

THE CHEMICAL INTERACTION OF OXYGEN AND OLEFINS

by

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J. L. Bolland

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Of the eleven published papers included in this thesis, all but those constituting Sections 4 and 12 were prepared for publication by myself. I personally carried out at least some of the experimental work on which each of these nine papers were based; the remaining work was carried out under my direction. Sections 4 and 12 represent co-operative investigations in which I played a full part in both the experimental work and the preparation of the papers for publication.

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SECTION 1

Introduction

All the material incorporated in this thesis has a common theme, in that it is concerned with the elucidation of the chemical mechanism by which non-conjugated olefins react with molecular oxygen. The constituent investigations are of two general types. On the one hand, since the oxidation mechanism is of the chain type, it is possible to bring changes on the mode of chain initiation and chain termination, in such a way as to provide a set of closely related chemical systems, which by exhibiting significant differences in kinetic behaviour build up a well-substantiated picture of the general oxidation mechanism. This work was carried out almost exclusively in the specially favourable case of ethyl linoleate, and is described in Sections 3-7.

In the second place, the elementary chemical processes which go to make up this mechanism may depend markedly on the detailed chemical structure of the olefin concerned. Sections 10-12 form part of a systematic investigation of this aspect of autoxidation. One class of olefins - the polyisoprenes - has been studied in rather greater detail: Sections 8 and 9 describe complementary investigations of the oxidation kinetics and of the nature of the primary

oxidation product as indicated by organo-analytical methods.

No attempt will be made here to relate in detail the various sections one to another, or to present the general context of published work into which they may be fitted: it is hoped that this requirement is adequately met by Section 2. Marginal references have been inserted in this latter section, to facilitate reference to the appropriate parts of the thesis.

Section 13 consists of a short communication which summarises the results of an investigation into the interaction of molecular oxygen and alcohols. It has been included in this thesis since it emphasises the respects in which another major class of substrate conforms to and diverges from the oxidative behaviour of the olefins.

SECTION 2

Kinetics of Olefin Oxidation

KINETICS OF OLEFIN OXIDATION

By J. L. BOWMAN, Ph.D.

The kinetics of olefin oxidation have been studied with the help of a number of investigators. The results of these studies are summarized in this section. The reaction of olefins with oxygen is a complex process involving a number of steps. The rate of reaction is affected by a number of factors, including the nature of the olefin, the concentration of oxygen, and the presence of catalysts. The reaction is generally first order with respect to the olefin and half order with respect to oxygen. The activation energy of the reaction is approximately 10 kcal/mole. The reaction is inhibited by a number of substances, including carbon dioxide and water. The reaction is also affected by the presence of metal ions, particularly copper and silver. The reaction is generally considered to be a free radical process. The mechanism of the reaction is still under investigation.

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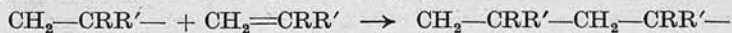
KINETICS OF OLEFIN OXIDATION

By J. L. BOLLAND, PH.D.

(THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION)

IN the twenty years that have elapsed since the independent existence of free radicals was established, the number of organic chemical reactions explainable 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:



The further step of measuring the absolute efficiencies of reactions of this type has recently been accomplished¹ 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.

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.

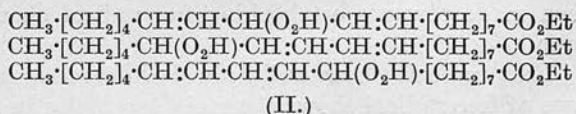
I. Chemical Nature of Oxidation Products³

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.

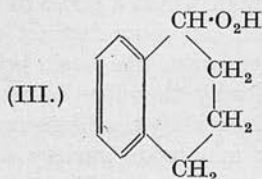
(a) The products formed in the autoxidation of mono-olefins,⁴ 1:4-dienes,⁵ and hydroaromatics⁶ are substantially pure α -hydroperoxides of which the following are representative examples:



(I.)



(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

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.

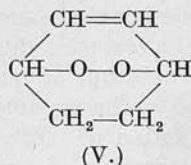
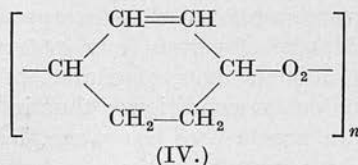
⁴ R. Criegee, H. Pilz, and H. Flygare, *Ber.*, 1939, **72**, 1799.

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.

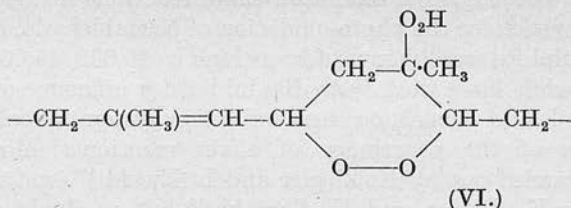
⁷ A. Bodendorf, *Arch. Pharm.*, 1933, **271**, 1.

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



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). (Sec. 9)



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

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. Bäckström¹⁵ 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 work¹⁶ 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. Ewald¹⁷ (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-

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

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 ethyllinoleate, $\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{Et}$, 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 $[\text{Bz}_2\text{O}_2]$, olefin $[\text{RH}]$, and oxygen $[\text{O}_2]$) as

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

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 $[\text{O}_2]/(k_c' [\text{RH}] + [\text{O}_2])$ is insufficiently sensitive to oxygen concentration to permit of more than a demonstration that pressure dependence is consistent with the factor $[\text{O}_2]/(\lambda_c + [\text{O}_2])$.

Photo-oxidation.—Systems consisting of oxygen and highly purified olefins absorb ultra-violet radiation of wave-length $> 2500 \text{ \AA}$. 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 circumstances²⁵ the rates of photo-oxidation of cyclohexene, methylcyclohexene, and ethyl linoleate conform to the relation

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

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

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 :

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

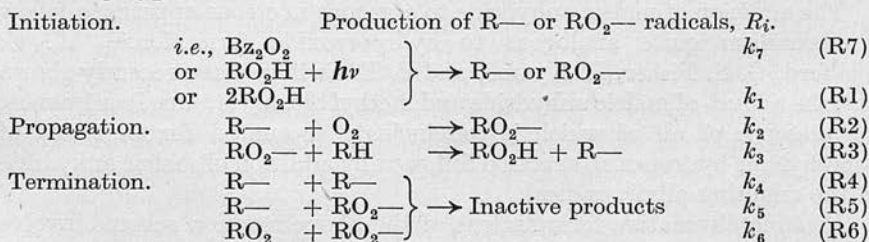
The autoxidation of mono-olefins follows precisely the same kinetic laws.²⁶ (Sec 1)

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 $[\text{RH}]$. 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 (Sec 2) being assumed to generate radicals suitable as oxidation chain carriers, the three rate equations reduce to the common form :

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

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 :



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

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

The correspondence between the experimental and the theoretical relation,

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 -methylene 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 realization²⁵ 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 linolenate²⁸ 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. Swift³² 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 -methylene 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

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 observation³³ 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 study³⁴ of the influence of quinol, Hq, on ethyl linoleate oxidation initiated by benzoyl peroxide and ethyl linoleate hydroperoxide leads to the two rate equations: (Sec 6)

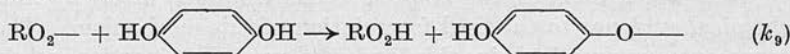
$$\text{Rate} = K_c[\text{Bz}_2\text{O}_2][\text{RH}]/[\text{Hq}] \quad (6)$$

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

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

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

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 identified³⁵ as (Sec 7)



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 :

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

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

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

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

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 $k_3k_6^{-1}$ and $k_2k_4^{-1}$ 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 $k_3k_6^{-1}$) measured under equivalent conditions at 10° for the photo- and benzoyl peroxide catalysed oxidations of *cyclohexene* are 17 and 16 respectively; (b) for the autoxidation and benzoyl peroxide initiated oxidations of ethyl linoleate the corresponding values of $k_3k_6^{-1}$ at 45° are 0.0226 and 0.0104 (mol.⁻¹ l.¹ sec.⁻¹); (c) at 45°, $k_2k_4^{-1}$ in the latter pair of systems is found to be 5.2×10^3 and 5.5×10^3 (mol.⁻¹ l.¹ sec.⁻¹), 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 applied²¹ to the experimental energies of activation associated with $k_3k_6^{-1}$ and $k_2k_4^{-1}$ 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 RO₂—, 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

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 solved³⁸ 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 Gee²⁵ 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 *cyclohexene* and *methylcyclohexene*, 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

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

(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)	
<i>cycloHexene</i>	15°	0.6 ₅	0.9 ₅
<i>Methylcyclohexene</i>	15	1.1	0.5 ₀
<i>Ethyl linoleate</i>	11	5.7	0.5 ₀
<i>Dihydromyrcene</i>	15	0.4 ₀	0.6 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 kcal./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 published¹ for the interaction of two hydrocarbon radicals, encountered as the chain-terminating process in vinyl polymerisation.

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 *cyclohexene*, obtained results consistent with the requirements of the same mechanism (though his explanation was in other, more complicated terms), while P. George⁴¹ has agreed that his observations on the benzoyl peroxide-catalysed oxidation of tetralin are capable of a re-interpretation which brings them into line.

c 10) VIII. The Propagation Processes, $\text{RO}_2- + \text{RH} \rightarrow \text{RO}_2\text{H} + \text{R}-$

$k_3 k_6^{-1}$ has been determined⁴² 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 $\text{RO}_2- + \text{RH} \rightarrow \text{RO}_2\text{H} + \text{R}-$ occurs at α -groups in a variety of unsaturated environments. The best available group values of $k_3 k_6^{-1}$ 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.

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.

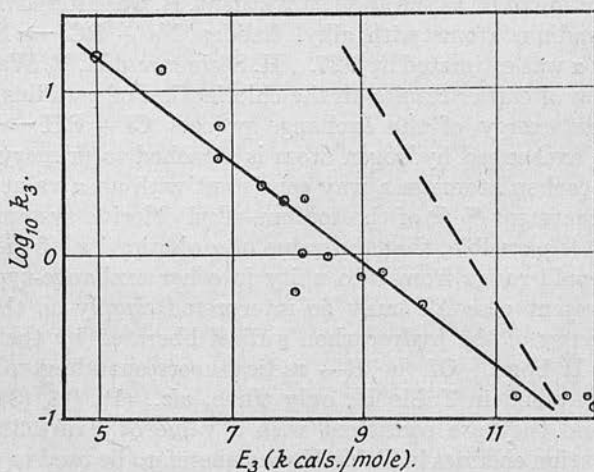
* E_3 is taken equal to $E_c - 15.5$ kcal.: from equation (4) $E_c = E_3 + \frac{1}{2}E_4 - \frac{1}{2}E_6$. E_6 is allotted the value of zero, and E_4 (the activation energy of dissociation of benzoyl peroxide) 31 kcal./mole.⁴²

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.*	$k_3 k_6^{-1/2} \times 10^4$ (mol. ^{-1/2} l. sec. ^{-1/2}).	$k_3 \times 10$ (mol. ⁻¹ l. sec. ⁻¹).	E_3 .	D_{C-H} .
			(kcal./mol.).	
1. —CH ₂ —CH=CH—CH ₂ — . (A) Variation in olefinic type .	6.5	5.0	9.7	80.2
2. —CH=CH—CH ₂ —CH=CH—	194	150	5.0	68.1
3. ϕ —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. ϕ —CH ₂ —CH=CH ₂	9.4	7.3	9.2	78.9
8. ϕ —CH ₂ —CH=CHMe	48	37	6.8	72.7
9. ϕ —CH ₂ —CH=CMe ₂	163	126	5.3	68.9
10. $\begin{array}{c} \text{CH}_3 \text{ (e)} \\ \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \\ \text{(b)} \quad \quad \quad \text{(a)} \end{array}$	(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).



⁴² J. H. McClure, R. E. Robertson, and A. C. Cuthbertson, *Canadian J. Res.*, 1942, **20B**, 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.

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 reactions⁴⁹ 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, $R\cdot + O_2 \rightarrow RO_2$

(Sec 12.)

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. Evans⁵⁰ 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 $k_2k_4^{-1}$ 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 shown⁵¹ to give $k_2k_4^{-1}$ 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 $R\cdot + R\cdot$ 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-

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 $k_2k_4^{-1}$ 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 molecule⁵³ 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 represented⁵⁴ 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. Podyapolskaya⁵⁵ detected concurrent first- and second-order reactions in the decomposition of methyl hydroperoxide. E. J. Harris⁵⁶ 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. Price⁵⁷ 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 Cass²⁷ 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 $k_1^{\frac{1}{2}}k_3k_6^{-\frac{1}{2}}[RH]$ at high oxygen pressures) when considered with $k_3k_6^{-\frac{1}{2}}$ 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 $RO_2 + RH$ 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 found⁵⁸ that methylcyclohexene to which *tert.*-butyl hydroperoxide and tetralin hydroperoxide have been added oxidises at a rate proportional to the respective peroxide

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.

(Sec 11)

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.

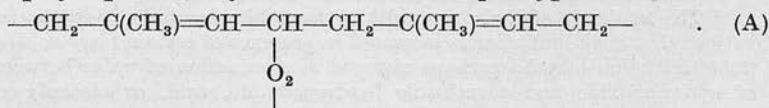
XI. Olefin-RO₂— Interaction as the Key Reaction

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 RO₂— and an olefinic centre which occurs most readily is the exchange of an α -methylene hydrogen atom, α -(mono)hydroperoxide will be the major primary product. If, however, circumstances favour the alternative of RO₂— radical addition at an olefinic double bond, fresh types of product will appear. Three distinct factors which may have this effect are exemplified below.

(i) *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 RO₂— type radicals and olefinic double bonds. If olefin-RO₂— radical interactions involving α -methylene hydrogen abstraction and double-bond addition respectively are compared⁵⁹ 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 -methylene groups in styrene no doubt contributes to the predominance of the polymeric type of reaction).

ecs.
Band 9) (ii) *Steric influences.* In the oxidation of the important group of $\Delta^{1:5}$ olefins, the polyisoprenes,⁶⁰ cyclisation of the RO₂— type chain carrier



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.

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 Robertson⁶⁴ 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:

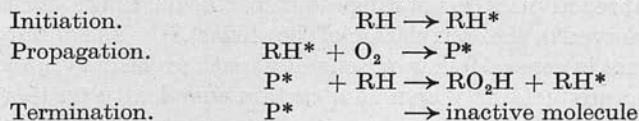
$$\text{Rate} = \text{const.}[\text{RH}]^2[\text{O}_2]^0 \quad (13)$$

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

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

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:



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 $\text{RH} \cdots \cdots \text{O}_2$. 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 links⁶⁶ 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. Medvedev⁶² 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.

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SECTION 3

The Thermal Oxidation of Ethyl Linoleate

Kinetic studies in the chemistry of rubber
and related materials

I. The thermal oxidation of ethyl linoleate

By J. H. Baxendale

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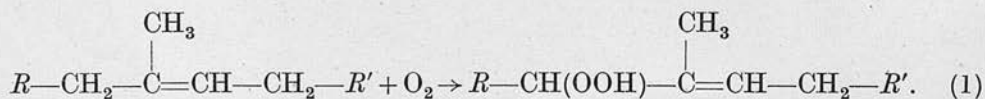
I. The thermal oxidation of ethyl linoleate

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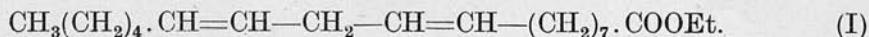
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The kinetics of the initial stages of the thermal oxidation of ethyl linoleate (by molecular oxygen) have been investigated in the temperature range 35–75° C. From consideration of chemical and kinetic evidence the reaction mechanism has been established: oxidation chains are initiated by thermal decomposition of ethyl linoleate hydroperoxide (which in the early stages of oxidation is substantially the sole product). The chain propagation reactions are identified as $R\cdot + O_2 \rightarrow RO_2\cdot$ and $RO_2\cdot + RH \rightarrow ROOH + R\cdot$ (where RH represents ethyl linoleate). Chain termination occurs by mutual destruction of the radical chain carriers, $R\cdot$ and $RO_2\cdot$.

