QUARTERLY REVIEWS

KINETICS OF OLEFIN OXIDATION

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In the twenty years that have elapsed since the independent existence of free radicals was established, the number of organic chemical reactions explicable in terms of free-radical intermediates has multiplied continuously. In the absence of conclusions based on rigorous reaction-kinetic analyses, identification of the elementary free-radical processes contained in such reaction mechanisms has been based largely on permissive evidence derived from the qualitative identification of final reaction products. This lag in the application of kinetic methods arises partly from their intrinsically more laborious nature and partly because intrusion of secondary reactions frequently renders a completely quantitative treatment of the main reaction extremely difficult. In recent years, however, substantial progress has been made towards establishing free-radical chemistry on a quantitative basis.

Free radicals show well-defined differences in reactivity. Thus each type of free radical shows a certain specificity in the reactions in which it will take part; again, the ease with which a series of radicals participate in a given general chemical reaction can show distinct variation. The application of reaction kinetics to determine the basic principles governing the reactivity of radicals in general may therefore be resolved into two parts. In the first place, it is necessary to identify the elementary reactions involving free radicals, which may occur in a wide variety of chemical reactions; secondly, having established the occurrence of a particular radical reaction, the influence on reaction efficiency resulting from alteration in the chemical structure of the radical and non-radical reactants should be followed. For example, a radical reaction which has been most carefully identified is the propagation process occurring in vinyl polymerisations:

$$CH_2{-}CRR'{-} + CH_2{=}CRR' \longrightarrow CH_2{-}CRR'{-}CH_2{-}CRR'{-}$$

The further step of measuring the absolute efficiencies of reactions of this type has recently been accomplished [1] and the influence of the identity of R and R′ contained in both the radical reactant and the monomer has been systematically investigated in recent extensive studies of copolymerisation.

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[1] *E.g.*, (*a*) G. M. Burnett and H. W. Melville, *Nature*, 1945, **156**, 661; *Proc. Roy. Soc.*, 1947, *A*, **189**, 456; (*b*) P. D. Bartlett and C. G. Swain, *J. Amer. Chem. Soc.*, 1945, **67**, 2273; 1946, **68**, 2381; (*c*) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.*, 1948, *A*, **192**, 309.

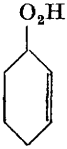
As a result, theories as to the basic factors influencing the addition of radicals to ethylenic double bonds have been formulated.[2]

The interaction of molecular oxygen with unsaturated hydrocarbon systems provides another reaction which is worthy of such systematic kinetic investigation. The chemistry of this reaction is simple, and is apparently common to a large range of compounds; experimentally, its course may be followed with a high degree of precision. It is our purpose here to summarise kinetic work that has been carried out in recent years on this topic. In the first place the argument in favour of a general mechanism of olefinic oxidation is outlined; we then discuss the influence of structural variations within the olefinic system on each of the elementary radical reactions which go to make up the oxidation mechanism.

I. Chemical Nature of Oxidation Products [3]

The primary products obtained by the combination of oxygen with various types of unsaturated hydrocarbon systems exhibit a common feature in containing the oxygen in unseparated pairs of atoms. The manner in which these pairs of oxygen atoms are linked to the hydrocarbon molecules does, however, vary from class to class of olefin.

(*a*) The products formed in the autoxidation of mono-olefins,[4] 1 : 4-dienes,[5] and hydroaromatics [6] are substantially pure α-hydroperoxides of which the following are representative examples:

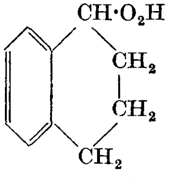


(I.)

$$CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH(O_2H)\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2Et$$
$$CH_3\cdot[CH_2]_4\cdot CH(O_2H)\cdot CH{:}CH\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2Et$$
$$CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH{:}CH\cdot CH(O_2H)\cdot[CH_2]_7\cdot CO_2Et$$

(II.)

(III.)



(*b*) Oxygen combines with conjugated (1 : 3) dienes by 1 : 4-addition to form either polymeric peroxides of the type (IV) [7] or under special conditions intramolecular (transannular) peroxides of type (V).[8]

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[2] Reviews of the present situation include those by F. R. Mayo, F. M. Lewis, and C. Walling, Faraday Soc. Discussion, 1947, **2**, 285; C. C. Price, *ibid.*, p. 304.

[3] For detailed reviews giving more extensive bibliography, see, *e.g.*, C. E. Hollis, *J. Oil Colour Chem. Assoc.*, 1944, **27**, 67; E. H. Farmer, *Trans. Faraday Soc.*, 1946, **42**, 228; S. Bergström and R. T. Holman, *Recent Advances in Enzymology*, 1948, **8**, 425.

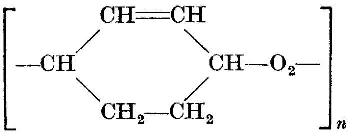
[4] R. Criegee, H. Pilz, and H. Flygare, *Ber.*, 1939, **72**, 1799.

[5] E. H. Farmer and A. Sundralingam, *J.*, 1943, 541; J. L. Bolland and H. P. Koch, *J.*, 1945, 445.

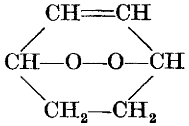
[6] M. Hartmann and M. Seiberth, *Helv. Chim. Acta*, 1932, **15**, 1390.

[7] A. Bodendorf, *Arch. Pharm.*, 1933, **271**, 1.

[8] G. O. Schenck and K. Ziegler, *Naturwiss.*, 1944, **32**, 157.



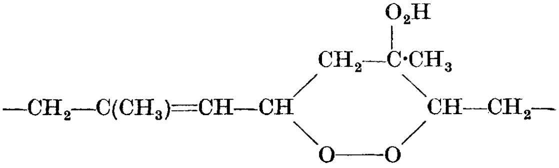
(IV.)



(V.)

Polymeric peroxides involving 1 : 2-addition are also encountered.[9] Transannular peroxides formally of the same type as (V) are obtained by the photo-oxidation of many polynuclear aromatic hydrocarbons.[10] Provided the *meso*-positions bridged by the peroxide group are suitably substituted with aromatic nuclei, these photo-peroxides possess the interesting property of dissociating with formation of molecular oxygen.

(*c*) A third type of peroxide which combines the essential character of these two contrasting types of product is apparently formed by the autoxidation of $\Delta^{1:5}$ systems.[11] Thus, when oxygen reacts with certain polyisoprenes it is largely incorporated in units of four oxygen atoms, two atoms being present in a hydroperoxide group and two in an intramolecular peroxide ring, according to the type of formulation (VI).



(VI.)

The chemistry of olefin oxidation thus follows a very simple formal pattern. In marked contrast is the multiplicity of oxidation products obtained from saturated hydrocarbons in the higher range of temperatures necessary for their oxidation.[12] The above analysis does, however, represent an over-simplification of the situation in at least two respects.

(i) In each of the three cases, (*a*)—(*c*), minor products are formed which bear the characteristics of the other types of product. Thus the oxidation product from 4-methylhept-3-ene contains some 10% of a dimeric peroxide [type (*b*)], while the product from dihydromyrcene [type (*c*)] certainly contains a minor proportion of polymeric peroxides [type (*b*)] and probably some mono-hydroperoxide [type (*a*)].

(ii) Small proportions of non-peroxidic products are apparently produced during oxidation of all olefins, particularly during advanced stages of reaction. These may include aldehydes, ketones, epoxides, acids, water, and carbon dioxide. These minor products assume an importance out of all proportion

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[9] H. Staudinger, *Ber.*, 1925, **58,** 1075 ; F. A. Bovey and I. M. Koltoff, *J. Amer. Chem. Soc.*, 1947, **69,** 2143.

[10] C. Dufraisse, *Bull. Soc. chim.*, 1939, **6,** 422, gives a summary of the many papers published by him and his co-workers on this topic.

