The Kinetics of Hydrocarbon Autoxidation in the Liquid Phase

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'We live in oxygen, the essential agent of respiration; oxygen bathes all the bodies and objects which surround us, and its great reactivity is well known. If then one were to effect by any means, a moderation or an excitation of the universal avidity of such an element, would there not result new perspectives in the chemistry of Nature, living and dead?' (C. Moureu and C. Dufraisse, 1926)

1 Introduction

The term autoxidation denotes the reaction of organic substances with molecular oxygen under mild conditions. It is to be distinguished from combustion. It is an everyday phenomenon, examples including the atmospheric deterioration of foods, rubber, paintwork, and lubricating oils. Much effort has gone into the development of antioxidants to inhibit such processes. Useful applications of autoxidation include the atmospheric drying of linseed oil paints, and the manufacture of phenol and acetone from cumene *via* oxidation to its hydroperoxide, and decomposition of the latter with strong acids:[1]

$$PhMe_2CH + O_2 \rightarrow PhMe_2CO_2H \xrightarrow{H^+} PhOH + MeCOMe \qquad (1)$$
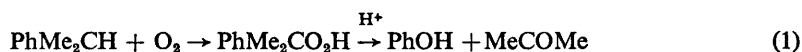
The synthetic applications of autoxidation have grown with the petrochemicals industry, since petroleum hydrocarbons may be oxidised in a controlled manner to starting materials for the production of detergents, organic solvents, man-made fibres, and so on.[1]

The scientific study of autoxidation began in the nineteenth century, when rubber and naturally-occurring oils were first examined. The complexity of these and other materials investigated inevitably meant slow progress, especially as the primary products of autoxidation were often transformed by secondary reactions. However, when simple compounds were studied under controlled conditions, it became apparent that many autoxidations are chain reactions, showing high quantum yields when photo-initiated, and sensitive to traces of impurities. The nature of the chain carriers was at first uncertain, energetic molecules and transient cyclic peroxides being among the species proposed. Eventually, the identification of hydroperoxides as primary products helped to establish the modern
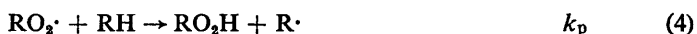
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[1] R. F. Goldstein and A. L. Waddams, 'The Petroleum Chemicals Industry,' Spon, London, 1967.

theory that autoxidations usually proceed by a free-radical mechanism. The essentials of this theory were summarised by Bolland[2] and Bateman.[3]

In practice, these hydroperoxides often react further, forming alcohols, ketones, esters, *etc.* In spite of the industrial importance of such reactions, however, their kinetic complexity excludes them from the present review. In the following sections the kinetics of hydroperoxide formation by a free-radical mechanism are considered, with brief notes on other primary products. Some account will also be given of autoxidations that involve singlet oxygen and carbanions, respectively, as reactive intermediates, since these are theoretically interesting and should prove invaluable for organic syntheses. Those interested in the history of autoxidation should consult the reviews by Milas,[4] and Moureu and Dufraisse.[5] Detailed information on many aspects of autoxidation may be found in recent books.[6-8]

2 Autoxidation Chains

The autoxidation of many hydrocarbons to hydroperoxides proceeds as follows:[3]

initiation $\rightarrow R\cdot$ (rate $= R_i$) (2)

propagation $R\cdot + O_2 \rightarrow RO_2\cdot$ k_o (3)

$RO_2\cdot + RH \rightarrow RO_2H + R\cdot$ k_p (4)

termination $2RO_2\cdot \rightarrow$ stable products $+ O_2$ $2k_t$ (5)

The radical $R\cdot$ is derived from the hydrocarbon RH by abstraction of a hydrogen atom. RO_2H is the hydroperoxide. The various k's are rate constants. The abstraction of hydrogen in reaction (4) occurs more readily if $R\cdot$ is stabilised by resonance. Consequently, hydrocarbons containing a hydrogen atom 'activated' by a neighbouring olefinic bond or aromatic system autoxidise at normal temperatures, whereas saturated hydrocarbons, benzene, *etc.* are much more stable. Where an allylic radical is formed by (4), the hydroperoxide produced may differ in structure from its parent hydrocarbon. For example, methyl linoleate,[9]

$$\overset{13}{C_5H_{11}}CH=\overset{11}{CHCH_2}CH=\overset{9}{CH}(CH_2)_7COOMe,$$ undergoes hydrogen abstraction at C-11, but the resulting allylic radical adds oxygen at C-9 or C-13, yielding the conjugated hydroperoxides $C_5H_{11}CH=CHCH=CHCH(OOH)(CH_2)_7COOMe$ and $C_5H_{11}CH(OOH)CH=CHCH=CH(CH_2)_7COOMe$. In air-saturated organic solvents the conversion of alkyl to alkylperoxyl radicals by reaction (3) usually proceeds quantitatively, so that only the latter contribute to chain termination.[3]

[2] J. L. Bolland, *Quart. Rev.*, 1949, **3**, 1.
[3] L. Bateman, *Quart. Rev.*, 1954, **8**, 147.
[4] N. A. Milas, *Chem. Rev.*, 1932, **10**, 295.
[5] C. Moureu and C. Dufraisse, *Chem. Rev.*, 1926—7, **3**, 113.
[6] 'Autoxidation and Antioxidants,' ed. W. O. Lundberg, Interscience, New York, 1961, 2 volumes.
[7] G. Scott, 'Atmospheric Oxidation and Antioxidants,' Elsevier, Amsterdam, 1965.
[8] L. Reich and S. S. Stivala, 'Autoxidation of Hydrocarbons and Polyolefins: Kinetics and Mechanisms,' Marcel Dekker, New York, 1969.
[9] H. H. Sephton and D. A. Sutton, *Chem. and Ind.*, 1953, 667.

In a typical autoxidation the propagation sequence may occur a hundred or more times for every act of initiation or termination. The rate of oxygen consumption, therefore, equals the rate of propagation:

$$- d[O_2]/dt = d[RO_2H]/dt = k_o[R\cdot][O_2] = k_p[RO_2\cdot][RH] \tag{6}$$

Furthermore, the concentration of alkylperoxyl radicals is minute, about 10^{-7} mol dm^{-3}, and its rate of change close to zero. Applying the principle of stationary states, we write

$$d[RO_2\cdot]/dt = 0 = R_i - 2k_t[RO_2\cdot]^2 \tag{7}$$

whence, eliminating $[RO_2\cdot]$ from (6) and (7):

$$- d[O_2]/dt = d[RO_2H]/dt = k_p[RH](R_i/2k_t)^{\frac{1}{2}} \tag{8}$$

The rate of autoxidation depends on the hydrocarbon concentration, but not on the oxygen concentration. Under mild conditions, oxygen consumption and hydroperoxide yield agree closely,[10-12] as required by equation (8). The kinetic chain-length (kcl), which is the average number of oxygen molecules consumed for each act of initiation, may be derived similarly:

$$kcl = k_p[RO_2\cdot][RH]/R_i = k_p[RH]/(2k_tR_i)^{\frac{1}{2}} \tag{9}$$

As shown by equations (8) and (9), the rate constant ratio $k_p/(2k_t)^{\frac{1}{2}}$ controls the susceptibility of a particular hydrocarbon to autoxidation. Its determination requires that the rates of autoxidation and initiation be measured accurately: the appropriate techniques will be discussed shortly. We must first, however, consider some primary products, other than hydroperoxides, produced by autoxidation.

Hydrocarbons containing conjugated double bonds, or based on the styrene skeleton, can copolymerise with oxygen.[12-15] In these cases, the propagation sequence involves addition of a peroxyl radical to the olefinic bond, instead of reaction (4). Taking styrene as an example:

$$RO_2\cdot + CH_2{=}CHPh \rightarrow RO_2CH_2\dot{C}HPh \tag{10}$$

The radical formed in (10) may add a further hydrocarbon unit

$$RO_2CH_2\dot{C}HPh + CH_2{=}CHPh \rightarrow RO_2CH_2CH(Ph)CH_2\dot{C}HPh \tag{11}$$

or undergo reaction (3). At sufficiently high oxygen concentrations, a 1:1 polyperoxide is formed.[13,14] This copolymerisation can occur with compounds, such as β-methylstryene,[14] which do not polymerise alone. Hydrocarbons such as indene,[14,15] which can undergo both reactions (4) and (10), produce hydroperoxide and polyperoxide simultaneously.

[10] K. R. Hargrave and A. L. Morris, *Trans. Faraday Soc.*, 1956, **52**, 89.

[11] G. A. Russell, *J. Amer. Chem. Soc.*, 1956, **78**, 1047.

[12] J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1967, **45**, 785, 793.

[13] F. R. Mayo, A. A. Miller, and G. A. Russell, *J. Amer. Chem. Soc.*, 1958, **80**, 2500 and previous papers.

[14] J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1966, **44**, 1113.

[15] G. A. Russell, *J. Amer. Chem. Soc.*, 1956, **78**, 1035, 1041.

At low oxygen concentrations, reaction (3) may be slow enough for some of the radicals formed in (10) to decompose to alkoxyl radicals, which initiate further autoxidation, and epoxide:[13,16]

$$RO_2C-C\cdot \rightarrow RO\cdot + -C-\!\!\!\!\bigvee_{O}\!\!\!\!-C- \tag{12}$$
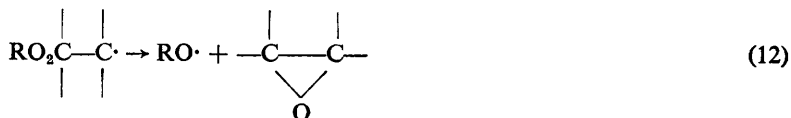
Certain mono-olefins also are known to yield epoxides,[16] which in some cases can be the major product of autoxidation.

