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Free-Radical Autoxidations of Hydrocarbons

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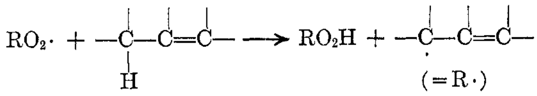
Since 1961, my associates and I have been making a fundamental study of the reactions of hydrocarbons with oxygen under mild conditions. This work has been supported on a continuing basis by a group of oil and chemical companies and intermittently by several government agencies. This account tells what we have been doing and why. Space limitations prevent discussion of some excellent work by others.[1]

Background

During the 1940's and early 1950's, an able group at the Natural Rubber Producers' Research Association[2] described many oxidations of aliphatic unsaturated hydrocarbons. As is now generally recognized, these oxidations are free-radical chain reactions, usually initiated by peroxides below 100°, which produce mostly isomeric allylic hydroperoxides by the chain-carrying steps 1 and 2. This process I shall call the

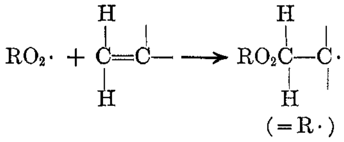


$$\mathrm{RO_2\cdot} + -\underset{\mathrm{H}}{\overset{|}{\mathrm{C}}}-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}- \longrightarrow \mathrm{RO_2H} + \underset{(=\mathrm{R\cdot})}{-\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-} \quad (1)$$

$$\mathrm{R\cdot} + \mathrm{O_2} \longrightarrow \mathrm{RO_2\cdot} \quad (2)$$

(hydrogen) *abstraction* mechanism.

At about the same time, several unsaturated hydrocarbons with terminal $=\mathrm{CH_2}$ groups, particularly those important in vinyl polymerization,[3,4] were found under similar conditions to give alternating 1:1 polyperoxides by a process (steps 3 and 2) that I shall call the *addition* mechanism. Here R· may contain up to about 30 molecules each of $\mathrm{O_2}$ and alkene.



$$\mathrm{RO_2\cdot} + \underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}=\overset{|}{\mathrm{C}}- \longrightarrow \underset{(=\mathrm{R\cdot})}{\mathrm{RO_2}\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{|}{\overset{|}{\mathrm{C}}}\cdot} \quad (3)$$

We began our work on oxidation in 1950 with the intention of applying the methods and reactivity equations of copolymerization[5] to autoxidation. We found unexpectedly that the initial products of oxidation of styrene at 50° depend on the oxygen pressure.[6]

Our observations are summarized in Figure 1;[7] here the top line represents the total rate of reaction of styrene as a function of oxygen pressure, and the other lines represent the contributions of separate products to the total. Scheme I represents the required expansion[7] of the addition mechanism reactions 3 and 2. Briefly, oxygen pressure is important in two reactions, 4 and 5, which compete with the basic chain step 2. Reaction 4 introduces excess styrene into the product; step 5 causes "unzipping" of the polyperoxide radical to styrene oxide, benzaldehyde, and formaldehyde. (The aldehydes correspond to "cleavage" of the double bond by oxygen; the reaction resembles superficially the cleavage by ozone.) Some reaction such as step 8 also competes with reaction 2, perhaps without any concentration effect, to regulate the molecular weight of the polyperoxide without much effect on the rate of oxidation. The over-all rate is determined by competition of reactions 3 and 9.

While this work on an ideal example of the addition mechanism was in progress, indications appeared that the realms of the abstraction and addition mechanisms of oxidation of alkenes are not as sharp as the distinctions between unsaturated hydrocarbons that will, or will not, polymerize. In a study of hydroperoxide

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(1) Reference 2 is a very competent short review. More extensive reviews are "Autoxidation and Antioxidants," Vol. I and II, W. O. Lundberg, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, and N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, "Liquid Phase Oxidation of Hydrocarbons," B. J. Hazzard, Transl., Plenum Press, New York, N. Y., 1967.

(2) D. Barnard, L. Bateman, J. I. Cunneen, and J. F. Smith in "The Chemistry and Physics of Rubber-Like Substances", L. Bateman, Ed., Maclaren and Sons Ltd., London, 1963, Chapter 17.

(3) F. A. Bovey and I. M. Kolthoff, *J. Am. Chem. Soc.*, **69**, 2143 (1947).

(4) C. E. Barnes, R. M. Elofson, and G. D. Jones, *ibid.*, **72**, 210 (1950).

(5) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

(6) A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.*, **78**, 1017 (1956); **86**, 5709 (1964) (correction).

(7) F. R. Mayo, *ibid.*, **80**, 2465, 6701 (1958).

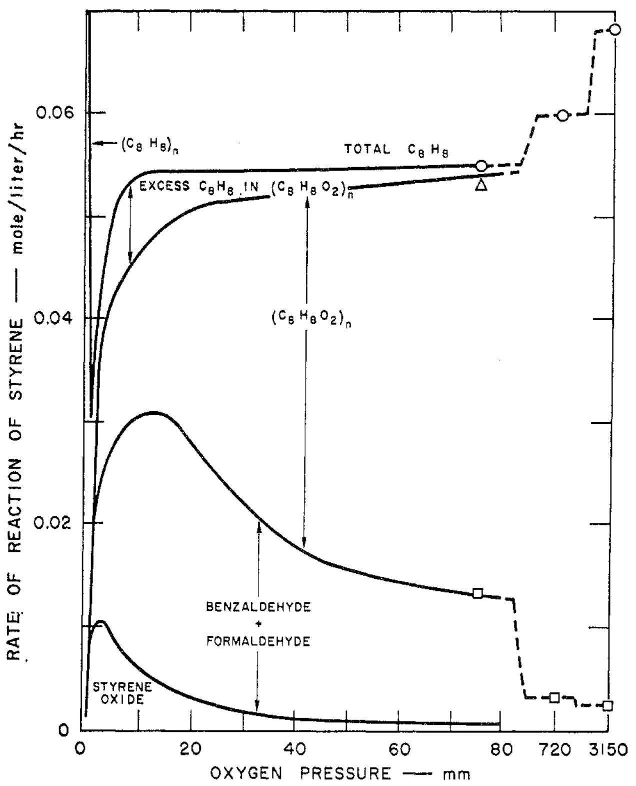

Figure 1. Rates and products of oxidation of styrene at 50° in the presence of 0.01 M ABN.[7]