[11] J. L. Bolland and H. Hughes, *J.*, in the press.

[12] C. F. Cullis and C. N. Hinshelwood, Faraday Soc. Discussion, 1947, **2,** 117.

to their relative abundance since they are associated with the appearance of deleterious properties during the oxidation of certain raw materials.

The proportion of non-peroxidic products may, of course, be greatly augmented by the use of appropriate oxidation conditions : thus in the very rapid oxidation of olefins occurring in presence of heavy-metal catalysts a high proportion of oxidation product may be found as ketones and alcohols.[13]

II. Oxidation Mechanism

Chain Character of Reaction.—The low-temperature liquid-phase autoxidation of olefins occurs by a chain mechanism. Chain reactions occurring in the gas phase may be recognised by several kinetic characteristics.[14] Three of these apply with equal force to chain reactions in liquid systems : small amounts of certain added substances (inhibitors and initiators, respectively) may give rise to spectacular decreases or increases in reaction rate ; further, if the reaction be accelerated photochemically, the quantum yield may exceed unity. The oxidation of olefins has been shown to fulfil these formal criteria. The pioneer work of H. L. J. Bäckström [15] demonstrated effectively the occurrence of oxidation chain reactions in the liquid phase. The quantum yields for the photo-oxidation of benzaldehyde, heptaldehyde, and sodium sulphite were shown to be as high as 10,000, 15,000, and 50,000 respectively, while later work [16] on the inhibitory influence of small quantities of alcohols and phenols on these oxidation systems supplied confirmatory evidence of the occurrence of chain reactions. Moreover, early experiments carried out by K. Ziegler and L. Ewald [17] (and more recently elaborated by K. Ziegler and K. Ganicke)[18] left no doubt that the free radicals generated by dissociation of hexaphenylethane could each result in the reaction of aldehydes and unsaturated hydrocarbons with numbers of oxygen molecules well in excess of unity.

Despite the spectacular success of these early investigations, published work on low-temperature oxidation kinetics, notwithstanding its obvious implications in so many commercial fields, was indeed scanty until the elucidation of the basic chemistry of olefinic oxidation apparently provided the stimulus of further inquiry into the detailed nature of the chain sequence by which these simple primary products are formed.

Chain reactions of the simplest (non-branching) type follow a common pattern in that reaction chains are initiated, propagated, and finally terminated. The essential rôle of the initiation step is to provide reactive intermediates or chain carriers which then set in train a series of facile reac-

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[13] A. H. Cook, *J.*, 1938, 1774 ; E. H. Farmer and A. Sundralingam, *J.*, 1942, 137 ; C. Paquot, *Bull. Soc. chim.*, 1941, **8**, 695.

[14] *E.g.*, C. N. Hinshelwood, " Kinetics of Chemical Change ", Oxford Univ. Press, 1940, p. 161.

[15] *J. Amer. Chem. Soc.*, 1927, **49**, 1460.

[16] H. N. Alyea and H. L. J. Bäckström, *ibid.*, 1929, **51**, 90; K.-K. Jeu and H. N. Alyea, *ibid.*, 1933, **55**, 575.

[17] *Annalen*, 1933, **504**, 162.

[18] *Ibid.*, 1942, **551**, 213.

tions. This propagation sequence may often be analysed into a succession of recurring cycles of reactions, the net result of each cycle being to produce one molecule of the primary product and reproduce the appropriate chain carrier ready for the next cycle. The termination of the chain occurs by the intervention of a further reaction which converts chain carriers into species incapable of carrying on the chain further. Provided the right balance exists between the efficiencies of these propagation and termination reactions, each chain will produce high yields of the primary reaction product. The nature of the overwhelming proportion of the product would thus be determined by the identity of the propagation reactions ; the products attributable to initiation and termination steps would be correspondingly trivial. In the temperature range at which olefins react at significant rates with oxygen (say, below 100°) this condition for high peroxide yield is fulfilled ; it is, however, possible to visualise experimental conditions (such as high temperatures) under which the chain lengths may be shortened sufficiently to increase the yield of the secondary products to appreciable amounts.

Reaction between pure olefins and oxygen is relatively slow at temperatures below, say, 50°. Circumstances exist in which the rate of oxidation is accelerated, without at the same time substantially affecting the nature of the oxidation product. These include (*a*) illumination with ultra-violet radiation, the presence of (*b*) peroxidic oxidation products (autocatalysis), or (*c*) dissociable molecules like benzoyl peroxide, and (*d*) enzymes.[19] Certain heavy-metal ions and co-ordination complexes strongly catalyse [13, 20] oxidation, but here the nature of the oxidation product so obtained is affected.

Final elucidation of the reaction mechanisms involved in oxidations stimulated by the above agencies, (*a*)—(*d*), has not been accomplished. Recently, however, a systematic correlation of the first three types of oxidation has been made.[21] These kinetic investigations are now summarised, with emphasis on the essential unity of the chain propagation and termination mechanisms, and the divergences in modes of chain initiation.

III. Kinetics of Olefinic Oxidation

The kinetic approach to the problem may be analysed into three stages. The identity of the elementary reactions, which by their consecutive occurrence make up the reaction mechanism as a whole, must be established. This first step (Section IV) is accomplished by determining the manner in which the rate of reaction depends on the various experimental variables (*i.e.*, the rate equation). Such kinetic evidence considered together with the best available chemical evidence as to the nature of the reaction products (and, on occasion, reaction intermediates) normally leads to a

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[19] S. Bergström and R. T. Holman, *Recent Advances in Enzymology*, 1948, **8**, 425.

[20] P. George, E. K. Rideal, and A. Robertson, *Proc. Roy. Soc.*, 1946, *A*, **185**, 288 ; P. George and A. Robertson, *Trans. Faraday Soc.*, 1946, **42**, 217.

[21] L. Bateman and J. L. Bolland, Proc. XIth International Congress of Pure and Applied Chemistry, 1947.

sound chemical formulation of the various steps. Secondly (Section V), the efficiency of various elementary reactions may be determined from the magnitude of the various characteristic constants which appear in the rate equation. Since, however, it is normally only possible to determine composite quantities involving more than one reaction velocity coefficient by this step, a third stage (Section VI) is necessary: by the application of special experimental techniques the efficiencies of individual elementary reactions may be evaluated.

IV. Identification of Elementary Reactions

Benzoyl Peroxide Catalysis.—The interaction between oxygen and the 1:4-dienic ester ethyl linoleate, $CH_3{\cdot}[CH_2]_4{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}CO_2Et$, in presence of benzoyl peroxide forms a specially favourable system for experimental study. Oxidation rates may be measured with sufficient precision to establish [22, 23] the complete relation between the rate of oxidation ascribable to the presence of benzoyl peroxide and the various reactant concentrations (benzoyl peroxide $[Bz_2O_2]$, olefin [RH], and oxygen $[O_2]$) as

$$\text{Rate} = k_c[\text{Bz}_2\text{O}_2]^{\frac{1}{2}}[\text{RH}]\frac{[\text{O}_2]}{k_c'[\text{RH}] + [\text{O}_2]} \quad . \quad . \quad . \quad (1)$$

where k_c and k_c' are constants which vary only with temperature. Similar rate equations are obtained with mono-olefins,[24] though here the factor $[O_2]/(k_c'[RH] + [O_2])$ is insufficiently sensitive to oxygen concentration to permit of more than a demonstration that pressure dependence is consistent with the factor $[O_2]/(\lambda_c + [O_2])$.

