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Peroxy Radicals

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The reaction of organic compounds with oxygen from the air is one of the most important of all chemical processes. While respiration and combustion are most familiar, there are also a host of less spectacular reactions which do not involve the complete degradation of the organic material to carbon dioxide and water. Many of these processes occur more or less spontaneously under comparatively mild conditions, and so they are known as *autoxidations*. With the exception of some photochemical oxidations and with the possible exception of certain organometallic compounds, the autoxidations of the majority of compounds proceed by free-radical chain processes which involve *peroxy radicals*.

For most organic substrates in solution the rate-controlling propagation step of the autoxidation chain involves the attack on the substrate by peroxy radicals at oxygen partial pressures above ~100 mm. Chain termination involves the mutual destruction of two peroxy radicals. For many autoxidations the primary oxidation product of a substrate RH is the corresponding hydroperoxide, ROOH. In these cases the chain can be represented by

Initiation

$$\text{initiator} \longrightarrow \text{R}\cdot \qquad (1)$$

Propagation

$$\text{R}\cdot + \text{O}_2 \longrightarrow \text{ROO}\cdot \qquad (2)$$

$$\text{ROO}\cdot + \text{RH} \longrightarrow \text{ROOH} + \text{R}\cdot \qquad (3)$$

Termination

$$\text{ROO}\cdot + \text{ROO}\cdot \longrightarrow \text{nonradical products} \qquad (4)$$

The addition of oxygen to the radical R· (reaction 2) is extremely fast and is probably diffusion controlled in many instances (*i.e.*, $k_2 \sim 10^9$ l./(mol sec)).

Peroxy radicals can also be formed from hydroperoxides either by oxidation with a one-electron transfer agent, *e.g.*, eq 5, or by oxidation with a free radical

$$\text{ROOH} + \text{Ce}^{4+} \longrightarrow \text{ROO}\cdot + \text{Ce}^{3+} + \text{H}^+ \qquad (5)$$

(eq 6). The latter reaction is often surprisingly fast.

$$\text{ROOH} + \text{X}\cdot \longrightarrow \text{ROO}\cdot + \text{XH} \qquad (6)$$

For example, the thermoneutral reaction between tetralin hydroperoxide and cumylperoxy radicals (or *vice versa*), eq 7, has a rate constant of about 10^3 l./(mol sec) at 30°.[1] Similarly, the reaction between phenoxy radicals and tetralin hydroperoxide, eq 8,

$$\text{ROOH} + \text{R'OO}\cdot \rightleftarrows \text{ROO}\cdot + \text{R'OOH} \qquad (7)$$

$$\text{C}_6\text{H}_5\text{O}\cdot + \text{ROOH} \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{ROO}\cdot \qquad (8)$$

has a rate constant of $\geq 2 \times 10^5$ l./(mol sec).[2] The reverse of this reaction, *i.e.*, eq −8, has a rate constant

$$\text{ROO}\cdot + \text{C}_6\text{H}_5\text{OH} \longrightarrow \text{ROOH} + \text{C}_6\text{H}_5\text{O}\cdot \qquad (-8)$$

of 5×10^3 l./(mol sec).[3-5]

Electron Spin Resonance Spectra. Peroxy radicals have been detected by esr spectroscopy in hydrocarbon autoxidations (both in the solid and liquid phase) and in the free-radical and ceric ion oxidation of hydroperoxides. Peroxy radicals have no hyperfine structure except that due to ^{17}O. The *g* values (line positions) of peroxy radicals are in the range 2.014–2.019.[6,7] This serves to distinguish them from other radicals commonly present in oxidizing systems (*e.g.*, R· or $\text{R}_2\text{NO}\cdot$) which have *g* values near that of the free electron (2.0023) as a consequence of the almost complete quenching of orbital angular momentum.

The line widths of most radicals increase with in-

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(1) J. A. Howard, W. J. Schwalm, and K. U. Ingold, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 6.

(2) J. R. Thomas, *J. Am. Chem. Soc.*, **86**, 4807 (1964).

(3) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963)

(4) J. A. Howard and K. U. Ingold, *ibid.*, **41**, 2800 (1963).

(5) I. T. Brownlie and K. U. Ingold, *ibid.*, **44**, 861 (1966).

(6) M. Bersohn and J. R. Thomas, *J. Am. Chem. Soc.*, **86**, 959 (1964).

(7) K. U. Ingold and J. R. Morton, *ibid.*, **86**, 3400 (1964).

creasing solvent viscosity and decreasing temperature as a consequence of the reduced averaging of anisotropic processes. In contrast, Thomas[8] has shown that the line widths of tertiary peroxy radicals decrease with increasing viscosity and decreasing temperature. For example, the line width of the *t*-butylperoxy radical, which is $\sim$30 G in pentane at 25°, drops to a limiting value of 14 G in solvents of high viscosity at this temperature and to a limiting value of 3 G at low temperatures (-60 to $-80°$). This unusual (though not completely unknown) behavior was attributed to additional spin–orbit relaxation mechanisms. The exact nature of the most important spin–orbit mechanism is still undetermined.

Ultraviolet Spectra. The uv absorption spectrum of the cyclohexylperoxy radical has been recorded by McCarthy and MacLachlan.[9] It extends from about 2600 to 3200 Å and has maxima at 2750 ($\epsilon_{\max} \sim 2 \times 10^3$ l./(mol cm)) and 2970 Å ($\epsilon_{\max} \sim 1 \times 10^3$ l./(mol cm)). Other peroxy radicals appear to absorb in the same region.[10]

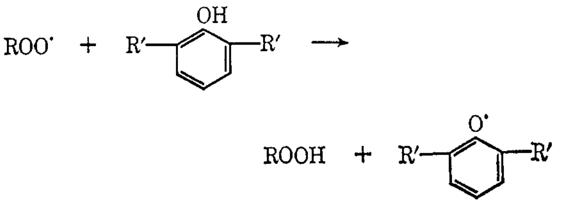
Reactions with Molecules. Peroxy radicals can enter into a wide variety of reactions with suitable substrates. The principal reactions with molecules are hydrogen atom abstractions, addition to unsaturated systems, radical displacement, and oxygen atom transfer. These reactions are considered in more detail below.

Hydrogen Atom Abstraction. The rate constant of hydrogen atom abstraction by a free radical depends primarily on the activation energy of the reaction which, of course, cannot be less than the heat of reaction. Since a reaction can only proceed rapidly if the activation energy is small, it is clear that only exothermic hydrogen atom abstractions are likely to be fast. Therefore, oxidations involving reaction 3 are only likely to be rapid if the bond which is formed (ROO–H) is at least as strong as that which is broken (R–H). Peroxy radicals are strongly resonance stabilized. Benson[11] has estimated the ROO–H bond strength to be about 90 kcal/mol, which means that this bond is stronger than a benzylic or allylic C–H bond ($\sim$84 kcal) or aldehyde C–H bond (86 kcal). It is comparable to a tertiary C–H bond in a saturated hydrocarbon (90–92 kcal). The resonance-weakened O–H, S–H, and N–H bonds of phenols, thiophenols, and aromatic amines provide readily abstractable hydrogen atoms.