In a few autoxidations hydrogen peroxide is formed.[12,17] The chain carriers are hydroperoxyl radicals. Taking cyclohexa-1,4-diene as an example:[12]

$$\text{cyclo-}C_6H_7\cdot + O_2 \rightarrow \text{benzene} + HO_2\cdot \qquad k_o \tag{13}$$

$$HO_2\cdot + \text{cyclo-}C_6H_8 \rightarrow H_2O_2 + \text{cyclo-}C_6H_7\cdot \qquad k_p \tag{14}$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad 2k_t \tag{15}$$

The formation of a stable aromatic system provides the impetus behind this propagation sequence.[12]

3 Measurement of Autoxidation Rates

The usual method for following autoxidation is to measure oxygen absorption from the gas phase into solution. Unless a thin layer of solution is used, efficient shaking or stirring is necessary to keep it saturated with oxygen. Accurate temperature control is needed in order to avoid spurious pressure changes, especially with volatile hydrocarbons, but high sensitivity can be achieved. Measurements may be automated in various ways, such as by recording the output from a pressure transducer,[18] or replenishing the absorbed oxygen by electrolysis of water.[19]

Since the maintenance of equilibrium between gas phase and solution is not easy, various techniques have been developed for following oxygen consumption in the solution itself. Thus, oxygen concentrations may be followed by u.v. spectrophotometry[20] or the oxygen electrode.[21] Similarly, reaction rates have been calculated from the heat liberated during autoxidation, as measured by a sensi-

[16] W. F. Brill, *Advances in Chemistry Series*, 1965, **51**, 70; D. E. van Sickle, F. R. Mayo, E. S. Gould, and R. M. Arluck, *J. Amer. Chem. Soc.*, 1967, **89**, 967, 977.

[17] A. Bromberg and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1969, **91**, 2860.

[18] H. Berger, A. M. W. Blaauw, M. M. Al, and P. Smael, *Advances in Chemistry Series*, 1968, **75**, 346.

[19] R. Marcuse, K. Remi, and P. O. Göthe, *Fette Seifen Anstrichm.*, 1964, **66**, 992.

[20] J. Betts and J. C. Robb, *Trans. Faraday Soc.*, 1968, **64**, 2402; 1969, **65**, 195, 2144; W. A. Pryor and R. A. Patsiga, *Spectroscopy Letters*, 1969, **2**, 61.
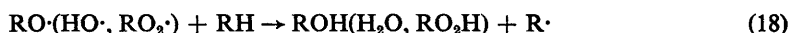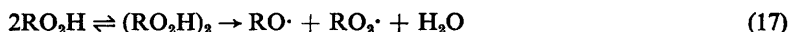
[21] J. W. Hamilton and A. L. Tappel, *J. Amer. Oil Chemists' Soc.*, 1963, **40**, 52; J. S. Bellin and C. A. Yankus, *Analyt. Chim. Acta*, 1967, **39**, 203; J. Heide-Jensen in 'Metal Catalysed Lipid Oxidation,' ed. R. Marcuse, Swedish Institute for Food Preservation Research, Göteberg, 1968, p. 75.

tive thermocouple,[22] and from a faint chemiluminescence[23] associated with peroxyl radical termination.

Autoxidation rates may be determined by product analysis also. Total hydroperoxide yields can be estimated by iodometry[24,25] or the stannous chloride method.[10] Gas–liquid chromatography is invaluable for analysing mixtures of hydroperoxides[26,27] or epoxides.[16] Polyperoxides have been determined by iodometry.[28] Detailed information on the analysis of these and other products may be found in recent publications.[25,28,29]

4 Measurement of Initiation Rates

Autoxidation chains are often initiated by the breakdown of traces of hydroperoxides to free radicals which can abstract hydrogen from hydrocarbons:[3]

$$RO_2H \rightarrow RO\cdot + HO\cdot \tag{16}$$

$$2RO_2H \rightleftharpoons (RO_2H)_2 \rightarrow RO\cdot + RO_2\cdot + H_2O \tag{17}$$

$$RO\cdot(HO\cdot, RO_2\cdot) + RH \rightarrow ROH(H_2O, RO_2H) + R\cdot \tag{18}$$

Even at low hydroperoxide concentrations, reaction (17) predominates over (16). The hydrogen-bonded dimer, $(RO_2H)_2$, has been detected by i.r. spectroscopy. Since autoxidation produces further hydroperoxide, the rate of initiation gradually increases, and a marked autoacceleration of the reaction may be observed. Bateman[3] has summarised the relevant kinetics.

For kinetic studies, it is best to maintain a constant initiation rate. To achieve this, the thermal- or photo-decomposition of organic peroxides or azo-compounds is commonly used as a source of radicals, and the extent of autoxidation is restricted in order to limit the build-up of hydroperoxide. For example, azo-di-isobutyronitrile decomposes as follows:

$$Me_2(CN)CN=NC(CN)Me_2 \rightarrow 2Me_2(CN)C\cdot + N_2 \tag{19}$$

Pairs of radicals are produced within a cage of solvent molecules. The radicals may react together before they can diffuse apart to initiate autoxidation chains. The rate of initiation cannot, therefore, be reliably calculated from initiator decomposition, but must be measured independently.[30] This is usually done by adding a small amount of phenolic antioxidant to the hydrocarbon and noting how the autoxidation rate increases as the antioxidant is destroyed.

[22] J. C. Robb and M. Shahin, *J. Inst. Petroleum*, 1958, **44**, 283; *Trans. Faraday Soc.*, 1959, **55**, 1753; J. A. Howard and J. C. Robb, *ibid.*, 1963, **59**, 1590.
[23] R. F. Vasil'ev and A. A. Vichutinskii, *Nature*, 1962, **194**, 1276; R. F. Vasil'ev, *Progr. Reaction Kinetics*, 1967, **4**, 305.
[24] F. W. Heaton and N. Uri, *J. Sci. Food Agric.*, 1958, **9**, 781.
[25] W. E. Link and M. W. Formo, ref. 6, vol. 1, chap. 10.
[26] F. R. Mayo, M. G. Syz, T. Mill, and J. K. Castleman, *Advances in Chemistry Series*, 1968, **75**, 38.
[27] R. Higgins, C. S. Foote, and H. Cheng, *Advances in Chemistry Series*, 1968, **77**, 102.
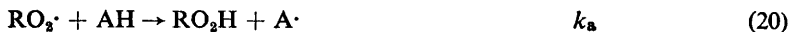[28] R. M. Johnson and I. W. Siddiqi, 'The Determination of Organic Peroxides,' Pergamon Press, London, 1970.
[29] W. O. Lundberg and P. Jarvi, *Progr. Chem. Fats and Other Lipids*, 1968, **9**, 379.
[30] C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, page 73.

In the presence of a simple chain-breaking antioxidant, such as 2,6-di-t-butyl-4-methylphenol,[31,32] reaction (5) is superceded by the termination sequence:

$$RO_2\cdot + AH \rightarrow RO_2H + A\cdot \qquad\qquad k_a \qquad\qquad (20)$$

$$RO_2\cdot + A\cdot \rightarrow \text{stable products} \qquad\qquad\qquad (21)$$

AH is the antioxidant, and A· the radical derived from it by loss of phenolic hydrogen. A stationary state treatment of reactions (2), (3), (4), (20), and (21), similar to that outlined in Section 2, leads to the expressions:

$$- d[O_2]/dt = d[RO_2H]/dt = k_p[RH]R_i/2k_a[AH] \qquad (22)$$

$$\text{kcl} = k_p[RO_2\cdot][RH]/R_i = k_p[RH]/2k_a[AH] \qquad (23)$$
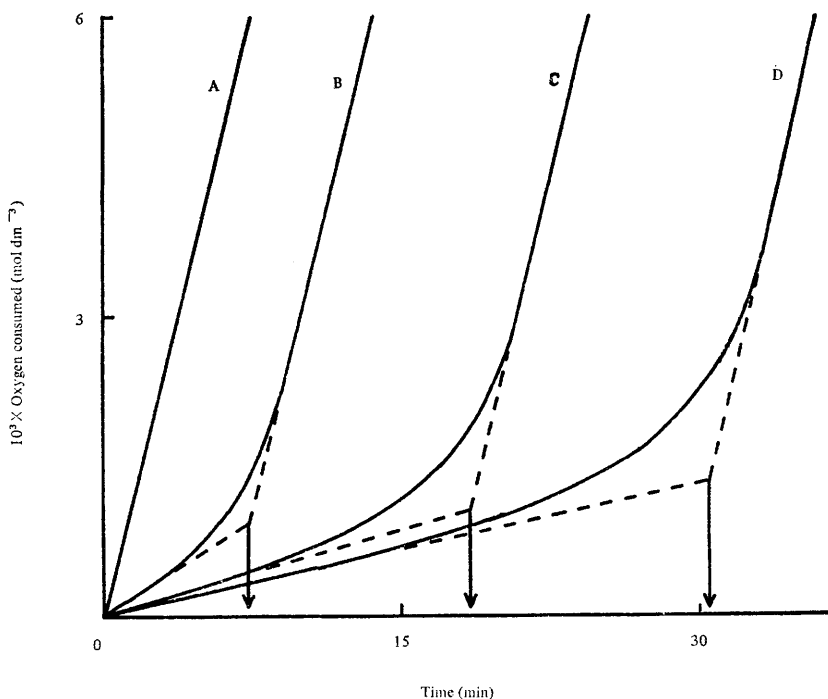
Figure 1 *Tangent-intercept method. Autoxidation of cumene at 68 °C initiated by 4·78 × 10⁻³ mol dm⁻³ azo-di-isobutyronitrile. The induction periods, marked by vertical arrows, are proportional to the initial concentration of the antioxidant 2,6-di-t-butyl-4-methylphenol,* [BMP]₀. A: *no antioxidant;* B,C,D: [BMP]₀ = 0·38, 0·96, *and* 1·53 × 10⁻⁴ mol dm⁻³ *respectively.* (J. Betts and J. C. Robb, unpublished results).