Photo-oxidation.—Systems consisting of oxygen and highly purified olefins absorb ultra-violet radiation of wave-length $>$ 2500 A. only very weakly and peroxidation is relatively slow. With formation of hydroperoxide, the optical density increases rapidly, and a state of complete absorption is finally reached. In these circumstances [25] the rates of photo-oxidation of *cyclo*hexene, methyl*cyclo*hexene, and ethyl linoleate conform to the relation

$$\text{Rate} = k_l I^{\frac{1}{2}}[\text{RH}]\frac{[\text{O}_2]}{\lambda_l + [\text{O}_2]} \quad . \quad . \quad . \quad . \quad (2)$$

where k_l and λ_l represent experimental constants and I is the absorbed light intensity.

Autoxidation.—When peroxide-free mono-olefins and 1 : 4-dienes are shaken with oxygen in the dark, the reaction rate accelerates as hydroperoxide products accumulate. The contribution to the total rate attributable to the autocatalytic influence of the α-hydroperoxides (RO_2H) has been

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[22] J. L. Bolland, *Proc. Roy. Soc.*, 1946, *A*, **186**, 218.

[23] *Idem*, *Trans. Faraday Soc.*, 1948, **44**, 669.

[24] In Sections IV, VIII, and X, reference is made to papers scheduled for publication in *Trans. Faraday Soc.* To facilitate future reference the Parts which they form in a series of papers " Kinetic Studies in the Chemistry of Rubber and Related Materials " is indicated. Here the reference is J. L. Bolland, Part VIII.

[25] L. Bateman, *ibid.*, 1946, **42**, 266; L. Bateman and G. Gee, *Proc. Roy. Soc.*, 1948, *A*, **195**, 376, 391.

followed in detail in the case of ethyl linoleate and found to follow the relation :

$$\text{Rate} = k_a[\text{RO}_2\text{H}][\text{RH}]\frac{[\text{O}_2]}{\lambda_a + [\text{O}_2]} \quad . \quad . \quad . \quad (3)$$

The autoxidation of mono-olefins follows precisely the same kinetic laws.[26]

Comparison of these three rate equations shows obvious parallelism in the way the rate of oxidation observed under the three different sets of conditions depends on $[\text{O}_2]$ and [RH]. In each case, one experimental variable, $[\text{Bz}_2\text{O}_2]$, I, and $[\text{RO}_2\text{H}]$, remains. The respective kinetic orders in which they appear may be correlated with the primary processes by which these three agencies would introduce radicals into the oxidation system. The normal decomposition of benzoyl peroxide has been the subject of many kinetic investigations, and despite more recent delineations of secondary reactions,[27] it is generally accepted that the primary reaction is unimolecular dissociation into free radicals. Photo-chemical production of radicals must be given by φI (where φ is the quantum yield of the radical-forming primary photo-process). Thermal decompositions of α-methylene hydroperoxides have not been systematically studied kinetically. The indications are, however, that in the case of ethyl linoleate hydroperoxide the rate-determining step is bimolecular.[22] These three primary processes being assumed to generate radicals suitable as oxidation chain carriers, the three rate equations reduce to the common form :

$$\text{Rate} = R_i^{\frac{1}{2}}k[\text{RH}]\frac{[\text{O}_2]}{k'[\text{RH}] + [\text{O}_2]} \quad . \quad . \quad . \quad (4)$$

in which R_i is written for the rate of formation of chain carriers.

The four kinetic characteristics embodied in this generalised relation can be accounted for in terms of a single chain-reaction mechanism of the following type :

$$\begin{array}{llllll}
\text{Initiation.} & & \multicolumn{2}{l}{\text{Production of R— or RO}_2\text{— radicals, } R_i.} & & \\
 & \textit{i.e.}, & \text{Bz}_2\text{O}_2 & \left.\begin{array}{l} \\ \\ \\ \end{array}\right\} \longrightarrow \text{R— or RO}_2\text{—} & k_7 & (\text{R7}) \\
 & \text{or} & \text{RO}_2\text{H} + h\nu & & & \\
 & \text{or} & 2\text{RO}_2\text{H} & & k_1 & (\text{R1}) \\
\text{Propagation.} & & \text{R—} + \text{O}_2 & \longrightarrow \text{RO}_2\text{—} & k_2 & (\text{R2}) \\
 & & \text{RO}_2\text{—} + \text{RH} & \longrightarrow \text{RO}_2\text{H} + \text{R—} & k_3 & (\text{R3}) \\
\text{Termination.} & & \text{R—} + \text{R—} & \left.\begin{array}{l} \\ \\ \\ \end{array}\right\} \longrightarrow \text{Inactive products} & k_4 & (\text{R4}) \\
 & & \text{R—} + \text{RO}_2\text{—} & & k_5 & (\text{R5}) \\
 & & \text{RO}_2 + \text{RO}_2\text{—} & & k_6 & (\text{R6})
\end{array}$$

In terms of this reaction scheme, the rate of oxidation is related to the velocity coefficient of the various elementary reactions (k_1—k_7) by

$$-\frac{d[\text{O}_2]}{dt} = R_i^{\frac{1}{2}}\frac{k_3}{\sqrt{k_6}}[\text{RH}]\frac{k_2\sqrt{k_6}[\text{O}_2]}{k_3\sqrt{k_4}[\text{RH}] + k_2\sqrt{k_6}[\text{O}_2] + \sqrt{k_4k_6R_i}} \quad . \quad (5)$$

The correspondence between the experimental and the theoretical relation,

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[26] J. L. Bolland and A. L. Morris, ref. 24, Part X.

[27] K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686 ; W. E. Cass, *ibid.*, p. 1976 ; D. J. Brown, *ibid.*, 1948, **70**, 1208.

(4) and (5), is complete, since the term $\sqrt{k_4 k_6 R_i}$ becomes negligible at chain lengths as great as those encountered here.

The chain carriers R— (formed by abstraction of an α-methylenic hydrogen atom from the olefin) or RO_2— (the corresponding peroxide radical) result either directly or indirectly from the initiating agency. Chain propagation proceeds by a two-stage cycle in which an oxygen molecule adds to the R-type radical and the resulting peroxide chain carrier abstracts a hydrogen atom from another olefin molecule to complete a hydroperoxide molecule and regenerate a hydrocarbon radical ready for the next cycle. Chain termination results from the interaction of chain carriers in pairs to form products no longer capable of continuing the propagation cycle.

Special weight should be given to two features of the photo-oxidation study : the square-root dependence of rate on I [equation (2)] and the realisation [25] of quantum yields greater than unity provide unequivocal evidence as to the nature of the chain-termination process and the chain character of the oxidation mechanism, respectively.

The identity of the chain carriers concerned cannot, of course, be determined from such kinetic investigations. Strong evidence is, however, furnished by the ultra-violet spectroscopic examination of the hydroperoxidic oxidation products of the $\Delta^{1:4:7}$ and $\Delta^{1:4}$ esters, ethyl linolenate [28] and ethyl linoleate,[29] which are found to be extensively conjugated ; in the latter case some 70% of the oxidised molecules contain conjugated diene groups. It is difficult to find a satisfactory alternative explanation for the transient existence at some stage in the formation of each hydroperoxide grouping of the radical R—. This radical,[30] embracing three resonance hybrid structures, two of which contain the double bonds in conjugation, may obviously undergo oxygen addition [by (R2)] in three alternative positions, two of which will result in the formation of conjugated peroxides (cf. II, p. 2).

The addition of maleic anhydride to α-groups in olefins appears to follow a mechanism quite analogous to hydroperoxide formation.[31] W. G. Bickford, G. S. Fisher, L. Kyame, and C. E. Swift [32] have recently shown that the adduct of maleic anhydride and methyl oleate contains four isomers, the presence of all of which is convincingly accounted for in terms of α-methylenic hydrogen abstraction followed by addition of maleic anhydride to the resulting allylic radical.

Possible alternative formulations of the above reaction scheme involve the chain carriers H— and HO_2—. Here, however, the requirements are that double-bond shift should either be absent or complete (depending on whether in the propagation reaction HO_2 + olefin the radical attacks at

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[28] E. H. Farmer, H. P. Koch, and D. A. Sutton, *J.*, 1943, 541.

