appeared to be largely induced, even at the lowest initial concentrations of t-BuO$_2$H. In both alkylbenzenes and alkanes, RO· and HO· radicals from homolysis of the peroxide readily produced solvent radicals. In alkylbenzene solvents, these radicals were the least reactive and most plentiful radicals and they combined with each other to give bibenzyls. However, in alkanes, the alkyl radicals were too reactive to accumulate. With hydroperoxide they produced alkylperoxy radicals; these scavenged the alkyl radicals to give mixed RO$_2$S, but at 180° these peroxides decomposed and induced more decomposition.

Decompositions of Other Hydroperoxides.—Some decompositions of n-BuO$_2$H, sec-BuO$_2$H, and α-cumyl O$_2$H in toluene at 170–182° gave rates from two to three times as fast as those found for t-BuO$_2$H. Yields of bibenzyl showed that these were at least 17–40% homolysis. From other products 21% of n-BuO·, 45% of sec-BuO·, and 60% of α-cumyl-O· radicals are estimated to cleave in toluene at 182° (50% t-BuO· in the previous section).

Implications for Autoxidation.—These results show that below 150° unimolecular homolysis of saturated hydroperoxides does not occur sufficiently rapidly to be a potential source of free radicals. Practically, this limitation is unimportant because faster routes to radical production are usually available (bimolecular decompositions of hydroperoxides[26] and their reactions with carbonyl compounds,[27,28] alkenes,[29–31] surfaces, and trace metals. Theoretically, the limitation is important because of the carelessness with which some workers have discussed unimolecular decompositions without considering the cofactors involved.

Registry No.—n-Butyl hydroperoxide, 4813-50-7; sec-butyl hydroperoxide, 13020-06-9; t-butyl hydroperoxide, 75-91-2; α-cumyl hydroperoxide, 80-15-9.

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