[31] C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Amer. Chem. Soc.*, 1955, **77**, 3233; C. E. Boozer, G. S. Hammond, C. E. Hamilton, and C. Peterson, *ibid.*, 1955, **77**, 3380.

[32] E. C. Horswill and K. U. Ingold, *Canad. J. Chem.*, 1966, **44**, 263, 269, 985.

These are valid for reasonably long autoxidation chains. If the antioxidant concentration is $[AH]_0$ initially, its value at time t will be given by $[AH] = [AH]_0 - R_1 t/2$ and equation (22) may be modified to:[33]

$$(- d[O_2]/dt)^{-1} = 2k_a[AH]_0/k_p[RH]R_1 - k_a t/k_p[RH] \qquad (24)$$

A linear graph of $(- d[O_2]/dt)^{-1}$ against t intercepts the time axis at $t = 2[AH]_0/R_1$, whence R_1 is readily calculated. The rate constant ratio k_a/k_p can be determined from the slope of the graph. This ratio measures the susceptibility of a hydrocarbon to autoxidation in the presence of a chain-breaking antioxidant.

With many hydrocarbons, however, reaction (5) may assume importance before the antioxidant has largely disappeared. As a result, the term $(- d[O_2]/dt)^{-1}$ diminishes more slowly than predicted by equation (24) and the initiation rate can be badly underestimated. This difficulty cannot be avoided by increasing $[AH]_0$ much above 10^{-4} mol dm^{-3}, since the autoxidation rate must be high enough to measure accurately.

For this reason, the tangent-intercept method[31,32] is often preferred (see Figure 1). Oxygen consumption is followed until all the antioxidant has disappeared and the autoxidation rate attains its maximum value. The induction period (IP) is measured as shown, and the initiation rate calculated from the equation IP $= 2[AH]_0/R_1$. This method allows for the onset of reaction (5) at low antioxidant concentrations. Its kinetic basis has been discussed elsewhere.[34]

5 Absolute Rate Constants

If hydrocarbon autoxidation is studied under stationary state conditions, the ratios $k_p/(2k_t)^{\frac{1}{2}}$ and k_p/k_a can be calculated from equations (8), (22), and (24). Typical values are shown in Table 1. These ratios are useful for predicting autoxidation rates, but not for relating hydrocarbon reactivity to structure, since they contain within themselves rate constants for both the propagation and termination steps. For this purpose, absolute rate constants are needed. Their determination has been described in detail elsewhere[35-40] and will only be outlined here.

Essentially, an autoxidation must be studied under non-stationary state conditions, so that the peroxyl radical concentration and autoxidation rate vary rapidly with time. In the rotating sector method,[35,36] a photo-initiated autoxidation is caused to approach and decline from its maximum (stationary state) rate by interposing between the light source and reaction vessel a rotating disc from

[33] D. S. Davies, H. L. Goldsmith, A. K. Gupta, and G. R. Lester, *J. Chem. Soc.*, 1956, 4926.
[34] C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, 'The Kinetics of Vinyl Polymerization by Radical Mechanisms,' London, 1958, p. 254.
[35] F. S. Dainton, 'Chain Reactions', Methuen, London, 1966, chap. 5.
[36] G. M. Burnett and H. W. Melville in 'Technique of Organic Chemistry,' ed. S. L. Friess, E. S. Lewis, and A. Weissberger, Interscience, New York, 1963, vol. 8, part 2, chap. 20.
[37] L. Bateman and G. Gee, *Trans. Faraday Soc.*, 1951, 47, 155.
[38] A. A. Vichutinskii, *Nature*, 1965, 206, 292.
[39] J. R. Thomas and K. U. Ingold, *Advances in Chemistry Series*, 1968, 75, 258.
[40] J. E. Bennett, D. M. Brown, and B. Mile, *Trans. Faraday Soc.*, 1970, 66, 386, 397.

Table 1 *Autoxidation of hydrocarbons at 30 °C*

Compound	$10^3 k_p/(2k_t)^{\frac{1}{2}}$	k_p	$\log A_p$	E_p	$10^{-6} \times k_t$	$\log A_t$	E_t	$10^3 \times k_p/k_a$	$10^{-3} \times k_a$	$\log A_a$	E_a	Ref.
Cyclohexane (65 °C)	0·03	0·07	—	—	3·4	9·5	19	—	—	—	—	a
Cyclohexene	2·5	6·1	9·1	48	2·8	10·8	25	0·23	27	8·9	26	b-d
Cumene	1·1	0·15	6·5	42	0·01	8·3	25	0·015	10	6·9	17	d-f
Ethylbenzene	0·16	0·70	6·0	36	10	7·0	0	0·22 (60 °C)	11 (60 °C)	—	—	g
Indan	1·7	4·8	—	—	4·1	—	—	—	—	—	—	a
Methyl linoleate	21	62	—	—	4·4	—	—	—	—	—	—	a
Styrene*	6·3	41	7·7	35	21	8·7	8	4·5	9	7·9	23	h
4-Methoxystyrene*	13	81	7·1	30	19	7·3	0	15 (40 °C)	9 (40 °C)	—	—	h
α-Methylstyrene	12	10	6·8	34	0·34	8·2	15	5 (65 °C)	8 (65 °C)	—	—	b
Tetralin	2·3	6·3	6·8	35	3·8	9·6	18	0·29	22	7·3	17	bdf

The hydrocarbons were autoxidised neat or in chlorobenzene solution. The antioxidant was 2,6-di-t-butyl-4-methylphenol. The units of k and A are dm³ mol⁻¹ s⁻¹. The units of E are kJ mol⁻¹. For a discussion of errors, see references b and h.

*A further termination reaction, which apparently involved abstraction of an α-hydrogen atom from the hydrocarbon by a peroxyl radical, was observed. The reported rate parameters at 30 °C are $k_x = 0.24$, $\log A_x = 7.8$, $E_x = 49$ for styrene and $k_x = 0.30$, $\log A_x = 5.9$, $E_x = 37$ for 4-methoxystyrene. This termination reaction was not observed with α-methylstyrene.

(a) J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1967, **45**, 793; (b) J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1966, **44**, 1113, 1119; (c) J. R. Thomas and K. U. Ingold, *Advances in Chemistry Series*, 1968, **75**, 258; (d) J. Betts and J. C. Robb, *Trans. Faraday Soc.*, 1968, **64**, 2402, 1969, **65**, 195, 2144; (e) D. G. Hendry, *J. Amer. Chem. Soc.*, 1967, **89**, 5433; (f) H. Berger, A. M. W. Blaauw, M. M. Al, and P. Smael, *Advances in Chemistry Series*, 1968, **75**, 346; (g) V. F. Tsepalov and V. Ya. Shlyapintokh, *Kinetika i Kataliz*, 1962, **3**, 870; A. A. Vichutinskii, *Russ. J. Phys. Chem.*, 1964, **38**, 1242; (h) J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1965, **43**, 2729, 2737.

which segments have been cut. From measurements of the average autoxidation rate as a function of sector speed the chain lifetime under steady illumination may be calculated. This is the average time that elapses between the initiation of an autoxidation chain and its termination. It is related to $2k_t$ by the equation:

$$\text{chain lifetime} = \frac{\text{population}}{\text{birth rate}} = \frac{[RO_2{}^{\cdot}]}{R_i} = \frac{1}{(2k_t R_i)^{\frac{1}{2}}} \tag{25}$$

Combination of $2k_t$ with $k_p/(2k_t)^{\frac{1}{2}}$ and k_p/k_a gives absolute values of k_p and k_a.

Alternatively, the photochemical pre- and after-effects may be studied,[35,37] as may the effect of adding small amounts of initiator or antioxidant to a thermally initiated autoxidation.[18,38] These methods require very sensitive measurements of autoxidation rate.[18,35-38] In recent years, electron spin resonance has been used to follow the self-termination of alkylperoxyl radicals [reaction (5)] directly.[39,40]

Some absolute rate constants are shown in Table 1. The A's and E's were calculated from the simple Arrhenius equation $\log k = \log A - E/2 \cdot 3RT$. These data are discussed in the next section. The k_p's are not directly comparable since, in passing from one hydrocarbon to another, the peroxyl radical is changed also. It is not immediately obvious which change has the greater influence on k_p. We shall see later how this problem is overcome by studying the co-oxidation of pairs of hydrocarbons. Meanwhile, an alternative and very elegant technique will be described.