In recent years the chemistry of unconjugated polyolefins has been extensively studied, and it has been abundantly demonstrated that a very important type of reactivity is that associated with methylene groups adjacent to a double bond (Farmer 1942). This α -methylene reactivity plays an essential role in many of the reactions of natural rubber, including the important one of oxidation: thus when rubber is oxidized photochemically the first identifiable product is a hydroperoxide of undiminished unsaturation (Farmer & Sundralingam 1943), which on the analogy of the characteristic behaviour of a series of simple unconjugated olefins (Criegee, Pilz & Flygare 1939; Farmer & Sundralingam 1942; Farmer & Sutton 1942, 1943; Sutton 1944) may be represented thus:



While photo-oxidation of such olefins does follow this course almost quantitatively in the initial stages, secondary reactions involving these primary products soon become of importance; in the case of thermal oxidation it is not in general possible to find conditions which make quantitative yields of hydroperoxide possible even at the outset. In embarking on a series of kinetic investigations designed to throw light on the precise mechanism of this type of oxidation, attention has in the first instance been devoted to olefins which can be oxidized thermally at a convenient rate and with quantitative production of hydroperoxide. The 1:4 olefinic esters appear to fulfil this requirement admirably, and the present paper describes an examination of the kinetics of the thermal oxidation of one of the simplest examples of this type, ethyl linoleate (I):



It will be shown that the oxidation products in the early stages of oxidation are simple and correspond exclusively to the type of reaction indicated by (1). The possibility thus arises of examining what appears to be the key reaction in the oxidation of many olefins of various types in absence of complicating secondary reactions.

EXPERIMENTAL

Ethyl linoleate was prepared from a sample of cotton-seed oil by the bromination-debromination procedure. The tetrabromostearic acid was repeatedly crystallized from ethyl acetate to give a product of melting-point $115.7 \pm 0.1^\circ \text{C}$ and bromine content 53.3 % (theoretical 53.3 %). The ethyl linoleate so obtained was carefully fractionated in a molecular still at 78°C . The final product had a peroxide content < 0.01 %, and as it was stored carefully *in vacuo*, this value did not increase appreciably during the investigation.

Ethyl stearate was prepared by esterifying B.D.H. stearic acid ('purified stearine') and recrystallizing the ester three times from ethanol. The final product melted at $33.3 \pm 0.1^\circ \text{C}$.

Benzoyl peroxide was recrystallized three times from ether, when a sample of peroxide content 6.42 % (theoretical 6.61 %) was obtained.

Rates of oxidation were measured in an apparatus of the constant-pressure type, indicated in figure 1. As the supply of ethyl linoleate available was strictly limited, the apparatus was designed to give accurate measurements of oxidation rates using a sample of about 0.2 g. The gas burette *A* (internal cross-section about 1 sq. cm. and length 20 cm.) and controlling manometers *B* and *C*, were immersed in a water thermostat, operating at $25.00 \pm 0.01^\circ \text{C}$, and were connected to the reaction vessel *D* (*ca.* 1-5 c.c. volume) by means of a 6 in. length of Thiokol tubing of external and internal diameters 15 and 2 mm. respectively. Vigorous agitation of the contents of the reaction vessel was achieved by connecting to an eccentric wheel driven at speeds of about 200 r.p.m. The reaction vessel was immersed in a subsidiary thermostat, the temperature of which was controllable to 0.05°C .

Prior to each run the required amount of ethyl linoleate (normally *ca.* 0.2 g.) was weighed into the nitrogen-filled reaction vessel and the glass-thiokol connexions sealed with picein. The apparatus was then thoroughly evacuated at 10^{-5} mm. and left overnight with free access to a liquid-oxygen trap.

During an oxidation run the di-octyl phthalate manometer *B* was used to indicate deviations from the chosen constant oxygen pressure in the apparatus; by observing the meniscus through a reading microscope (magnification $10 \times$), pressure alterations of 0.005 mm. Hg could readily be detected. The upward movement of the mercury level in the gas burette was actuated by the evolution of gas from the small electrolytic cell *E*. The method of automatic control of the gas burette, originally described by Kohman (1929), was used. A thermionic relay, based on the original design of Hershberg & Huntress (1933), was incorporated in the device. Details of the circuit, designed by Dr G. F. Bloomfield of these laboratories,* are

* The British Rubber Producers' Research Association.

included in figure 1. Since the current through the platinum control contacts sealed into the reverse side of the wide-limbed mercury manometer was only a few microamperes, the repeated making and breaking of the contacts, even in an atmosphere of oxygen, caused no sign of contamination of the mercury surface. Provided the current through the electrolytic cell was regulated so that the cell was on and off for approximately equal periods, the pressure variation during the control cycle did

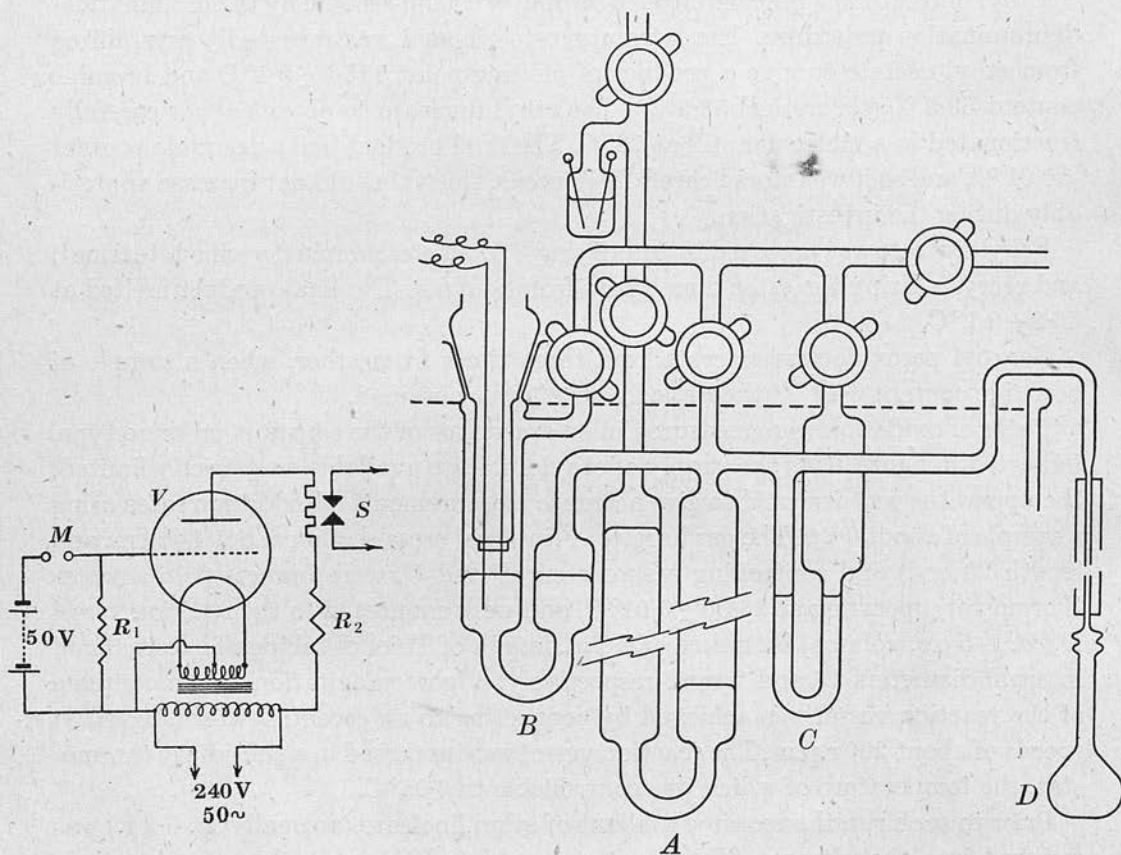


FIGURE 1. Apparatus for measuring rates of oxidation and circuit of electronic relay. *V* represents a PX4 valve, *S* a Sunvic hot-wire vacuum switch (type 602V), *M* the contacts in the manometer, *C* and *R*₁ and *R*₂ resistances of 5 megohms and 5000 ohms respectively.

not exceed 0.02 mm. During an oxidation run, therefore, the automatic device was employed to maintain the oxygen pressure close to the selected standard value, while at regular intervals the exact time at which the standard pressure was obtained—as indicated on the octoil manometer—was noted and the current burette level measured to 0.01 mm.

The thiokol tubing, forming the flexible connexion to the reaction vessel, was baked out *in vacuo* for 16 hr. at 100° C before use; after such treatment only negligible amounts of permanent and condensable gases penetrated into the apparatus over periods of many days.

The peroxide content of oxidation products was, when possible, determined by the colorimetric ferrous thiocyanate method described by Bolland, Sundralingam, Sutton & Tristram (1941) and the iodometric method of Dastur & Lea (1941). Both methods were found capable of giving reproducible results, but the iodometric method suffered the disadvantage of requiring an inconveniently large sample if accurate results were to be obtained for peroxide contents less than 0.1 g.mol. peroxide/g.mol. ethyl linoleate.

Standard experimental conditions, under which the oxidation of ethyl linoleate proceeded at a readily measurable rate, were chosen as follows: temperature, 45° C; oxygen pressure, 100 mm. Hg; concentration of ethyl linoleate, 100 %; and weight of linoleate sample, 0.2 g.

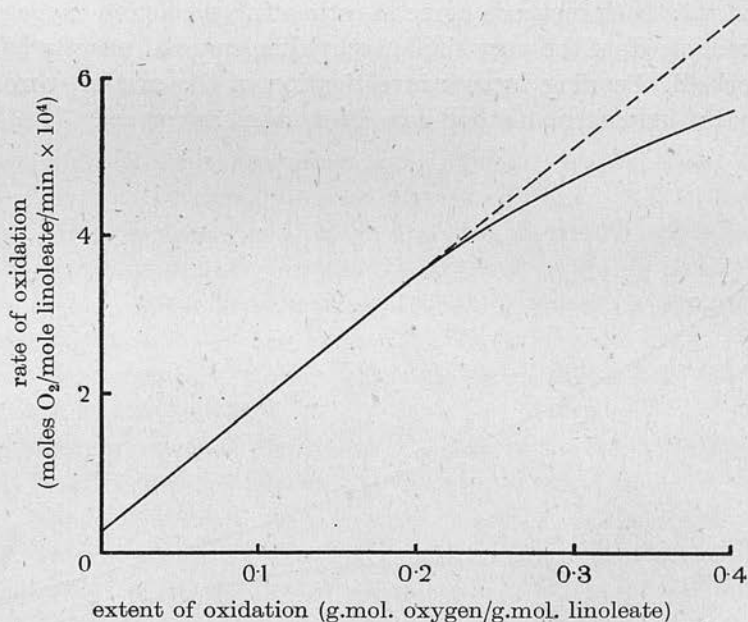


FIGURE 2. Oxidation of ethyl linoleate at 25° C and 100 mm. oxygen pressure.

The course of a typical oxidation run under such conditions is shown in figure 2. Oxidation commences without any apparent inhibition period. During the introduction of up to 0.2 g.mol. oxygen/g.mol. ethyl linoleate a linear relation between the experimentally determined rates of oxidation and the extent of oxidation is satisfied. At higher extents of oxidation the curve deviates from linearity until at about 1.0 g.mol. oxygen/g.mol. linoleate the maximum rate of oxidation is reached. In this investigation, attention has been concentrated on the earlier stages of oxidation, during which, there is reason to believe, the complications associated with secondary reactions—such as peroxide decomposition and molecular intercondensation—are of minor importance.

Formation of volatile products. In the case of a sample of ethyl linoleate oxidized at 45° C the formation of products condensable in liquid oxygen was found to corre-

spond to 1 mol. for every 70 and 100 mol. oxygen reacted during the introduction of the first and second 0.2 g.mol. oxygen/g.mol. ethyl linoleate respectively. Analyses indicated that at least 90% of the volatile products was water.

Peroxide formation. Measurement of the peroxide content carried out at the conclusion of or during the course of oxidation runs at 45°C have shown that divergent results are obtained from the two analytical methods—ferrous thiocyanate and Dastur-Lea iodometric—employed. This is illustrated in figure 3, where the fraction (Y) of oxygen atoms in the oxidized linoleate which are active in oxidizing Fe^{++} or HI respectively is plotted against the total extent of oxidation. This represents the first instance encountered where more than half the total reacted oxygen is active towards either ferrous thiocyanate or hydriodic acid (in particular, it may be mentioned that both methods agree in estimating the active oxygen content of oxidation products from the very similar ethyl linolenate at exactly half the total oxygen absorbed). Pending further investigation of the matter, peroxide determinations by the iodometric method have been taken as correct.

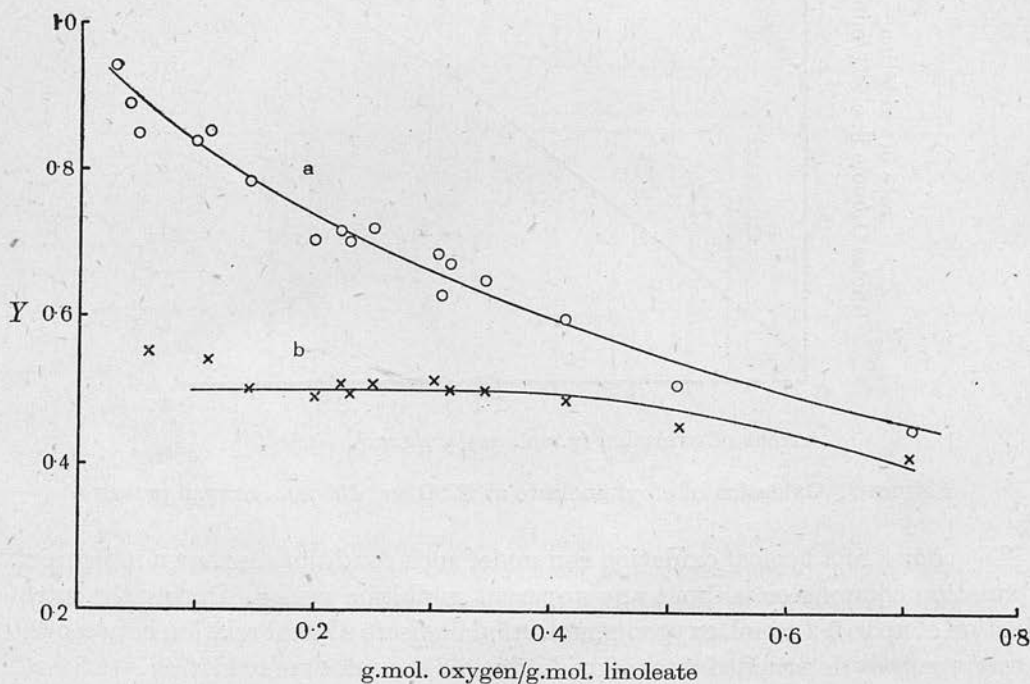


FIGURE 3. Determination of peroxide content of oxidized ethyl linoleate. Y represents the fraction of oxygen atoms in oxidation products active in oxidation of ferrous ion (curve a) and KI (curve b).

Active hydrogen content. The active hydrogen content of samples of oxidized ethyl linoleate was determined by the method described by Bolland (1941). Duplicate analyses gave the following results: the peroxide contents (based on iodometric estimations and on measured extent of oxidation of samples) of three samples were

0.290, 0.272 and 0.120 g.mol. peroxidic oxygen/g.mol. ethyl linoleate respectively; the corresponding active hydrogen contents were determined as 0.143, 0.141 and 0.062 g.mol. active hydrogen/g.mol. ethyl linoleate. In each case the active hydrogen content was, within experimental error, half the peroxidic oxygen content.

Chromatographic analysis of oxidation products. Samples of oxidation products were dissolved in 40–60° C petrol ether and passed through a short (*ca.* 10 cm.) column of activated alumina (Savory & Moore) in an atmosphere of nitrogen. The chromatogram was eluted with a further quantity of 40–60° petrol ether, which was collected in several separate successive portions. These were evaporated down *in vacuo* at room temperature and the residues weighed. In one experiment a solution of 4.2500 g. oxidized ethyl linoleate, containing 0.184 g.mol. oxygen/g.mol. ethyl linoleate, in 150 c.c. petrol ether was chromatographed in the above fashion. The first 250 c.c. petrol ether passing through the column contained 3.4121 g. residue, the next 100 c.c. 0.0075 g., and a further 100 c.c. 0.0010 g. As all three residues contained only negligible amounts of peroxide, the separation between oxidized and non-oxidized ethyl linoleate was taken to be complete at this stage. The oxidized portion remaining in the chromatogram accordingly amounted to 0.8294 g., containing 1.01 g.mol. oxygen/g.mol. ethyl linoleate. A similar experiment with an oxidized ethyl linoleate sample containing 0.20 g.mol. oxygen/g.mol. ethyl linoleate gave a very similar result in indicating that the average oxygen content of the oxidized molecules was 1.05 g.mol. O₂/g.mol. ethyl linoleate.

The effect of altering the various experimental conditions in turn from their standard values was investigated.

Ethyl linoleate concentration. The linear character of the rate of oxidation *v.* extent of oxidation relation was not altered by dilution of ethyl linoleate with its most closely related saturated ester, ethyl stearate. Further, as figure 4 shows, the slope of the linear curve is proportional to the concentration of ethyl linoleate.