Since ROO· is a comparatively unreactive radical it is quite selective in its abstraction from hydrocarbons and has a strong preference for the most weakly bound hydrogen atom. The selectivity of peroxy radicals is similar to that of bromine atoms (D^0(H–Br) = 87 kcal). Peroxy radicals are less selective than polystyryl radicals but more selective than *t*-butoxy, methyl, and phenyl radicals or chlorine atoms.[12] The high selectivity of peroxy radicals means that they abstract hydrogen in marked preference to deuterium, and the abstraction reactions therefore generally exhibit a large deuterium kinetic isotope effect.[5,13,14]

The rate constants listed in Table I have been selected to illustrate some of the major features of the hydrogen atom abstraction reaction. Abstraction from hydrocarbons, even when they contain allylic or benzylic hydrogen, is generally a rather slow process at 30° [15] (*cf.* reactions I–V in Table I). Although the R–H bond strength is the most important factor in determining the rate constant for hydrogen abstraction from RH, steric and polar factors can also play a significant role. Differences in rate constant which must almost certainly be of steric origin have been observed both for changes in the structure of the peroxy radical and for changes in the structure of the oxidizing substrate. Thus, the tertiary cumylperoxy radical is less reactive than the secondary tetralylperoxy radical toward cumene (reactions II and III) and also toward tetralin (reactions IV and V). In general, primary and secondary peroxy radicals appear to be about three to five times more reactive in abstraction as tertiary peroxy radicals.[16,17]

Steric retardation by the substrate can best be illustrated by the effect of two *o*-alkyl groups on the rate of abstraction of hydrogen from phenols (*cf.* reactions VII, VIII, and IX). Thus 2,6-di-*t*-butylphenol is less reactive than 2,6-dimethylphenol (reaction IX *vs.* VIII). However, the latter compound is more reactive than phenol itself because the abstraction is accelerated by electron donation from the methyl groups to a greater extent than it is retarded by their steric effect.[4] The measured rate constants can be corrected for the polar accelerating effects of the *o*-alkyl groups. When this is done, it is found that the steric effect of two *o*-methyl groups has reduced the rate of reaction 9 to about 60% of the value it would have had in the absence of steric retardation. Two *o*-*t*-butyl groups reduce the rate to about 20% of its theoretical sterically nonhindered value. The rates of reaction 9 at 65° for a number of di-*o*-alkylphenols have



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[8] J. R. Thomas, *J. Am. Chem. Soc.*, **88**, 2064 (1966).

[9] R. L. McCarthy and A. MacLachlan, *J. Chem. Phys.*, **35**, 1625 (1961).

[10] R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **57**, 1107 (1961).

[11] S. W. Benson, *J. Am. Chem. Soc.*, **87**, 972 (1965).

[12] K. U. Ingold, *Pure Appl. Chem.*, **15**, 49 (1967).

[13] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **40**, 1851 (1962).

[14] J. A. Howard, K. U. Ingold, and M. Symonds, *ibid.*, **46**, 1017 (1968).

[15] J. A. Howard and K. U. Ingold, *ibid.*, **45**, 793 (1967).

[16] B. S. Middleton and K. U. Ingold, *ibid.*, **45**, 191 (1967).

[17] J. A. Howard and K. U. Ingold, *ibid.*, **46**, 2655, 2661 (1968).

Table I

Rate Constants for Hydrogen Atom Abstraction by Peroxy Radicals

Reacn.	Temp, °C	Substrate	Peroxy radical	k, l./(mol sec)	k_H/k_D
I	30	Ethylbenzene	1-Phenethyl	1.3[a]	
II	30	Cumene	Cumyl	0.18[a]	14 ± 5[b]
III	30	Cumene	Tetralyl	0.5[c]	
IV	30	Tetralin	Tetralyl	6.4[a]	
V	30	Tetralin	Cumyl	1.65[c]	
VI	30	Tetralin hydroperoxide	Cumyl	600[c]	17–30[c]
VII	65	Phenol	Poly(peroxystyryl)	5×10^3 [d,e]	~15[d]
VIII	65	2,6-Dimethylphenol	Poly(peroxystyryl)	20×10^3 [e,f]	
IX	65	2,6-Di-*t*-butylphenol	Poly(peroxystyryl)	5×10^3 [e,f]	10.5[f]
X	65	2,6-Di-*t*-butyl-4-methylphenol	Poly(peroxystyryl)	18×10^3 [e,f]	10.6[g]
XI	65	2,6-Di-*t*-butyl-4-nitrophenol	Poly(peroxystyryl)	1×10^3 [e,f]	
XII	65	Diphenylamine	Poly(peroxystyryl)	20×10^3 [h]	3 ± 0.5

[a] Reference 16. [b] Reference 14. [c] Reference 1. [d] Reference 3. [e] The rate constant has been corrected on the basis of our measured propagation constant for styrene at this temperature as noted in ref 5. [f] Reference 4. [g] Reference 13. [h] Reference 5.

been correlated[4] with the degree of steric protection the substituents afford the phenolic hydroxyl group as determined by infrared spectroscopy.[18] The abstraction of hydrogen from phenols and aromatic amines is much more rapid than from benzylic hydrocarbons.

The importance of dipolar contributions to the transition state

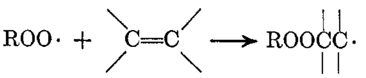
$$\mathrm{PhX{:}H{\cdot}OOR} \longleftrightarrow \mathrm{PhX^{+}{\cdot}H{:}^{-}OOR} \longleftrightarrow \mathrm{PhX{\cdot}H{:}OOR}$$

can be estimated from the influence of *meta* and *para* substituents on the reaction rate (*cf.* reactions IX, X, and XI in Table I). The rate constants can be correlated by the Hammett equation using Brown's electrophilic substituent constants, σ^+, since these normally give better correlations for hydrogen atom abstractions than the usual Hammett σ constants; that is

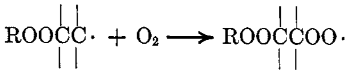
$$\log k/k_0 = \rho\sigma^+$$

where k and k_0 are the rate constants for the substituted and unsubstituted compounds, respectively. Hydrogen abstraction from ring-substituted cumenes by the cumylperoxy radical at 30° gives $\rho = -0.29$.[14] This value is considerably smaller than the values obtained for abstraction by the poly(peroxystyryl)peroxy radical at 65° from phenols[3] (-1.5), 2,6-di-*t*-butylphenols[4] (-1.1), and diphenylamines[19] (-0.89). The negative values of ρ mean that all these reactions are facilitated by electron-donating substituents on the ring. The polar effect is clearly greater for phenols and amines than for cumene.