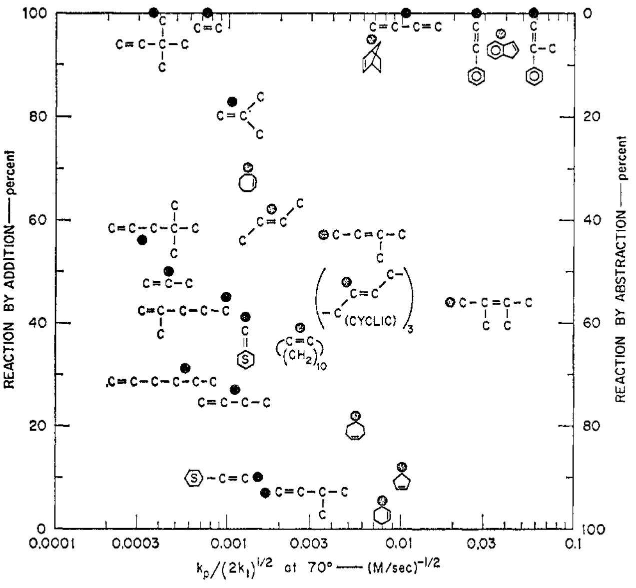

Figure 2. Rates and products of oxidation of alkenes, corrected to 70°. k_p ($= k_1 + k_3$) and k_t are rate constants for chain propagation and termination.

yields, Hargrave and Morris[8] found a yield as low as 43% with 2-methyl-1-nonene. Gasson and coworkers[9] showed that oxidation of α-diisobutylene, t-$BuCH_2C(Me){=}CH_2$, gave the corresponding epoxide and the cleavage product, t-$BuCH_2COMe$ ($+CH_2O$?), as major primary products. I confirmed this finding, found yields of hydroperoxides in the range 10–20%, and found that there were numerous reports of epoxide formation and cleavage in oxidations of alkenes.[10]

Though nearly ideal examples of oxidations of alkenes by both abstraction[8] and addition mechanisms[11] were known, it was now apparent that in many, perhaps most, alkene oxidations both reactions 1 and 3 occur simultaneously. Obtaining good data on this competition seemed to be the most important remaining problem in autoxidations of alkenes. The Air Force Office of Scientific Research concurred and supported this study at Stanford Research Institute for 4 years beginning in 1961.

An important feature of our oxidation research has been our use of added initiators and low conversions. Azonitriles were used below 100°, di-t-butyl peroxide above 100°. Knowledge of both radical production and oxygen consumption gives kinetic chain lengths and measures the contributions of chain propagation and of chain initiation and termination to the products found. Much has been made of "steady rates" in oxidations without added initiator. At least in the autoxidation of cyclopentene,[12] this steady rate is only a transition between initial autocatalysis and later retardation and depletion of substrate, without much other significance. Our use of low conversions, 1% for alkanes, 5–10% for alkenes, assists in isolating the primary reactions and in minimizing involvement of the more reactive primary products.

Competitions between the Addition and Abstraction Mechanisms

Dr. Dale E. Van Sickle was responsible for most of this work, mostly product studies. Allylic hydroperoxides, the related allylic alcohols, aldehydes, ketones, and acids of the same number of carbon atoms, and the last unit in the low molecular weight polyperoxides, $(\text{–}\overset{|}{C}{=\!=}\overset{|}{C}\overset{|}{\underset{|}{C}}O_2(\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}O_2\text{–})_nH$, are assumed to arise through abstraction reaction 1 and secondary reactions. Epoxides, aldehydes, and ketones formed by cleavage at the double bond, and the remaining polyperoxide residues, are taken as products of the addition mechanism. Figure 2 summarizes the initial rates of oxidation,[7,13–18] corrected to unit rate of initiation at 70°, for 25 unsaturated hydrocarbons and the per cent oxidation occurring by the addition and abstraction mechanisms at the temperatures of the experiments (50–90°, except 110° for ethylene and propylene).

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(8) K. R. Hargrave and A. L. Morris, *Trans. Faraday Soc.*, **52**, 89 (1956).

(9) E. J. Gasson, A. F. Millidge, G. R. Primavesi, W. Webster, and D. P. Young, *J. Chem. Soc.*, 2161 (1954).

(10) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2497 (1958).

(11) Summaries and literature reviews are in the paper by F. R. Mayo, A. A. Miller, and G. A. Russell, *ibid.*, **80**, 2500, 6701 (1958).

(12) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *ibid.*, **87**, 4832 (1965).

(13) F. R. Mayo and A. A. Miller, *ibid.*, **78**, 1023 (1956); **80**, 6697 (1958) (correction).

(14) G. A. Russell, *ibid.*, **78**, 1035, 1041 (1956).

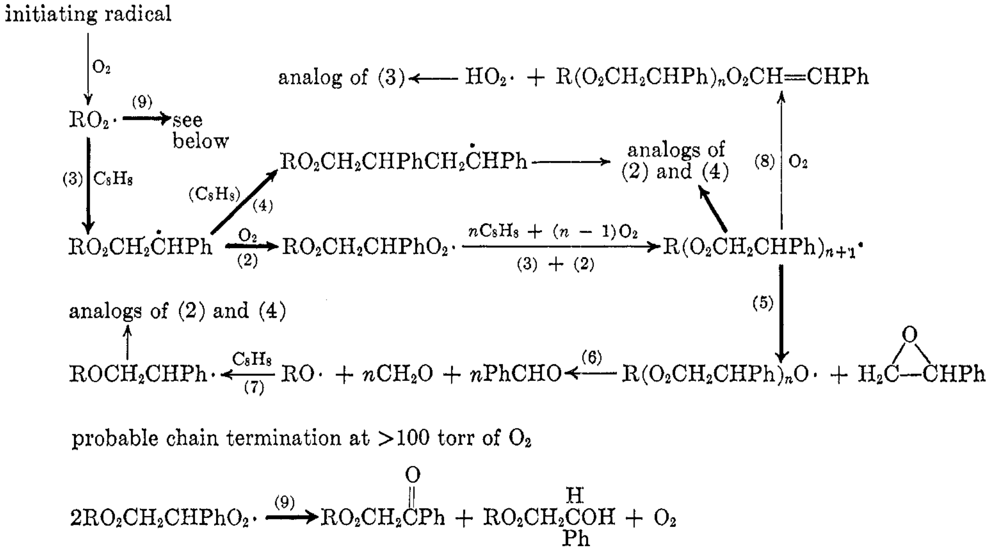
(15) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *ibid.*, **87**, 4824 (1965).