[29] J. L. Bolland and H. P. Koch, *J.*, 1945, 445.

[30] A quantum-mechanical treatment of this radical has recently been given by W. E. Moffitt and C. A. Coulson, *Trans. Faraday Soc.*, 1948, **44,** 81.

[31] A. Delalande, Proc. XIth International Congress of Pure and Applied Chemistry, 1947.

[32] *J. Amer. Oil Chem. Soc.*, 1948, **25,** 254.

the α-methylene position or at the double bond). While spectroscopic and chemical evidence both appear to rule out this possibility's being of general occurrence, note should be taken of the observation [33] that in presence of lipoxidase ethyl linoleate may give a completely conjugated oxidation product.

Inhibition by Phenolic Antioxidants.—In the above three oxidation systems, only the chain-initiation step was different. The complementary process of altering the chain-termination mechanism without affecting the other elementary reaction may be achieved simply by introducing a phenolic inhibitor into the oxidation system.[15, 16, 34]

A systematic study [34] of the influence of quinol, Hq, on ethyl linoleate oxidation initiated by benzoyl peroxide and ethyl linoleate hydroperoxide leads to the two rate equations :

$$\text{Rate} = K_c[\text{Bz}_2\text{O}_2][\text{RH}]/[\text{Hq}] \quad . \quad . \quad . \quad . \quad (6)$$

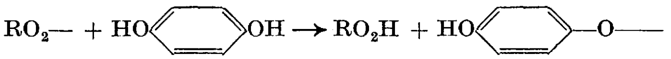
and

$$\text{Rate} = K_a[\text{RO}_2\text{H}]^2[\text{RH}]/[\text{Hq}] \quad . \quad . \quad . \quad . \quad (7)$$

where K_c and K_a are constants.* These equations are obviously special cases of the general relation

$$\text{Rate} = R_i k_{\text{Hq}}[\text{RH}]/[\text{Hq}] \quad . \quad . \quad . \quad . \quad (8)$$

Kinetics of this type are consistent with a reaction mechanism, the initiation and propagation of which are identical with those deduced for the uninhibited oxidations, with the chain termination now involving an RO_2-type chain carrier and a quinol molecule. The chemical course of this step is identified [35] as



(k_9)

from correlation of diminishing strength of phenolic O–H bond in a series of phenolic compounds and the increasing efficiency with which they partake in this reaction. The semiquinone radicals are apparently of sufficient stability to discontinue the propagation of the oxidation chain, and disappear by dismutation in pairs to benzoquinone and quinol.

V. Relative Efficiencies of Elementary Reactions

If we compare the experimental rate equations with the theoretical equations deduced by stationary-state methods from the suggested chain mechanism, certain relations involving the velocity coefficients of the elementary reactions obviously arise :

$$k = R_i^{\frac{1}{2}} k_2 k_6^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$k' = k_3 k_6^{-\frac{1}{2}} . k_2^{-1} k_4^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$k_{\text{Hq}} = k_3 k_9^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The composite quantities $k_3 k_6^{-\frac{1}{2}}$, $k_2 k_4^{-\frac{1}{2}}$, and $k_3 k_9^{-1}$ may thus be evaluated in terms of experimentally determined constants and the rate of chain

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[33] S. Bergström and R. T. Holman, *Nature*, 1948, **161**, 55.

[34] J. L. Bolland and P. ten Have, *Trans. Faraday Soc.*, 1947, **43**, 201.

[35] *Idem*, Faraday Soc. Discussions, 1947, **2**, 252.

* These equations apply only to the inhibitor concentration range in which *all* chains are terminated by the inhibitor.

initiation. If the approximation is made that the latter is equal to the rate of a photo- or thermal decomposition of the peroxide concerned, comparative estimates for $k_3k_6^{-\frac{1}{2}}$ and $k_2k_4^{-\frac{1}{2}}$ can be made for oxidation systems which differ only in mode of chain initiation. For example, (*a*) the chain lengths (which are, at constant rates of chain initiation, proportional to $k_3k_6^{-\frac{1}{2}}$) measured under equivalent conditions at 10° for the photo- and benzoyl peroxide catalysed oxidations of *cyclo*hexene are 17 and 16 respectively; (*b*) for the autoxidation and benzoyl peroxide initiated oxidations of ethyl linoleate the corresponding values of $k_3k_6^{-\frac{1}{2}}$ at 45° are 0·0226 and 0·0104 (mol.$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$); (*c*) at 45°, $k_2k_4^{-\frac{1}{2}}$ in the latter pair of systems is found to be $5{\cdot}2 \times 10^3$ and $5{\cdot}5 \times 10^3$ (mol. $^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$), respectively. The agreement is as close as can be expected in view of the assumption involved, namely, that the number of chain carriers formed by the decomposition of one molecule of peroxide is independent of both the identity of the peroxide and the method of decomposition. Tests applied [21] to the experimental energies of activation associated with $k_3k_6^{-\frac{1}{2}}$ and $k_2k_4^{-\frac{1}{2}}$ further substantiate the identity of chain mechanism throughout these three types of oxidation.

Judged by the kinetic characteristics (outlined in Section VI) the five separate oxidation systems fitted into a close-knit picture of the oxidation of hydroperoxide-forming olefins: when considered together they argue a formidable case in favour of the oxidation mechanism suggested. The close quantitative correlations between the various systems indicated in this section must be regarded as very material confirmatory evidence.

It is worth defining the respective contributions made by kinetic and chemical evidence to the final formulation of this mechanism. The kinetic arguments summarised in this and the preceding section establish the essential form of the elementary reactions; for example, in one propagation step (the faster one) one chain carrier and an oxygen molecule are concerned, while in a second propagation step another chain carrier and an olefin molecule participate. It is only when the chemical identity of the product [aided in this particular instance by an indication (p. 8) as to the identity of one of the chain carriers] is considered that the most convincing chemical formulation of the chain carriers, as R— and RO_2—, respectively, becomes evident. The kinetic and chemical evidence are each indispensable to the final conclusions. Several authors have on the basis of product-identification speculated on the nature of the autoxidation mechanism. The kinetic evidence now accumulated has shown that of these, the views of Farmer *et al.*[36, 28] have proved essentially correct; other views, *e.g.*, the earlier non-chain formulation of F. D. Gunstone and T. P. Hilditch,[37] have been controverted.

VI. Absolute Velocities of Elementary Reactions

We have seen that only functions involving pairs of velocity coefficients can be deduced from measurements of overall rates of oxidation and rates of chain initiation. A third experimentally determinable characteristic of

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[36] E. H. Farmer, G. F. Bloomfield, A. Sundralingam, and D. A. Sutton, *Trans. Faraday Soc.*, 1942, **38**, 348.

[37] *J.*, 1946, 1022.

the oxidation reaction is required before the individual velocity coefficients can be finally disentangled. The same problem occurs in the polymerisation field. Here it has been solved [38] by determination of the life-time of the growing polymer chains. The rotating-sector technique as applied, notably by H. W. Melville, to photo-polymerisation is directly applicable to olefin oxidation—since the prerequisite that chain termination should occur through mutual destruction of pairs of chain carriers is fulfilled.