Oxygen pressure. A series of short measurements of the rate of oxidation of a sample of partly oxidized ethyl linoleate (oxygen content *ca.* 0.1 g.mol./oxygen/g.mol. linoleate) was carried out while the oxygen pressure was maintained at a succession of widely varying values in the range 4–760 mm. Any increase in the rate of oxidation arising from an increase in extent of oxidation was corrected for by interspersing the series with measurements at a selected standard pressure (actually 17 mm.). A lower limit was placed on the range of pressures employed by the necessity of ensuring that the rate of diffusion of oxygen into the liquid phase did not become a rate-controlling factor. At the lowest pressure included in the series of experiments, from which figure 5 was constructed, a twofold increase in the rate of shaking the reaction vessel had no effect on the rate of oxidation.

The results of similar sets of measurements at 22 and 65° C are incorporated in table 1.

Temperature. Oxidation runs carried out in the temperature range 35–75° C conformed to the character shown in figure 2. The slopes of the initial portions of the rate of oxidation *v.* extent of oxidation curves are recorded in table 1.

Oxidation of ethyl linoleate in presence of benzoyl peroxide. In a short series of oxidation runs at 45° C, the effect of addition of benzoyl peroxide in various concentrations was determined. In each experiment the oxidation was followed sufficiently far to give an accurate (extrapolated) value of the rate of oxidation at zero extent of oxidation. The initial rates of oxidation conformed accurately to the equation

$$(\text{Rate})_0 = 1.20 \times 10^{-3}[C]^{\frac{1}{2}} + 0.30 \times 10^{-4}, \quad (2)$$

where $[C]$ represents the gram-molecular fraction of dibenzoyl peroxide (cf. figure 6).

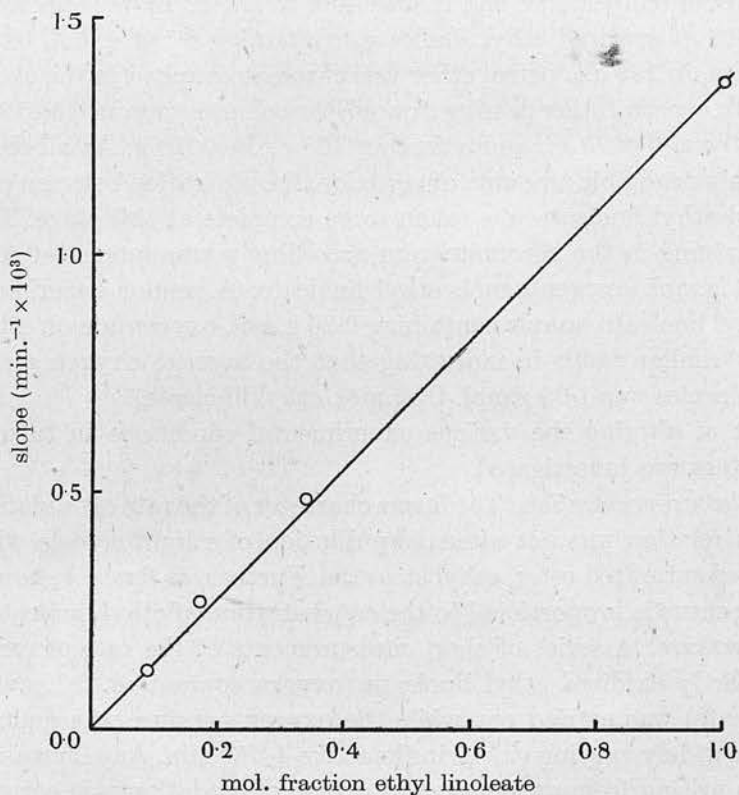


FIGURE 4. Dependence of rate of oxidation on concentration of ethyl linoleate at 45° C and 100 mm. oxygen pressure.

Thermal decomposition of ethyl linoleate hydroperoxide. It will be shown below that the thermal decomposition of the linoleate hydroperoxide plays an important role in the oxidation mechanism suggested, and this reaction has therefore been studied in some detail. A full account will be published elsewhere; it is sufficient for present purposes to note the main conclusions:

(a) Decomposition is substantially bimolecular with respect to peroxide concentration, the velocity constant at 45° C, for example, being 1.50×10^{-4} (g.mol. peroxide/g.mol. linoleate)⁻¹ min.⁻¹.

(b) Not more than one molecule of water is formed for every two peroxide molecules decomposed.

(c) The temperature coefficient corresponds to an apparent energy of activation of 26 kcal./g.mol.

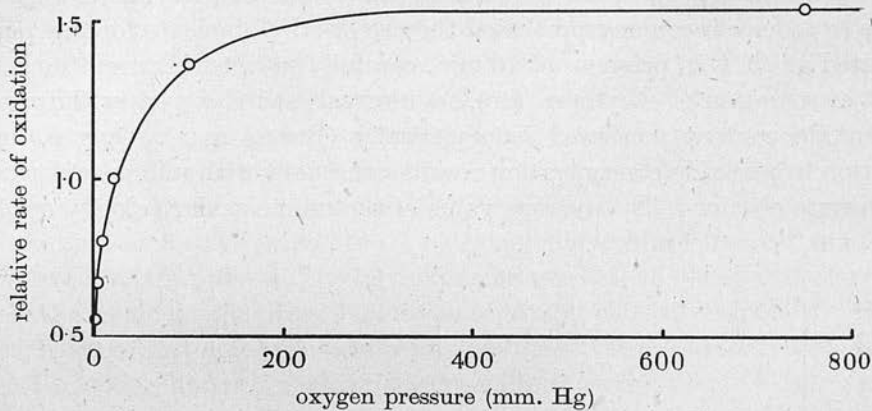


FIGURE 5

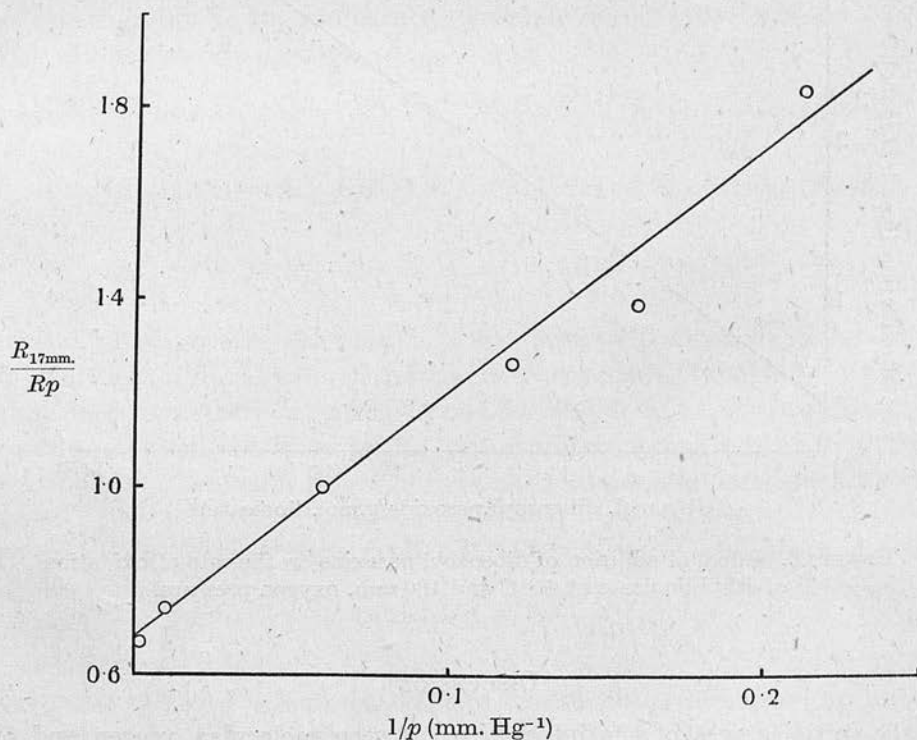


FIGURE 5A

FIGURES 5, 5A. Dependence of rate of oxidation of ethyl linoleate on oxygen pressure at 45° C. $R_{17\text{mm.}}$ and R_p represent the rates of oxidation at 17 mm. and p mm. oxygen pressure respectively.

Thermal decomposition of dibenzoyl peroxide. It has been demonstrated that the thermal decomposition of dibenzoyl peroxide in benzene solution is a unimolecular reaction (McClure, Robertson & Cuthbertson 1942). This has been checked under conditions more closely approximating to those under which the oxidation runs were carried out: for this purpose a 6.10 molar % solution of dibenzoyl peroxide in ethyl stearate (reasons of economy precluded the use of ethyl linoleate for this purpose) was heated at 45° C in presence of 10 mm. carefully purified nitrogen (included to prevent evaporation of ethyl stearate). At intervals samples were withdrawn and the peroxide content measured iodometrically (Braun 1942). Over a fourfold diminution in peroxide concentration results consistent with unimolecular decomposition were obtained. The average value of the unimolecular velocity coefficient at 45° C was $3.0 \times 10^{-5} \text{ min.}^{-1}$.

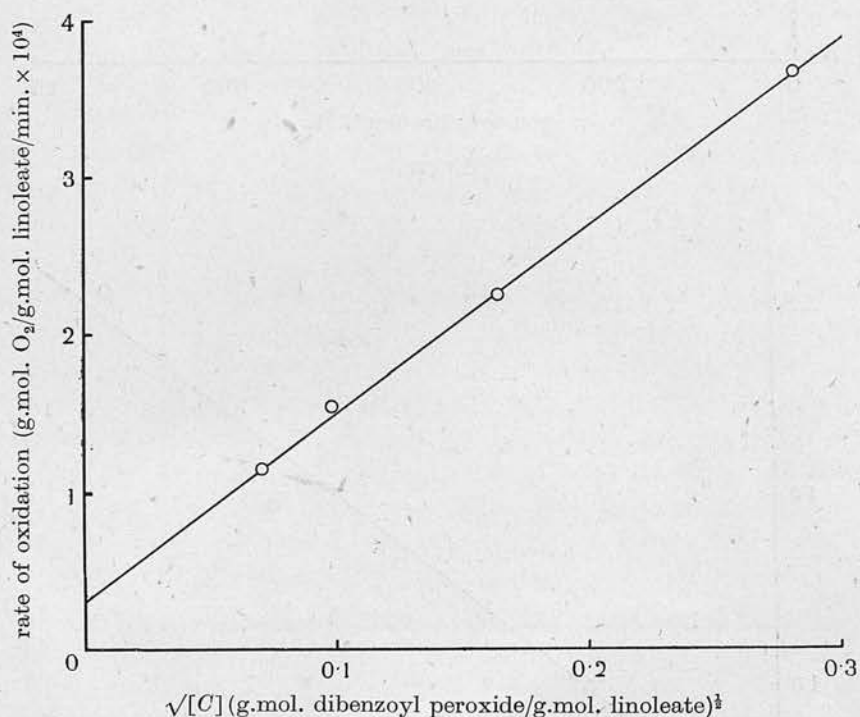
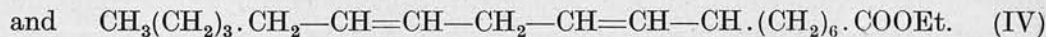


FIGURE 6. Effect of addition of dibenzoyl peroxide on the rate of oxidation of ethyl linoleate at 45° C and 100 mm. oxygen pressure.

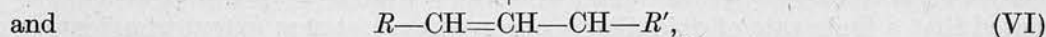
DISCUSSION

In the initial stages of the interaction between molecular oxygen and ethyl linoleate, peroxide groups are formed exclusively: determination of the peroxide content of oxidation products by the Dastur-Lea iodometric method of estimation shows that formation of non-peroxidic products does not become appreciable until some 0.4 g.mol. oxygen/g.mol. ethyl linoleate has reacted. This quantitative aspect

of the reaction is emphasized by the almost complete absence of such volatile products as water and carbon dioxide; in sharp contrast, during the thermal oxidation of certain other olefinic materials, such as rubber, which give only fractional yields of peroxide, water and carbon dioxide are formed from the outset.* The active hydrogen estimations quoted on p. 223 show that the peroxide groups formed in the thermal oxidation of ethyl linoleate, as in the case of other olefinic substances (Criegee, Pilz & Flygare 1939; Farmer & Sundralingam 1942, 1943; Farmer & Sutton 1942, 1943; and Sutton 1944) are of the hydroperoxidic type. While no formal proof is offered here that these hydroperoxide groups are disposed in the α -position to a double bond, the observation (Bolland & Koch 1945) that the introduction of a hydroperoxide group may result in the formation of a conjugated diene chromophore in the oxidized molecule represents very strong evidence that the double bonds are not destroyed in the process. The obvious inference is that the alternative reactive points in the molecule, the three α -methylene groups, constitute the site of reaction. Farmer, Koch & Sutton (1943) have pointed out that the most satisfactory explanation of the diene conjugation which accompanies the oxidation of 1:4 unsaturated esters lies in the formation, at some point in the oxidation mechanism, of free radicals, formally derivable from the parent ester by abstracting a hydrogen atom from an α -methylene group. In the comparatively simple case of ethyl linoleate only three radicals of this type are possible:



The factor which governs the relative probabilities with which these three radicals are formed must of necessity be the resonance energy made available, by the breaking of the (α -methylene) carbon hydrogen bond, for stabilizing the resulting free radicals. Calculations of the resonance energies concerned have been made by Orr† (Bolland & Orr 1945), who estimates that the resonance energies associated with the radical systems

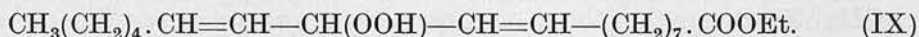
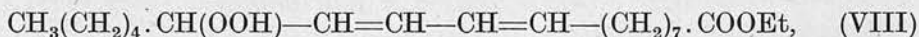


are 30.5 and 18.7 kcal./g.mol. respectively. On this basis formation of the radical (II) is very much more probable than formation of (III) or (IV). Though the position

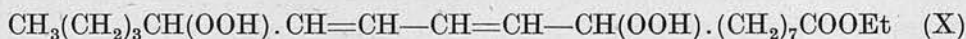
* Thus if rubber is oxidized in the temperature range 25–100° C, about 0.05 g.mol. H₂O and 0.02 g.mol. CO₂ are formed per g.mol. of oxygen reacted.

† I wish to thank Dr W. J. C. Orr for making available these calculations and for the benefit of discussion on the importance of resonance energies in the present problem.

into which substituents (e.g. —OOH) are introduced into the radical by succeeding reaction processes may well be affected by other factors, it is probably of significance that the formation of products of the types (VII) and (VIII) will be favoured at the expense of (IX) by the resonance energy (*ca.* 7 kcal./g.mol.) associated with their conjugated structure:



It is important to note that formation of radicals is less likely from mono-hydroperoxide molecules than from the unoxidized ester: in the case of the isomers (VII) and (VIII) the resonance energy made available by radical formation is some 23 kcal./g.mol. (i.e. the resonance energy of radical (V) less that of the conjugated diene structure), while in the case of the non-conjugated hydroperoxide (IX) the resonance energy concerned will be that of the allyl radical (VI), viz. 19 kcal./g.mol. It is thus to be anticipated that the oxidative attack on ethyl linoleate mono-hydroperoxide is relatively difficult, so that in the early stages of oxidation the formation of even the most probable di-hydroperoxides, e.g.



is small. The distribution of the hydroperoxide groups as determined from chromatographic analysis of oxidation products containing up to 0.2 g.mol. O_2 /g.mol. linoleate (cf. p. 223) provide confirmation of this view.

On chemical and spectroscopic evidence alone, it thus appears that in the early stage of the thermal oxidation of ethyl linoleate α -methylene hydroperoxides are formed quantitatively and in restricted variety, and that the intermediate formation of free radicals of type (II) form an essential part of the oxidation mechanism. The kinetic measurements, as will appear in the sequel, are entirely compatible with this general picture, and in addition fill in much detail regarding the oxidation mechanism, in a manner which it is beyond the possibility of purely chemical investigation to provide.