Addition. Most of our knowledge of the addition mechanism of oxidation comes from the extensive studies of Mayo and coworkers. Under 1 atm of oxygen they have shown that certain readily polymerizable or copolymerizable olefins such as styrene, α-methylstyrene, and methyl methacrylate give mainly a 1:1 copolymer of oxygen and olefin.[20,21]



$$\mathrm{ROO\cdot} + \mathrm{{>}C{=}C{<}} \longrightarrow \mathrm{ROOC{-}C\cdot} \quad (10)$$



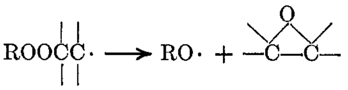
$$\mathrm{ROOC{-}C\cdot} + \mathrm{O_2} \longrightarrow \mathrm{ROOC{-}COO\cdot} \quad (11)$$

The peroxy radical always adds to the double bond in such a way as to produce the more stable β-peroxy alkyl radical, *e.g.*, eq 12. Addition is favored over the

$$\mathrm{ROO\cdot} + \mathrm{C_6H_5CH{=}CH_2} \longrightarrow \mathrm{C_6H_5\dot{C}HCH_2OOR} \quad (12)$$

abstraction of an allylic hydrogen when the double bond is conjugated with an aromatic, carbonyl, nitrile, or another vinyl group. However, even olefins which give mainly hydroperoxides form some addition products.[22]

Most olefins, and perhaps all olefins under the right conditions, yield a certain amount of epoxide on oxidation (eq 13). The relative rates of reactions 11 and 13



$$\mathrm{ROOC{-}C\cdot} \longrightarrow \mathrm{RO\cdot} + \mathrm{{-}C{-}C{-}}\ (\text{epoxide, O bridging}) \quad (13)$$

determine whether the polymeric peroxide or the epoxide (along with compounds from the simultaneously formed alkoxy radical) will be the main product. At a given oxygen pressure, the greater the stability of the β-peroxy alkyl radical the more likely it is to react with oxygen rather than undergo unimolecular decomposition.

Both secondary and tertiary poly(peroxy) radicals derived from substrates such as styrene and α-methylstyrene appear to be somewhat more reactive than the corresponding monomeric peroxy radicals.[17] The addition of peroxy radicals to substituted styrenes is subject to polar and steric effects similar to those of the abstraction reaction.

Radical Displacement.[23] The autoxidation of organoboron compounds is a free-radical chain reaction which almost certainly involves a radical displacement

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(18) K. U. Ingold and D. R. Taylor, *Can. J. Chem.*, **39**, 471 (1961).
(19) I. T. Brownlie and K. U. Ingold, *ibid.*, **45**, 2419 (1967).
(20) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2497 (1958).
(21) F. R. Mayo, A. A. Miller, and G. A. Russell, *ibid.*, **80**, 2500 (1958).
(22) D. E. van Sickle, F. R. Mayo, and R. M. Arluck, *ibid.*, **87**, 4824, 4832 (1965).
(23) C. Walling, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 166.

on boron as one of the propagation steps[24,25] (eq 14).

$$ROO\cdot + BR_3 \longrightarrow [ROO\dot{B}R_3] \longrightarrow ROOBR_2 + R\cdot \qquad (14)$$

For many boron compounds this reaction is so extremely fast that it was not realized until quite recently that a chain reaction was involved. The oxidation is difficult to inhibit with the usual phenol and amine free-radical inhibitors, but it can be inhibited with the stable radical, galvinoxyl.

Other alkyl derivatives of group III metals also react readily with oxygen, presumably by the same sort of mechanism. For organometallic compounds containing highly ionic carbon–metal bonds oxidation in ionizing solvents probably involves a carbanion pathway (see below). Grignard reagents appear to oxidize by a free-radical pathway[26] which may also involve a displacement reaction.

Oxygen Atom Transfer. The autoxidations of trialkyl phosphites[27,28] and trialkyl phosphines[29] occur by rapid chain reactions. Propagation involves the intermediate formation of a phosphoranyl radical with nine electrons on phosphorus, as was first proposed by Walling and Rabinowitz[27,30] (eq 15 and 16). The

$$ROO\cdot + P(OR)_3 \longrightarrow [ROO\dot{P}(OR)_3] \longrightarrow RO\cdot + OP(OR)_3 \qquad (15)$$

$$ROO\cdot + PR_3 \longrightarrow [ROO\dot{P}R_3] \longrightarrow RO\cdot + OPR_3 \qquad (16)$$

presence of unoccupied d orbitals in phosphorus makes this expansion of the valence shell possible. Boron, which has only six electrons, does not have to undergo valence shell expansion in its reaction with peroxy radicals.

The alkoxy radicals formed in reactions 15 and 16 also react very rapidly with phosphite[31] and phosphine by a similar mechanism. In the latter case cleavage can occur by two paths (eq 17), and the products are

$$RO\cdot + PR_3 \longrightarrow [RO\dot{P}R_3] \begin{array}{l} \nearrow OPR_3 + R\cdot \\ \searrow ROPR_2 + R\cdot \end{array} \qquad (17)$$

therefore a mixture of alkylated and partially dealkylated products.[29]

The cooxidation of phosphorus trichloride with hydrocarbons is a rapid chain reaction[30] which yields phosphoryl chlorides (eq 18) and substantial amounts

$$PCl_3 + 0.5O_2 + RH \longrightarrow RPOCl_2 + HCl \qquad (18)$$

of phosphorus oxychloride (eq 19). This reaction

$$PCl_3 + 0.5O_2 \longrightarrow POCl_3 \qquad (19)$$

occurs by a complex sequence of competing and successive steps involving a number of chain-carrying radicals including the peroxy radicals $ROO\cdot$, $RPCl_3OO\cdot$, and $PCl_4OO\cdot$.[32]

Electron-Transfer Reactions. The ready autoxidation of some carbanions has been known for many years. Largely as a result of the work of Dr. G. A. Russell the mechanisms of these reactions have now been fairly well clarified. The rates of oxygen absorption by triphenylmethane[33] ($pK_a = 28$) and diphenylmethane[34] ($pK_a = 30$) in basic dimethyl sulfoxide solution are equivalent to the rates of ionization of the hydrocarbons. The reactions correspond, at least kinetically, to the simple fast addition of oxygen to the carbanion (eq 20 and 21). However, the changes in

$$RH + B^- \xrightarrow{\text{slow}} R:^- + HB \qquad (20)$$

$$R:^- + O_2 \xrightarrow{\text{fast}} ROO^- \qquad (21)$$

multiplicity suggest that reaction 21 is in fact a two-step process.[35]

$$R:^- + \uparrow\cdot O{-}O\cdot\uparrow \longrightarrow R\cdot\uparrow\ \uparrow O_2\cdot^- \longrightarrow R\cdot\downarrow\ \uparrow O_2\cdot^- \longrightarrow ROO^- \qquad (21)$$