Bateman and Gee [25] have in this way estimated the average time-interval τ required for the completion of a cycle of propagation processes (pp. 8 and 19) in an oxidation chain in four representative olefins : mono-olefins in *cyclo*hexene and methyl*cyclo*hexene, a 1 : 4-diene in ethyl linoleate, and a 1 : 5-diene in 2 : 6-dimethylocta-2 : 6-diene (dihydromyrcene). This work is notable for the extreme care taken in overcoming the very real difficulties arising from the relatively high optical density and the by no means negligible " dark " rate of oxidation of the partly oxidised olefins. τ is related directly to k_3 and k_6 by

$$k_3 = \nu_L[\mathrm{RH}]^{-1}\tau^{-1} \quad \text{and} \quad k_6 = \tau^{-2}\nu_L R_L$$

(where R_L and ν_L are respectively the rate and chain length of oxidation under the given experimental conditions). As the primary quantum yield of chain carriers (φ on p. 7) is uncertain, it is preferable in evaluating k_3 and k_6 from these equations to use values of ν_L calculated from the benzoyl peroxide-catalysed oxidation when carried out under identical conditions of temperature and oxidation rate.

Bateman and Gee's final figures for k_3 and k_6 (Table I) established the important point that the efficiency with which two RO_2— radicals interact is quite insensitive to the structure of the hydrocarbon residue in the radical.

TABLE I

Olefin.	Temp	k_3.	$k_6 \times 10^{-6}$.
		(mol.$^{-1}$ l. sec.$^{-1}$)	
*cyclo*Hexene	15°	$0{\cdot}6_5$	$0{\cdot}9_5$
Methyl*cyclo*hexene . .	15	$1{\cdot}1$	$0{\cdot}5_0$
Ethyl linoleate . . .	11	$5{\cdot}7$	$0{\cdot}5_0$
Dihydromyrcene . . .	15	$0{\cdot}4_0$	$0{\cdot}6_5$

The temperature coefficient of τ is found to be negligible. After reviewing their possible experimental errors, Bateman and Gee place an upper limit of 5 kcals./mole to the energy of activation for the RO_2— radical interaction. This energy figure and also the absolute value of k_6 accord fairly well with the data as yet published [1] for the interaction of two hydrocarbon radicals, encountered as the chain-terminating process in vinyl polymerisation.

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[38] (1) Rotating-sector method : Ref. 1 (*a*), (*b*), (*c*) ; (2) diffusion method, T. T. Jones and H. W. Melville, *Proc. Roy. Soc.*, 1940, *A*, **175**, 392 ; viscosity method, Ref. 1 (*d*).

VII. Influence of Olefinic Structure on Propagation Processes

In delineating the effect that alterations in olefin structure may have on the various elementary processes, the first essential is, of course, to ascertain that these very alterations do not introduce changes in the reaction mechanism. A classical warning of the dangers of using overall reaction-rate measurements (even under the most strictly reproduced conditions) to compare the reactivities of closely related molecules is implicit in the work of Hughes, Ingold *et al.*[39] on the replacement reactions of alkyl halides, where the fine balance between two competing mechanisms may be upset by small changes in the alkyl grouping. The oxidation mechanism (p. 7) has been rigorously shown to apply to representative members of three groups of unsaturated hydrocarbons, 1 : 4-dienes, mono-olefins, and hydroaromatics in ethyl linoleate, methyl oleate, and tetralin, respectively. A wealth of rather less systematic data supports the view that the mechanism applies to all mono-olefins irrespective of the degree of alkyl substitution at the double bond or the α-carbon atoms. S. S. Medvedev,[40] in an earlier paper on the benzoyl peroxide-catalysed oxidation of *cyclo*hexene, obtained results consistent with the requirements of the same mechanism (though his explanation was in other, more complicated terms), while P. George [41] has agreed that his observations on the benzoyl peroxide-catalysed oxidation of tetralin are capable of a re-interpretation which brings them into line.

VIII. The Propagation Processes, $\mathbf{RO_2— + RH \rightarrow RO_2H + R—}$

$k_3k_6^{-\frac{1}{2}}$ has been determined [42] for some 25 olefins belonging to these three groups in a series of strictly comparable experiments throughout which the same chain initiator, benzoyl peroxide, was used. By suitable choice of olefins, the influence of several characteristic structural features have been separated so that it is possible to estimate the efficiency with which the hydrogen-exchange reaction $RO_2— + RH \rightarrow RO_2H + R—$ occurs at α-groups in a variety of unsaturated environments. The best available group values of $k_3k_6^{-\frac{1}{2}}$ at 45° are collected in Table II. Absolute values of k_3 are calculated on the assumption that k_6 remains constant throughout at 6×10^5 (mol.$^{-1}$ l. sec.$^{-1}$).

Variations in the energy of activation (E_3) required for this exchange reaction resulting from changes in the identity of RH may readily be determined, since such variations are reflected in the overall energy of activation (E_c) for the benzoyl peroxide-catalysed oxidation. The correlation between the energies of activation thus found and the corresponding k_3 values for a series of olefins is quite consistent and may be represented by a linear log k_3–E_3 plot (see figure). Interpolated values of E_3* corresponding to the various group-values of k_3 are included in Table II.

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[39] See E. D. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.

[40] *Acta Physicochim. U.R.S.S.*, 1938, **9**, 395.

[41] *Trans. Faraday Soc.*, 1946, **42**, 268.

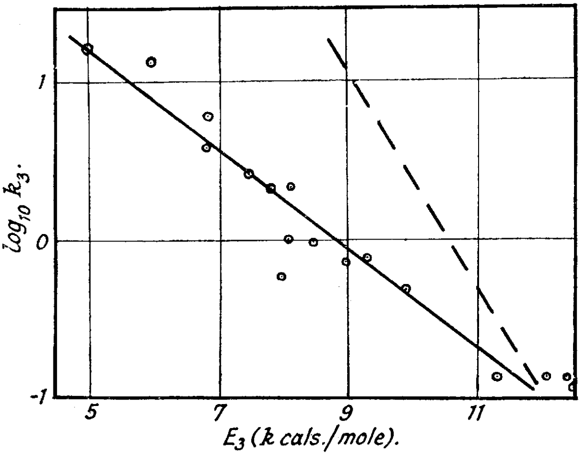
* E_3 is taken equal to $E_c - 15{\cdot}5$ kcals. : from equation (4) $E_c = E_3 + \frac{1}{2}E_i - \frac{1}{2}E_6$. E_6 is allotted the value of zero, and E_i (the activation energy of dissociation of benzoyl peroxide) 31 kcals./mole.[43]

The slope of the curve in the figure is distinctly less than that expected (indicated by the slope of the broken line) if the frequency factor (*A*) in

TABLE II

Grouping.*	$k_3k_6^{-\frac{1}{2}} \times 10^4$ (mol.$^{-\frac{1}{2}}$ l. sec.$^{-\frac{1}{2}}$).	$k_3 \times 10$ (mol.$^{-1}$ l. sec.$^{-1}$).	E_3.	D_{C-H}.
			(kcals./mol.).	
1. $—CH_2—CH=CH—CH_2—$.	6·5	5·0	9·7	80·2
(*A*) Variation in olefinic type .				
2. $—CH=CH—CH_2—CH=CH—$	194	150	5·0	68·1
3. $\phi—CH_2—$	4·6	3·6	10·2	81·4
(*B*) Variation in double-bond substitution.				
4. $—CH_2—CH=CH_2$ . . .	1·74	1·35	11·6	85·0
5. $—CH_2—CH=CHMe$ . . .	5·4	4·2	10·0	80·9
6. $—CH_2—CH=CMe_2$ . . .	26	20	7·9	75·5
7. $\phi—CH_2—CH=CH_2$ . . .	9·4	7·3	9·2	78·9
8. $\phi—CH_2—CH=CHMe$ . .	48	37	6·8	72·7
9. $\phi—CH_2—CH=CMe_2$ . . .	163	126	5·3	68·9
10. $\overset{(b)}{—CH_2}—\overset{CH_3\,(c)}{\overset{\vert}{C}}=CH—\overset{(a)}{CH_2—}$	(*a*) 16·3 (*b*) 6·5 (*c*) 2·2	12·6 5·0 1·72	8·5 9·7 11·2	77·1 80·2 84·0
(*C*) Variation in α-group substitution.				
11. $R—CH=CH·CH_3$	2·2	1·72	11·2	84·0
12. $—CHMe—CH=CH—R$ . .	21	16·2	8·1	76·1

* The reactivities given refer to the α-methylene group in the grouping (except in groups 10 and 11).