Kinetic analysis

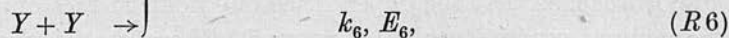
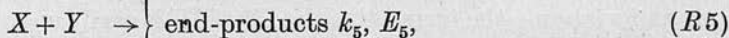
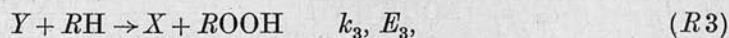
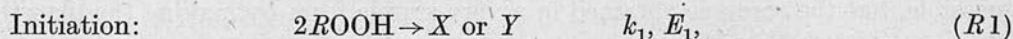
Under all experimental conditions examined, the course of oxidation (cf. figure 2) shows the well-known characteristics of the autocatalytic reaction, but it is to be noted that a finite rate of oxidation is observed even at zero extent of oxidation. This points to the composite nature of the oxidation, and, indeed, examination has shown that it is permissible to attribute the overall rate of oxidation to two distinct types of reaction, which may with advantage be considered independently. The results of the oxidation rate measurements detailed in the experimental section may be summarized by the following expression:

$$\text{rate of oxidation} = \frac{d[\text{ROOH}]}{dt} = K \cdot [\text{ROOH}][\text{RH}] \cdot f([\text{O}_2]) + f'([\text{RH}], [\text{O}_2]), \quad (3)$$

where $[RH]$, $[ROOH]$ and $[O_2]$ represent the concentration of ethyl linoleate, ethyl linoleate hydroperoxide and oxygen in the liquid phase. The first term is identified with oxidation, which being catalysed by the sole product oxidation (i.e. hydroperoxide) is responsible for the autocatalytic aspects of the oxidation and represents the predominant mode of reaction in all but the very initial stages of oxidation. The form of the second, peroxide-independent, term $f'([RH], [O_2])$ has not as yet been completely established. This type of oxidation obviously is of prime importance in the earliest stages of the oxidation of peroxide-free ethyl linoleate in so far as it provides the initial concentration of peroxide, from which the peroxide-catalysed oxidation develops in autocatalytic fashion. In the discussion following, however, attention is concentrated entirely on the peroxide-catalysed oxidation.

Any reaction mechanism which may be advanced for the peroxide-catalysed oxidation of ethyl linoleate must fulfil three essential requirements: (a) it must account for the kinetic characteristics of the oxidation, (b) it must provide a satisfactory explanation of the catalytic action of peroxide, and (c) it must be consistent with information derived from chemical evidence.

In considering many alternatives, the reaction scheme (*R1-R6*) alone has been found to satisfy the first two of these three criteria. This mechanism requires that the thermal oxidation of ethyl linoleate should, in common with many different types of oxidation, be a chain reaction,* and that chains should be initiated by the formation of free radicals from the thermal decomposition of linoleate hydroperoxide, and terminated by the mutual destruction of the particular radicals which act as chain carriers. In the somewhat generalized formulation below, these chain carriers are denoted by *X* and *Y*:



where k_1 to k_6 and E_1 to E_6 represent the reaction velocity coefficient and energies of activation of the elementary reactions (*R1*) to (*R6*) respectively.

Two limiting forms which the rate equation deduced from the above mechanism may assume, will be discussed in the first instance. The stationary concentration of the chain carrier, *X*, will be determined by the rate at which it is formed by the propagation reaction (*R3*) and the rate at which it is destroyed by termination

* Formal confirmation of this view has been obtained from measurements of the effect of inhibitors on the rate of oxidation of ethyl linoleate (J. L. Bolland & P. ten Have, unpublished work).

reactions (*R4*) and (*R5*); [*Y*] is controlled in similar fashion by propagation reaction (*R2*) and termination reactions (*R5*) and (*R6*). If the value of [*O*₂] is sufficiently high relative to [*RH*]' (i.e. at sufficiently high oxygen pressure) the stationary concentration of *X* and *Y* will be adjusted so that [*X*] is very large in comparison with [*Y*]. Under these circumstances chain termination will be effected entirely by (*R6*), and the rate equation becomes

$$d[\text{ROOH}]/dt = k_3 \sqrt{(k_1/k_6)} [\text{ROOH}] [\text{RH}]. \quad (4)$$

Similarly, when [*O*₂] is sufficiently low the stationary concentration of *X* assumes a value low relative to that of *Y*, and termination by (*R4*) predominates. Under these conditions

$$d[\text{ROOH}]/dt = k_2 \sqrt{(k_1/k_4)} [\text{ROOH}] [\text{O}_2]. \quad (5)$$

Equation (4) is in complete accord with our experimental results at high oxygen pressures, since in the pressure range 100–700 mm. the rate of oxidation was found to be proportional to the hydroperoxide content (figure 2) and ethyl linoleate concentration (figure 4) and almost independent of oxygen pressure (figure 5). The increasing influence of the oxygen pressure on the rate of oxidation as the former is reduced from 100 to 4 mm. is apparent from figure 5. The intervention of experimental difficulties prevent reliable rate measurements being made below about 4 mm. oxygen pressure, but if it is legitimate to extrapolate the straight line shown in figure 5A it follows that equation (5) is obeyed at still lower oxygen pressures.

In order to derive a kinetic equation applicable at all oxygen pressures, reaction (5) has to be considered as well as (4) and (6). No simple general solution is then possible, but the result is obtained in a very simple form by making the plausible assumption that $k_5^2 = k_4 k_6$:

$$\frac{d[\text{ROOH}]}{dt} = k_3 \sqrt{\frac{k_1}{k_6}} [\text{ROOH}] [\text{RH}] \frac{k_2 \sqrt{k_6} [\text{O}_2]}{k_2 \sqrt{k_6} [\text{O}_2] + k_3 \sqrt{k_4} [\text{RH}] + \sqrt{(k_1 k_4 k_6)} [\text{ROOH}]}. \quad (6)$$

When the oxidation chain length is large—as is shown below to be the case in the present system—the term $\sqrt{(k_1 k_4 k_6)} [\text{ROOH}]$ is easily shown to be of quite negligible importance, so that the dependence of oxidation rate on oxygen pressure is of the form found experimentally (cf. figure 5A where 1/rate is shown to be a linear function of 1/*p*).

The oxidation chain length, ν , under any particular set of conditions in which the suggested mechanism holds good, is given by

$$\nu = \frac{R}{\alpha R_D} = \frac{1}{\alpha} \frac{k_3}{\sqrt{(k_1 k_6)}} \frac{[\text{RH}]}{[\text{ROOH}]} \frac{k_2 \sqrt{k_6} [\text{O}_2]}{k_2 \sqrt{k_6} [\text{O}_2] + k_3 \sqrt{k_4} [\text{RH}]}, \quad (7)$$

where *R* represents the rate of oxidation, *R*_{*D*} the rate of thermal decomposition of ethyl linoleate hydroperoxide, and α is the average number of fresh chain carriers resulting from the decomposition of one hydroperoxide molecule.

Under 'standard' conditions of temperature (45° C), oxygen pressure (100 mm.) and initial linoleate concentration (100 %), equation (7) reduces to

$$\nu = \frac{9.6}{\alpha[\text{ROOH}]}, \quad (8)$$

when $[\text{ROOH}]$ is expressed in g.mol. peroxidic oxygen/g.mol. ethyl linoleate. For example, at extent of oxidation 0.1 g.mol./oxygen/g.mol. ethyl linoleate the chain length is 96, if α is assumed to be unity. It is of interest that the amount of water formed during oxidation is consistent with a chain length of this order. On the basis that one molecule of water is formed for every two peroxide molecules thermally decomposed (cf. p. 224), the average chain length during the introduction of the first and second 0.2 g.mol./oxygen/g.mol. ethyl linoleate is 40 and 55 respectively, compared with values of approximately 96 and 32 calculated from (8).

Oxidation of ethyl linoleate catalysed by dibenzoyl peroxide

The manner in which the thermal decomposition of dibenzoyl peroxide may initiate chain reactions of the radical type (Smith 1945), and the nature of the reaction products with cyclohexene (Farmer & Michael 1942) indicate that the thermal decomposition of dibenzoyl peroxide results in the production of free radicals. While these are almost certainly phenyl $\text{C}_6\text{H}_5\cdot$ - and benzoate $\text{C}_6\text{H}_5\text{COO}\cdot$ -radicals, details of the mechanism whereby they are formed are by no means established (McClure *et al.* 1942). If these radicals are capable of initiating oxidation chains in ethyl linoleate, a reaction mechanism differing from that suggested above (*R1-R6*), only in so far as the initiation step is concerned, is to be anticipated. On this basis, the resulting rate of oxidation will be given by

$$\frac{d[\text{ROOH}]}{dt} = k_3 \sqrt{\frac{k_7}{k_6}} \sqrt{[C]} [\text{RH}] \frac{k_2 \sqrt{k_6} [\text{O}_2]}{k_2 \sqrt{k_6} [\text{O}_2] + k_3 \sqrt{k_4} [\text{RH}]}, \quad (9)$$

where $[C]$ and k_7 represent the concentration and the (unimolecular) reaction velocity coefficient for the thermal decomposition of dibenzoyl peroxide.

The underlying reason for the appearance of the square root of the rate of chain initiation in the theoretical rate equations ($\sqrt{k_1} [\text{ROOH}]$ and $\sqrt{k_7} \sqrt{[C]}$ in equations (6) and (9) respectively) lies in the assumption that chain termination occurs by mutual deactivation of two chain carriers. Accordingly, the proof by direct experiment (cf. equation (2)) that the rate of oxidation catalysed by dibenzoyl peroxide is in fact proportional to $\sqrt{[C]}$ provides valuable confirmation of the correctness of the suggested chain termination mechanism (*R4-R6*).

When comparing the chain lengths of oxidation, initiated by dibenzoyl peroxide and linoleate hydroperoxide, conditions must be chosen under which the rates of peroxide decomposition are equal. Thus at 45° C the rate of decomposition (1.5×10^{-6} g.mol. peroxide/g.mol. ethyl linoleate/min.) is the same in samples of ethyl linoleate containing 0.05 g.mol. dibenzoyl peroxide/g.mol. ethyl linoleate and 0.10 g.mol. linoleate hydroperoxide/g.mol. ethyl linoleate respectively. Since the rates of oxidation (at 100 mm. oxygen pressure) of these samples are 3.2×10^{-4} and

1.4×10^{-4} g.mol. O_2 /g.mol. linoleate/min., the respective chain lengths are 213 and 96. In view of uncertainty as to the number and chain-starting efficiency of the radicals formed by the decomposition of the two different peroxides, it is felt that the correspondence between the chain lengths is satisfactory and provides convincing evidence that the thermal oxidation of ethyl linoleate is in fact initiated by hydroperoxide decomposition.

Identity of chain carriers

The foregoing discussion of the oxidation of ethyl linoleate, catalysed by ethyl linoleate hydroperoxide and dibenzyl peroxide, shows that the mechanism (*R1-R6*) does satisfy the first two of the three requirements given on p. 229; in particular, the nature of the chain-initiation and chain-termination steps have, it is felt, been fully established. It is important to note that no assumptions regarding the actual form that the chain carriers *X* and *Y* take have been involved.

In deciding the identity of the chain carriers the remaining requirement—consistency between kinetic and chemical conclusions—is of importance: due weight must be given to the spectroscopic evidence which points conclusively to the formation during the oxidation chain of linoleate radicals (of types (V) and (VI)) which is denoted, in conformity with the other abbreviated formulae, by *R*—. In order to reconcile this view and the requirement that one propagation reaction must, from kinetic analysis, involve an oxygen molecule and the other an ethyl linoleate molecule, *X* is identified as *R*— and *Y* as RO_2 —, i.e. molecules with the radical end-group $O-O$ — substituted in one of the three alternative α -methylene groups.

The precise sequence of reactions by which *R*— or RO_2 — radicals are in the first instance formed from the decomposition of the hydroperoxide has not been determined, but doubtless all the possible free radicals which might be primary products of decomposition could generate *R*— radicals by the removal of hydrogen atoms from ethyl linoleate molecules.

It is not of course possible to determine the correct chemical formulation of the three termination reactions from kinetic evidence; in the case of (*R4*) and (*R5*) the possible alternatives to the formation of *R-R* and *R-O-O-R* bridges between linoleate molecules are not obvious. On the other hand, in the third termination reaction (*R6*) cross-linking must almost certainly be accompanied by the elimination of oxygen or the introduction of oxygenated groups in the neighbourhood of the α -methylene groups concerned. In the early stages of oxidation such cross-linking will be of minor significance; when, however, oxidation reaches more advanced stages, and the chain length presumably becomes short (cf. equation (8)), this type of reaction will become increasingly important and may make a definite contribution towards the 'drying' phenomena which materials like ethyl linoleate exhibit.

An alternative which is formally satisfactory from the kinetic standpoint is that the chain carriers are *H*— and HO_2 —. As this view, however, provides no possible explanation of the conjugated structure of the oxidation products, it is not considered tenable.

The activation energies of the elementary reactions

The apparent energy of activation calculated from the temperature coefficient of the oxidation rate is a composite quantity, and according to (4) equal to $E_3 + \frac{1}{2}(E_1 - E_6)$ under conditions of very high oxygen pressure. Extrapolation of directly determined rates of oxidation (normally at 100 mm.) to infinite pressure may be carried out by means of the equation

$$R_\infty/R_p = 1 + \frac{\gamma}{p}[RH], \quad (10)$$

which, it was noted earlier, is in agreement both with experiment and the approximate theoretical equation (6). Table 1 includes measurements of the constant γ at three temperatures, determinations of the slope of the linear rate of oxidation v . extent of oxidation curves in the temperature range 35–75° C, and the corresponding values at infinite oxygen pressure calculated from (10). The energy of activation derived from the last set of figures is 17.2 kcal./g.mol. (cf. figure 7).

TABLE 1

temp. ° C	γ mm. Hg	R_∞/R_{100}	slope $\times 10^3$ min. ⁻¹	
			100 mm.	$p = \infty$
22	2.6	1.03	—	—
35	—	1.06	0.58	0.61
45	7.7	1.08	1.36	1.47
54	—	1.12	2.72	3.04
65	18	1.18	6.9	8.2
75	—	1.26	10.5	13.2

From equations (4) and (5) the ratio of rates of oxidation at infinite pressure and a very low oxygen pressure (p) may be written

$$\frac{R_\infty}{R_p} = \frac{k_3}{k_2} \sqrt{\frac{k_4}{k_6} \frac{[RH]}{\beta p}}, \quad (11)$$

where $\beta p = [O_2]$.

This relation is of the same form as the limiting expression derived from (10) when $p \ll \gamma$. If, therefore, the assumption that the linear $1/R$ v . $1/p$ relation may be extrapolated to lower pressures than those actually investigated is made, then

$$\frac{k_3}{k_2} \sqrt{\frac{k_4}{k_6} \frac{1}{\beta}} = \gamma, \quad (12)$$

and
$$E_\gamma = E_3 - E_2 + \frac{1}{2}(E_4 - E_6) - \Delta H_s, \quad (13)$$

where E_γ is the apparent activation energy calculated from the temperature coefficient γ , and ΔH_s is the heat of solution of oxygen in ethyl linoleate. The value of E_γ obtained from figure 7 is 8.7 kcal./g.mol., and ΔH_s is taken as zero: thus

Horiuti (1933) found negligible values for the heat of solution of oxygen in a series of six organic liquids. Inserting these values in (13)

$$E_3 - E_2 + \frac{1}{2}(E_4 - E_6) \approx 8.7 \text{ kcal./g.mol.} \quad (14)$$

We also have $E_3 + \frac{1}{2}(E_1 - E_6) = 17.2 \text{ kcal./g.mol.}$, or inserting the value of E_1 (26 kcal./g.mol.) deduced from the kinetics of the thermal decomposition of ethyl linoleate hydroperoxide,

$$E_3 - \frac{1}{2}E_6 = 4.2 \text{ kcal./g.mol.} \quad (15)$$

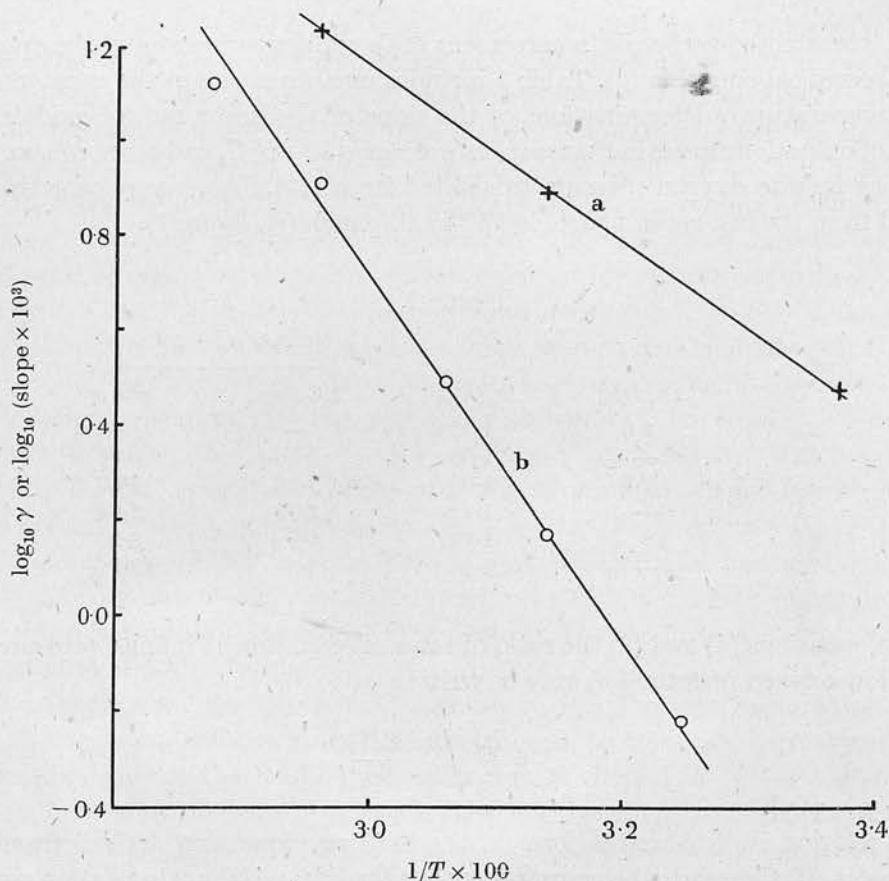


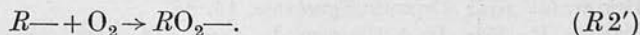
FIGURE 7. Dependence on temperature of γ (curve *a*) and the slope of the rate of oxidation v . extent of oxidation relation (curve *b*).