For more acidic hydrocarbons, such as fluorene[35] ($pK_a = 21$) or 9-phenylfluorene[35] ($pK_a = 16$), the reaction involves the carbanion in equilibrium with the hydrocarbon.

$$RH + B^- \overset{\text{fast}}{\rightleftharpoons} R:^- + HB \qquad (20)$$

$$R:^- + O_2 \xrightarrow{\text{slow}} ROO^- \qquad (21)$$

The oxidation of 2-nitropropane in basic solution[35] involves long kinetic chains and proceeds only when catalyzed. Chain propagation occurs by electron transfer from the carbanion to the peroxy radical (eq 22).

$$R:^- + ROO\cdot \longrightarrow R\cdot + ROO^- \qquad (22)$$

Although transition metals such as cobalt and manganese normally catalyze the autoxidation of organic substrates, it has been observed that at high concentrations the metals may sometimes inhibit the reaction. Inhibition is probably generally due to chain termination by the electron-transfer reactions[36] 23 and 24.

$$ROO\cdot + Co^{2+} \longrightarrow ROO^- + Co^{3+} \qquad (23)$$

$$ROO\cdot + Mn^{2+} \longrightarrow ROO^- + Mn^{3+} \qquad (24)$$

The reaction of peroxy radicals with Mn^{2+} is as fast as hydrogen abstraction from the more efficient amine and phenolic inhibitors ($\sim 2 \times 10^5$ l./(mol sec)[36]).

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(24) A. G. Davies and B. P. Roberts, *Chem. Commun.*, 298 (1966); *J. Chem. Soc., B*, 17 (1967).

(25) P. G. Allies and P. B. Brindley, *Chem. Ind.* (London), 319 (1967).

(26) R. C. Lamb, P. W. Ayers, M. K. Toney, and J. F. Garst, *J. Am. Chem. Soc.*, **88,** 4261 (1966).

(27) C. Walling and R. Rabinowitz, *ibid.*, **81,** 1243 (1959).

(28) W. G. Bentrude, *Tetrahedron Letters*, 3543 (1965).

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(30) C. Walling and M. S. Pearson, "Topics in Phosphorus Chemistry," Vol. III, Interscience Publishers, New York, N. Y., 1966, p 1.

(31) C. Walling and M. S. Pearson, *J. Am. Chem. Soc.*, **86,** 2262 (1964).

(32) F. R. Mayo, L. J. Durham, and K. S. Griggs, *ibid*,. **85,** 3156 (1963).

(33) G. A. Russell and A. G. Bemis, *ibid.*, **88,** 5491 (1966).

(34) G. A. Russell, A. G. Bemis, E. J. Geels, E. G. Janzen, and A. J. Moye, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 174.

(35) G. A. Russell, *et al.*, "Selective Oxidation Processes," Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, p 112.

(36) K. U. Ingold, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 296.

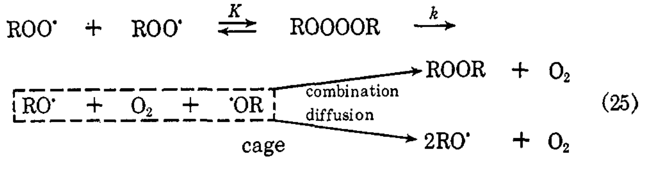
Table II
Chain Termination Constants for Hydrocarbon Oxidation at 30°

Peroxy radical	$2k_t$, M^{-1} sec^{-1}	Examples
Primary, $RCH_2OO\cdot$	$2\text{–}4 \times 10^8$	*p*-Xylene, octene-1
Secondary, $RR'CHOO\cdot$	$20\text{–}40 \times 10^6$ (benzylic)	Ethylbenzene, styrene
	$1\text{–}10 \times 10^6$ (allylic)	Heptene-3, methyl oleate
	$6\text{–}8 \times 10^6$ (cyclic)	Cyclohexene, tetralin
Tertiary, $RR'R''COO\cdot$	$0.1\text{–}60 \times 10^4$	Cumene, α-methylstyrene
Hydroperoxy, $HOO\cdot$	2.0×10^6	Hydrogen peroxide[a]
	1.2×10^9	1,4-Cyclohexadiene

[a] Pulse radiolysis of aqueous hydrogen peroxide (D. J. Currie and F. S. Dainton, *Trans. Faraday Soc.*, **61,** 1156 (1965); G. E. Adams, J. W. Boag, and B. D. Michael, *Proc. Roy. Soc.* (London), **A289,** 321 (1966)).

Reactions with Radicals. The reactions of peroxy radicals with radicals can be conveniently subdivided into reactions with peroxy radicals (the self-reaction), reactions with amino radicals, reactions with phenoxy radicals, and reactions with alkyl radicals.

The Self-Reaction. We have measured the rate constants for chain termination during the oxidation of a number of hydrocarbons giving a wide variety of peroxy radicals.[1,14,15,17,37] The results are summarized in Table II in terms of the types of peroxy radical involved. In general, chain-termination rate constants increase along the series tertiary peroxy < secondary peroxy < primary peroxy. With the possible exception of the hydroperoxy radical in nonaqueous media, none of these reactions is diffusion controlled. That is, since the rate constants are less than ~10^9 l./(mol sec), we know that reaction does not occur at every encounter between two peroxy radicals. The slowness of the reaction between tertiary peroxy radicals is due primarily to the fact that the decomposition of a tetroxide intermediate to alkoxy radicals and oxygen requires a significant activation energy.[38–40] The differences in the rate constants for the self-reactions of peroxy radicals are due primarily to differences in the activation energy for tetroxide decomposition.[39] For tertiary peroxy radicals the over-all process can be represented as



(25)

Formation of di-*t*-butyl tetroxide is exothermic by 5–6 kcal/mol,[40,41] and its activation energy for decomposition to alkoxy radicals is ~10–15 kcal/mol.[39,40] Bartlett and Guaraldi[40] have provided convincing evidence for the existence of this tetroxide by directly monitoring by esr the *t*-butylperoxy radical concentration present in equilibrium with the tetroxide at very low temperatures. At temperatures below −85° the peroxy radical concentration does not change with time but can be reversibly increased and decreased by raising and lowering the temperature. At a temperature of −70° the more stable di-*t*-butyl trioxide is produced[42] (eq 26), and this breaks down at −30° to

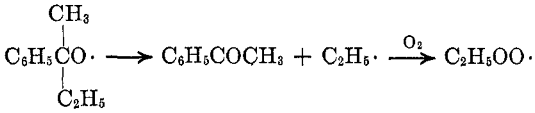
$$RO\cdot + ROO\cdot \longrightarrow ROOOR \qquad (26)$$

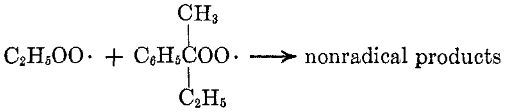
give, among other products, di-*t*-butyl peroxide (eq 27 and 28).