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[42] J. H. McClure, R. E. Robertson, and A. C. Cuthbertson, *Canadian J. Res.*, 1942, **20***B*, 103 ; S. Kamenskaya and S. Medvedev, *Acta Physicochim. U.R.S.S.*, 1940, **13**, 565 ; K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1690.

the Arrhenius equation, Rate $= Ae^{-E/RT}$, remained independent of olefinic architecture (so that alterations in E_3 accounted quantitatively for variations in reaction velocity). The apparent decrease in frequency factor in sympathy with decrease in activation energy has the apparent effect of nullifying some 50% of the latter.

Careful measurements of the activation energy and frequency factor of a variety of reactions had earlier established such behaviour as common in ionic reactions.[43] The probability that this generalisation extends also to radical reactions seems probable in view of R. A. Gregg and F. R. Mayo's observations [44] on the (hydrogen) transfer reaction occurring in the polymerisation of styrene and also the above evidence.

Thermochemically the reaction (R3) is of extreme simplicity since variations in heat of reaction may be related directly to variations in the strength of one chemical bond : the heat of reaction is the resultant of two terms, namely, the dissociation energies of the $\alpha\beta$ C–H bond in the olefin being broken and the O–H bond being formed in the hydroperoxidic grouping. The latter may safely be assumed insensitive to changes in the structural details of the hydrocarbon residue to which the peroxide group is attached. Correlation may therefore be looked for between the activation energy (E_3) and the energy required to rupture the $\alpha\beta$ C–H bond.

The activation energies of series of related exothermic reactions have in certain cases been shown to bear a well-defined relation to their heat of reaction. E. T. Butler and M. Polanyi [45] suggested that a simple linear relationship

$$\Delta E = \alpha . \Delta H \qquad . \quad . \quad . \quad . \quad . \quad (12)$$

represented the variation of changes in activation energy (ΔE) with changes in heat of reaction (ΔH) as the alkyl substituent, R, was altered in the general reaction of sodium atoms with alkyl halides $\mathrm{Na} + \mathrm{RCl} \longrightarrow \mathrm{NaCl} + \mathrm{R}$—. The constant α was estimated at 0·27. H. Steiner and H. R. Watson,[46] from a recalculation of earlier results on the chlorination of paraffins, report that the activation energy of the exchange process $\mathrm{Cl} + \mathrm{RH} \longrightarrow \mathrm{HCl} + \mathrm{R}$— varies as the exchanged hydrogen atom is attached to primary, secondary, and tertiary carbon atoms in a way consistent with an α value of 0·22. A theoretical treatment [47, 45] of the sodium–alkyl chloride system shows that equation (12) is plausible, that the value of α obtained is of the right order and that α could range from 0 to unity in other exchange-type reactions.

In the present case ΔH may be interpreted simply as the change in resonance energy of the hydrocarbon radical liberated by the dissociation of the $\alpha\beta$ C–H bond. Of the R— radicals corresponding to the olefinic groupings contained in Table II, only three, *viz.*, (1), (2), (3), have been calculated, and they are consistent with a value of α of 0·39.

The activation energies in Table II may therefore be used to give a rough

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[43] R. A. Fairclough and C. N. Hinshelwood, *J.*, 1937, 538.

[44] Faraday Soc. Discussion, 1947, **2,** 329.

[45] *Trans. Faraday Soc.*, 1943, **39,** 19.

[46] Faraday Soc. Discussion, 1947, **2,** 88.

[47] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1938, **34,** 11.

estimate of the resonance energies of various other α-hydrocarbon radicals differing structurally in much more subtle respects—and the corresponding carbon–hydrogen dissociation energies (D_{C-H} in Table II). Apart from the obvious influence of alteration in the type of unsaturated grouping, introduction of methyl substituents gives rise to some minor effects which include : (i) Increase in degree of methyl substitution at the double bond may increase methylenic reactivity (cf. 4, 5, 6 ; and 7, 8, 9). (ii) In unsymmetrically methyl-substituted double bonds (*e.g.*, 10) the α-methylene group more distant from the methyl group is activated while the adjacent group is unaffected—if not indeed slightly reduced in reactivity. (iii) The degree of substitution of the α-grouping influences its reactivity (cf. 11, 1, 12). The strength of $\alpha\beta$ C–H bonds is in the order primary $>$ secondary $>$ tertiary. In saturated hydrocarbons parallel variations are observed.[48]

The influence of such structural features on the ease of hydrogen-atom detachment from groups in olefins extends to a much wider field than oxidation of olefins, since this process almost certainly forms the rate-determining factor in the many other important reactions [49] in which the α-methylene groups of olefins are involved. The ease with which reaction (R3) can be studied experimentally in quantitative clear-cut fashion makes it an admirable prototype for α-methylenic reactivity in general.

IX. The Propagation Step, $R— + O_2 \rightarrow RO_2$

The addition of oxygen molecules to atoms and radicals is, in general, one of extreme facility. The ease with which even highly resonance-stabilised hydrocarbon radicals combine with oxygen has long been recognised, while C. E. H. Bawn and A. G. Evans [50] have shown the combination of sodium and oxygen to require a very small activation energy.

From experimental measurements of the dependence of oxidation rate on oxygen pressure [cf. equation (4)] the term $k_2k_4^{-\frac{1}{2}}$ may be evaluated. The number of olefins for which such measurements are feasible is unfortunately rather restricted. Representative members of 1 : 4-dienes, mono-olefins, and hydroaromatics have, however, been shown [51] to give $k_2k_4^{-\frac{1}{2}}$ values, which differ by no more than a factor of 2. Here, however, the two individual velocity coefficients cannot be separated with confidence, since no direct measurements (by the rotating-sector method) of the absolute efficiency of the R— + R— interaction have been made. Extreme experimental difficulties would attend their evaluation in oxidation systems ; a more promising approach lies in the determinations of the efficiency of the termination reaction (k_t) in polymerisation, in which two essentially hydrocarbon radicals are involved. Such data as are available [1, 52] suggest that k_t diminishes with increasing reactivity of the monomer in the chain-

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[48] J. O. Smith and H. S. Taylor, *J. Chem. Physics*, 1939, **7**, 390 ; E. C. Baughan and M. Polanyi, *Nature*, 1940, **146**, 685 ; E. C. Baughan, M. G. Evans, and M. Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 385 ; A. D. Walsh, *ibid.*, 1946, **42**, 270.

[49] E. H. Farmer, *ibid.*, 1942, **38**, 340.

[50] *Ibid.*, 1937, **33**, 1580.

[51] J. L. Bolland, ref. 24, Part IX.

[52] G. Dixon-Lewis, Faraday Soc. Discussion, 1947, **2**, 319.

propagation step. This in turn implies that the rate of interaction of the two hydrocarbon radicals decreases with increase in the resonance energy of the radicals. The most probable interpretation of the observed constancy of $k_2k_4^{-\frac{1}{2}}$ is that in passing from olefin to olefin changes in both k_2 and k_4 occur which do, however, to a first approximation cancel each other out. This is not unreasonable, since the diradical attributes of the oxygen molecule [53] prompt the suggestion that both (R2) and (R4) belong to the same formal type of reaction and should be influenced by changes in exothermicity [twice as great in (R4) as in (R2)] in much the same way. It seems likely that radical interactions are not so sensitive to alterations in heat of reaction as the exchange-type reaction.

X. Peroxide Decomposition

It is very generally accepted that the decomposition of the peroxides formed during various types of oxidation plays an essential rôle in the further progress of the reaction. In contrast to the situation arising in the combustion of saturated hydrocarbons, the kinetic consequences of decomposition of α-hydroperoxides formed during the oxidation of olefins is simple and clear-cut. The decomposition of α-hydroperoxides has not yet been examined from a kinetic standpoint to a degree commensurate with its significance.