If a hydrocarbon, R^1H, is autoxidised in the presence of a sufficient quantity of hydroperoxide, R^2O_2H, the following chain transfer reaction occurs efficiently.[41]

$$R^1O_2{}^{\cdot} + R^2O_2H \rightarrow R^1O_2H + R^2O_2{}^{\cdot} \tag{26}$$
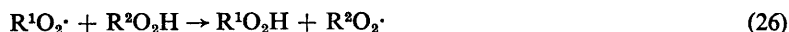
As a result, $R^2O_2{}^{\cdot}$ radicals alone participate in chain propagation and termination

$$R^2O_2{}^{\cdot} + R^1H \rightarrow R^2O_2H + R^{1\cdot} \qquad\qquad k_p{}^{21} \tag{27}$$

$$2R^2O_2{}^{\cdot} \rightarrow \text{stable products} + O_2 \qquad\qquad 2k_t{}^{22} \tag{28}$$

since reaction (27) is invariably followed by (3) and (26), re-forming the $R^2O_2{}^{\cdot}$ radicals. The rate of autoxidation is therefore given by:[41]

$$- \text{d}[O_2]/\text{dt} = \text{d}[R^1O_2H]/\text{dt} = k_p{}^{21} [R^1H](R_i/2k_t{}^{22})^{\frac{1}{2}} \tag{29}$$

If $2k_t{}^{22}$ is known, *e.g.* from rotating sector studies, $k_p{}^{21}$ may be calculated. Values for various combinations of peroxyl radical and hydrocarbon are shown in Table 2. The method depends upon the availability of a stable hydroperoxide, R^2O_2H, to form the desired peroxyl radical and upon the efficiency of reaction (26).[41]

6 Structure and Reactivity
The rate constants in Table 2 clearly depend on the chosen hydrocarbon, rather

[41] J. A. Howard, W. J. Schwalm, and K. U. Ingold, *Advances in Chemistry Series*, 1968, **75**, 6; J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1968, **46**, 2655, 2661.

Table 2 *Absolute rate constants* ($k_p{}^{21}$, $dm^3\ mol^{-1}\ s^{-1}$) *at 30 °C, determined by the hydroperoxide method*

Peroxyl radical	Hydrocarbon						
	Toluene	Ethylbenzene	Cumene	Tetralin	Styrene	α-Methylstyrene	9,10-Dihydroanthracene
n-Butyl	0·1	0·55	0·45	6·4	14	25	310
s-Butyl	0·1	0·5	0·4	4·2	6·3	12	140
t-Butyl	0·05	0·20	0·22	2·0	1·05	—	—
Cumyl	0·03	0·18	0·18	1·65	2·1	—	—
Cyclohexyl	—	0·5	—	4·5	6·8	14	160
Dihydroanthracyl	—	0·6	—	6·5	21	33	330
Tetralyl	0·1	0·5	0·5	6·3	8·8	16	240

Data taken from J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1968, **46**, 2655, 2661.

than the peroxyl radical. This is not unexpected, since the variable alkyl portion in $R^2O_2\cdot$ is somewhat remote from its reactive centre. Moreover, the e.s.r. spectra of various alkylperoxyl radicals are almost identical, indicating that the unpaired electron is largely located on the peroxy-group.[40] The least reactive radicals, cumylperoxyl and t-butylperoxyl, are both tertiary. Their reactivity is probably diminished by steric hindrance.[41]

Similar considerations apply to the k_p and k_a values in Table 1. The former vary considerably from one hydrocarbon to another, whereas the latter change but little with the peroxyl radical attacking a given antioxidant. The lowest k_p is displayed by cyclohexane, which is alone among the hydrocarbons listed in not giving a resonance-stabilised radical by reaction (4) or (10). Since alkylperoxyl radicals are electrophilic, k_p and k_a are susceptible to polar influences. Thus, they generally increase slightly in solvents of high dielectric constant, although specific solvent effects such as hydrogen bonding can be equally important.[42] Similarly, they are influenced by the presence of electron-donating or -withdrawing substituents in the aromatic rings of hydrocarbons such as cumene[11,43,44] and styrene,[45] and of phenolic[46] and other chain-breaking[47] antioxidants. It is considered that some charge separation must occur in the transition states of reactions (4), (10), and (20). For example, the transition state of (10) in styrene autoxidation has been represented as follows:[45]

$$\underset{(1)}{RO_2\cdot CH_2{=}CHPh} \leftrightarrow \underset{(2)}{RO_2{-}\overset{\delta^-}{CH_2}{\doteq}\overset{\delta^+}{CHC_6H_5}} \leftrightarrow \underset{(3)}{RO_2CH_2{-}\dot{C}HPh} \qquad (30)$$

The unpaired electron in (3) occupies an orbital extending over the aromatic ring. However, ring-substituents also favour resonance-stabilisation of these transition states,[45,46] so that the extent of their polar influence is uncertain. This subject has been discussed in detail elsewhere.[42-47]

The self-termination of alkylperoxyl radicals is more complicated than was implied by equation (5). E.s.r. studies have shown that at low temperatures they combine reversibly to form tetroxides:[40,48]

$$2RO_2\cdot \rightleftharpoons RO_4R \qquad (31)$$

At higher temperatures self-termination presumably proceeds *via* irreversible decomposition of these tetroxides.[40,48] In the case of primary and secondary alkylperoxyl radicals an α-hydrogen atom is transferred:[49]

[40] D. G. Hendry and G. A. Russell, *J. Amer. Chem. Soc.*, 1964, **86**, 2368; J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1964, **42**, 1044, 1250.

[43] G. A. Russell and R. C. Williamson, *J. Amer. Chem. Soc.*, 1964, **86**, 2357.

[44] J. A. Howard, K. U. Ingold, and M. Symonds, *Canad. J. Chem.*, 1968, **46**, 1017.

[45] J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1965, **43**, 2737.

[46] J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1963, **41**, 1744; M. A. Da Rooge and L. R. Mahoney, *J. Org. Chem.*, 1967, **32**, 1.

[47] I. T. Brownlie and K. U. Ingold, *Canad. J. Chem.*, 1967, **45**, 2419, 2427.

[48] K. Adamic, J. A. Howard, and K. U. Ingold, *Chem. Comm.*, 1969, 505.

[49] G. A. Russell, *J. Amer. Chem. Soc.*, 1957, **79**, 3871; J. A. Howard and K. U. Ingold, *ibid.*, 1968, **90**, 1056, 1058.

$$R_2CO + O_2 + R_2CHOH \qquad (32)$$

Replacement of this hydrogen by deuterium reduces $2k_t$ by about half.[40,45,49] Tertiary alkylperoxyl radicals cannot self-terminate in this manner, but react instead to give pairs of alkoxyl radicals within a solvent cage:[40,41]

$$R_3CO_4CR_3 \rightarrow 2R_3CO\cdot + O_2 \qquad (33)$$

The alkoxyl radicals may combine within the cage, yielding a peroxide $R_3CO_2CR_3$, but they usually diffuse apart. Some initiate further autoxidation chains, whilst others fragment to smaller radicals which *can* terminate efficiently by (32). The appropriate sequence for cumyloxyl radicals is:[44]

$$PhMe_2CO\cdot \xrightarrow{O_2} PhCOMe + MeO_2\cdot \qquad (34)$$

$$MeO_2\cdot + PhMe_2CO_2\cdot \rightarrow CH_2O + O_2 + PhMe_2COH \qquad (35)$$
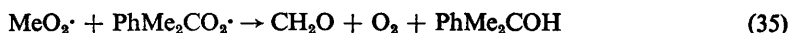
In support of this mechanism, cumene autoxidises more rapidly in the presence of its hydroperoxide.[41,44] This is because cumyloxyl radicals transfer readily with the hydroperoxide to re-form cumylperoxyl radicals

$$PhMe_2CO\cdot + PhMe_2CO_2H \rightarrow PhMe_2COH + PhMe_2CO_2\cdot \qquad (36)$$

thereby eliminating the termination sequence (34) and (35). Furthermore, if cumene is autoxidised using a mixture of $^{16}O^{-16}O$ and $^{18}O^{-18}O$, 'scrambling' of the oxygen isotopes by (33) occurs much more rapidly than chain termination.[50] The lowest $2k_t$ values in Table 1 are displayed by the tertiary hydrocarbons, cumene, and α-methylstyrene.

Some equilibrium constants for reaction (31) have been reported.[40,48] On the assumption that (31) is a rapid pre-equilibrium preceding the slower reactions (32) and (33), these equilibrium constants can be combined with $2k_t$ values at several temperatures to give a detailed picture of the tetroxide decomposition.[40,48]

7 Co-oxidation Studies

If two hydrocarbons, R^1H and R^2H, are co-oxidised, four propagation steps must be considered. These are[51]

$$R^1O_2\cdot + R^1H \rightarrow R^1O_2H + R^1\cdot \qquad k_p^{11} \qquad (37)$$

$$R^1O_2\cdot + R^2H \rightarrow R^1O_2H + R^2\cdot \qquad k_p^{12} \qquad (38)$$

$$R^2O_2\cdot + R^2H \rightarrow R^2O_2H + R^2\cdot \qquad k_p^{22} \qquad (39)$$

[50] P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, 1963, **85**, 2407.
[51] G. A. Russell, *J. Amer. Chem. Soc.*, 1955, **77**, 4583.

and reaction (27). Each is invariably followed by reaction (3). The relative rates of hydrocarbon disappearance are given by:

$$\frac{d[R^1H]}{d[R^2H]} = \frac{d[R^1O_2H]}{d[R^2O_2H]} = \frac{[R^1O_2\cdot](k_p{}^{11}[R^1H] + k_p{}^{12}[R^2H])}{[R^2O_2\cdot](k_p{}^{22}[R^2H] + k_p{}^{21}[R^1H])} \quad (40)$$