$$ROOOR \longrightarrow RO\cdot + ROO\cdot \qquad (27)$$

$$RO\cdot + RO\cdot \longrightarrow ROOR \qquad (28)$$

In the autoxidation of hydrocarbons giving tertiary peroxy radicals a certain fraction of chain termination generally involves primary or secondary peroxy radicals formed *via* β scission of the tertiary alkoxy radicals produced in reaction 25. For example, with *sec*-butylbenzene


$$C_6H_5\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C}}O\cdot \longrightarrow C_6H_5COCH_3 + C_2H_5\cdot \xrightarrow{O_2} C_2H_5OO\cdot \qquad (29)$$


$$C_2H_5OO\cdot + C_6H_5\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C}}OO\cdot \longrightarrow \text{nonradical products} \qquad (30)$$

The most interesting question presently unanswered about the self-reaction of tertiary peroxy radicals relates to the effect of the structure of R on the tetroxide equilibrium constant K_{25} and the tetroxide unimolecular decomposition rate constant k_{25}. The over-all rate for the reaction giving molecular products directly varies by a factor of about 60 along the peroxy radical series *t*-butyl < cumyl < 2-phenylbutyl-2 < 1,1-diphenylethyl.[17] It seems unlikely that the ratio of radical diffusion from the cage to radical combination in the cage can differ greatly from one pair of alkoxy radicals to another. The difference in the over-all rates of reaction is probably chiefly associated with a difference in k_{25}.

In 1957 Russell[43] suggested that the self-reaction of secondary (and primary) peroxy radicals involved the decomposition of a tetroxide by way of a cyclic transition state in which one of the α-hydrogen atoms is transferred to give the products ketone, alcohol, and oxygen.

The Russell mechanism provides a very attractive

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[37] J. A. Howard and K. U. Ingold, *J. Am. Chem. Soc.*, **90,** 1058 (1968).

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

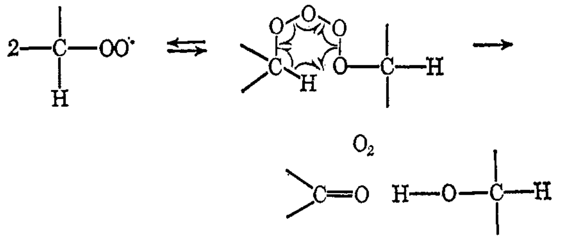
[39] J. R. Thomas and K. U. Ingold, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 258.

[40] P. D. Bartlett and G. Guaraldi, *J. Am. Chem. Soc.*, **89,** 4799 (1967).

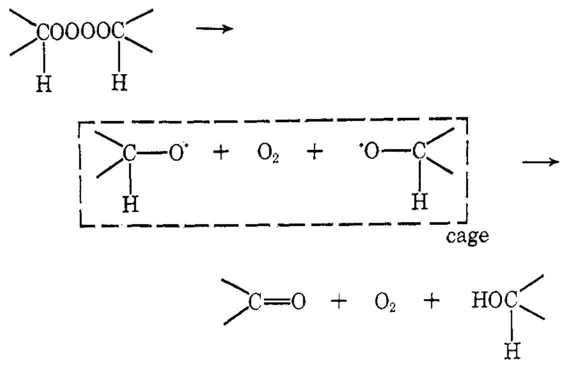
[41] S. W. Benson, *ibid.*, **86,** 3922 (1964).

[42] P. D. Bartlett and P. Günther, *ibid.*, **88,** 3288 (1966).

[43] G. A. Russell, *ibid.*, **79,** 3871 (1957).


(31)

explanation for the observed low activation energy and rapid termination reactions of secondary peroxy radicals compared with tertiary peroxy radicals. These phenomena are not easily accounted for by an alternative hypothesis involving the prior decomposition of the tetroxide to alkoxy radicals and their subsequent rapid disproportionation in the cage.



(32)

Unlike the tertiary peroxy radicals virtually all interactions of secondary peroxy radicals are chain terminating in solution at 30°.[17,44] However, nonterminating interactions have been observed for primary and secondary peroxy radicals at room temperature in the gas phase,[45] and such nonterminating reactions may also occur in the liquid phase at higher temperatures. In the liquid phase the termination process for secondary peroxy radicals exhibits a deuterium isotope effect, $k_H/k_D = 1.37 \pm 0.14$ at 30°, when the α hydrogen of the peroxy radical is replaced by deuterium.[37] Termination is slower for peroxy radicals derived from saturated hydrocarbons than for structurally similar peroxy radicals derived from unsaturated hydrocarbons in which the peroxy group is adjacent to a π-electron system.[37] This may reflect either the greater stability of a conjugated carbonyl compound or the activation of the α hydrogen by the π system.

The Wigner spin-conservation rule requires that the oxygen evolved in the self-reaction of secondary peroxy radicals should be formed in an excited singlet state if this reaction proceeds by the Russell mechanism and provided the tetroxide is an intermediate rather than merely a transition state.[46] In the latter case, triplet ground-state oxygen, ${}^3\Sigma_g^-$, could be formed by a reaction of radicals with like spin.[38] In the transition state the four oxygen atoms must all lie in a plane with the carbon and hydrogen out of the plane if the oxygen is formed in its first excited state, ${}^1\Delta_g$ (which is 22 kcal above the ${}^3\Sigma_g^-$ state). A skew-boat transition-state structure which would give rise to oxygen in its second excited state, ${}^1\Sigma_g^+$ (37 kcal above ${}^3\Sigma_g^-$), would appear to be configurationally more favorable.

A small amount of the oxygen evolved from *sec*-butylperoxy radicals has been trapped with 9,10-diphenylanthracene to produce the corresponding transannular peroxide.[47] The formation of such a peroxide is commonly assumed to be a unique diagnostic test for singlet oxygen. If this assumption is correct, which is by no means certain, the possibility still exists that the singlet oxygen was formed in some minor process not representative of the major reaction. However, the simple interpretation that singlet oxygen is formed in the main reaction, *i.e.*, eq 33, is supported by the fact

$$2sec\text{-}C_4H_9OO\cdot \rightleftarrows sec\text{-}C_4H_9OOOOC_4H_9\text{-}sec \longrightarrow sec\text{-}C_4H_9OH + C_2H_5COCH_3 + {}^1O_2 \quad (33)$$

that under similar conditions no transannular peroxide could be detected in the self-reactions of *t*-butylperoxy radicals.[47] In this case the oxygen is presumably formed in the triplet ground state (eq 34).

$$2t\text{-}C_4H_9OO\cdot \rightleftarrows t\text{-}C_4H_9OOOOC_4H_9\text{-}t \longrightarrow 2t\text{-}C_4H_9O\cdot + {}^3O_2 \quad (34)$$

Transannular peroxide was not formed in the self-reaction of hydroperoxy radicals[47] (eq 35).

$$2HOO\cdot \longrightarrow 2HO\cdot \text{ or } HOOH + {}^3O_2 \quad (35)$$

The absence of nonterminating interactions, the deuterium isotope effect, the difference in the termination constants of saturated and unsaturated peroxy radicals, and the probable evolution of singlet oxygen all suggest that the Russell mechanism is the most important termination process for secondary peroxy radicals at room temperature.