It is obviously not possible to evaluate the four activation energies involved from (14) and (15). E_4 , since it corresponds to recombination of hydrocarbon radicals, may, however, be taken to be about 6 kcal./g.mol. On this assumption, E_2 is estimated at $-1.5 \text{ kcal./g.mol.}$ E_3 and E_6 are interrelated in accordance with (15). Without making any assumptions as to the magnitude of E_6 (which may well be different from E_4) we may therefore estimate E_3 at not less than 4.2 kcal.

In view of uncertainty as to some of the energies introduced in the above argument (especially E_7 and ΔH_s), it is not perhaps surprising that the value of E_2 so derived is negative. It seems, however, permissible to conclude that the energy of activation required for



is significantly in excess of that for



The thermochemistry of the elementary reactions

A further test which must be applied to the individual reactions which comprise the suggested reaction mechanism is their soundness from the energetic point of view: thus the propagation and termination reactions, to which only small energies of activation have been assigned above, would require to be exothermic or only very slightly endothermic. Rough estimates of these heats of reaction can readily be made from the bond energies appropriate to the various reactants and products. The bond energies employed here are carbon-hydrogen 99 kcal. (Baughan 1941; Kynch & Penney 1942), carbon-oxygen 87 kcal. (Baughan, Evans & Polanyi 1941) and oxygen-hydrogen 110 kcal. The most reliable estimate at present available of the oxygen-oxygen bond strength in hydroperoxides (D_{O-O}) is that calculated from the data of Stathis & Egerton (1940) on the heats of combustion of ethyl and propyl hydroperoxides, viz. 56 kcal.; preliminary measurements of the heat of oxidation of ethyl linoleate and ethyl linolenate provide confirmation of this value.

The termination reactions will clearly be exothermic. The condition that the propagation step ($R2'$) should be exothermic is $D'_{O-O} > 54$ kcal., where D'_{O-O} represents the oxygen-oxygen bond energy in the peroxide radical, RO_2 . This requirement will obviously be fulfilled provided D'_{O-O} is not significantly less than D_{O-O} . D'_{O-O} does in fact exceed D_{O-O} if we accept Pauling's (1940) treatment of the electronic structure of the peroxide ion, on the analogy of which the RO_2 radical may be described as $R-O^{\cdot\cdot}O$, the three-electron bond serving to make $D'_{O-O} > D_{O-O}$; Pauling's quantitative interpretation of the three-electron bond would suggest that $D'_{O-O} \sim \frac{3}{2}D_{O-O}$.

Since it is unlikely that D'_{O-O} will exceed D_{O-O} by more than 41 kcal., the energetic requirement for the second propagation reaction ($R3'$) is considered fulfilled.

The final conclusion is that the set of elementary reactions which permit of the complete interpretation of the kinetic data is also satisfactory from the thermochemical point of view.

I wish to express my thanks to Dr G. Gee for the benefit of many helpful and stimulating discussions during the course of the above work, which forms part of the programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

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SECTION 4

The Primary Thermal Oxidation Product
of Ethyl Linoleate

112. The Course of Autoxidation Reactions in Polyisoprenes and Allied Compounds. Part IX. The Primary Thermal Oxidation Product of Ethyl Linoleate.

By J. L. BOLLAND and H. P. KOCH.

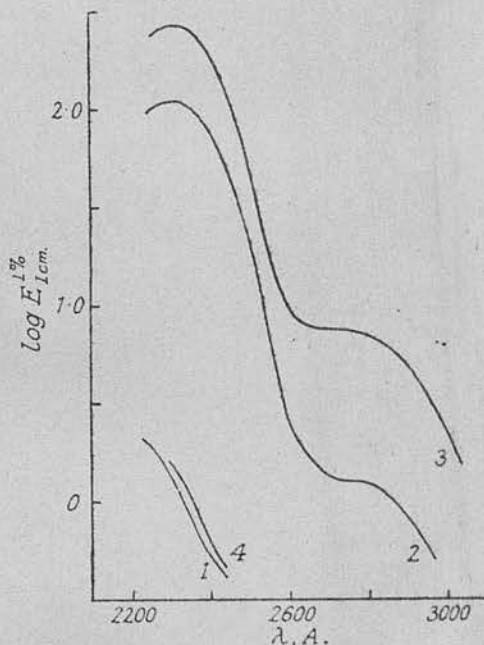
The primary product of the thermal reaction between ethyl linoleate and molecular oxygen is a mono-hydroperoxide which is shown by spectrographic analysis to contain at least 70% of conjugated diene isomers resulting from rearrangement of the unsaturated system $\cdot\text{C}=\text{C}-\text{C}=\text{C}\cdot$. One of the first decomposition products appears to be ketonic according to similar evidence. The observed displacement of double bonds can be accounted for by a free-radical mechanism of oxidation.

IN Part IV (Farmer and Sutton, J., 1943, 119) it was reported that the photo-oxidation of methyl oleate gives rise to an unsaturated hydroperoxide which can be isolated from unchanged ester by selective adsorption on alumina; and it was subsequently demonstrated by spectrographic measurements (Part VII, Farmer, Koch, and Sutton, *ibid.*, p. 541) that conjugated diene and triene units are formed during the thermal peroxidation of more highly unsaturated esters of the drying-oil type, $\text{CHR}_1\cdot\text{CH}=\text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_2\cdot\text{CH}=\text{CHR}_2$. Quantitative chromatographic and absorption-spectra analysis has since been employed in the investigation of the course of thermal oxygenation of ethyl linoleate (I), and the nature of the primary reaction product is now described.

Chemical Examination.—Pure ethyl linoleate and oxygen gas react readily on shaking in the dark at 45°, and the extent of peroxidation as determined iodometrically (Dastur and Lea, *Analyst*, 1941, 66, 90) is in satisfactory agreement with accurate volumetric measurements of oxygen absorption at intakes lower than 4%. Peroxidised samples withdrawn during these early stages of oxidation evolve one molar volume of methane per mole of incorporated oxygen in high-vacuum Zerewitinoff determinations, indicating that all the primary oxygen groups formed are hydroperoxidic. Furthermore, by chromatographic adsorption of the peroxide from a known weight of oxidised material in light petroleum solution, followed by weighing of the unoxidised ester in the eluate, it can be shown that only one such hydroperoxide group is present in each of the adsorbed oxygenated molecules. It must therefore be assumed on the basis of the chemical evidence alone that the primary oxidation product of ethyl linoleate (I) is a monohydroperoxide.

Ultra-violet Spectra.—The absorption curves of pure ethyl linoleate, two oxidised samples, and the chromatographically recovered unchanged ester (all in alcoholic solution) are plotted in the accompanying figure. The most characteristic feature of the spectra given by the oxidised samples, apart from weak selective absorption near 2750 Å., is the intense band at 2315 Å., which is removed by adsorption on alumina and must therefore be associated with the peroxido-ester present in the samples. By allowing for the feeble absorption of unchanged ester at 2315 Å. ($E_{1\text{cm.}}^{1\%} = 1.25$), the maximum molecular extinction coefficient of ethyl linoleate peroxide can be calculated from the expression $\epsilon = 32(100 + m)[(\log I_0/I)_{\text{max.}} - 1.25lc/10]/\text{mlc}$, where m is the oxygen intake per 100 g. of starting material, and c the total solute concentration (in g./l.) of the spectroscopic solution contained in a cell of l cm. length. This ϵ value was obtained from the spectra of a number of independently autoxidised samples, and the results are in Table I.

Ethyl linoleate spectra.



1. Pure starting material.
2. After 1.6% oxygen absorption.
3. „ 5.4% oxygen absorption.
4. „ chromatographic removal of oxygenated fraction.

TABLE I.

Oxygen intake (%)	0.431	0.629	1.20	1.95*	2.6	3.3	1.6†	2.65†	5.4†
$\epsilon_{\text{max.}}$ of oxidation product	22,900	23,000	22,300	22,500	21,100	18,000	22,100	20,000	15,900

* Reaction vessel packed with glass fragments.

† Results of preliminary runs (cf. Experimental).

Up to an oxygen intake of about 2% the extinction coefficient is reproducible within the limits of error of the spectrographic assay, so that its average value of 22,700 can be regarded as a characteristic constant of ethyl linoleate peroxide formed during thermal oxygenation. The subsequent decline from this figure may be due to the onset of secondary intermolecular or peroxide decay reactions.

Analysis of 2315 Å. Absorption Intensity.—It was reported in Part VII that a typical mono-olefinic hydroperoxide such as that of cyclohexene does not display high-intensity absorption in the ultra-violet which is exclusively characteristic of conjugated unsaturated centres. The peroxido-ester band at 2315 Å. must therefore be due to a rearrangement of double bonds into conjugation, and it may be compared in Table II with the

bands of analogous terminally disubstituted butadienes in alcoholic solution. Clearly, the extinction maximum of the ester hydroperoxide is located in the wave-length region typical of six similar conjugated linoleic compounds, while the smaller hexadiene molecules exhibit maxima at slightly higher frequencies. The presence of the hydroperoxide group on a carbon atom adjoining the conjugated system would not be expected to affect the position of this typical diene band, an assumption that is borne out by the spectrum of cyclohexene hydroperoxide in which the olefinic and peroxidic absorptions are roughly additive (Koch, unpublished observation), and further supported by the negligible effect of 1:6-oxy-substitution on the absorption wave-length of 2:4-hexadiene given in the table. The close similarity of the band position of the peroxido-ester to that of analogous conjugated linoleates is therefore not surprising.

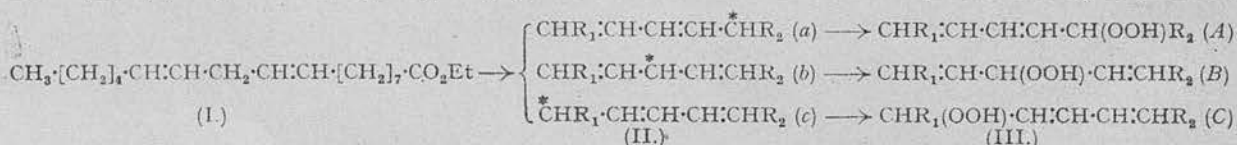
TABLE II.

Constitution of diene.	$\lambda_{\max.}$ (A.)	$\epsilon_{\max.}$	Ref.
Ethyl linoleate hydroperoxide	2315	22,700	This paper
$\Delta^{10:12}$ -Linoleyl alcohol	2325	32,000	4
$\Delta^{10:12}$ -Methyl linoleate	2325	29,700	4
$\Delta^{10:12}$ -Linoleic acid	2325	32,500	4
$\Delta^{9:11}$ -Linoleic acid	2325	26,600	4
"	2300	~33,000 ¹	5
Alkali-isomerised potassium linoleate	2340	24,400 ²	6
2:4-Hexadiene	2270	22,500 ³	7
1:6-Diethoxy-2:4-hexadiene	2280	26,800	7
1:6-Diacetoxy-2:4-hexadiene	2280	27,300	7

¹ Measured in hexane. According to Booker *et al.* (*loc. cit.*), diene intensities are frequently somewhat higher in hexane than in alcohol. ² The linoleate is measured as a charged anion after heating with strong alkali which appears to have a gradual destructive effect superimposed on its isomerising agency. Our previous assumption (Part VII) that the maximum $E_{1\text{cm}}^{0.1\%}$ value recorded by Mitchell *et al.* corresponds to the presence of 100% conjugated diene may therefore be inaccurate, and the calculated $\epsilon = 24,400$ value low. It is, moreover, subject to the uncertain "solvent effect" of the highly polar medium in which the measurements are made. ³ Probably low, owing to doubtful purity of the specimen (cf. Booker *et al.*, *loc. cit.*, p. 1461). ⁴ Kerns, Belkengren, Clark, and Miller, *J. Opt. Soc. Amer.*, 1941, **31**, 271. ⁵ Van der Hulst, *Rec. Trav. chim.*, 1935, **54**, 639. ⁶ Mitchell, Kraybill, and Zscheile, *Ind. Eng. Chem. Anal.*, 1943, **15**, 1. ⁷ Booker, Evans, and Gillam, *J.*, 1940, 1453.

As regards the ϵ values recorded in the table, the maximum intensity of the linoleate hydroperoxide absorption at 2315 A. appears to be unduly low if full conjugation is to be assumed, and the inconsistencies of the data from Kerns's laboratory—all obtained with extensively purified materials by an accurate photoelectric method—are rather unexpected. The extinction coefficient of a conjugated diene in this spectral region depends on the dipole moment of the excited state and may therefore be affected by changes in either the length or the charge of the dipole involved. Since the constitutional distinctions between the four linoleic compounds of Kerns *et al.* are all due to chemical modifications at carbon atoms far removed from the chromophoric centre, alterations of dipole charge could hardly occur, but spatial differences might be responsible for the observed intensity variations. Butadiene itself, in fact, is known at room temperature to consist of an equilibrium mixture of single-bond *cis*- and *trans*-isomers, in which the predominating and more elongated *s-trans*-displays considerably greater absorption near 2200 A. than the *s-cis*-form (Rasmussen, Tunnicliff, and Brattain, *J. Chem. Physics*, 1943, **9**, 432; Sugden and Walsh, *Trans. Faraday Soc.*, 1945, **41**, 76). In the absence of other evidence, however, and in view of the relatively high intensities of the 1:6-oxy-substituted hexadienes, it is difficult to see why the extinction coefficient of a fully conjugated peroxido-linoleate should be lower than that of all the other compounds under discussion. The most probable conclusion would therefore be that the conjugative displacement of double bonds has been incomplete. If the range of ϵ values obtained by Kerns *et al.* is taken as a theoretical standard of extinction for a pure compound of this type, the linoleate oxidation product appears to contain between 70 and 85% of conjugated isomers. Although this estimate cannot be made more precise, a rearrangement of about 70% must be regarded as the minimum allowed by the available evidence, since diene intensities larger than 32,500 are unknown and not to be expected (Booker, Evans, and Gillam, *loc. cit.*; Koch, *Chem. and Ind.*, 1942, **61**, 273).

Course of Autoxidation Reaction.—On the basis of the free-radical mechanism of oxidation suggested in Part VII, oxidative attack at the active methylene group of ethyl linoleate (I) results in the formation of a free radical (II), which is a resonance hybrid composed of the three equivalent canonical structures (a)—(c). The hydroperoxidic product (III) derived from the radical would then be expected to contain the three isomeric forms (A)—(C). Quantitatively, 67% conjugation will result if these three are produced in equal amounts,



but if the conjugated forms (A) and (C) are favoured owing to their resonance energy, up to 100% conjugation might occur. It is not possible to distinguish between these possibilities on the above experimental evidence which characterises the primary oxidation product as a monohydroperoxide at least 70% conjugated. The postulated intermediate formation of a free radical of type*(II) is also in accord with kinetic evidence (Bolland, *Proc. Roy. Soc., A*, in the press).

Spectral Evidence of Decomposition.—The absorption curves of all the thermally autoxidised samples show a well-defined shoulder at 2750 Å. which is absent from pure mono-olefin peroxide spectra and cannot be attributed to triene conjugation since no fine structure is revealed even on careful inspection of the photographic records (cf. Fig. 2 in Part VII). The intensity of this band increases markedly on keeping the peroxidised ester for some time at 45° in a vacuum and is evidently associated with a small amount of secondary decomposition product. The absorption region in question is that typical of conjugated diene ketones; thus, the spectrum of crotonylideneacetone, $\text{CH}_3\text{CH}:\text{CH}:\text{CH}:\text{CO}-\text{CH}_3$, displays a broad and intense maximum near 2730 Å. (Jones and Lahey, *Chem. Abs.*, 1943, 37, 3342). There can be little doubt that the long-wave bands shown in the figure are due to small amounts of the analogous diene ketone resulting from decomposition of the conjugated hydroperoxide. According to this interpretation, about 1% of the peroxide present in the sample characterised by curve 2 has decomposed in such a manner. The ketone of crossed conjugation which might be produced in even smaller amounts by secondary decay of the hypothetical unconjugated hydroperoxide (III, B) would be expected to absorb at shorter wave-lengths, where its extinction could be neglected relatively to that of the conjugated hydroperoxide present.