If the autoxidation chains are long, interconversion of peroxyl radicals by (38) and (27) proceeds much more quickly than chain initiation or termination. The radical concentrations $[R^1O_2\cdot]$ and $[R^2O_2\cdot]$ may therefore be eliminated from (40) by noting that $k_p{}^{12}[R^1O_2\cdot][R^2H] = k_p{}^{21}[R^2O_2\cdot][R^1H]$. It follows that[26,51]

$$\frac{d[R^1H]}{d[R^2H]} = \frac{d[R^1O_2H]}{d[R^2O_2H]} = \frac{r_1[R^1H]/[R^2H] + 1}{r_2[R^2H]/[R^1H] + 1} \quad (41)$$

in which $r_1 = k_p{}^{11}/k_p{}^{12}$ and $r_2 = k_p{}^{22}/k_p{}^{21}$. If $d[R^1H]/d[R^2H]$ is measured at several values of $[R^1H]/[R^2H]$, the reactivity ratios r_1 and r_2 can be found graphically.[26,52] If oxygen consumption is measured, only one hydrocarbon or hydroperoxide need by analysed,[52] since $- d[O_2]/dt = - d[R^1H + R^2H]/dt = d[R^1O_2H + R^2O_2H]/dt$. For accuracy, low conversions must be employed. This keeps $[R^1H]/[R^2H]$ effectively constant and avoids interconversion of peroxyl radicals by reaction (26) as hydroperoxide accumulates.[26]

For long autoxidation chains the rate of oxygen consumption is given by[8,51]

$$\frac{- d[O_2]}{dt} = \frac{(r_1[R^1H]^2 + 2[R^1H][R^2H] + r_2[R^2H]^2)R_i{}^{\frac{1}{2}}}{(r_1{}^2\delta_1{}^2[R^1H]^2 + 2\phi r_1 r_2 \delta_1 \delta_2[R^1H][R^2H] + r_2{}^2\delta_2{}^2[R^2H]^2)^{\frac{1}{2}}} \quad (42)$$

in which $\delta_1 = (2k_t{}^{11})^{\frac{1}{2}}/k_p{}^{11}$, $\delta_2 = (2k_t{}^{22})^{\frac{1}{2}}/k_p{}^{22}$, $\phi = k_t{}^{12}/(k_t{}^{11}k_t{}^{22})^{\frac{1}{2}}$ and the self-termination constants are defined as follows:

$$R_i = 2k_t{}^{11}[R^1O_2\cdot]^2 + 4k_t{}^{12}[R^1O_2\cdot][R^2O_2\cdot] + 2k_t{}^{22}[R^2O_2\cdot]^2 \quad (43)$$

The definition of $k_t{}^{12}$ allows for a statistical factor of 2 favouring 'cross-termination' between unlike peroxyl radicals.[51] A derivation of (42) has been published.[8,51] If the rate of oxygen consumption is measured accurately over a range of hydrocarbon concentrations, 'best' values of r_1, r_2 and ϕ may be calculated from equation (42) using a high-speed computer.[53] In view of the industrial importance of co-oxidation, this recently developed method should find wide application. It demands less experimental work than the use of (41).

Some co-oxidation data are shown in Table 3. Despite the wide variations in r_1 and r_2, the product $r_1 r_2$ is comparatively constant. This is because the ratios r_1 and r_2 are largely dependent on the reactivities of the hydrocarbons, rather than their peroxyl radicals. A large r_1 indicates that $R^1O_2\cdot$ attacks R^1H rather than R^2H; but in that case $R^2O_2\cdot$ will behave similarly (see Section 6) making r_2 small.

[52] D. G. Hendry, *Advances in Chemistry Series*, 1968, **75**, 24.
[53] C. Chevriau, P. Naffa, and J. C. Balaceanu, *Bull. Soc. chim. France*, 1964, 3002; L. Sajus, *Advances in Chemistry Series*, 1968, **75**, 59; E. Niki, Y. Kamiya, and N. Ohta, *Bull. Chem. Soc. Japan*, 1969, **42**, 512.
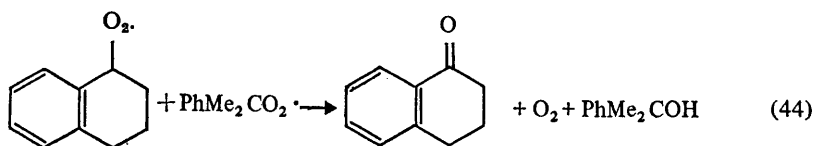
Table 3 *Co-oxidation of hydrocarbons*

R¹H	R²H	Temp. (°C)	r_1	r_2	r_1r_2	ϕ	Ref.
Buta-1,3-diene	Styrene	30	1·5	0·7	1·0	—	a
		50	2·2	0·42	0·9	—	a
		80	2·8	0·30	0·8	—	a
Cumene	Tetralin	30	0·11	12·8	1·4	5·9	b
		56	0·18	7·0	1·3	3·8	b
		60	0·13	4·6	0·6	—	c
		80	0·21	5·0	1·05	4·3	d
Styrene	Tetralin	60	2·3	0·43	1·0	—	c
		70	2·7	0·49	1·3	3·9	d
Cumene	Styrene	60	0·05	20	1·0	—	c
		60	0·1	13	1·3	5·3	e

(a) D. G. Hendry, *Advances in Chemistry Series*, 1968, 75, 24; (b) J. A. Howard, W. J. Schwalm, and K. U. Ingold, *Advances in Chemistry Series*, 1968, 75, 6; (c) F. R. Mayo, M G. Syz, T. Mill, and J. Castleman, *Advances in Chemistry Series*, 1968, 75, 38; (d) E. Niki, Y. Kamiya, and N. Ohta, *Bull. Chem. Soc. Japan.*, 1969, 42, 512; (e) C. Chevriau, P. Naffa, and J. C. Balaceanu, *Bull Soc. chim. France*, 1964, 3002.

These opposing effects tend to cancel in r_1r_2. Since $\phi > 1$, cross-termination of peroxyl radicals must be favoured.

It is an interesting feature of co-oxidations that the autoxidation of a tertiary hydrocarbon can be retarded by low concentrations of a secondary hydrocarbon, even though the latter by itself would autoxidise more quickly.[11] This is illustrated for cumene and tetralin by curve D in Figure 2. The explanation is that cumylperoxyl radicals attack tetralin rather than cumene (see Tables 2 and 3) and the tetralylperoxyl radicals so formed, possessing α-hydrogen atoms, are able to cross-terminate efficiently with the remaining cumylperoxyl radicals:[51]

$$+ \text{PhMe}_2 \text{CO}_2 \cdot \longrightarrow \quad + \text{O}_2 + \text{PhMe}_2 \text{COH} \qquad (44)$$

As the tetralin concentration is increased, the autoxidation rate passes through a minimum, because of an overall increase in reactivity of the hydrocarbon mixture towards peroxyl radicals.[51] The co-oxidation of secondary hydrocarbons with tetralin (curves A, B, and C) is free from this effect, because their peroxyl radicals can self-terminate efficiently.

8 Transition Metal Compounds

Compounds of transition metals play an important role in many everyday autoxidations, whether usefully, as in the drying of linseed oil paints, or hurtfully, as in the deterioration of lubricating oils in contact with metallic surfaces. At low
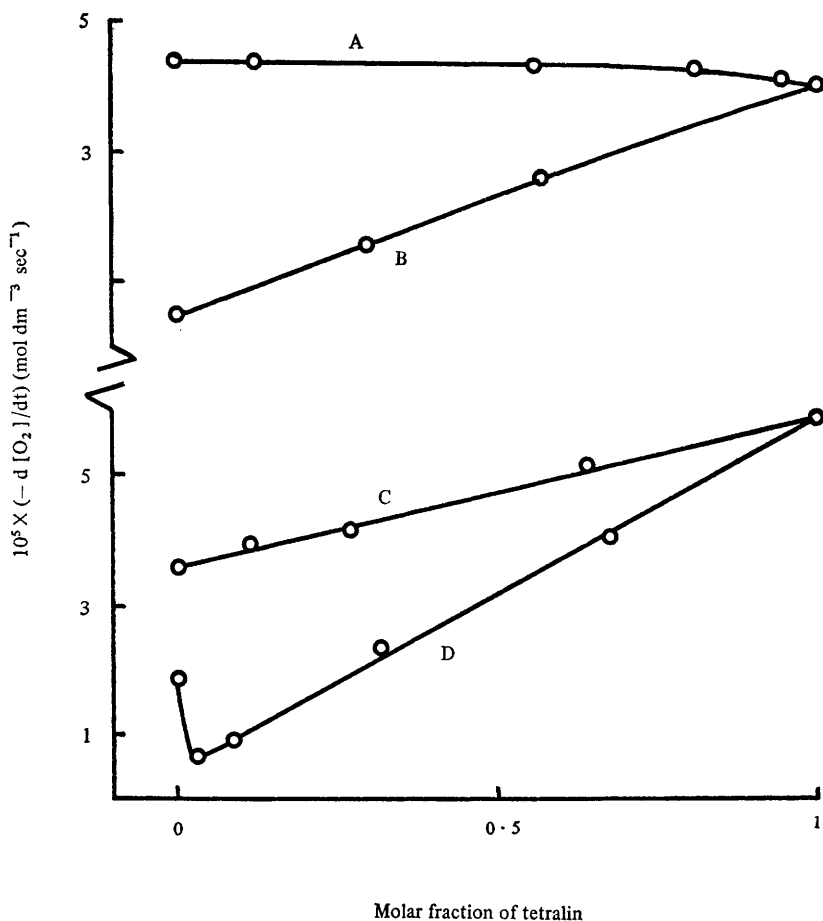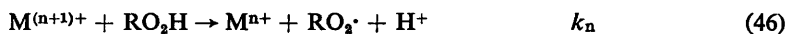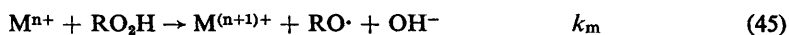
Figure 2 *Co-oxidation of tetralin with other hydrocarbons.* A: *cyclohexene*, B: *ethylbenzene initiated by* 0·06 mol dm⁻³ *azo-di-isobutyronitrile at* 60 °C (J. Alagy, G. Clément, and J. C. Balaceanu, *Bull. Soc. chim. France*, 1959, 1325, 1961, 1792); C: *indan*, D: *cumene initiated by* 0·02 mol dm⁻³ *t-butyl perbenzoate at* 90 °C (G. A. Russell, *J. Amer. Chem. Soc.*, 1955, **77**, 4583; 1956, **78**, 1047).

concentrations their chief effect is to initiate autoxidation by converting hydro-peroxides to radicals:[54,55]

$$M^{n+} + RO_2H \rightarrow M^{(n+1)+} + RO\cdot + OH^- \qquad k_m \qquad (45)$$

$$M^{(n+1)+} + RO_2H \rightarrow M^{n+} + RO_2\cdot + H^+ \qquad k_n \qquad (46)$$

[54] N. Uri, ref. 6, vol. 1, chap. 2.
[55] Y. Kamiya, S. Beaton, A. Lafortune, and K. U. Ingold, *Canad. J. Chem.*, 1963, **41**, 2020, 2034; Y. Kamiya and K. U. Ingold, *ibid.*, 1964, **42**, 1027, 2424.