Although acylperoxy and aroylperoxy radicals do not have a hydrogen atom in the α position, the reported rate constants for chain termination in the autoxidations of aldehydes are quite large, *e.g.*, 7.5×10^6 and 2.1×10^8 l./(mol sec) for decanal and benzaldehyde, respectively, in solution,[48] and 8.9×10^{10} and 2.7×10^{10} l./(mol sec) for acetaldehyde and propionaldehyde, respectively, in the vapor phase.[49] These values may indicate no more than the rough order of magnitude of the termination rate constants. The molecular

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[44] R. Hiatt, T. Mill, and F. R. Mayo, *J. Org. Chem.*, **33**, 1416 (1968); R. Hiatt, T. Mill, K. C. Irvin, and J. H. Castleman, *ibid.*, **33**, 1428 (1968).

[45] See, for example: S. S. Thomas and J. G. Calvert, *J. Am. Chem. Soc.*, **84**, 4207 (1962); J. Heicklen and H. S. Johnston, *ibid.*, **84**, 4394 (1962).

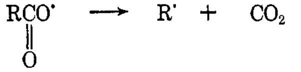
[46] It has also been suggested (R. Kellogg, private communication) that oxygen and ketone are initially formed in their triplet states and that the excited ketone is rapidly quenched to its singlet ground state by the caged oxygen. The oxygen is thereby raised to an excited singlet state.

[47] J. A. Howard and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 1056 (1968).

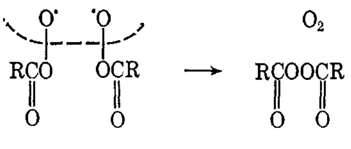
[48] H. R. Cooper and H. W. Melville, *J. Chem. Soc.*, 1994 (1951); T. A. Ingles and H. W. Melville, *Proc. Roy. Soc.* (London), **A218**, 175 (1953).

[49] C. A. McDowell and L. K. Sharples, *Can. J. Chem.*, **36**, 268 (1958).

oxygen evolved in the termination process appears to come from both radicals.[50] A mechanism similar to that outlined by reaction 25 is presumably possible, with acyloxy radicals (if not aroyloxy) undergoing extensive decarboxylation in the cage (eq 36). A four-center cyclic transition state has also been suggested[50] (eq 37). This reaction might involve radicals of like spin,[38] giving peroxide and $^3\Sigma_g{}^-$ oxygen without the formation of an intermediate. However, reaction 37 appears rather unlikely because tertiary alkyl peroxy radicals might be expected to interact in a similar way, and yet their termination rate constants are very much lower than those of the acylperoxy and aroylperoxy radicals. On the whole, a six-center cyclic transition state, analogous to the Russell transition state for secondary peroxy radicals, would appear to be most likely (eq 38).



$$\underset{\displaystyle \overset{\|}{O}}{RCO^{\cdot}} \longrightarrow R^{\cdot} + CO_2 \qquad (36)$$



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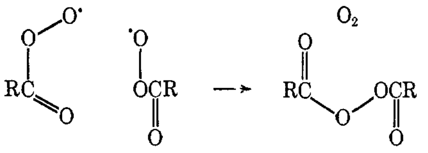
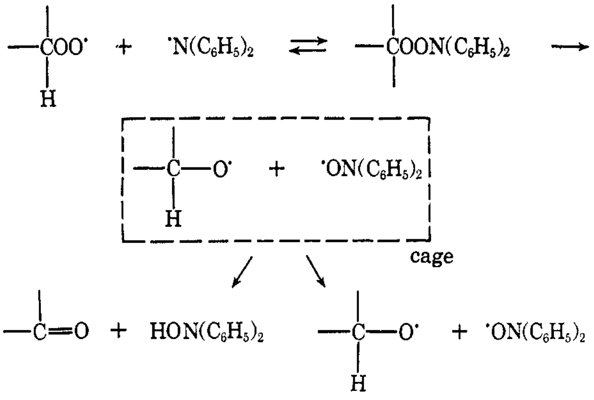


(38)

Reactions with Amino Radicals. The reaction of tertiary peroxy radicals with diphenylamino radicals at 65° can lead to the production of the diphenylnitroxide radical in up to 50% yield[51] (eq 39). The efficiency

$$ROO\cdot + (C_6H_5)_2N\cdot \longrightarrow RO\cdot + (C_6H_5)_2NO\cdot \qquad (39)$$

of nitroxide formation is considerably lower for secondary or primary peroxy radicals (about 10–15% maximum). A plausible explanation for the greater efficiency of nitroxide formation by tertiary peroxy radicals is that the primary and secondary peroxy radicals undergo a hydrogen atom exchange in the cage to give a carbonyl compound and a hydroxylamine (eq 40). Such a hydrogen atom transfer is clearly not possible for a tertiary peroxy radical. Peroxy radicals can also react with the aromatic rings of diarylamino radicals.[51]



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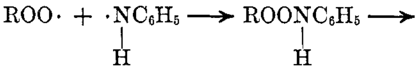
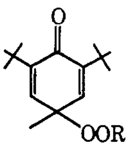
The reaction of peroxy radicals with primary aromatic amines does not yield nitroxide radicals derived directly from the amine in significant quantities.[52] It seems likely that the main products will be an alcohol and an aromatic nitroso compound (eq 41). If these



$$ROO\cdot + \cdot\underset{\displaystyle H}{\underset{|}{N}}C_6H_5 \longrightarrow ROO\underset{\displaystyle H}{\underset{|}{N}}C_6H_5 \longrightarrow ROH + O{=}NC_6H_5 \qquad (41)$$

are indeed the products, they may be formed directly or by a disproportionation in the cage between RO· and $C_6H_5N(H)O\cdot$.

Reactions with Phenoxy Radicals. The reaction of 2,4,6-trialkylphenols with peroxy radicals yields peroxycyclohexadienones by radical coupling reactions.[53–56] For example, 2,6-di-*t*-butyl-4-methylphenol gives 2,6-di-*t*-butyl-4-alkylperoxy-4-methyl-2,5-cyclohexadien-1-one (**1**), and 2,4-di-*t*-butyl-6-methylphenol gives both the 4- and 6-alkylperoxycyclohexadienones, **2** and **3**.