(16) D. E. Van Sickle, F. R. Mayo, R. M. Arluck, and M. G. Syz, *ibid.*, **89**, 967 (1967).

(17) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Org. Chem.*, **32**, 3680 (1967).

(18) D. G. Hendry, F. R. Mayo, and D. Schuetzle, *Ind. Eng. Chem., Prod. Res. Develop.*, in press.

Scheme I
Autoxidation of Styrene[a]



[a] Important competitions marked by boldface arrows.

The eight alkenes that give 80–100% reaction by the addition mechanism have conjugated unsaturation, or no allylic hydrogen atoms, or unreactive allylic hydrogen atoms (as in norbornene), or a combination of methyl groups and a terminal (vinyl) double bond (as in isobutylene). The simplest cyclic alkenes with five or six carbon atoms and two open-chain alkenes containing tertiary allylic hydrogen atoms react 80–100% by the abstraction mechanism. The other 13 compounds listed, 52% of the total, 62% of the unconjugated alkenes, fall between these extremes and give >20% of each group of products. This proportion is largely unaffected by change of solvent or temperature,[19] and the balance between the two routes is close enough for most alkenes that useful prediction of products is difficult.

The most reactive alkenes are tetramethylethylene and those with conjugated unsaturation. In general, the alkenes with terminal unsaturation (indicated with solid points in Figure 2) are the least reactive; those with two substituents on the C-2 atom or with tertiary allylic hydrogen atoms are more reactive. We assume that the low rate of oxidation of butadiene,[18] compared to other conjugated hydrocarbons, is due mostly to a high termination constant for the unhindered, largely primary, allylic peroxide radical and that the high reactivity of tetramethylethylene is due to a relatively slow termination, about 95% of the peroxy radicals being tertiary peroxy radicals. These small effects of termination constants will be discussed under Cooxidation.

Whenever the competition between addition and abstraction favors addition, the competition between reaction 2, leading to dimeric or higher peroxides, and reaction 5, leading to epoxides and alkoxy radicals (and then to ethers or alcohols), becomes important. Table I shows how results of both competitions depend upon the structure of the alkene and on the oxygen pressure.[19] The ratios k_2/k_5 differ by a factor of more than 10^4, the substituted benzyl radicals in the styrene having the least tendency to attack the peroxide link and the highly hindered cyclooctyl radical having the most tendency.

This treatment of epoxide yields applies only to the early stages of the oxidation of alkenes or to alkenes where aldehydes are only minor products of oxidation. If and as aldehydes accumulate in a reaction mixture, the cooxidation of the aldehyde with the alkene results in formation of epoxide by two additional routes,[15,19] by a reaction like 5 where the penultimate group is an acylperoxy radical and by a nonradical epoxidation by the peracids formed from oxidation of aldehydes. Thus some of the very high yields of epoxides reported in the literature, particularly for 2-butene and cyclooctene,[15,19] depend on the formation of aldehydes by cleavage at the double bond. Since every reaction like 5 must produce an alkoxy radical, the primary formation of alcohols and ethers measures the contribution of step 5.

The Oxidation of Isobutane

At the inception of our oxidation program at Stanford Research Institute, hydroperoxides were well known to be the principal products of liquid-phase oxidations of alkylbenzenes but they were only minor products (except for H_2O_2) in gas-phase oxidations.[20–22] We set out to find the reason for the difference in the case of isobutane and ended up with a correlation of temperature and concentration effects in both phases.

The liquid-phase oxidation of isobutane at 125° was known[23] to give about 75% yield of *t*-butyl hydroperoxide, 21% of *t*-butyl alcohol, and about 2% of acetone

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[19] D. E. Van Sickle, F. R. Mayo, E. S. Gould, and R. M. Arluck, *J. Am. Chem. Soc.*, **89**, 977 (1967).

[20] J. H. Knox, *Trans. Faraday Soc.*, **56**, 1225 (1960).

[21] A. P. Zeelenberg and A. F. Bickel, *J. Chem. Soc.*, 4014 (1961).

[22] Except in the presence of HBr (E. R. Bell, F. H. Dickey, J. H. Raley, F. F. Rust, and W. E. Vaughan, *Ind. Eng. Chem.*, **41**, 2597 (1949)).

[23] D. E. Winkler and G. W. Hearne, *ibid.*, **53**, 655 (1961).

Table I

Evaluation of k_2/k_5 for Various β-Peroxyalkyl Radicals[19]

Alkene	Reaction temp., °C	% reactn by addn	k_2/k_5, M^{-1}	Calcd yield of epoxide,[a] %	O_2 pressure[b] for $k_2[O_2] = k_5$, atm
Cyclooctene (in C_6H_6)	70	70	2.2	41	45
Tetramethylethylene	50	44	32	25	3
Cycloheptene	60	22	34	14	3
Cycloheptene (in C_6H_6)	90	22	25	15	4
2-Methyl-1-pentene	70	45	110	18	0.9
2-Butene	70	62	110	23	0.9
Trimethylethylene	60	57	150	19	0.7
Cyclopentene	50	12	220	4	0.5
α-Methylstyrene	50	100	6,000–11,000	3	0.02
Styrene	50	100	53,000–154,000	< 1	0.002

[a] Calculated for 1 atm of O_2 from experimental yields at higher pressures.[19] [b] Calculated oxygen pressure at which half the RO_2–C–C· radicals would add O_2 and half would rearrange to epoxide.