4

Metals such as cobalt and manganese, which can alternate between adjacent valency states and undergo both reactions (45) and (46), decompose hydroperoxides catalytically. When equilibrium has been established between the two valency states of the metal, $k_m[M^{n+}][RO_2H] = k_n[M^{(n+1)+}][RO_2H]$ and the initiation rate is given by

$$R_i = (k_m[M^{n+}] + k_n[M^{(n+1)+}])[RO_2H] = 2k_mk_n[M][RO_2H]/(k_m + k_n) \tag{47}$$

in which $[M] = [M^{n+}] + [M^{(n+1)+}]$. The autoxidation rate, which is given by equation (8), depends on the square root of the total metal concentration. As hydroperoxide accumulates, the autoxidation accelerates. The hydroperoxide concentration eventually attains a maximum value, at which its decomposition by reactions (45) and (46) exactly counterbalances its formation by (4). On the assumption that the alkoxyl radicals produced in (45) react quantitatively with hydrocarbon according to (18), it may be shown that:[8,55]

$$- d[O_2]/dt = k_p^2[RH]^2/2k_t \tag{48}$$

The limiting autoxidation rate is thus independent of the total metal concentration. This interesting result has been observed in various autoxidation systems.[55] Nevertheless, equation (48) may not be a reliable source of $k_p/(2k_t)^{\frac{1}{2}}$ values, since its derivation takes no account of alkoxyl radical attack upon hydroperoxide [reaction (36)]. Moreover, the polarity of a medium rich in hydroperoxide and metal ions would probably affect the value of $k_p/(2k_t)^{\frac{1}{2}}$.[55]

Compounds of transition metals have been reported to initiate autoxidation by oxidising particularly reactive hydrocarbons[56,57]

$$M^{(n+1)+} + RH \rightarrow M^{n+} + R\cdot + H^+ \tag{49}$$

such as linoleic acid.[57] In the absence of hydroperoxides, reaction with molecular oxygen has also been observed.[58-60] Uri[59] has formulated this as follows:

$$Co^{2+}(XH)\cdot O_2 \rightarrow Co^{3+}(X^-) + HO_2\cdot \tag{50}$$

in the case of bis(*N*-butylsalicylaldimino)cobalt(II) and similar compounds. Complex formation between chelate and oxygen apparently precedes the radical-producing step (50).[59,60]

In their lower valency states, transition metals can also terminate autoxidation chains by reducing alkylperoxyl radicals to hydroperoxides and other products.[55,59-61] Uri reports that, for the chelates mentioned above, this termination is second-order in metal concentration, so that these compounds display the

[56] W. A. Waters, *Discuss. Faraday Soc.*, 1968, **46**, 158.
[57] F. W. Heaton and N. Uri, *J. Lipid Res.*, 1961, **2**, 152.
[58] L. N. Denisova, E. T. Denisov, and T. G. Degtyareva, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1966, 1095.
[59] A. T. Betts and N. Uri, *Makromol. Chem.*, 1966, **95**, 22; *Advances in Chemistry Series*, 1968. **76**, 160.
[60] C. Copping and N. Uri, *Discuss. Faraday. Soc.*, 1968, **46**, 202.
[61] V. P. Shcheredin and E. T. Denisov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1967, 1428.

unusual feature of initiating autoxidation at low concentrations, but behaving as antioxidants at higher concentrations.[59,60]

The behaviour of transition metals in autoxidation systems is, of course, strongly dependent on the ligands attached to them.[54,55] In this section they have been written as 'naked ions' merely for convenience. A detailed account of their chemistry in autoxidation systems has been given by Reich and Stivala.[8]

9 Antioxidant Behaviour

In Section 4 we saw how simple phenolic antioxidants terminate autoxidation chains by hydrogen-atom transfer. If the phenolic hydrogen is replaced by deuterium, k_a is markedly reduced.[62,63] In the simplest cases the phenoxyl radical formed by (20) combines with a second alkylperoxyl radical to yield a substituted cyclohexadienone.[31,32] For example, the 2,6-di-t-butyl-4-methylphenoxyl radical reacts thus:

$$RO_2\cdot \ + \qquad\qquad\qquad \longrightarrow \qquad\qquad\qquad \tag{51}$$
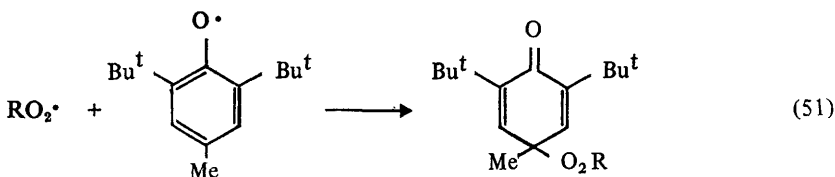
Some phenoxyl radicals disappear by self-coupling reactions also.[32] Phenoxyl radicals having either or both ortho positions free are sufficiently reactive to initiate further autoxidation by abstracting hydrogen from the hydrocarbon or its hydroperoxide:

$$A\cdot \ + \ RH(RO_2H) \rightarrow AH + R\cdot(RO_2\cdot) \tag{52}$$
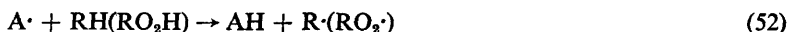
This chain-transfer reaction can lead to considerable kinetic complications, as has been discussed in detail elsewhere.[63,64] Some rate constants for (52) have been reported.[64,65]

In addition to phenols, primary and secondary aromatic amines are popular antioxidants.[7,8] These also terminate autoxidation chains by reaction (20): replacement of the amine hydrogen by deuterium lowers k_a.[47,66] The aminoradicals so formed do not usually disappear by reaction (21); instead, they react with alkylperoxyl radicals as follows:[47,66]

$$RO_2\cdot \ + \ R_2N\cdot \rightarrow RO\cdot + R_2NO \tag{53}$$

[62] J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1962, **40**, 1851.
[63] J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1964, **42**, 2324.
[64] L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, 1967, **89**, 5619.
[65] M. B. Neiman, U. G. Mamedova, P. Blenke, and A. L. Buchachenko, *Doklady Akad. Nauk S.S.S.R.*, 1962, **144**, 392; Yu. G. Mamedova, A. L. Buchachenko, and M. B. Neiman, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1965, 911; J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 4807.
[66] I. T. Brownlie and K. U. Ingold. *Canad. J. Chem.*, 1966, **44**, 861.

The nitroxide, R_2NO, is itself a weak antioxidant. The alkoxyl radicals initiate further autoxidation. Amino-radicals can also chain-transfer by reaction (52).[47,65,66] Simpler kinetics are, however, followed by the *p*-phenylenediamines, which apparently transfer both amino-hydrogens in succession to alkylperoxyl radicals:[31,47]

$$2RO_2\cdot + RNHC_6H_4NHR \rightarrow 2RO_2H + RN{=}C_6H_4{=}NR \qquad (54)$$
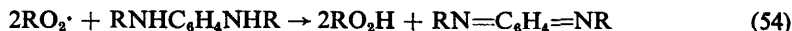
Because they simply reduce the lifetime of autoxidation chains already begun, chain-breaking antioxidants are comparatively ineffective for suppressing autoxidations with high initiation rates. This situation arises, for example, in hydrocarbons in which large amounts of hydroperoxide have accumulated. For this reason, an important class of antioxidants has been developed to suppress the initiation act. One group of compounds, which includes the zinc dialkyldithio-phosphates and other organic sulphur compounds,[67] destroys hydroperoxides by non-radical producing mechanisms. Another group suppresses the decomposition of hydroperoxides to radicals by traces of heavy metals. The chelating agents involved, such as various organic hydroxy-acids[68] and derivatives of ethylene-diaminetetra-acetic acid,[68] act by precipitating the metals from solution or modifying their redox potentials sufficiently that one of reactions (45) and (46) is prevented. This 'protective' action is not possible, however, if the metal is already strongly chelated, as in the phthalocyanines.[68] Where photo-initiation is important, light absorbers such as carbon black are effective antioxidants.[7]

Mixtures of antioxidants can suppress autoxidation more strongly than might be expected from consideration of their separate efficiencies. This phenomenon, known as synergism, is most commonly encountered when a hydroperoxide destroyer and chain-breaker are combined. The former reduces the initiation rate to a low level and the latter terminates any autoxidation chains that are started. Synergistic combinations of chain-breakers are known also. 4-Methoxyphenol and 2,4,6-tri-t-butylphenol (TBP) provide an example.[64] 4-Methoxyphenol is the better scavenger of alkylperoxyl radicals, but its own radical can initiate further autoxidation by reaction (52). This is prevented by TBP, which scavenges the 4-methoxyphenoxyl radicals. The 2,4,6-tri-t-butylphenoxyl radicals themselves disappear by (21) to complete the termination sequence.