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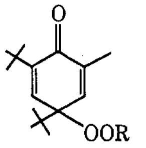

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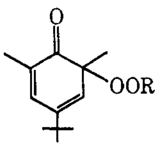
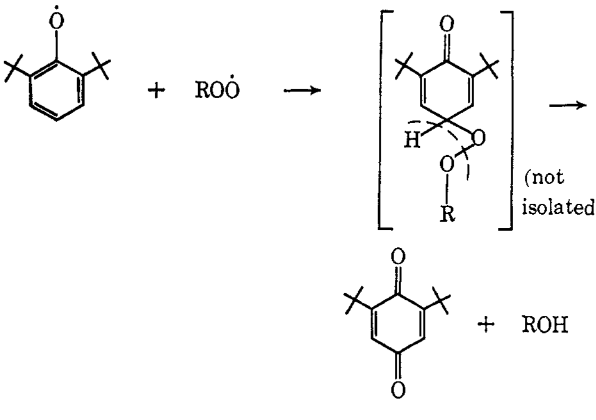


3

The reaction with 2,6-dialkylphenols yields diphenoquinones (by phenoxy radical coupling) and quinones[56] (eq 42). The reaction with 2,4-di-*t*-butylphenol yields



(42)

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(50) C. A. McDowell and S. Sifniades, *Can. J. Chem.*, **41**, 300 (1963).

(51) K. U. Ingold, *Am. Chem. Soc. Div. Petrol. Chem. Preprints*, **13** (2) C15 (1968).

(52) K. Adamic, unpublished results.

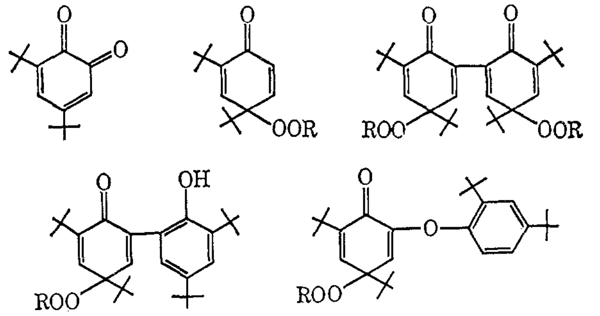
(53) T. W. Campbell and G. M. Coppinger, *J. Am. Chem. Soc.*, **74**, 1469 (1952).

(54) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

(55) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3233 (1955).

(56) E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 263 (1966).

a number of products including the following products of peroxy-phenoxy radical coupling.[57]



Reactions with Alkyl Radicals. At low oxygen partial pressures (commonly ~10 mm) the reaction between peroxy radicals and alkyl radicals becomes an important termination reaction in low-temperature autoxidations. The importance of this process increases with an increase in the stability of the alkyl radical since the more stable alkyl radicals react more slowly with oxygen (eq 43). Reaction 43 is extremely fast. It is considered in

$$\mathrm{ROO\cdot + R\cdot \longrightarrow ROOR} \qquad (43)$$

more detail in the following section.

Unimolecular Decomposition. The unimolecular decomposition of β-peroxy alkyl radicals to alkoxy radical and epoxide (reaction 13) has been already described. Decomposition may also occur by the reverse of reaction 2. The stability of the peroxy radical toward this

$$\mathrm{ROO\cdot \longrightarrow R\cdot + O_2} \qquad (-2)$$

redissociation depends on the strength of the bond formed between the radical R· and oxygen. The bond strength is 47 kcal/mol for H–OO·; 26–29 kcal for alkyl-OO·, and 13–15 kcal for resonance-stabilized radicals such as allyl and benzyl.[11] Benson[11] has estimated the equilibrium constant of reaction 2 over a range of temperatures for a number of peroxy radicals. The HOO· radical can play an important role in oxidations up to at least 1000° even at quite low partial pressures of oxygen. The saturated alkyl peroxy radicals are quite stable below 300–400° and they may therefore be important in cool flame reactions. However, the unsaturated resonance-stabilized radicals are much less stable. At 0.1 atm of oxygen the R· and ROO· concentration will be equal (under equilibrium conditions) at 200° for the allyl radical and at only 100° for the benzyl radical.[11] The triphenylmethylperoxy radical is even more unstable. Janzen and coworkers[58] have shown by esr measurements that the reaction of the triphenylmethyl radical with oxygen is reversible in a solid crystal lattice permeable to oxygen (eq 44).

$$\mathrm{(C_6H_5)_3C\cdot + O_2 \rightleftharpoons (C_6H_5)_3COO\cdot} \qquad (\Delta H = -9 \pm 1\ \mathrm{kcal/mol}) \quad (44)$$

Since the reaction of the triphenylmethyl radical with the triphenylmethylperoxy radical is rapid ($2k_{45}$ = 1.5×10^8 l./(mol sec)[17]) (eq 45); it is not surprising

$$\mathrm{(C_6H_5)_3C\cdot + (C_6H_5)_3COO\cdot \longrightarrow (C_6H_5)_3COOC(C_6H_5)_3} \qquad (45)$$

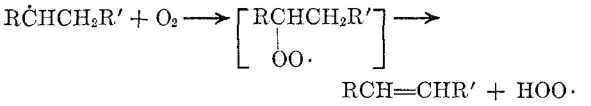
to find that both triphenylmethane[59,60] and triphenylmethyl hydroperoxide[17] are rather efficient inhibitors of the autoxidation of other hydrocarbons such as cumene and tetralin.

$$\mathrm{ROO\cdot + (C_6H_5)_3C\cdot \longrightarrow ROOC(C_6H_5)_3} \qquad (46)$$

The equilibrium constant of reaction 44 has been calculated to be 60 atm^{-1} at 30° from the measured rates of oxidation of tetralin and 9,10-dihydroanthracene in the presence of triphenylmethyl hydroperoxide.[17] This value is in satisfactory agreement with Janzen's estimate[58] of approximately 25 atm^{-1} at 27°.

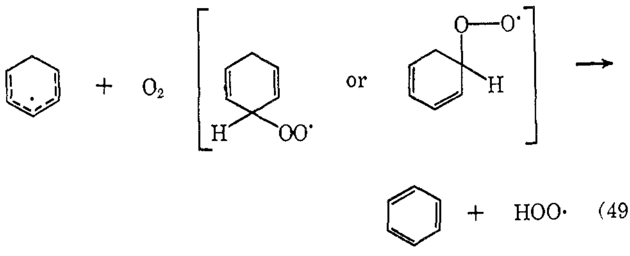
Reversibility of reaction 2 may explain the fact that alkylaromatic hydrocarbons such as toluene, ethylbenzene, and cumene inhibit the vapor-phase oxidation of *n*-heptane at 300–400°.[61] Furthermore, as Russell was first to point out,[62] an equilibrium for reaction 2 provides a ready explanation of the fact that hydrocarbons which yield very stable alkyl radicals tend to give dialkyl peroxides on oxidation rather than hydroperoxides.