and 1% of isobutyl derivatives. The gas-phase oxidation at about 1 atm and 300° was known [21,24] to give mostly isobutylene. Dr. Theodore Mill began his study between these regions with the di-*t*-butyl peroxide initiated oxidation at about 1 atm and 155°. He found that the kinetic chains were very short and that the principal products were acetone and methanol. Further work by Dr. Mill and by Dr. David L. Allara (with support of the U. S. Army Edgewood Arsenal) and by Dr. Dale G. Hendry on liquid-phase oxidations has now accounted for all the major features of the early stages of the oxidation of isobutane.[25] The reactions are shown in Scheme II.[26]

In neat liquid isobutane the reaction chains are fairly long and the principal product is *t*-butyl hydroperoxide, formed by the chain steps 10 and 11. The amount of alcohol formed (13 and 14) depends on the rate of chain initiation (13 *vs.* 11). Termination occurs mostly by step 12. In the gas phase at 155° and low total pressures, where there is not enough isobutane to sustain reaction 11, the *t*-butylperoxy radicals react mostly with each other. The *t*-butoxy radicals formed in reaction 13, not being restrained by any liquid cage, separate readily. In the gas phase at low pressures there is insufficient isobutane to sustain reaction 14 and so nearly all the *t*-butoxy radicals cleave to acetone and methyl radicals by reaction 15. The methyl radicals react with oxygen (reaction 16), and the resulting methylperoxy radicals then undergo reaction 17, 18, or 19. Methylperoxy radicals are so much more reactive in chain termination than *t*-butylperoxy radicals[25] that most of the chain termination in the gas phase must take place by reaction 18 rather than by reaction 12. However, the large proportion of methanol in the product indicates that many methylperoxy radicals must be converted to methoxy radicals by reaction 19.

The transition from the liquid-phase to the gas-phase reaction is a fairly smooth one, in both rates and products. In the liquid-phase reaction at 100°, dilution with carbon tetrachloride favors radical interactions 12 and 13 at the expense of propagation 11, and the yields of *t*-butyl alcohol (20) and of acetone (15) increase at the expense of *t*-butyl hydroperoxide (11). Similarly, increasing concentration (pressure) of isobutane in the gas-phase oxidation at 100° increases the yield of *t*-butyl hydroperoxide at the expense of *t*-butyl alcohol, metha-

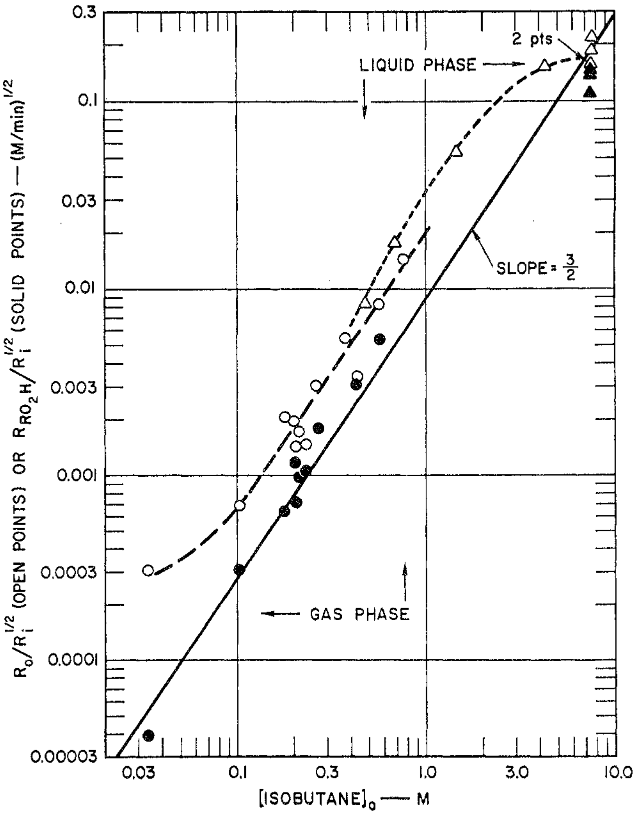

Figure 3. Rates of oxidation of isobutane at 100°.

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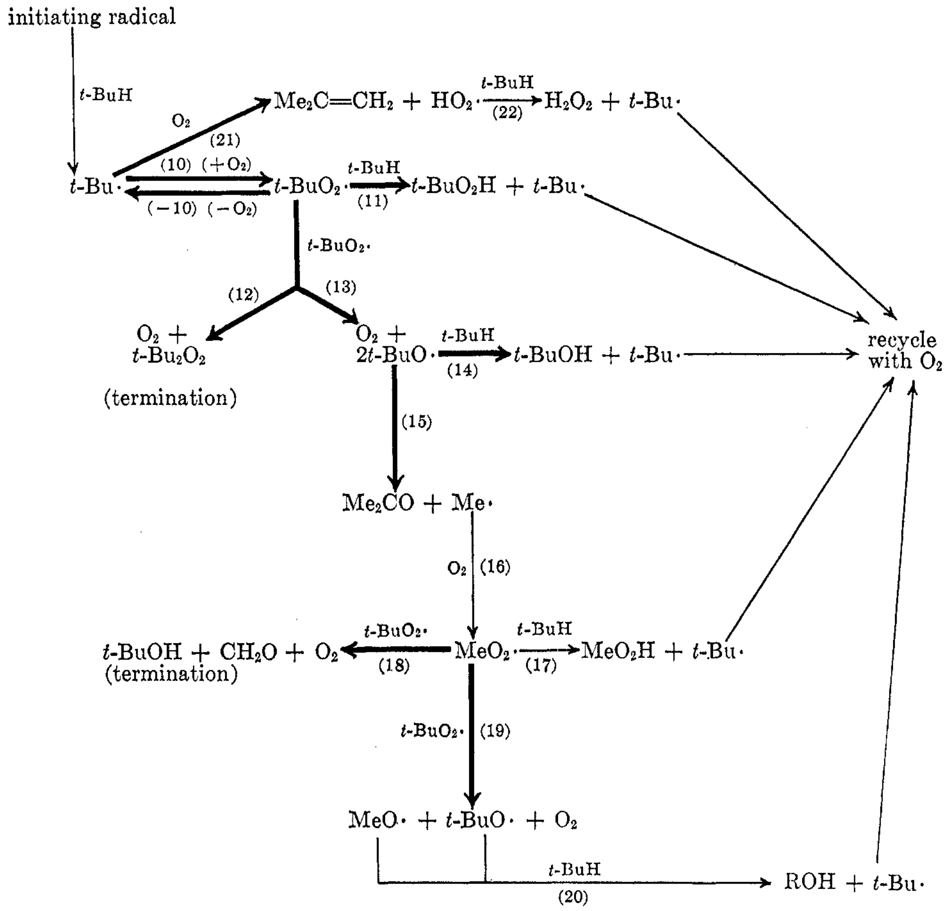
(24) J. Hay, J. H. Knox, and J. M. C. Turner, "Tenth Symposium (International) on Combustion," The Combustion Institute, 1965, p 331.