It is not uncommon for a single antioxidant to act in several ways. For example, (stilbene dithiolate)nickel scavenges peroxyl radicals,[60] destroys hydroperoxides[60] and absorbs u.v. radiation.[69] The separate assessment of each mode of action is commercially and theoretically important.[70] Further details on antioxidant behaviour may be found in recent publications.[7,8,68,71]

[67] D. Barnard, L. Bateman, M. E. Cain, T. Colclough, and J. I. Cuneen, *J. Chem. Soc.*, 1961, 5339; L. Bateman, M. E. Cain, T. Colclough, and J. I. Cuneen, *ibid.*, 1962, 3570; T. Colclough and J. I. Cuneen, *ibid.*, 1964, 4790; A. J. Burn, *Advances in Chemistry Series*, 1968, **75**, 323.
[68] N. Uri, ref. 6, vol. 1, chap. 4.
[69] N. Uri, private communication.
[70] J. D. Holdsworth, G. Scott, and D. Williams, *J. Chem. Soc.*, 1964, 4692; H. Low, *Ind. Eng. Chem. Product Research and Development*, 1966, 5, 80.
[71] K. U. Ingold, *Chem. Rev.*, 1961, **61**, 563; *Advances in Chemistry Series*, 1968, **75**, 296.

10 Purification of Hydrocarbons and Spontaneous Initiation

In view of the sensitivity of hydrocarbon autoxidation to impurities, careful purification is essential prior to kinetic studies. Usually, hydrocarbons are refluxed with a hydroperoxide destroyer and fractionally distilled under nitrogen. Any hydroperoxides formed during storage can be reduced to minute levels by percolation through a column of chromatographic alumina or iron-free[72] silica gel. Gas–liquid chromatography, invaluable for assessing hydrocarbon purity, has been used preparatively with volatile materials.[22] Privett[73] has reviewed the preparation of the commercially important polyunsaturated fatty acids from natural sources. Storage under nitrogen is recommended.[57,73]

Even rigorously purified hydrocarbons autoxidise to some extent. Various sources of 'spontaneous initiation' have been suggested. These include the effect of trace metals at levels requiring neutron-activation analysis for their detection,[54] glass surfaces,[74] and a direct radical-forming reaction between hydrocarbon and molecular oxygen.[17,74,75] In the case of hydrocarbons derived from natural sources, adventitious traces of photosensitisers may be active.[76] These can produce hydroperoxides by the mechanism outlined in Section 13 and decomposition of these hydroperoxides initiates the usual autoxidation chain.[76] Natural background radiation appears to be unimportant as a source of radicals.[54]

11 Low Oxygen Concentrations

So far, we have considered autoxidations in which alkyl radicals react exclusively according to (3). At low oxygen concentrations, however, they survive long enough to participate in the additional termination steps:[3]

$$R\cdot + RO_2\cdot \rightarrow \text{stable products} \qquad 4k_{t_1} \qquad (55)$$

$$2R\cdot \rightarrow \text{stable products} \qquad 2k_{t_2} \qquad (56)$$

As a result, the autoxidation rate $(R = -\,d[O_2]/dt)$ falls below its limiting value (R_∞) at high oxygen concentrations. On the basis of reactions (2)—(5), (55), and (56), assuming long kinetic chains, it may be shown that:[54]

$$[(R_\infty/R)^2 - 1][O_2] = k_{t_2}k_p^2[RH]^2/k_ik_o^2[O_2] + 2\phi k_p(2k_{t_2})^{\frac{1}{2}}[RH]/k_o(2k_t)^{\frac{1}{2}} \qquad (57)$$

The termination constants are defined by

$$R_i = 2k_t[RO_2\cdot]^2 + 4k_{t_1}[R\cdot][RO_2\cdot] + 2k_{t_2}[R\cdot]^2 \qquad (58)$$

and $\phi = k_{t_1}/(k_tk_{t_2})^{\frac{1}{2}}$. A linear plot of $[(R_\infty/R)^2 - 1][O_2]$ against $[O_2]^{-1}$ gives $k_o/(2k_{t_2})^{\frac{1}{2}}$ and ϕ, provided that $k_p/(2k_t)^{\frac{1}{2}}$ has already been obtained from rate

[72] J. F. Ford, V. O. Young, and R. C. Pitkethly, *Advances in Chemistry Series*, 1968, **76**, 207.
[73] O. S. Privett, *Progr. Chem. Fats and Other Lipids*, 1968, **9**, 407.
[74] D. J. Carlsson and J. C. Robb, *Trans. Faraday Soc.*, 1966, **62**, 3403.
[75] E. T. Denisov, *Kinetika i Kataliz*, 1963, **4**, 53; *Russ. J. Phys. Chem.*, 1964, **38**, 1; L. N. Denisova and E. T. Denisov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1965, 1702; L. Dulog, *Makromol. Chem.*, 1964, 76 119.
[76] H. R. Rawls and P. J. van Santen, *Tetrahedron Letters*, 1968, 1675.

measurements at high oxygen concentrations, using equation (8). If oxygen uptake is measured, the work involved is tedious, since a fresh experiment is required for each rate determination at a new oxygen concentration. Consequently, few results have been published since the surveys of Bateman[3] and Uri,[54] to which the reader is referred for further details. Recently however, the chemiluminescence method[23] has been employed to follow in a single experiment the decline in autoxidation rate (R) as a pre-saturated solution becomes depleted in oxygen. Since the thermocouple,[22] oxygen electrode,[21] and spectrophotometric[20] methods should prove equally labour-saving, further research in this field may be anticipated.

The efficiency of reaction (3) derives from the fact that molecular oxygen is a biradical: k_0 values ranging from 10^6 to 10^8 dm^3 mol^{-1} s^{-1} have been reported.[3,54,77] In most air-saturated hydrocarbons, which contain $\geqslant 10^{-3}$ mol dm^{-3} of oxygen, conversion of alkyl to alkylperoxyl radicals proceeds quantitatively. However, in the case of particularly reactive materials,[3] such as ethyl linolenate and 2,6-dimethylhepta-2,5-diene, reaction (4) can compete with (3) even at moderate oxygen concentrations, say $> 2 \times 10^{-3}$ mol dm^{-3}. At low oxygen concentrations antioxidant behaviour may change markedly.[78] Thus, the diarylnitroxides are relatively inert towards alkylperoxyl radicals, but scavenge alkyl radicals efficiently.[47] Cupric compounds also scavenge alkyl radicals efficiently.[79]

12 Autoxidation of Polymers

The autoxidation of polymers has been copiously reviewed elsewhere,[7,8,80,81] but will be briefly mentioned here because of its everyday importance. As regards the basic chain mechanism, it resembles the autoxidation of low-molecular-weight hydrocarbons in the liquid phase.[8,82] Some significant differences should, however, be noted. Thus, the autoxidation of solid polymers is frequently controlled by diffusion of oxygen into the material,[8] rather than by chemical factors, so that kinetic studies must be restricted to thin films.[83] Furthermore, the physical properties of a polymer may be transformed at comparatively small extents of autoxidation, owing to the marked molecular weight changes caused by scission or cross-linking of the polymer molecules.[8,84] In relating the autoxidation characteristics of a polymer to its structure, resort is often made to model compounds of low molecular weight.[81,82] These are easier to prepare in a high state of purity, and their autoxidation products are more easily handled. For

[77] C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.*, 1949, **198A**, 252; D. G. Hendry, F. R. Mayo, and D. Scheutzle, *Ind. Eng. Chem.*, *Product Research and Development*, 1968, **7**, 136.

[78] R. Marcuse and P. O. Frederiksson, *J. Amer. Oil Chemists' Soc.*, 1969, **46**, 262.

[79] R. Marcuse and P. O. Frederiksson in 'Metal Catalysed Lipid Oxidation,' ed. R. Marcuse, Swedish Institute for Food Preservation Research, Göteburg, 1968, p. 97.

[80] M. Tryon and L. A. Wall, ref. 6, vol. 2, chap. 19; W. L. Hawkins, *Oxidation and Combustion Reviews*, 1965, **1**, 169; L. Reich and S. S. Stivala, *Reviews in Macromolecular Chemistry*, 1967, **1**, 249.

[81] P. M. Norling, T. C. P. Lee, and A. V. Tobolsky, *Rubber Chem. Technol.*, 1965, **38**, 1198; J. I. Cuneen, *ibid.*, 1968, **41**, 182.

[82] N. Uri, *Chem. and Ind.*, 1967, 2060.

[83] N. Grassie and N. A. Weir, *J. Appl. Polymer Sci.*, 1965, **9**, 963.