EXPERIMENTAL.

Ethyl linoleate was prepared from cottonseed oil (*Org. Synth.*, 1942, 22, 75). The intermediate tetrabromostearic acid had m. p. $115.7^\circ \pm 0.1^\circ$ and theoretical bromine content, 53.3%. The final product was free from conjugated isomers, as selective absorption near 2315 Å. was negligible (cf. figure).

Samples of ethyl linoleate, carefully shielded from light, were shaken vigorously at 45° under an oxygen pressure of about 100 mm. The volume of oxygen absorbed was determined accurately in a constant-pressure gas burette system attached to the reaction vessel. In a preliminary series of runs oxygen was absorbed by a stationary surface exposed to the atmosphere at 35° in the dark, in amounts determined by weighing.

The peroxide content of the oxidised samples was estimated by the method of Dastur and Lea (*loc. cit.*). Extended experience with this method has shown (Bolland, *loc. cit.*) that the peroxidic oxygen content corresponds quantitatively with the amount of oxygen absorbed (in the range, 1–4%, and presumably also at lower degrees of oxidation).

Duplicate active hydrogen analyses (Bolland, *Trans. Inst. Rubber Ind.*, 1941, 16, 257) of three samples of oxidised ethyl linoleate, gave severally 0.286, 0.282, and 0.124 mol. of methane per mol. of ethyl linoleate, and the corresponding peroxide contents (based on iodometric estimations and on measured extents of oxidation) were 0.290, 0.272, and 0.120 mol. of absorbed oxygen per mol. of ethyl linoleate.

For chromatographic separation of the peroxide from the unoxidised ester, a short column of activated alumina (Savory and Moore) was found effective; light petroleum (b. p. 40–60°) was employed as solvent and eluent, and the operation carried out under a slight pressure of purified nitrogen. Ethyl linoleate (containing less than 0.01% of peroxidic oxygen) recovered in this manner from an oxidised sample containing 2% of peroxidic oxygen, and freed from solvent in a vacuum, gave the spectrum indicated in the figure; it is virtually identical with that of the starting material. The rapid diminution in the amount of residue in successive portions of the eluate (all of which gave negligible peroxide tests) showed that the separation was quantitative. In one instance 4.2500 g. of oxidised ethyl linoleate, containing 1.83% of peroxidic oxygen, yielded a total of 3.4206 g. of ethyl linoleate. It follows that the 0.8294 g. of oxidised material remaining in the column contained 1.01 mols. of oxygen per mol. of ester.

The ultra-violet spectra were obtained by means of a Hilger quartz spectrograph equipped with the Spekker photometer and a condensed tungsten-steel spark source of light. The maximum optical densities ($\log_{10} I_0/I$) at 2315 Å. were determined by visual examination and interpolation of the match-points on Kodak B-10 plates with an error not greater than 2%. The photometer was carefully calibrated before each measurement by the determination of blank match-points, and the recording of spectra was completed in each case within 20 mins. of admitting air to the specimen in order to prevent further significant oxidation.

The authors express their gratitude to Dr. G. Gee for his encouragement and criticism during the course of this work, which forms part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

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113. The System Lead Chloride-Water at 15° to 35°.

By T. P. GOULDEN and L. M. HILL.

The solubility of lead chloride in water has been redetermined for the temperature range 15–35°; the following average results were obtained (g. per 100 g. of saturated solution): 15°, 0.866; 20°, 0.968; 25°, 1.075; 30°, 1.179; 35°, 1.298. Determinations of lead and chloride in these solutions showed a slight excess of the latter equivalent to about 0.004 g. of lead chloride.

MANY determinations of the solubility of lead chloride are on record. Ditte (*Compt. rend.*, 1881, 92, 718), Lichty (*J. Amer. Chem. Soc.*, 1903, 25, 474), Demassieux (*Compt. rend.*, 1913, 156, 892), and Flottmann (*Z. anal. Chem.*, 1928, 73, 30) each made measurements at a number of temperatures, and numerous single-temperature determinations, mostly at 25°, have been reported. In spite of this mass of data it was difficult to select a series of trustworthy values for the temperature range 15–35°.

A characteristic of aqueous lead chloride solutions which has often been noted, particularly by Ley (*Ber.*, 1897, 30, 2192) and Benrath (*Z. physikal. Chem.*, 1908, 64, 693), is the slight hydrolysis which occurs. In our work a careful watch was kept for this by means of determinations of lead and chloride ions, but when it was found that the differences between the ionic concentrations were only slightly outside the limits of experimental error, and were within the limits of accuracy required from our data, the subject of hydrolysis was not pursued further.

SECTION 5

The Benzoyl Peroxide - Catalysed Oxidation of Ethyl Linoleate

KINETIC STUDIES IN THE CHEMISTRY OF
RUBBER AND RELATED MATERIALS

VI. THE BENZOYL PEROXIDE-CATALYSED OXIDATION OF ETHYL LINOLEATE

By J. L. BOLTON

Received January 1957

A kinetic study of the autoxidation of ethyl linoleate is given in an earlier paper (1) of this series. In that reaction mechanism the reaction time of which was the formation of the radical by the thermal decomposition of ethyl benzoyl peroxide. A critical test of the mechanism of the reaction mechanism was proposed. The reaction mechanism of the autoxidation of ethyl linoleate by catalysis will be proposed and tested using the conditions of experiment. Several papers have previously reported the results of the kinetic study of the autoxidation of ethyl linoleate. These have been reported and detailed and described. The rate of the autoxidation is first order in the peroxide concentration and the rate of oxidation of ethyl linoleate is a temperature dependence. The reaction mechanism for the autoxidation of ethyl linoleate is the radical mechanism and is proposed.

The rate of autoxidation of ethyl linoleate is first order in the benzoyl peroxide concentration and is first order in the concentration of ethyl linoleate. It was therefore possible to measure the rate of the reaction by a kinetic method and the autoxidation time was measured with the same. It is a kinetic study of the autoxidation of ethyl linoleate and the reaction mechanism is proposed.

Some of the kinetic results are given in this paper. The results have been published previously, however, this article is a critical review of the results.

Experimental

The rate of autoxidation was measured in the absence of any inhibitor. The reaction time and the rate of autoxidation were measured by the kinetic method. The results are given in this paper. The results are given in this paper.

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KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS.

VI. THE BENZOYL PEROXIDE-CATALYSED OXIDATION OF ETHYL LINOLEATE.

By J. L. BOLLAND.

Received 18th September, 1947.

A kinetic analysis of the autocatalysed oxidation of ethyl linoleate given in an earlier paper¹ of this series suggested a chain-reaction mechanism, the initiation step of which was the formation of free radicals by the thermal decomposition of ethyl linoleate hydroperoxide. A critical test of the correctness of the proposed mechanism can obviously be provided by detailed comparison of the autocatalysed oxidation with that initiated by catalysts known to produce free radicals under the conditions of experiment. Benzoyl peroxide is a particularly valuable source of free radicals in this connection since firstly, the kinetics of thermal dissociation have been worked out in detail and secondly, the ease of thermal dissociation is such as to promote conveniently measurable rates of oxidation of many olefins in a temperature range in which the oxidation chains are long and secondary reactions of the initial oxidation products are unimportant.

The rates of oxidation can be measured rather more precisely in the benzoyl peroxide-initiated oxidation than in the autocatalysed oxidation of ethyl linoleate. It has therefore been possible to submit the former system to a more searching kinetic examination than was possible with the latter, and it is gratifying that the results obtained fully substantiate the reaction mechanism previously advanced.¹

Some of the general conclusions arrived at in this paper have already been published,² without, however, their detailed experimental justification being given.

Experimental.

The rates of oxidation were measured in the manner already described.¹ More accurate results and more convenient operation were obtained by substituting a Pyrex spiral made from 1.2 mm. quill tubing for the neoprene connection between the reaction vessel and the gas-burette system. In the present

¹ Bolland, *Proc. Roy. Soc. A*, 1946, 186, 218.

² Bolland and Gee, *Trans. Faraday Soc.*, 1946, 42, 236 and 244.

experiments, initial rates of oxidation were invariably required. The increase in rate of oxidation as oxidation proceeded was always sufficiently gradual, for extrapolation of rate measurements to zero extent of oxidation to be made with precision: it is estimated that the error in determining the initial rate of oxidation was in general not more than 1%.

Materials.—Ethyl linoleate and ethyl stearate were prepared as already described.¹ Methyl oleate prepared from olive oil was kindly supplied by Dr. D. A. Sutton; it was refractionated on a molecular still. All three esters were finally purified by careful chromatographing on an alumina column.

The Experimental Rate Equation.

The parameters which can be varied experimentally in the benzoyl peroxide-catalysed oxidation of ethyl linoleate are (i) benzoyl peroxide and (ii) ethyl linoleate concentrations, (iii) the oxygen pressure and (iv) the temperature. These factors were systematically varied and the results are dealt with in order below.

(i) **Benzoyl Peroxide Concentration** $[Bz_2O_2]$.—The effect of $[Bz_2O_2]$ on the initial rate of oxidation (R_0) of ethyl linoleate was determined carefully at 35, 45 and 55° c. at an oxygen pressure of 100 mm. Hg. The experimental results

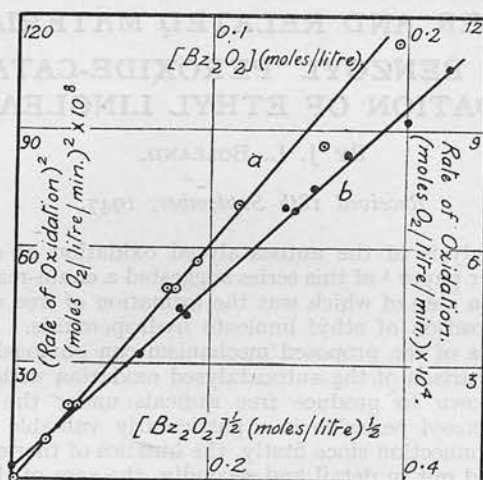


FIG. 1.—Influence of benzoyl peroxide concentration on rate of oxidation (R_0) of ethyl linoleate at 45° c.:

- (a) relation between R_0^2 and $[Bz_2O_2]$;
 (b) relation between R_0 and $[Bz_2O_2]^{1/2}$.

at 45° c., are presented in Fig. 1. It is apparent that the data agree either with the relationship $R_0 = \text{constant} \times [Bz_2O_2]^{1/2}$, or with $R_0^2 = \text{constant} \times [Bz_2O_2]$, the intercept at $[Bz_2O_2] = 0$ being too small to permit any definite choice between these two forms. Similar relationships are obeyed accurately at 35 and 55° c.

(ii) **Olefin Concentration, [RH].**—Ethyl stearate and methyl oleate were used as diluents in determining the influence of olefin concentration on the initial rate of oxidation. By plotting the ratio of initial rates of oxidation in diluted and undiluted samples of olefin against ethyl linoleate concentration, a direct proportionality is found between initial rate of oxidation and [RH] (Fig. 2). The straight lines (a) and (b) in Fig. 2 join the points representing the relative rates of oxidation of pure ethyl linoleate (1.00) and pure methyl oleate (0.08₅) and pure linoleate (1.00) and pure ethyl stearate (ca. 0.00₅) respectively. The rates recorded in Fig. 2 refer to infinite oxygen pressure, extrapolations being carried out by means of eqn. (1).

(iii) **Oxygen Pressure.**—The influence of variation of oxygen pressure was followed by carrying out a series of short oxidation runs at different oxygen pressures on a sample of ethyl linoleate containing benzoyl peroxide. Any

rate increase throughout the series arising from autocatalysis was allowed for by interspersing the runs with measurements at a convenient standard pressure.

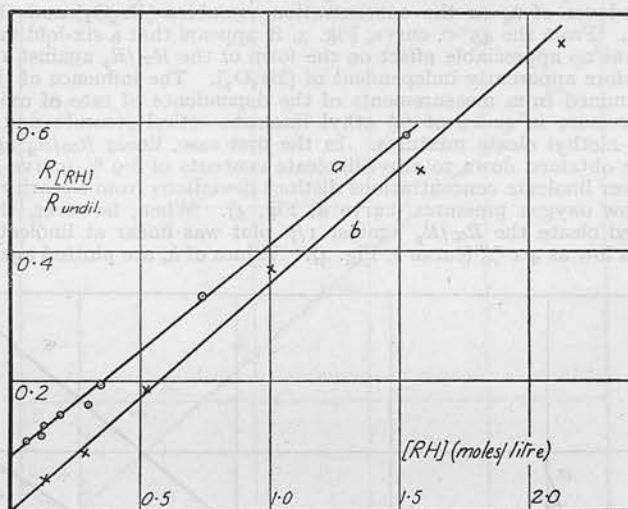


FIG. 2.—Influence of ethyl linoleate concentration, [RH], on rate of oxidation at 55° c. in ethyl linoleate-methyl oleate (curve *a*) and ethyl linoleate-ethyl stearate (curve *b*) mixtures. Curves *a* and *b* are drawn to pass through the point for pure ethyl linoleate.

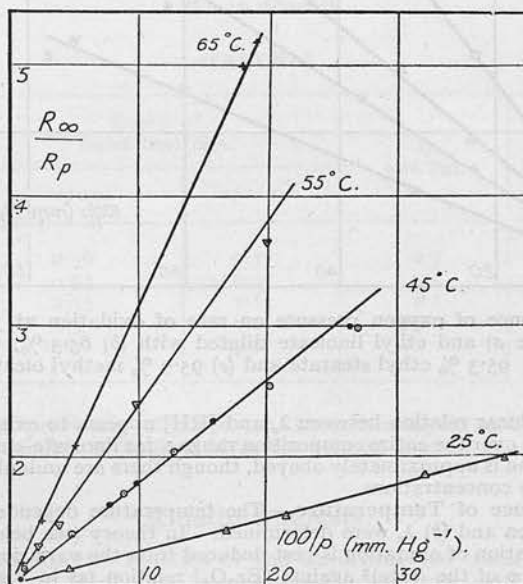


FIG. 3.—Influence of oxygen pressure (*p*) on rate of oxidation of ethyl linoleate. [Bz_2O_2] at 45° c. is 0.026 and 0.160 moles/l. for full and open circles respectively.

The rate of oxidation and oxygen pressure (*p*) were found to be accurately related by the equation

$$R_{\infty}/R_p = 1 + \lambda_c/p \quad (1)$$

where R_p and R_{∞} are the rates of oxidation when the oxygen pressure is *p* mm.

Hg and infinite respectively. Fig. 3 gives typical sets of experimental data of this kind, for the four temperatures 25, 45, 55 and 65° c.

Before the precise form of the experimental rate equation can be defined, the dependence of λ_c on the concentration variables $[Bz_2O_2]$ and $[RH]$ must be known. From the 45° c. curve, Fig. 3, it appears that a six-fold variation in $[Bz_2O_2]$ has no appreciable effect on the form of the R_∞/R_p against $1/p$ curve: λ_c is therefore apparently independent of $[Bz_2O_2]$. The influence of $[RH]$ on λ_c was determined from measurements of the dependence of rate of oxidation on oxygen pressure in series of (a) ethyl linoleate—ethyl stearate and (b) ethyl linoleate—methyl oleate mixtures. In the first case, linear R_∞/R_p against $1/p$ plots were obtained down to ethyl linoleate contents of 8.9% (curve c, Fig. 4), but at lower linoleate concentrations distinct deviations from linearity appeared at very low oxygen pressures (curve d, Fig. 4). When, however, the diluent was methyl oleate the R_∞/R_p against $1/p$ plot was linear at linoleate concentrations as low as 4.1% (curve e, Fig. 4). Values of λ_c are plotted against $[RH]$

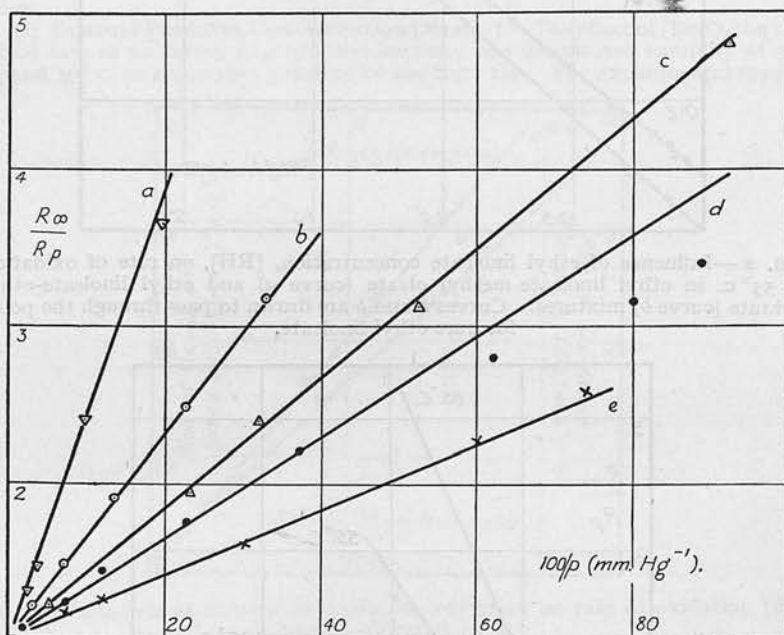


FIG. 4.—Influence of oxygen pressure on rate of oxidation at 55° c. of ethyl linoleate (curve a) and ethyl linoleate diluted with (b) 65.3%, (c) 91.1% and (d) 95.3% ethyl stearate and (e) 95.9% methyl oleate.

in Fig. 5. A linear relation between λ_c and $[RH]$ appears to exist for linoleate-oleate mixtures over the entire composition range; for linoleate-stearate mixtures the same relation is approximately obeyed, though there are undoubted deviations at low linoleate concentrations.