(25) D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, Advances in Chemistry Series, No. 73, American Chemical Society, Washington, D. C., in press.

(26) Some important related papers on interactions of alkylperoxy radicals are: J. R. Thomas, *J. Am. Chem. Soc.*, **87**, 3935 (1965); J. R. Thomas and K. U. Ingold, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., in press; K. U. Ingold, *Preprints, Div. Petrol. Chem.*, **13** (2), C16 (1968); P. D. Bartlett and G. Guaraldi, *J. Am. Chem. Soc.*, **89**, 4799 (1967); on similar oxidation mechanisms with cumene: T. G. Traylor and C. A. Russell, *ibid.*, **87**, 3698 (1965); D. G. Hendry, *ibid.*, **89**, 3433 (1967).

Scheme II
Autoxidation of Isobutane[a]



[a] Important competitions are marked by boldface arrows.

nol, and acetone. In a gas-phase oxidation at 100°, when radical interactions 12 and 13 were minimized by the extremely low rate of initiation and when reaction 11 was favored by using 13 atm of isobutane, a 92% yield of hydroperoxide was obtained.

Figure 3 shows that there is also a smooth transition in over-all rates between the two phases. In undiluted liquid isobutane, most of the chain termination occurs by reaction 12 and the rate of oxidation is the conventional first order in isobutane and one-half order in initiator. However, in dilute solution or in the gas phase most of the chain termination occurs by reaction 18. Now the rate of hydroperoxide formation (and to a first approximation the over-all rate of oxidation) becomes three-halves order in isobutane and one-half order in initiator; the higher order in isobutane appears because participation of isobutane in reaction 14 decreases the cleavage of *t*-butoxy radicals in reaction 15, an essential step in the chain termination under these conditions.

Figure 3 shows how the rates of hydroperoxide formation and over-all rates of oxidation at unit rate of initiation depend on the concentration of isobutane at 100°. The rates of oxidation in the high-pressure gas-phase reaction and in carbon tetrachloride solution are remarkably similar. In fact, a major remaining problem is to account for the close similarity.[25] Walling and Wagner[27] found a large effect of solvent and phase change on the competition between reactions like 14 and 15 for *t*-butoxy radicals. Since phase change should produce a larger effect on oxidation rate than we have observed, there must be other and compensating effects.

Benson[28] has accounted for the formation of isobutylene as a major product at and above 300° as follows. Although reaction 10 is faster than reaction 21 at any temperature, it is reversible at high temperatures where step 21 is not. Therefore, the products of the chain oxidation at high temperatures depend on whether the concentration of isobutane is sufficient to remove *t*-$BuO_2\cdot$ radicals by reaction 11 before they are diverted to isobutylene by reactions −10 and 21. Medley and Cooley[29] have shown that higher pressures offset the effects of higher temperatures in gas-phase oxidations and permit formation of oxygenated products, but their data reveal little about the routes by which these products are formed. This area deserves further attention for both theoretical and practical ends.

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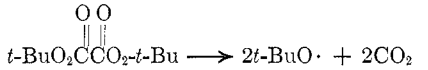
[27] C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

[28] S. W. Benson, *ibid.*, **87**, 972 (1965).

[29] H. D. Medley and S. D. Cooley, *Advan. Petrol. Chem. Refining*, **3**, 309 (1960).

Homolytic Decompositions of Hydroperoxides

Since hydroperoxides are important primary but unstable products of many autoxidations, their reactions under oxidation conditions are important. Further, some of the steps in their decompositions are identical with some steps in autoxidations. Dr. Richard Hiatt initiated work on the chain decomposition of *t*-butyl hydroperoxide at the University of Toronto[30] and continued it at Stanford Research Institute[31] from 1964 to 1966. He and others showed that the chain decomposition of *t*-butyl hydroperoxide, induced, for example, by di-*t*-butylperoxy oxalate, is represented by reactions 23, 24, 12, and 13. Chains are initiated by reaction 23, terminated by 12, and propagated by 24 and 13. The competition between reactions 12 and 13 determines the kinetic chain length and measures the ratio k_{12}/k_{13}, also important in autoxidation (Scheme II). In dilute solutions of hydroperoxide, in hydroxylic solvents, or at higher temperatures, this simple picture is complicated



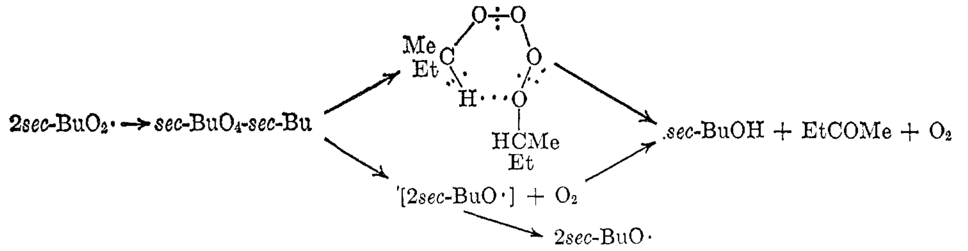
$$t\text{-BuO}_2\overset{\overset{\text{O}}{\|}}{\text{C}}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{O}_2\text{-}t\text{-Bu} \longrightarrow 2t\text{-BuO}\cdot + 2\text{CO}_2 \qquad (23)$$