The decomposition of tetralin hydroperoxide is better represented [54] as a first- rather than a second-order reaction, while measurements carried out on oxidised ethyl linoleate appeared to suggest that the peroxide decomposition follows a bimolecular process. Kinetic investigations of the thermal decomposition of the hydroperoxides derived from low-molecular saturated hydrocarbons have emphasised the complexity of this type of reaction: S. Medvedev and A. Podyapolskaya [55] detected concurrent first- and second-order reactions in the decomposition of methyl hydroperoxide. E. J. Harris [56] came to a similar conclusion with ethyl and *n*-propyl hydroperoxides, though here the decomposition was at least partly heterogeneous.

Interpretation of such kinetic data must of course be made with some reserve, since the observed rates of decomposition may not measure the rate of primary dissociation into radicals. The initial dissociation process may initiate a chain sequence of decomposition reactions, or on the other hand the proportion of radical fragments which recombine to re-form peroxide molecules may be significant (as suggested by C. C. Price [57] in the decomposition of benzoyl peroxide). In addition, the peroxide may decompose in an alternative way, without the liberation of radicals (as, for example, in the case of tetralin hydroperoxide, where it is suggested that the major course of decomposition may consist of intramolecular dehydration to

[53] L. Pauling, " Nature of the Chemical Bond ", Cornell Univ. Press, 1940, p. 271; G. W. Whitehead, " The Theory of Resonance ", John Wiley & Sons, New York, 1944, p. 206.

[54] K. I. Ivanov, V. K. Savinova, and E. G. Mikhailova, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **25**, 34.

[55] *Acta Physicochim. U.R.S.S.*, 1935, **2**, 487.

[56] *Proc. Roy. Soc.*, 1939, *A*, **173**, 126.

[57] *Ann. N.Y. Acad. Sci.*, 1943, **44**, 351.

α-tetralone). Any of these three complications could obviously result in the reaction order of the overall reaction and that of the radical-producing process being different. This situation is well illustrated by the recent refined kinetic examinations of the thermal decomposition of benzoyl peroxide. Bartlett and Nozaki and also Cass [27] found that the decomposition shows deviations from a strictly first-order course, which are, however, satisfactorily accounted for by the occurrence of a chain-decomposition reaction initiated by the radical fragments set free by the dissociation of peroxide molecules. The fact that the kinetics of chain reactions—*e.g.*, polymerisation or oxidation —initiated by benzoyl peroxide may follow the simple course expected from its straightforward unimolecular dissociation, is readily explained: the primary products of dissociation may initiate polymerisation or oxidation chains in preference to the chain decomposition of further molecules of peroxide. The complicating factors encountered in peroxide decomposition kinetics are then missing from the chain reactions the peroxides may initiate.

A wide variety of olefins autoxidise according to the ethyl linoleate pattern (p. 7) in giving in the initial stages a linear relationship between rate of oxidation and extent of oxidation.[58] The implication of this kinetic characteristic is [cf. equation (3)] that the chain initiation (*i.e.*, the production of chain-starting radicals from the peroxide) is bimolecular with respect to α-hydroperoxide concentration.* The slopes of the linear autoxidation curves (equal to $k_1^{\frac{1}{2}} k_3 k_6^{-\frac{1}{2}}[\mathrm{RH}]$ at high oxygen pressures) when considered with $k_3 k_6^{-\frac{1}{2}}$ values (Table II) yield an estimate of k_1, the bimolecular velocity coefficient of the radical-producing peroxide decomposition process. Comparisons of k_1 throughout a series of olefins, all of which give as oxidation products secondary α-hydroperoxides, show that any variations are relatively trivial. Small but definite differences are, however, detected on passing to olefins that give (*a*) mainly a tertiary α-hydroperoxide and (*b*) a certain proportion of primary hydroperoxide; the rates of radical production are apparently in the order tertiary > secondary > primary. The differences must, however, be regarded as small since this reaction, in contrast to the $\mathrm{RO_2}$— + RH step, is endothermic. The values of k_1 for secondary and tertiary hydroperoxides differ only by an amount corresponding to about one kcal./mol. in activation energy. On this basis variations in oxygen–oxygen dissociation energy probably do not exceed this figure.

From the proportionality between rate of oxidation and the square-root of the rate of chain initiation [equation (4)] interesting conclusions as to the nature of the latter process may be drawn. Thus it is found [58] that methyl*cyclo*hexene to which *tert.*-butyl hydroperoxide and tetralin hydroperoxide have been added oxidises at a rate proportional to the respective peroxide

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[58] J. L. Bolland and A. L. Morris, ref. 24, Part X.

* The tendency of hydroperoxides to react bimolecularly is emphasised by observations that chain initiation is increased in presence of certain fatty acids and alcohols. Chain initiation may be perhaps pictured as elimination of water between a molecule of hydroperoxide and a molecule (hydroperoxide, acid, or alcohol) containing an hydroxyl group. One factor which may play a dominant rôle in favouring bimolecular as opposed to unimolecular dissociation may well be preliminary formation of hydrogen bonds between pairs of reactant molecules.

concentrations. The peroxide decomposition process responsible for chain initiation is on this evidence bimolecular. It remains to be seen whether the lower order of the *overall* decomposition of tetralin hydroperoxide arises from a concurrent unimolecular decomposition in which radicals are not generated or from the chain character of the decomposition. It is certainly true that the kinetics of the oxidation reactions initiated by peroxide can shed very considerable light on their own mechanism of decomposition.

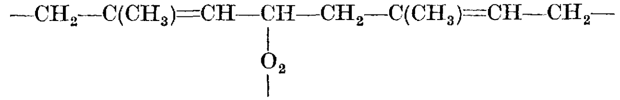
XI. Olefin–RO_2— Interaction as the Key Reaction

We may summarise the conclusions of the preceding four sections regarding the influences of olefinic structure on the various elementary processes comprising the autoxidation mechanism (p. 7) in this way : the efficiencies with which the initiation process (R1) and the termination reaction (R6) occur are sensibly the same for a variety of non-conjugated unsaturated hydrocarbons ; in addition, the resultant influence of the propagation and termination reactions involving the R-type chain carrier is negligible. The remaining chain-propagation step (R3) (see above), on the other hand, is sufficiently sensitive to the nature of RH to introduce considerable variations in oxidation-chain length throughout this same range of olefins ; (R3) must thus be regarded as the key reaction in controlling rates of autoxidation.

This same reaction also has a determining influence on the chemical nature of the primary peroxidic product obtained by oxidation of any given olefin. So long as the mode of reaction between RO_2— and an olefinic centre which occurs most readily is the exchange of an α-methylenic hydrogen atom, α-(mono)hydroperoxide will be the major primary product. If, however, circumstances favour the alternative of RO_2— radical addition at an olefinic double bond, fresh types of product will appear. Three distinct factors which may have this effect are exemplified below.

(1) *Thermochemical influence.* The polymeric peroxides formed during the autoxidation of such hydrocarbons as α-terpinene and styrene must be built up by a succession of addition reactions involving RO_2— type radicals and olefinic double bonds. If olefin–RO_2— radical interactions involving α-methylenic hydrogen abstraction and double-bond addition respectively are compared [59] from the thermochemical point of view, the olefinic systems in which the balance is most likely to be in favour of the latter mode of reaction is undoubtedly just such conjugated olefins (though, of course, the absence of α-methylenic groups in styrene no doubt contributes to the predominance of the polymeric type of reaction).