[84] J. B. Lawrence and N. A. Weir, *Chem. Comm.*, 1966, 257.

example, 2,6,10,14-tetramethylpentadecane has been studied as a model compound for polypropylene.[82] The mobility of alkylperoxyl radicals is restricted in solid polymers[8,82] and some doubt exists concerning the mechanism of chain termination in the absence of added antioxidants.[8]

13 Singlet Oxygen[27,85-88]

This species is conveniently prepared by photolysis in the presence of a suitable sensitiser, S, which can transfer its triplet excitation energy to oxygen by collision:[27]

$$^1S + h\nu \rightarrow {}^3S \tag{59}$$

$$^3S + {}^3O_2 \rightarrow {}^1S + {}^1O_2 \tag{60}$$
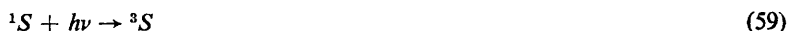
The superscripts refer to the singlet and triplet states. Reaction (60) proceeds quantitatively in air-saturated organic solvents.[27] The singlet oxygen combines with an olefinic hydrocarbon or decays to its triplet ground state:[27]

$$^1O_2 + RH \rightarrow RO_2H \qquad\qquad k_c \tag{61}$$

$$^1O_2 \rightarrow {}^3O_2 \qquad\qquad k_d \tag{62}$$

Compounds such as rubrene, which contain a cyclic dienoid system, yield transannular peroxides.[85] Mono-olefins yield hydroperoxides by (61), accompanied by a 1:2 shift of the double bond.[27,85] Since no allylic radicals are involved, the products differ from those of free-radical autoxidation.[27,85] The quantum yields for production of triplet sensitiser, Φ_S, and peroxide, Φ_P, are related by:[27]

$$\Phi_P = \Phi_S k_c[RH]/(k_c[RH] + k_d) \tag{63}$$

Hence, k_d/k_c can be determined from a linear graph of Φ_P^{-1} against $[RH]^{-1}$. In practice, the reactivities of two hydrocarbons are usually compared by making them compete for singlet oxygen and determining the reactivity ratio k_c^1/k_c^2 from[27,86]

$$d[R^1]/d[R^2H] = d[R^1O_2H]/d[R^2O_2H] = k_c^1[R^1H]/k_c^2[R^2H] \tag{64}$$

in which k_c^1 and k_c^2 refer respectively to combination of $^1O_2$ with R^1H and R^2H.

Singlet oxygen may also be produced by reaction of hypochlorite with hydrogen peroxide[27,87] or by electrodeless discharge through oxygen gas.[88] In each case, equation (64) and a modified version of (63) apply.[27] Some recent data are shown in Table 4. As shown by the values of k_d/k_c and k_c^1/k_c^2, the behaviour of $^1O_2$ is independent of its mode of production, but varies slightly with solvent. The reactivity ratios, k_c^1/k_c^2, illustrate its electrophilic character and sensitivity to

[85] K. Gollnik, *Adv. Photochem.*, 1968, **6**, 2; *Advances in Chemistry Series*, 1968, **77**, 78. For an earlier theory concerning these photosensitised autoxidations, see K. Gollnik and G. O. Schenk, *Pure and Applied Chemistry*, 1964, **9**, 507.
[86] K. R. Kopecky and H. J. Reich, *Canad. J. Chem.*, 1965, **43**, 2265.
[87] C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, 1964, **86**, 3879; W. H. Schuller and R. V. Lawrence, *Ind. Eng. Chem. Product Research and Development*, 1967, **6**, 266.
[88] E. J. Corey and W. C. Taylor, *J. Amer. Chem. Soc.*, 1964, **86**, 3881.

Table 4 *Addition of singlet oxygen to mono-olefins at* 30 °C

R^1H	R^2H	k_c^1/k_c^2		Ref.
		Photo-sensitised	$OCl^- - H_2O_2$	
1-Methylcyclopentene	1-Methylcyclohexene	$9 \cdot 8 \pm 1 \cdot 1$ (15 °C)		a
2,3-Dimethylbut-2-ene	2-Methylbut-2-ene	41	35 (25 °C)	b
2-Methybut-2-ene	2-Methylpent-2-ene	$1 \cdot 32$	$1 \cdot 28$ (25 °C)	b
cis-4-Methylpent-2-ene	2-Methylpent-2-ene	$0 \cdot 014$	$0 \cdot 011$ (4 °C)	b
trans-4-Methylpent-2-ene	2-Methylpent-2-ene	$0 \cdot 0025$	$0 \cdot 0020$ (4 °C)	b
		k_d/k_c (mol dm^{-3})		
		Photo-sensitised	$OCl^- - H_2O_2$	
2-Methylpent-2-ene	—	$0 \cdot 13, 0 \cdot 05*$, $0 \cdot 18\dagger$	$0 \cdot 16$ (25 °C)	b

(a) Average value for the sensitizers Eosin Y, Erythrosin B, Hematoporphyrin, Methylene Blue, and Rose Bengal in methanol solution. Olefin consumption measured by gas–liquid chromatography. Data from K. R. Kopecky and H. J. Reich. *Canad. J. Chem.*, 1965, **43**, 2265; (b) in 50–50 methanol–t-butanol solution. Sensitizer was Rose Bengal. Hydroperoxide production measured by gas–liquid chromatography. Data from R. Higgins, C. S. Foote, and H. Cheng, *Advances in Chemistry Series*, 1968, **77**, 102.
*In t-butanol solution.
†In methanol solution.

olefin structure. In particular, substitution of alkyl groups at the olefinic bond favours reaction (61).

The addition of singlet oxygen to mono-olefins is thought to proceed by a concerted mechanism, with the C–O bond formed and the (allylic) C–H bond broken being *cis* to one another:[27,85,89]

(65)

The products formed depend upon the availability of this allylic hydrogen, and alkyl substituents at the double bond have little or no 'Markovnikoff' directing effect.[85] Thus, in the case of 2-methylbut-2-ene secondary and tertiary hydroperoxides are formed in nearly equal amounts:[27]

$$Me_2C{=}CHMe + {}^1O_2 \rightarrow CH_2{=}C(Me)CH(O_2H)Me \ (51\%)$$
$$+ \ Me_2C(O_2H)CH{=}CH_2 \ (49\%) \qquad (66)$$

[89] F. A. Litt and A. Nickon, *Advances in Chemistry Series*, 1968, **77**, 118.

Singlet oxygen is very selective in its reactions and should prove a useful reagent for organic syntheses.[87] Its chemistry has recently been surveyed in detail.[85]

14 Autoxidation of Carbanions

We finally consider the autoxidation of carbanions,[90-93] formed by treating hydrocarbon with a strong base:

$$RH + B^- \rightleftharpoons R^- + BH \tag{67}$$

$$R^- + O_2 \rightarrow RO_2^- \tag{68}$$

The acidity of the hydrocarbon determines which of reactions (67) and (68) is rate-controlling. In the case of diphenyl- and triphenyl-methane, for which $pK_a = 30$ and 28 respectively, the carbanion R^- reacts avidly with oxygen. Hence, the autoxidation rate simply equals the ionisation rate. Replacement of the acidic hydrogen by deuterium lowers this rate six- or ten-fold.[91] In the case of fluorene, a more acidic hydrocarbon with $pK_a = 20$, no deuterium isotope effect is observed since reaction (68) is much slower than the rapid pre-equilibrium (67).[91]

Russell has pointed out that (68), as written, would be spin-forbidden.[90,91] He has therefore suggested that R^- may be converted to a free radical, by donating an electron to an acceptor X, before combining with oxygen. A plausible reaction sequence would be

$$R^- + X \rightarrow R\cdot + X^{-}\cdot \tag{69}$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \tag{70}$$

$$RO_2\cdot + X^{-}\cdot \rightarrow RO_2^- + X \tag{71}$$

which is equivalent to (68). In support of this mechanism, the autoxidation of fluorene is catalysed by substituted nitrobenzenes,[90] and proceeds most rapidly in the presence of the powerful acceptor 3-trifluoromethylnitrobenzene.[91] The rates of these catalysed autoxidations correlate well with rates of electron transfer to the nitrobenzenes, as measured by e.s.r.[90,91]

The hydroperoxide formed by (68) may sometimes be isolated in good yield, but often undergoes further change. Thus, the autoxidation of 9-alkylfluorenes in pyridine solution, with benzyltrimethylammonium hydroxide as base, proceeds as far as the hydroperoxides below -15 °C, but at higher temperatures gives 9-alkylfluorenols by reaction of these hydroperoxides with the parent carbanions:[92]

[90] G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, *Advances in Chemistry Series*, 1965, **51**, 112.
[91] G. A. Russell, A. G. Bemis, E. J. Geels, E. G. Janzen, and A. J. Moye, *Advances in Chemistry Series*, 1968, **75**, 174.
[92] Y. Sprinzak, *J. Amer. Chem. Soc.*, 1958, **80**, 5449.
[93] G. A Russell, A. J. Moye, E. G. Janzen, S. Mak, and E. R. Talaty, *J. Org. Chem.*, 1967, **32**, 13˘.

$$(72)$$
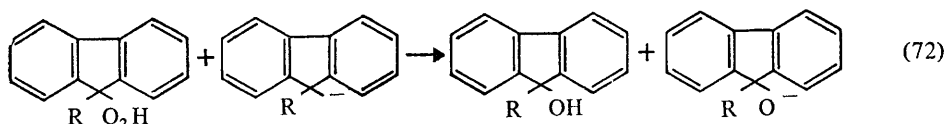
Various reactions of hydroperoxide with base or solvent have also been reported.[90-92] In some cases, formation of dehydrogenated, as well as oxygenated, products may occur. For example, substituted toluenes autoxidise to the corresponding stilbenes, as well as to benzoic acids.[93] The versatility of carbanion autoxidations, which proceed under mild conditions, could make them invaluable for organic synthesis.

15 Conclusion

Owing to limitations of space, many aspects of autoxidation kinetics have had to be omitted from this Review. Nonetheless, I hope that the reader will have found it a useful introduction to the subject and guide to the literature. The basic mechanism of autoxidation is now well understood and the next decade should witness the further development of quantitative rules relating the reactivity of hydrocarbons[3,8] and antioxidants[33,68] to their structure. A detailed understanding of many commercially important autoxidations must await further research. In this respect, the use of a computer to solve realistic kinetic equations based on complicated autoxidation mechanisms[94] holds promise for the future.

I am indebted to Professor J. C. Robb and Dr. N. Uri for reading the manuscript.

[94] L. R. Mahoney, *J. Amer. Chem. Soc.*, 1967, **89**, 1895.