$$t\text{-BuO}\cdot + t\text{-BuO}_2\text{H} \longrightarrow t\text{-BuOH} + t\text{-BuO}_2\cdot \qquad (24)$$

$$2t\text{-BuO}_2\cdot \rightleftarrows t\text{-BuO}_4\text{-}t\text{-Bu} \begin{array}{ll} \nearrow t\text{-Bu}_2\text{O}_2 + \text{O}_2 & (12) \\ \searrow 2t\text{-BuO}\cdot + \text{O}_2 & (13) \end{array}$$

by cleavage of alkoxy radicals and their reaction with solvent. The autoxidation steps 14 and 15 divert the simple peroxide decomposition chain (24 and 13) by protecting the hydroperoxide from the action of alkoxy radicals or by making possible, through reaction 15, a much faster termination than reaction 12. Thus studies of peroxide reactions have strengthened, and been strengthened by, studies of autoxidation. Both reactions 12 and 13 seem to proceed through a pair of *t*-butoxy radicals, constrained in a solvent cage, with separation facilitated by increasing temperature and decreasing viscosity of the medium. In the gas phase few, if any, of the *t*-butoxy radicals combine; chain termination probably occurs by reactions like 18.

In induced decompositions of secondary hydroperoxides in solution up to 100°, one pair of initiating radicals decomposes no more than two molecules of hydroperoxide.[31] Probably most interactions of *sec*-$RO_2\cdot$ radicals are terminating. From isotope effects in the oxidation of α-deuterioethylbenzene, Russell[32] first proposed a cyclic intermediate for this termination as in eq 25a. Three recent communications support this suggestion.[33,34]



(25a)

(25b)

(25c)

However, in the gas phase, nonterminating reactions like 25c have been noted for primary and secondary $RO_2\cdot$ radicals, even at room temperature.[35] They may become important in the liquid phase above 100°. Termination by route 25b then becomes a possibility. While work on secondary hydroperoxides by both Hiatt and Mill establishes that chain lengths in induced liquid-phase decompositions are very short, product compositions and poor material balances have raised the possibilities of other mechanisms and of secondary reactions. There is very little information available on allylic hydroperoxides or allylic peroxy radicals.

Dr. Hiatt's work[31] on metal-catalyzed decompositions of hydroperoxides suggests that the principal function of transition metal compounds in many peroxide decompositions and in most metal-catalyzed autoxidations of alkanes and alkylbenzenes is to initiate conventional chains by generating free radicals from hydroperoxides. This conclusion does not exclude the possibility that some metals with high oxidation potentials may initiate chains directly or that metals may have additional effects in oxidations of oxygen-containing compounds.[36] The complex kinetics of metal-catalyzed oxidations and peroxide decompositions are ascribed[31] 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 reactions progress.

Cooxidations of Hydrocarbons

There has been considerable interest in oxidations of mixtures of hydrocarbons since Russell[37] first showed that 3 mole % of tetralin would reduce the rate of oxidation of cumene by two-thirds, even though neat tetralin oxidizes ten times as fast as cumene alone at the same temperature (90°) and rate of initiation. Some later work[38] is summarized in Figure 4. The copolymer

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

[31] R. Hiatt, T. Mill, and F. R. Mayo, *J. Org. Chem.*, **33,** 1416 (1968); R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *ibid.*, **33,** 1421, 1428 (1968); R. Hiatt, K. C. Irwin, and C. W. Gould, *ibid.*, **33,** 1430 (1968); R. Hiatt and K. C. Irwin, *ibid.*, **33,** 1436 (1968).

[32] G. A. Russell, *J. Am. Chem. Soc.*, **79,** 3871 (1957).

[33] J. A. Howard and K. U. Ingold, *ibid.*, **90,** 1056, 1058 (1968).

[34] T. Mill and R. S. Stringham, *ibid.*, **90,** 1062 (1968).

[35] S. S. Thomas and J. G. Calvert, *ibid.*, **84,** 4207 (1964); J. Heicklen and H. S. Johnston, *ibid.*, **84,** 4394 (1964); and earlier papers of both groups.

[36] R. van Helden and E. C. Kooyman, *Rec. Trav. Chim.*, **80,** 57 (1961).

[37] G. A. Russell, *J. Am. Chem. Soc.*, **77,** 4583 (1955).

composition equation[5] has been important in correlating product studies and in interpreting rate studies. For low conversions and long kinetic chains, it relates the composition of the product $\Delta[\text{A}]/\Delta[\text{B}]$ formed from two reactants A and B to the composition of the feed in terms of two reactivity ratios. For cooxidations in the

$$\frac{-\Delta[\text{A}]}{-\Delta[\text{B}]} = \frac{r_\text{a}[\text{A}]/[\text{B}] + 1}{r_\text{b}[\text{B}]/[\text{A}] + 1} \qquad (26)$$

$$r_\text{a} = \frac{k_\text{aa}\ (\text{for AO}_2\cdot + \text{A})}{k_\text{ab}\ (\text{for AO}_2\cdot + \text{B})} \qquad r_\text{b} = \frac{k_\text{bb}\ (\text{for BO}_2\cdot + \text{B})}{k_\text{ba}\ (\text{for BO}_2\cdot + \text{A})}$$

presence of sufficient oxygen, all carbon radicals are converted to peroxy radicals and eq 26 then permits solution for the two reactivity ratios. Thus the relative rates of attack on two hydrocarbons by each of two peroxy radicals may be determined from product compositions alone. No rate data are required, and the results are independent of initiation and the chain termination constants. Efforts to use rates of oxidation of mixtures to determine r_a and r_b have met with only limited success,[39] for reasons discussed elsewhere.[40]

The original tetralin–cumene results were explained[37] on the two bases that tetralin is about 20 times as reactive as cumene toward peroxy radicals and that it also has a considerably higher termination constant than cumene. Thus a small proportion of tetralin in cumene is readily converted to tetralylperoxy radicals, which then increase chain termination and decrease the rate of oxidation of cumene. This paper[37] is probably the first discussion to bring out the very large difference in rates of chain termination for *t*- and *sec*-peroxy radicals.