(iv) **Influence of Temperature.**—The temperature dependence of (a) the rate of oxidation and (b) λ_c were determined. In theory (see below) the overall energy of activation of oxidation is best deduced from the variation of the square root of the slope of the $(rate)^2$ against $[Bz_2O_2]$ relation (as in Fig. 1) with temperature. Provided chromatographed samples of ethyl linoleate were used, the rate of oxidation at zero $[Bz_2O_2]$ was sufficiently low for this characteristic to be almost undistinguishable from the slope of the linear R_0 against $[Bz_2O_2]^{\frac{1}{2}}$ curves. Values of this slope determined at an oxygen pressure of 100 mm. are collected in column 2, Table I. The corresponding slopes at infinite oxygen pressures (column 3) were calculated from a relation analogous to eqn. (1). They give an accurately linear $\log(\text{slope})$ against $1/T$ curve, the slope of which corresponds to an overall energy of activation (E_0) of 20.5 kcal./mole. The ex-

perimental values of λ_0 quoted in the same table also give a linear $\log \lambda_0$ against $1/T$ curve, the apparent energy of activation (E_a) being 9.5 kcal./mole. See p. 676.

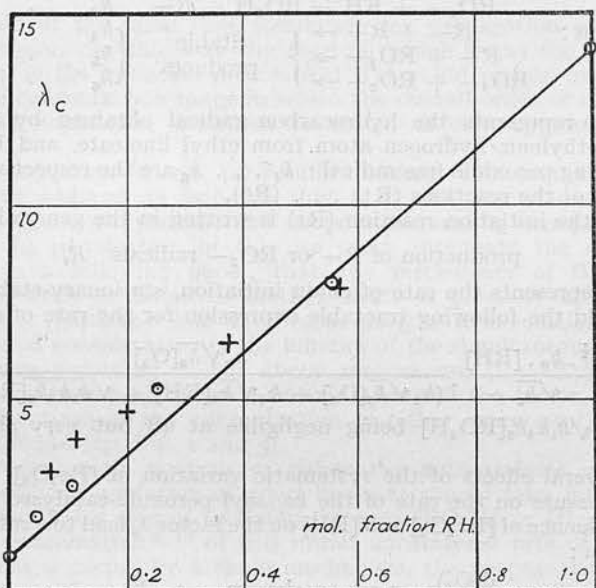


FIG. 5.—Dependence of λ_0 on $[RH]$, with ethyl stearate (+) and methyl oleate (O) as diluents.

TABLE I

Temp. °C.	Slope $\times 10^3$. (moles./litre) ^{1/2} /min.		λ_c (mm. Hg).	λ_a (mm. Hg).
	100 mm.	$p = \infty$.		
25	0.36	0.37	2.7	2.6
35	0.93	0.97	—	—
45	2.35	2.54	8.1	7.7
55	6.3	7.2	14.0	—
65	14.0	17.0	21	18

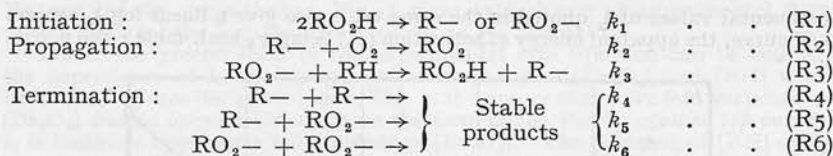
The values of λ previously obtained for the autocatalytic oxidation of ethyl linoleate¹ are included in Table I under the column heading λ_a .

Kinetic Analysis.

Investigation of the kinetics of the autocatalysed oxidation of ethyl linoleate¹ showed that the experimental oxidation rates obeyed the relationship

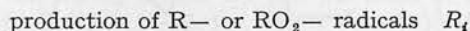
$$-\frac{d(O_2)}{dt} = k_2[RO_2H][RH] \frac{p}{\lambda_a + p} \quad (2)$$

where RO_2H represents the α -methylene hydroperoxide of ethyl linoleate and k_2 and λ_a are constants. This relation was then shown to be consistent with the chain reaction scheme, (R1)-(R6):



where R- represents the hydrocarbon radical obtained by extraction of an α -methylene hydrogen atom from ethyl linoleate, and $\text{RO}_2\text{-}$ the corresponding peroxidic free radical; $k_1 \dots k_6$ are the respective velocity coefficients of the reactions (R1) \dots (R6).

If now the initiation reaction (R1) is written in the generalised form :



where R_i represents the rate of chain initiation, stationary-state methods readily yield the following tractable expression for the rate of oxidation.

$$-\frac{d(\text{O}_2)}{dt} = \frac{R_i^{\frac{1}{2}} \cdot k_3 \cdot [\text{RH}]}{\sqrt{k_6}} \cdot \frac{k_2 \sqrt{k_6} [\text{O}_2]}{(k_2 \sqrt{k_6} [\text{O}_2] + k_3 \sqrt{k_4} [\text{RH}] + \sqrt{k_1 k_4 k_6} [\text{RO}_2\text{H}])} \quad (3)$$

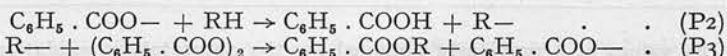
the term $\sqrt{k_1 k_4 k_6} [\text{RO}_2\text{H}]$ being negligible at all but very short chain lengths.*

The several effects of the systematic variation of $[\text{Bz}_2\text{O}_2]$, $[\text{RH}]$ and oxygen pressure on the rate of the benzoyl peroxide-catalysed oxidation, and the influence of $[\text{Bz}_2\text{O}_2]$ and $[\text{RH}]$ on the factor λ_c lead to a rate equation of the form :

$$-\frac{d(\text{O}_2)}{dt} = k_c [\text{Bz}_2\text{O}_2]^{\frac{1}{2}} [\text{RH}] \cdot \frac{p}{k'_c [\text{RH}] + p} \quad (4)$$

where k_c is a constant at any given temperature and $k'_c = \lambda_c / [\text{RH}]$.

Eqn. (4) is clearly equivalent to the theoretical expression, (3), provided $R_i = k_1 [\text{Bz}_2\text{O}_2]$. It has on several occasions³⁻⁵ been demonstrated that the thermal decomposition of benzoyl peroxide is to a close approximation a first-order reaction. Recent detailed kinetic investigations^{6, 7, 8} of the decomposition have stressed the occurrence of secondary reactions which give rise to small deviations from first-order kinetics. Cass, and Nozaki and Bartlett account satisfactorily for the deviation from first-order kinetics in terms of a chain decomposition initiated by radical fragments arising from unimolecular peroxide breakdown. While the precise reaction sequence involved in this chain type of decomposition has not as yet been elucidated in general, the experiments of Cass on the identity of the decomposition products of benzoyl peroxide when certain ethers are used as solvents strongly suggests that here at least the chains are propagated by the reaction cycle :



* This equation requires the simplifying assumption that $k_4 k_6 = k_5^2$. It is, however, possible to derive a rate equation without introducing this condition. The resulting relation differs from (3) only in predicting a rather more complex connection between rate of oxidation and oxygen pressure. We have preferred to use the less rigorous but more easily tested eqn. (3), because the wide range of conditions over which it accounts satisfactorily for the effect of oxygen pressure on the rate of benzoyl peroxide-catalysed oxidation makes it evident that the underlying assumption is at least a good approximation to the truth.

³ McClure, Robertson and Cuthbertson, *Can. J. Res., B.*, 1942, **20**, 103.

⁴ Kamenskaya and Medvedev, *Acta Physicochim.*, 1941, **13**, 565.

⁵ Brown, *J. Amer. Chem. Soc.*, 1940, **62**, 2657.

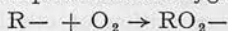
⁶ Cass, *ibid.*, 1946, **68**, 1976.

⁷ Nozaki and Bartlett, *ibid.*, 1946, **68**, 1686.

⁸ Barnett and Vaughan, *J. Physic. Chem.*, 1947, **51**, 926.

⁹ Cass *J. Amer. Chem. Soc.*, 1947, **69**, 500.

If this mechanism is applicable to olefins the reaction (P₃) would certainly be suppressed completely in presence of oxygen by the reaction,



which would at the same time commence the propagation phase of an oxidation chain. In this way the reaction which forms the rate determining step in the initiation process (i.e. R₁) would remain unimolecular even in the concentration range in which the overall order of the benzoyl peroxide decomposition, measured *in vacuo*, departs appreciably from unity.

In the derivation of eqn. (4) results obtained with methyl oleate as diluent were adduced as evidence that both the rate of oxidation (at given [Bz₂O₂], oxygen pressure and temperature) and λ_c were proportional to [RH]. In justification of this we must anticipate the conclusion, contained in a following paper, that the mechanism of the benzoyl peroxide-initiated oxidation of methyl oleate is precisely analogous to that for ethyl linoleate. For the present purpose it is sufficient to state that a detailed consideration of the kinetics of the simultaneous oxidation of two olefins according to the above mechanism, (R₂)-(R₇), leads to the conclusion that both the rate of oxidation and the factor, λ_c, should be linear functions of the concentration of either component—and this in fact was found (cp. Fig. 2 and 5).

A rigorous kinetic analysis of either the autocatalytic or benzoyl peroxide catalysed-oxidation of ethyl linoleate should take into account the small but finite rate of oxidation at zero [RO₂H] or [Bz₂O₂]. Experimental examination^{2, 10} of this initial uncatalysed rate of oxidation indicates that it occurs by a chain mechanism, the propagation and termination steps of which are represented by (R₂)-(R₆), while the chain-initiation step involves bimolecular interaction between oxygen and the olefin. The generalised form in which (3) is written thus requires no amendment on this account; but since R₄ now becomes, in the case of the benzoyl peroxide-initiated reaction, $k_7[Bz_2O_2] + k_8[O_2][RH]$, it follows that the exact relation between rate and [Bz₂O₂] (at any given oxygen pressure, [RH] and temperature) should not be:

$$\text{rate} \propto [Bz_2O_2]^{\frac{1}{2}}, \text{ but } (\text{rate})^2 \propto [Bz_2O_2] + \text{constant.}$$

Reference to Fig. 1 makes it apparent that this latter law is in fact obeyed (curve *a*), and also that the rate of oxidation at zero [Bz₂O₂] is here so small that the approximation involved in our comparison of the experimental and theoretical expressions for the rate of oxidation (i.e. eqn. (4) and (3)) is fully justified. It should be stressed that this holds true only for carefully chromatographed samples of ethyl linoleate: the presence of polar impurities, presumably mainly free linoleic acid, increases the intercept at zero [Bz₂O₂] to appreciable proportions.

Comparison of the Autocatalytic and Benzoyl Peroxide Catalysed Oxidations.

The conclusion that the mechanisms operating in these two oxidation systems differ only in the manner of chain initiation is so far supported by three experimental findings.

(i) The similarity of the eqn. (2) and (4) above, governing the overall rates of oxidation of the two systems; (ii) the similarity of the rate equations for the two oxidation systems in presence of the chain terminator, hydroquinone;¹¹ (iii) the fact that the rate equations for both systems conform to a single generalised equation, both when hydroquinone is absent (cp. eqn. (3) above) and present (eqn. (1), Part IV)¹¹ provided

¹⁰ A detailed account of these experiments is now in preparation.

¹¹ Bolland and ten Have, *Trans. Faraday Soc.*, 1947, **43**, 201.

expressions for the rate of chain initiation are introduced which agree with the observed order of the thermal decomposition of the peroxides concerned, bimolecular decomposition of ethyl linoleate hydroperoxide, and unimolecular decomposition of benzoyl peroxide.

These arguments, which are based on experimentally-determined reaction orders, may be supplemented by comparison of certain quantitative characteristics of the autocatalysed and benzoyl peroxide-catalysed oxidation systems. Three such factors are:

- (a) the chain length of oxidation,
- (b) the term λ_0 ,
- (c) the energies of activation of the elementary reactions

(a) This comparison has already been made,¹ and shows that if the rate of chain initiation is taken as equal to the rate of peroxide decomposition and if conditions are chosen so that R_i is the same then the chain length in the benzoyl peroxide-initiated oxidation is 2.2 times that for the autoxidation.

(b) The values of λ_a and λ_0 included in Table I make it obvious that over the temperature range 25°-65° c. the value of λ is the same whether the chain initiator is linoleate hydroperoxide or benzoyl peroxide.

(c) At high oxygen pressures, when the eqn. (4) simplifies to

$$-\frac{d(O_2)}{dt} = \frac{R_i^{\frac{1}{2}} k_2 [RH]}{\sqrt{k_6}}$$

the overall energy of activation for the autoxidation and benzoyl peroxide-catalysed oxidation (E_a and E_0 respectively) may be written in terms of the energies of activation of the elementary reactions (R1)-(R7) as $\frac{1}{2}E_1 + E_3 - \frac{1}{2}E_6$ and $\frac{1}{2}E_7 + E_3 - \frac{1}{2}E_6$. Taking E_a and E_1 as 17.2 and 26 kcal./mole¹ respectively, $E_3 - \frac{1}{2}E_6$ for the autoxidation becomes 4.2 kcal./mole; the best available values for E_0 and E_7 are 20.8 and 31 kcal./mole, giving a second estimate of $E_3 - \frac{1}{2}E_6$ based on the benzoyl peroxide catalysed oxidation of 5.0 kcal./mole.

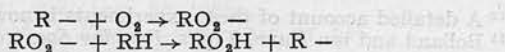
It is further found that values of E_1 are very similar for the two oxidation systems. For the autoxidation¹ the determined value of E_1 was 8.7 kcal./mole, compared with the figure of 9.5 kcal./mole for the benzoyl peroxide-catalysed reaction (p. 673). In terms of the activation energies of the elementary reactions this means that for the two oxidation systems, very similar estimates of $E_2 - E_3 - \frac{1}{2}(E_4 - E_6)$ and (since $E_3 - \frac{1}{2}E_6$ is the same for both systems) $E_2 - \frac{1}{2}E_4$ are obtained.

These various correlations between the two types of oxidation system are sufficiently exact to provide very strong confirmatory evidence for the correctness of the mechanisms of oxidation, deduced for each system when considered independently.

The author is indebted to Dr. G. Gee and Dr. L. Bateman for valuable advice and criticism. This work forms part of the programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

Summary.

Kinetic investigation of the interaction of oxygen and ethyl linoleate in presence of benzoyl peroxide leads to the conclusion that oxidation chains are initiated by the unimolecular dissociation of benzoyl peroxide into radicals, which in turn lead to the production of R-radicals. The propagation reactions are



and termination occurs through mutual interaction of pairs of the chain carriers, $R -$ or $RO_2 -$. (RH represents ethyl linoleate, $R -$ the radical produced by removal therefrom of an α -methylene hydrogen atom, and $RO_2 -$ the corresponding peroxide radical.)

Comparison of various kinetic features of the oxidation of ethyl linoleate initiated by benzoyl peroxide, and the autoxidation of the same olefin indicate that the chain-propagation and chain-termination steps of these two systems are identical.

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SECTION 6

The Inhibitory Effect of Hydroquinone
on the Thermal Oxidation
of Ethyl Linoleate

KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS.

IV. THE INHIBITORY EFFECT OF HYDROQUIN- ONE ON THE THERMAL OXIDATION OF ETHYL LINOLEATE.

BY J. L. BOLLAND AND P. TEN HAVE.*

Received 2nd May, 1946.