(ii) *Steric influences.* In the oxidation of the important group of $\Delta^{1:5}$ olefins, the polyisoprenes,[60] cyclisation of the RO_2— type chain carrier



$$—CH_2—C(CH_3)=CH—\underset{\substack{| \\ O_2 \\ |}}{CH}—CH_2—C(CH_3)=CH—CH_2— \qquad . \quad (A)$$

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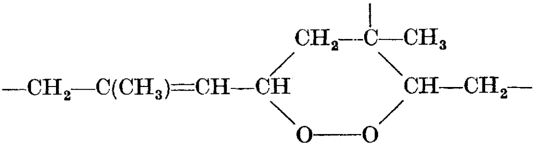
[59] J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, 1946, **42**, 244.

[60] J. L. Bolland and P. ten Have, *ibid.*, 1949, **45**, 93.

to give



(B)

occurs to the virtual exclusion of *inter*molecular α-methylenic hydrogen exchange.* The particular spacing of neighbouring double bonds in this type of olefin, leading as it does to the possibility of forming six-membered cyclic peroxides, may be seen to be the factor mainly responsible for the peroxide structure obtained.

(iii) *Concentration effects.* Schenk and Ziegler[8] have succeeded in preparing transannular peroxides from three cyclic conjugated olefins (including ascaridole from α-terpinene) by interaction of the olefins with oxygen at such high dilutions that intramolecular recombination of the RO_2— diradical, produced by addition of an oxygen molecule to the conjugated system, is of comparable probability to intermolecular (polymerisation) reactions with other olefin molecules.

Heterogeneity of Peroxide Products.—While the rates of the RO_2— + olefin reaction shows undoubted variations with olefinic structures, its exothermic nature ensures that reactivities do not range over spectacular limits (such as, for example, are observed in the epoxylation of the olefins).[61] As a result this key reaction does not in general follow one chemical path exclusively, and the resulting peroxidic products may assume a certain complexity on this account. For example, polymeric peroxides are by no means completely absent from the overwhelmingly mono-hydroperoxidic product obtained from certain mono-olefins. Again, in unsymmetrically-substituted olefins attack does not always proceed exclusively at one type of α-grouping. Thus in the simple olefinic grouping $—\overset{(b)}{CH_2}—\overset{(a)}{C}(CH_3)=CH—\overset{(c)}{CH_2}—$ it is estimated (Table II) that hydrogen abstraction will proceed at α-groups (*a*), (*b*), and (*c*) in the ratio 1 : 3 : 9·5. In general, subsequent addition of oxygen may in each case occur at two alternative sites (one of which results in the shifting of the double bond from its original position). Hence, of the six constituents comprising the primary oxidation, the two major ones each represent only some 33% of the total.

XII. Oxidation of Peroxide-free Olefins

In the most general terms the autoxidisability of an olefin can be measured by the time taken for it to absorb some significant amount of oxygen. One factor which must be of very real importance in this connection

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[61] D. Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692.

* The completion of the diperoxidic primary product [(VI) on p. 3] occurs by addition of oxygen to radical (B) and α-methylenic hydrogen abstraction by the resulting peroxide radical (C). In this way the chain-propagation cycle on p. 8 is modified to contain four steps. Since, however, the two steps (A) ⟶ (B) and (B) ⟶ (C) are fast in comparison with (C) ⟶ (VI), a close parallelism between the oxidation kinetics of this type of diene and the α-monohydroperoxide-forming olefins is maintained.[60]

is undoubtedly the initial rate of oxidation of the peroxide-free olefin: its value decides the rate at which the hydroperoxide concentration is built up, and hence the time taken for the autocatalysed reaction to assert itself.

The kinetics of oxidation of some peroxide-free olefins have been followed,[62-65] without, however, any generally applicable picture of the mechanism being evolved. George and Robertson [64] have made a careful kinetic study of the initial stages of the oxidation of tetralin and have reached some interesting conclusions. Their experimental data show that the initial rate of oxidation is expressed by the simple relation:

$$\text{Rate} = \text{const.}[\text{RH}]^2[\text{O}_2]^0 \quad . \quad . \quad . \quad . \quad (13)$$

while in the presence of four different types of inhibitors the oxidation rate conforms to

$$\text{Rate} = \text{const.}[\text{RH}]^2[\text{O}_2]^0/(1 + k_I[I]) \quad . \quad . \quad . \quad (14)$$

where $[I]$ represents inhibitor concentration. Introducing the reasonable assumption that the inhibitors function as oxidation-chain terminators, George and Robertson conclude that the two rate equations (13) and (14) are both explicable only in terms of a chain mechanism in which the chain carriers are energy-rich molecules and not, as one of the same authors suggests is the case for other tetralin oxidation systems, radicals.

The complete mechanism suggested may be represented as:

Initiation.		$\text{RH} \longrightarrow \text{RH}^*$
Propagation.	$\text{RH}^* + \text{O}_2$	$\longrightarrow \text{P}^*$
	$\text{P}^* + \text{RH}$	$\longrightarrow \text{RO}_2\text{H} + \text{RH}^*$
Termination.	P^*	$\longrightarrow$ inactive molecule

Asterisked molecules are considered to be activated, P* being visualised as either a vibrationally excited hydroperoxide molecule or a complex which can be represented by $\text{RH}\cdots\cdots\cdots\text{O}_2$. The inhibitors when present cause chain termination by interaction with this chain carrier.

General objections to the occurrence of energy chains of this type in liquid media may perhaps be advanced, and certainly a mechanism in which the chain carriers are radicals is *a priori* more attractive: the energy chains suggested by George and Robertson contain on the average some 600 links [66] each of which must involve the transfer of vibrational energy from one chain carrier to the next in a highly specific manner before a chain carrier (and again only one of the two chain carriers must be involved) finally dissipates its activating vibrational energy. Also a reaction between the chain carrier P* and an inhibitor molecule, in which the latter is thereby removed from the system, is much more difficult to visualise than the corresponding radical reaction.

The possibility of more than one chain reaction proceeding simultaneously and independently (*e.g.*, of the material and energy chain types) is one of

[62] S. Medvedev, *Acta Physicochim. U.R.S.S.*, 1938, **9**, 395.

[63] J. L. Henderson and H. A. Young, *J. Physical Chem.*, 1942, **46**, 670

[64] P. George and A. Robertson, *Proc. Roy. Soc.*, 1946, *A*, **185**, 309.

[65] P. George, *ibid.*, p. 337.

[66] P. George, E. K. Rideal, and A. Robertson, *ibid.*, p. 305.

real interest, and the extension of George and Robertson's work to other olefins is of some importance.

Non-peroxidic Oxidation Products.—It is an undoubted fact that, side by side with the peroxidic primary products, other oxygenated groupings appear during autoxidations. Kinetic measurements when considered alone may give a quite illusory impression of simplicity of mechanism : the reactions by which secondary products arise will affect the kinetics of the overall reaction only if their occurrence happens to have repercussions on one of the rate-determining steps in the peroxidation mechanism. It is only after careful chemical analysis of the products that a true impression is gained of the complexity of the reaction.

We may note two important effects which the occurrence of secondary processes may have. S. Medvedev [62] in his study of the autoxidation of tetralin demonstrated that the secondary product, α-tetralone, had an undoubted influence in diminishing the rate of oxidation, and that certain characteristics of the detailed kinetic course followed by this oxidation could be explained in terms of tetralone formation. A similar effect has recently been identified in the autoxidation of certain aliphatic olefins—and in particular in polyisoprenes.

Secondary reactions accompanying the main peroxidation reaction, to which all commercially important olefinic raw materials are susceptible, result in notable alterations in their physical properties. These include the development of rancidity in fats (by formation of aldehydes), gelling of drying oils (by the formation of conjugated diene groupings in oxidised molecules which may then the more easily cross-link), and the mechanical failure of polymers (through the concurrent oxidative scission of the chains). The detailed mechanism by which these secondary reactions occur, and their relation to the main course of oxidation, has not as yet been established.