The two bases of explanation above now seem to be such strict requirements for strong retarding effects that very few hydrocarbon systems can meet them.[40] The essential very slow termination in cumene depends on exclusive attack at tertiary C–H bonds and little cleavage of cumyloxy to methyl radicals. Figure 4 shows rates of oxidation of several cumene mixtures.[38] Only 2,3-dimethylbutane is enough like cumene to give a rate which is a linear function of composition. (Isobutane should behave similarly.) Most other hydrocarbons depress the rate of oxidation, the extent depending on their reactivity in chain propagation. Even in *sec*-butylbenzene there is more cleavage of 2-phenyl-2-butoxy radicals and enough *sec*-C–H attack to give a higher rate of termination, a slower rate of oxidation, and no retardation by tetralin.[38] Marked accelerations in oxidations of hydrocarbon mixtures (at constant rate of initiation) are unknown and improbable.[40]

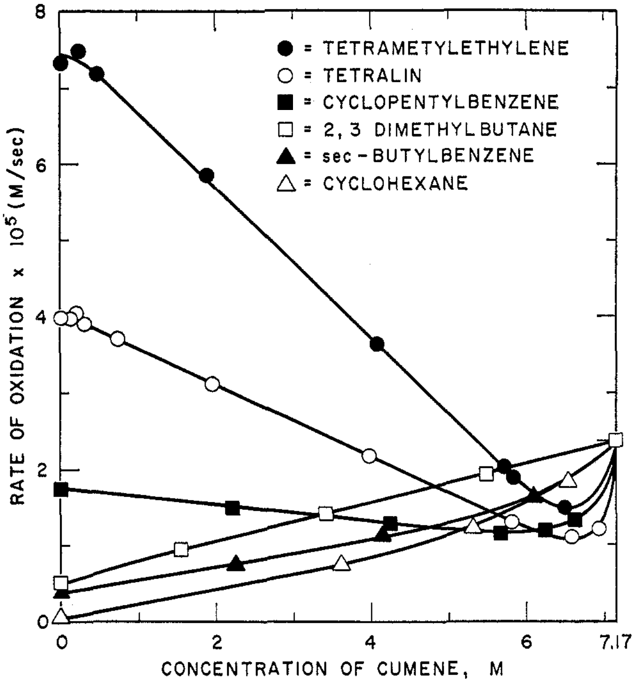

Figure 4. Cooxidations of cumene and other hydrocarbons with 0.06 *M* ABN at 60°. Data are from ref 38.

A major objective of cooxidation research has been to find out how much the selectivity of $\text{RO}_2\cdot$ radicals is affected by changes in the structure of R. If the structure of R has no effect, then $r_\text{a} = 1/r_\text{b}$ and $r_\text{a}r_\text{b} = 1$. In both copolymerization and cooxidation, $r_\text{a}r_\text{b}$ products have frequently, perhaps usually, been less than unity, corresponding to a tendency (often large in copolymerization) for the reactants to alternate in reaction due to polar or steric effects.[5] There are no established examples of the opposite tendency for $r_\text{a}r_\text{b}$ to be significantly greater than unity.

Accurate determination of reactivity ratios by eq 26 requires more care in analyses than most workers have been willing to employ. In our own work[40,41] on all six combinations of butadiene, styrene, tetralin, and cumene, four of the $r_\text{a}r_\text{b}$ products are in the range 0.84–1.0. The smallest product found was 0.6 for cumene and tetralin. In this combination, tetralin was 4.6 times more reactive than cumene toward the tetralin peroxy radical, 7.7 times more reactive toward the cumylperoxy radical. That this effect may be steric, due to the slow reaction of the tertiary cumylperoxy radical with cumene,[42] is suggested by our results with decalin–tetralin mixtures,[40] for which $r_\text{t} = 12$, $r_\text{d} = 0.04$, and $r_\text{t}r_\text{d} = 0.5$. This product probably represents about the minimum value for an $r_\text{a}r_\text{b}$ product and the maximum effect of R on selectivity of $\text{RO}_2\cdot$ in cooxidations of hydrocarbons. We propose[40] that the effect is largely due to steric hindrance of the attack of a decalylperoxy radical on decalin and that the products of reactivity ratios for hydrocarbons less than 0.5 or greater than 1.0 are suspect. Most of the results in the literature[38,39,43] fall

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Table II
Comparison of Absolute and Relative Rates of Oxidation of Hydrocarbons at 30–60°[a]

Hydrocarbons	$10^5k_p/(2k_t)^{1/2}$		Relative k_p (cumene = 1), $BO_2\cdot$[d]	k_p	$k_t \times 10^{-6}$
	30°[b]	60°[c]	50°	30°[b]	30°[b]
α-Methylstyrene	1300			10	0.3
Styrene	890	2000	10.4	41	21
Tetramethylethylene	320	1000		2.6	0.32
Cyclopentene	280		12.7	8.8	3.1
Tetralin	230	616	7.0	6.3	3.8
Cyclohexene	230	510	5.7	6.1	2.8
Cumene	150	356	1.00	0.18	0.0075
				0.16[e]	0.0095[e]
				0.80[e]	0.025[e]
Allylbenzene	49			10	220
Ethylbenzene	21	53		1.30	20
sec-Butylbenzene	18	45	0.9	0.08	0.09
Cyclohexylbenzene	15	60		0.06	0.08
n-Butylbenzene	8.1	39		0.56	24
1-Octene (1-hexene)	6.2	37		1.0	130
p-Xylene	4.9	16.1		0.84	150
o-Xylene	3.3	16.3		0.42	77
Mesitylene		13.9			
m-Xylene	2.8	11.8			150
Toluene	1.4	5.3		0.24	150

[a] Rate constants in moles/(liter second). [b] Howard and Ingold.[42] [c] Sajus.[39] [d] Butadiene peroxy radicals.[41] [e] D. G. Hendry,[26] at 30 and 60°, respectively.

outside these limits. The above discussion does not apply to oxidations of substrates containing elements other than carbon or hydrogen; polar effects of R on $RO_2\cdot$ radicals might be large and interesting.