In the gas-phase oxidation of simple alkanes above 300° the major initial products are olefins containing the same number of carbon atoms as the parent alkanes.[63–65] This has been attributed to a hydroperoxy radical chain reaction (eq 47 and 48). Russell[62] suggested and we have confirmed[66] that the production of benzene by the autoxidation of 1,4-cyclohexadiene at 30° involves a similar chain (eq 49 and 50).



$$\mathrm{R\dot{C}HCH_2R' + O_2 \longrightarrow \left[\begin{array}{c} RCHCH_2R' \\ | \\ OO\cdot \end{array}\right] \longrightarrow RCH{=}CHR' + HOO\cdot} \qquad (47)$$

$$\mathrm{RCH_2CH_2R' + HOO\cdot \longrightarrow R\dot{C}HCH_2R' + H_2O_2} \qquad (48)$$



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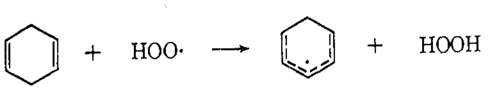

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[57] E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 269 (1966).

[58] E. G. Janzen, F. J. Johnston, and C. L. Ayers, *J. Am. Chem. Soc.*, **89**, 1176 (1967).

[59] G. A. Russell, *ibid.*, **78**, 1047 (1956).

[60] D. G. Hendry and G. A. Russell, *ibid.*, **86**, 2371 (1964).

[61] J. J. Giammaria and H. D. Norris, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, 16 (1962).

[62] G. A. Russell, *J. Chem. Educ.*, **36**, 111 (1959).

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

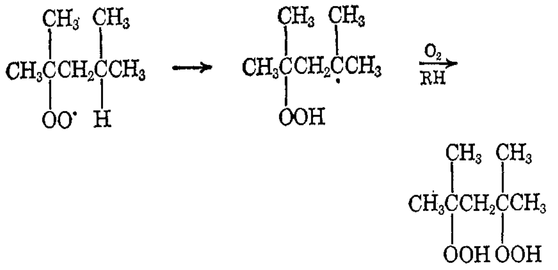
[64] A. P. Zeelenberg and A. F. Bickel, *J. Chem. Soc.*, 4014 (1961).

[65] J. H. Knox and C. H. J. Wells, *Trans. Faraday Soc.*, **59**, 2786, 2801 (1963).

[66] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **45**, 785 (1967).

The formation of the aromatic ring provides the driving force which leads to this propagation sequence. There seems to be little doubt that the reaction proceeds through an unstable alkylperoxy radical intermediate. Evidence for this intermediate has been obtained in pulse radiolysis studies of aerated aqueous solutions of benzene.[67] More convincingly, at 30° neat 1,4-dihydronaphthalene is oxidized to an organic hydroperoxide, but a 0.1 *M* solution in chlorobenzene gives mainly naphthalene and hydrogen peroxide.[66] However, only organic hydroperoxide is formed from 0.1 *M* 9,10-dihydroanthracene at 30°. The balance between the reactions leading to an ROO· chain and those leading to an HOO· chain is extremely sensitive to temperature, concentration, and hydrocarbon structure.

Intramolecular hydrogen abstractions can also yield dihydroperoxides, cyclic ethers, or carbonyl compounds and olefins.[68] The products of these unimolecular peroxy radical reactions depend on the experimental conditions. For example, the oxidation of 2,4-dimethylpentane at 120° in the liquid phase gives an 89% yield (based on oxygen consumed) of the corresponding 2,4-dihydroperoxide[69] (eq 51). In contrast, the vapor-phase oxidation of 2-methylpentane in the cool-flame temperature range (250–300°, [RH] = 50–150 mm, $[O_2]/[RH] = 2$) yields substantial quantities of the O-heterocycles, 2,2-dimethyltetrahydrofuran (**4**) and 2,4-dimethyltetrahydrofuran[70] (eq 52). Many carbonyl compounds and olefins are also produced in this reaction (eq 53).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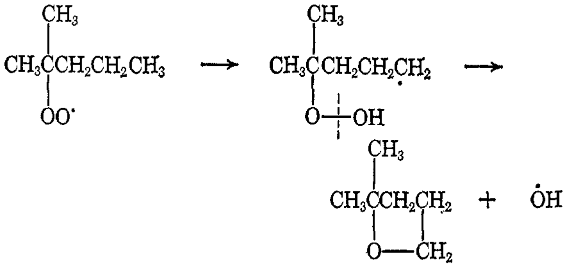
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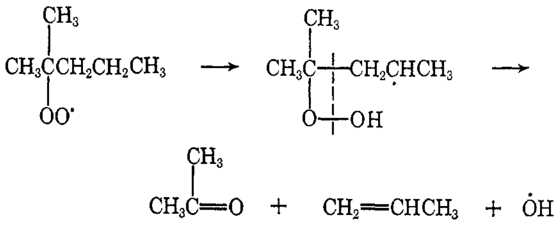
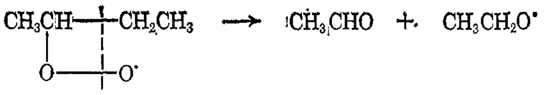
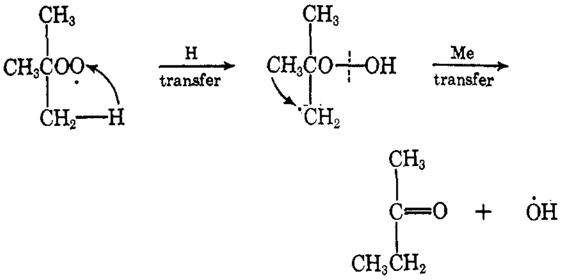

(53)

It has frequently been suggested[71] that in the liquid phase reactions analogous to eq 53 actually involve a direct isomerization of the peroxy radical (eq 54). However, this seems unlikely compared either with β scission of the corresponding alkoxy radical or with a reaction analogous to (53).


(54)

Extremely interesting isomerizations involving intramolecular transfer of alkyl groups (rather than hydrogen) have been observed in some gas-phase oxidations.[68] For example, the slow combustion and cool-flame oxidation of isobutane[72] gives methyl ethyl ketone in quite high yields. The isomerization to the rearranged carbon skeleton is believed to occur after intramolecular hydrogen transfer (eq 55).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(68) A. A. Fish, *Quart. Rev.* (London), **18**, 243 (1964).

(69) F. F. Rust, *J. Am. Chem. Soc.*, **79**, 4000 (1957).

(70) A. A. Fish, *Proc. Roy. Soc.*, **A298**, 204 (1967); Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968; *Angew. Chem. Intern. Ed. Engl.*, **7**, 45 (1968).

(71) See, *e.g.*, N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, "Liquid Phase Oxidation of Hydrocarbons," Plenum Press, New York, N. Y., 1967, Chapter 1, p 5, and Chapter 9, p 326.

(72) C. F. Cullis, A. A. Fish, and D. W. Trimm, *Proc. Roy. Soc.* (London), **A273**, 427 (1963).