In conjunction with the valuable work of Howard and Ingold[42] on absolute rate constants in oxidation, our data on relative rates in cooxidations[40,41] bring out some additional relations, as shown in Table II. Values in the first two columns are proportional to the over-all rates of oxidation of individual hydrocarbons at unit rate of initiation. The agreement between the two groups of workers at two different temperatures is satisfactory. These values depend on both the propagation and the termination constants, with the R in $RO_2\cdot$ changing every time the hydrocarbon changes. The values in the third column are the relative reactivities of the same hydrocarbons toward the peroxy radical involved in the oxidation of butadiene.[41] Values in the last two columns are the absolute values of the propagation and termination constants for the same oxidations as determined by Howard and Ingold;[42] here also the peroxy radical changes every time the hydrocarbon changes.

The interesting and unexpected result from Table II is that the over-all rates of oxidation are usually better than the absolute rate constants for propagation as a measure of the *relative* rates of reaction of the hydrocarbons toward a *common* peroxy radical. Large termination constants are reduced by the exponent $^1/_2$ in the over-all rates and largely offset by large propagation constants for the same radical and *vice versa*. Thus, in spite of its small termination constant, the over-all rate of oxidation of cumene is not much different from those of other hydrocarbons in Table II, using reactivity in cooxidation with butadiene as a guide.

For many studies of oxidation processes, relative reactivities toward the same radical are desired. The accurate and convenient methods of Hendry,[41] using butadiene as the standard for comparison, and of Howard, Schwalm, and Ingold,[44] using an added hydroperoxide in the oxidation of a series of hydrocarbons, provide such information. In the absence of such data, the over-all rate of oxidation of the hydrocarbon at a known rate of initiation now seems to be a better substitute than was anticipated, large effects of termination constants on oxidation rates notwithstanding. These relations have not been tested with the least unreactive hydrocarbons or with compounds containing other elements.

Future Research in Autoxidation

Since we initiated our oxidation program at Stanford Research Institute in 1961, several important problems have been resolved, but new ones have appeared. Reactions of secondary and allylic hydroperoxides and peroxy radicals and high-pressure gas-phase oxidations have already been mentioned. Several other problems, some now being investigated in this laboratory, are outlined below.

From rate constants and their ratios obtained from oxidations of normal butane and isobutane, rates and products of oxidation of isopentane can be predicted fairly well. Relatively few additional standards may

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(44) J. A. Howard, W. J. Schwalm, and K. U. Ingold, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., in press.

permit extension of such predictions to many other alkanes.

While Howard and Ingold[42] have provided individual rate constants for a variety of unsaturated hydrocarbons and alkylbenzenes (Table II), the practically equally important alkanes have been neglected. From our data on over-all rates of oxidation of isobutane[25] and rate constants for termination by $2t\text{-BuO}_2\cdot$ radicals,[26] the activation energy for this chain propagation appears to be about 16 kcal/mole, high enough and important enough to deserve confirmation.

In alkanes with chains of more than five carbon atoms, intramolecular reactions of peroxy radicals can become important. Some time ago, Rust[45] reported high yields of dihydroperoxides from liquid-phase oxidations of 2,4-dimethylpentane and 2,5-dimethylhexane, and Jones and Fenske[46] reported important yields of cyclic ethers from gas-phase oxidations of longer *n*-alkanes. This area received further attention at the recent Oxidation Symposium.[47,48] Accurate determinations of some ratios of rate constants for inter- and intramolecular reactions seem scarce but important.

In oxidations of unsaturated hydrocarbons, some cleavage to carbonyl compounds occurs by an unknown mechanism. Thus, the 5% styrene converted to aldehydes at 4 atm of oxygen (Figure 1)[7] and the corresponding 20% conversion of α-methylstyrene to acetophenone and formaldehyde[49] occur by some process that is kinetically indistinguishable from one of the chain propagation steps 2 or 3. The same kind of reaction occurs in oxidations of polyisoprenes[50,51] and apparently with other unsaturated polymers. Related to this cleavage is the formation of 80% yields of formaldehyde in the gas-phase oxidation of ethylene[52] and similar cleavages with other alkenes. The mechanism proposed by Knox[53] does not allow for reaction 5 (epoxide formation).

Although considerable information is now available on reactions and selectivities of alkylperoxy radicals, rather little is known about selectivities of alkoxy radicals. These are often important chain carriers, and there is reason[15,19] to think that their selectivities may be unusual and worth investigation.

Most commercial liquid-phase oxidations involve reaction temperatures of 150–200°, added metal catalyst, and rates so high that the kinetic chains must be very short and many of the products must arise from chain initiation and termination. These over-all reactions must be very complicated, but a better understanding should help to control and direct them. For example, the conversion of cyclohexyl hydroperoxide to adipic acid may proceed by three or more routes, depending on how the cyclohexane ring opens and on whether the mechanism is radical or nonradical (*e.g.*, the cleavage of cyclohexanone by a peracid). Further, polar effects, so important in copolymerization,[5] may appear in cooxidations of polar compounds. The best approach to such complex reactions seems to require a step-by-step extension of what we know to what we do not know.

My discussion of peroxide decompositions indicated that homogeneous metal catalysis had limited applications to the oxidations of saturated hydrocarbons. However, when unsaturated hydrocarbons[54] or oxygen[36] or nitrogen compounds are involved, and at higher conversions of hydrocarbons, specific catalyses are known. There is also great interest, both fundamentally and practically, in the combined effect of cobalt and bromine on the oxidation of alkylbenzenes to acids. Hay and Blanchard[55] have made significant contributions to this problem but have by no means exhausted important possibilities.

Research on heterogeneous catalysis of oxidation in the gas phase[56] has yielded a few very valuable processes but little understanding of what goes on. Perhaps improved understanding of homogeneous oxidation will assist in understanding heterogeneous processes.

Finally, I am very much interested in the oxidation and aging of polymers and in applying to these processes what we have learned about autoxidations of hydrocarbons. The types of competing free-radical reactions must be much the same, but viscosity effects[57] and intramolecular reactions seem destined to play much more important roles.

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