The manner in which inhibitors interfere with various types of chemical chain reactions, such as oxidation and polymerisation, is a problem which has attracted effort on a scale commensurate with its technical importance. It is, however, fair to say that in no case has the precise chemical mechanism of inhibition yet been determined. Granted that oxidations proceed by chain-type reactions, nearly all of our present understanding of the nature of antioxidant action is due to Bäckström and his collaborators. The salient points established in a series of papers published in 1927-33 were that the inhibitor intervened by providing an alternative and very efficient mode by which the long oxidation chains could be terminated prematurely,¹ and further that in the process the inhibitor molecules themselves underwent oxidation.² Bäckström was, however, not in a position to identify the precise nature of the chemical reaction involved, since the chain mechanism of autoxidation (in absence of inhibitor) of the systems with which he was concerned, was then by no means established.

¹ Bäckström, *J. Amer. Chem. Soc.*, 1927, 49, 1460.

² Alyea and Bäckström, *J. Amer. Chem. Soc.*, 1929, 51, 90.

* Seconded by The Netherlands Indies Govt. to the B.R.P.R.A.

Evidence of sufficiently diverse character—chemical,³ kinetic,^{4, 5} spectroscopic,³ and thermochemical⁶—has been accumulated to establish the mechanism by which certain mono-olefins and 1-4 dienes react with molecular oxygen. As a first step in a programme of work on the mechanism of autoxidation, the effect of inhibitors on such oxidation systems has been investigated. In the present paper we describe in some detail the effect of addition of hydroquinone on the oxidation of ethyl linoleate; a succeeding paper (Part V of the series) considers the characteristics of other representative phenolic inhibitors, and allows us to identify the chemical reactions responsible for the antioxidant properties of this particular type of compound and to assess some of the factors which make for efficient inhibition of olefin oxidation.

Experimental.

The experimental technique used in determining rates of oxidation was in general that already outlined.⁴ It was, however, found convenient to use a flexible spiral constructed from 2 mm. Pyrex quill tubing as connection between reaction vessel and the gas burette system. The spiral could be immersed in the water thermostat heating the reaction vessel, but in practice sufficiently good thermostatic control was achieved by surrounding the spiral with a tissue paper envelope.

The inhibitor was introduced into the reaction vessel as a dilute solution in purified acetone, delivered from a micrometer syringe. The solvent was then evaporated off in a current of nitrogen and the ethyl linoleate and (where required) dibenzoyl peroxide weighed into the reaction vessel. It was in this way possible to introduce accurately amounts of inhibitor of 10⁻³ % and upwards on a 0.2 g. sample of fatty ester.

The ethyl linoleate was obtained as before.⁴ Samples which had been subjected to a two-fold molecular distillation at 68° c.,⁷ were used in some experiments; in others (indicated by asterisks in Tables I and II) the linoleate used was further purified by chromatographic fractionation on an alumina column. Dibenzoyl peroxide was recrystallised three times from ether; the hydroquinone was a B.D.H. sample recrystallised three times from benzene under nitrogen before use.

When studying the uninhibited oxidation of ethyl linoleate it was found of real diagnostic value to compare the kinetic features of oxidation initiated in the first place by ethyl linoleate hydroperoxide (i.e. autoxidation) and in the second by dibenzoyl peroxide. For similar reasons we have here investigated the effect of addition of hydroquinone on both oxidation systems.

(A) **Effect of Hydroquinone on Dibenzoyl Peroxide Initiated Oxidation of Ethyl Linoleate.**—Suitable standard values of the various experimental variables were chosen: hydroquinone, dibenzoyl peroxide and ethyl linoleate concentrations 1.4×10^{-4} , 0.030 and 1.00 mole/mole fatty ester, oxygen pressure 100 mm. and temperature 45° c. These five variables were altered in turn with the results detailed in Table I. The initial rate of oxidation was in each case determined from the smoothed experimental extent of oxidation — time curve by graphical extrapolation of its slope to zero extent of oxidation. Variation of ethyl linoleate concentration was obtained by dilution with carefully purified ethyl stearate.

$(Bz_2O_2)_0$, $(Hq)_0$ and $(RH)_0$ represent the initial concentrations (moles/mole fatty ester) of dibenzoyl peroxide, hydroquinone, and ethyl linoleate

³ Bolland and Koch, *J. Chem. Soc.*, 1945, 445.

⁴ Bolland, *Proc. Roy. Soc., A*, 1946, 186, 218.

⁵ Bolland and Gee, *Trans. Faraday Soc.*, 1946, 42, 236.

⁶ Bolland and Gee, *ibid.*, 1946, 42, 244.

⁷ Farmer and Sutton, *J. Soc. Chem. Ind.*, 1946, 65, 164.

respectively and p_{O_2} the oxygen pressure. The initial rate of oxidation, $(R_a)_0$ is given in moles O_2 /mole linoleate/min. R_u represents the corresponding rate of oxidation in absence of inhibitor. The chain length (ν) of oxidation is calculated on the assumption (a) that each molecule

TABLE I

$[Hq]_0$ $\times 10^4$	$[Bz_2O_2]_0$ $\times 10^2$	$[RH]_0$	p_{O_2} (mm.)	Temp. (°C.)	$(R_a)_0$	R_u	K $\times 10^2$	K' $\times 10^2$	ν
(mole/mole ester)					(mole O_2 /mole ester/min. $\times 10^4$)				

(a) Standard experimental conditions.

1.40	3.0	1.00	100	45	0.059	2.23	1.65	1.65	6.1
nil	3.0	1.00	100	45	—	2.23	—	—	241

(b) Variation of hydroquinone concentration.

0.154	2.67	1.00	100	45	0.50	2.11	1.73	1.73	63.0
0.286	2.76	1.00	100	45	0.262	2.15	1.63	1.63	31.6
0.776	3.26	1.00	100	45	0.128	2.32	1.84	1.84	13.0
2.97	3.50	1.00	100	45	0.036	2.40	1.95	1.95	3.8
5.46	3.32	1.00	100	45	0.018	2.34	1.80	1.80	1.8
9.05	3.18	1.00	100	45	0.010	2.29	1.72	1.72	1.1

(c) Variation of dibenzoyl peroxide concentration.

1.53	0.75	1.00	100	45	0.0161	1.19	1.73	1.73	6.2
1.40	1.44	1.00	100	45	0.0324	1.59	1.79	1.79	6.8
1.46	6.18	1.00	100	45	0.110	3.13	1.64	1.64	6.7
2.60	7.30	1.00	100	45	0.074	3.39	1.79	1.79	3.7

(d) Variation of ethyl linoleate concentration.

*1.30	2.94	0.175	100	45	0.0127	0.392	1.89	0.33	8.3
*1.40	3.28	0.110	100	45	0.0067	0.256	1.58	0.17	6.1

(e) Variation of oxygen pressure.

1.47	3.02	1.00	30.0	45	0.050	2.24	1.09	5.0	5.6
1.48	3.18	1.00	7.5	45	0.048	2.27	1.40	18.0	5.1
1.67	3.31	1.00	3.5	45	0.045	2.34	1.38	39.4	4.5

(f) Variation of temperature.

*0.616	2.86	1.00	100	52	0.400	4.06	1.50	1.50	17.0
0.660	1.03	1.00	100	52	0.140	2.52	1.46	1.46	1.7
0.723	2.91	1.00	100	52	0.342	4.09	1.49	1.49	14.2
*1.50	3.10	1.00	100	52	0.166	4.22	1.40	1.40	6.5
*0.653	3.15	1.00	100	38.2	0.0350	1.14	1.78	1.78	12.1
*0.793	3.00	1.00	100	38.2	0.0305	1.21	1.76	1.76	9.2

of dibenzoyl peroxide which decomposes results in the initiation of one oxidation chain and (b) that the unimolecular rate constants for the decomposition at 38, 45, and 52° C. are respectively 1.10, 3.0 and 8.25×10^{-6} min.⁻¹.

(B) Effect of Hydroquinone on the Autoxidation of Ethyl Linoleate. —Samples of ethyl linoleate were allowed to react with molecular oxygen at 45° C. until suitable extents of oxygen uptake were reached; the hydroperoxide content of these oxidised samples was based on volumetric measurements of the oxygen uptake, the final oxidation rate at the conclusion of the preparation, and iodometric determination of the peroxidic oxygen content.⁸ These samples, stored *in vacuo* at 0° C., were used to

⁸ Dastur and Lea, *Analyst*, 1941, 66, 90.

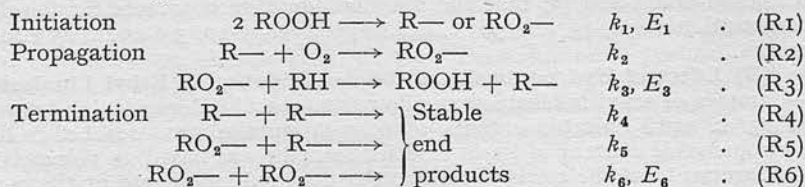
provide material for a series of oxidation runs, in presence of hydroquinone, in which the experimental conditions were systematically varied. Table II summarises the data so obtained.

TABLE II

$[\text{Hq}]_0$ $\times 10^4$	$[\text{ROOH}]_0$ $\times 10^2$	$[\text{RH}]_0$	f_{O_2} (mm.)	Temp. (°C.)	$(R_a)_0$	R_u	K $\times 10^2$	K' $\times 10^2$	ν
(mole/mole ester)					(mole O ₂ /mole ester/min. $\times 10^4$)				
nil	18.0	0.82	100	45	—	2.50	—	—	51
(a) Variation of hydroquinone concentration.									
1.22	18.1	0.819	100	45	0.181	2.52	2.84	2.33	3.7
1.40	18.1	0.819	100	45	0.155	2.52	2.80	2.30	3.2
*1.40	17.7	0.823	100	45	0.140	2.32	2.98	2.48	3.0
2.75	18.1	0.819	100	45	0.079	2.58	2.80	2.30	1.6
6.73	18.1	0.819	100	45	0.031	2.52	2.6	2.20	0.6
11.5	18.1	0.819	100	45	0.026	2.52	3.85	3.16	0.5
(b) Variation of ethyl linoleate hydroperoxide concentration.									
*0.28	2.55	0.975	100	55	0.173	1.15	3.56	3.46	5.0
*0.28	4.33	0.957	100	55	0.290	1.44	3.75	3.59	3.0
*2.70	9.9	0.910	100	55	0.106	2.87	3.17	2.88	2.0
*2.98	19.4	0.806	100	55	0.404	5.60	3.08	2.58	2.0
*3.12	27.4	0.726	100	55	0.550	6.9	2.65	1.92	1.5
(c) Variation of ethyl linoleate concentration.									
*0.28	6.3	0.350	100	45	0.052	0.26	2.60	0.91	8.3
*0.256	5.2	0.287	100	45	0.030	0.18	2.47	0.71	7.3
(d) Variation of oxygen pressure.									
1.50	18.1	0.819	725	45	0.150	2.52	2.90	0.33	3.1
1.40	18.1	0.819	100	45	0.157	2.52	2.84	2.32	3.3
1.60	18.1	0.819	11.0	45	0.125	2.52	2.58	19.0	2.6
(e) Variation of temperature.									
3.02	18.1	0.819	100	55	0.290	5.40	2.46	2.01	1.7
13.3	18.1	0.819	100	55	0.063	5.40	2.38	1.95	0.4
2.80	18.1	0.819	100	65	1.150	11.0	2.17	1.78	2.1
12.1	18.1	0.819	100	65	0.250	11.0	2.06	1.69	0.5

Kinetic Analysis.

Oxidation Mechanism in Presence of Hydroquinone.—In absence of hydroquinone the oxidation of ethyl linoleate by molecular oxygen has been shown⁴ to proceed mainly by the following chain mechanism:



where R refers to the linoleate residue obtained by removal of an α -methylene hydrogen atom, and the radical nature of the chain carriers is indicated by a dash; the reaction velocity coefficients and activation

energies of the several elementary reactions, (R1)-(R6), are denoted by the symbols k and E . Reaction (R1) represents chain initiation by thermal decomposition of ethyl linoleate hydroperoxide, which forms the sole oxidation product; the exact manner in which the initial chain carrier arises cannot as yet be formulated, but it is known that the decomposition is a second order reaction. In addition we may distinguish two additional ways in which oxidation chains may be initiated: the first, which is only of prime importance in the initial stages of autoxidation involves direct interaction between oxygen and ethyl linoleate⁵



the second arises from the presence of traces of free (linoleic) acid which normally contaminate samples of ethyl linoleate prepared as above, even after molecular distillation, and which interact with linoleate hydroperoxide molecules. Removal of this free acid may be accomplished by chromatographing the linoleate through alumina; consistent results are obtained for both chromatographed and unchromatographed samples, when the data are treated as follows.

The rate of autoxidation of ethyl linoleate at high oxygen pressures (R_u) may be expressed as follows, if it is assumed that all three types of initiators lead to identical propagation and termination mechanisms:

$$R_u = R_1 \frac{k_3}{\sqrt{k_6}} [\text{RH}] \quad (\text{I})$$

where R_1 is the total rate of chain initiation; here

$$R_1 = \alpha_1 k_1 [\text{ROOH}]^2 + \alpha_8 k_8 [\text{O}_2][\text{RH}] + f[\text{acid}][\text{ROOH}]$$

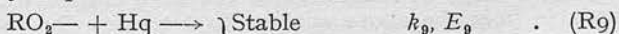
α_1 and α_8 represent respectively the number of oxidation chains actually initiated by the decomposition of one molecule of peroxide and the interaction of one molecule of oxygen and RH. Similarly in the case of the oxidation in presence of dibenzoyl peroxide the initiation steps are (R8) and



The appropriate expression for R_1 may be written

$$R_1 = \alpha_7 k_7 [\text{Bz}_2\text{O}_2] + \alpha_8 k_8 [\text{O}_2][\text{RH}]$$

On the basis of Bäckström's work, it is to be anticipated that in the presence of hydroquinone in sufficient quantity the normal chain termination reactions, (R4)-(R6) would be completely replaced by the two reactions, involving hydroquinone and either of the two chain carriers:



Assuming that the initiation and propagation reactions remain as indicated above and that termination occurs exclusively by reactions (R9) and (R10) the precise form of the expressions for the rate of oxidation derived by normal stationary state methods depends on whether the chain carrier produced in the first instance by the initiation process is $\text{R} \cdot$ or $\text{RO}_2 \cdot$. If this is, in fact, $\text{RO}_2 \cdot$

$$-\frac{d[\text{O}_2]}{dt} = R_a = R_1 \frac{k_3[\text{RH}]}{[\text{Hq}]} \cdot \frac{k_2[\text{O}_2]}{k_2 k_9 [\text{O}_2] + k_3 k_{10} [\text{RH}] + k_9 k_{10} [\text{Hq}]} \quad (2)$$

$$= R_u^2 \frac{k_6}{k_3 [\text{RH}] [\text{Hq}]} \cdot \frac{k_2 [\text{O}_2]}{k_2 k_9 [\text{O}_2] + k_3 k_{10} [\text{RH}] + k_9 k_{10} [\text{Hq}]} \quad (3)$$

If, however, the initial chain carrier is $\text{R} \cdot$, an additional factor

$$(\text{I} + k_9 [\text{Hq}] / k_3 [\text{RH}])$$

must be introduced into (2) and (3). Since (see below) $k_3 [\text{RH}] / k_9 [\text{Hq}] \sim \nu$, this difference is only of importance when the inhibitor concentration is

sufficiently high to reduce the chain length to small proportions. In this region measurements of the rate of oxygen uptake are of doubtful significance, since the production of CO_2 (especially if dibenzoyl peroxide is present) water and other volatile products is certainly comparable with the oxygen absorbed; moreover it is known that high inhibitor concentrations have a marked accelerating influence on the decomposition of ethyl linoleate hydroperoxide, thus introducing uncertainty as to the true value of R_1 . No attempt is made here to examine these aspects of the reaction; since it is therefore not possible to decide between $\text{R}-$ and RO_2- as the initial chain carrier, the latter is chosen for the sake of simplicity.

Two limiting cases of (3) may be noted:

(a) if $k_9 \gg k_{10}$ so that the only important termination reaction is $\text{RO}_2- + \text{Hq}$,

$$R_a = R_u^2 \cdot \frac{k_6}{k_3 k_9} \cdot \frac{I}{[\text{RH}][\text{Hq}]} \quad (4)$$

(b) if $k_{10} \gg k_9$ so that the only important termination reaction is $\text{R}- + \text{Hq}$,

$$R_a = R_u^2 \cdot \frac{k_6 k_2}{k_3^2 k_{10}} \cdot \frac{[\text{O}_2]}{[\text{RH}]^2 [\text{Hq}]} \quad (5)$$

From (4) and (5) constants K and K' may be defined:

$$K = \frac{k_6}{k_3 k_9} = \frac{R_a}{R_u^2} \cdot [\text{Hq}] \cdot [\text{RH}] \quad (6)$$

and
$$K' = \frac{k_6 \cdot k_2}{k_3^2 \cdot k_{10}} \cdot [\text{O}_2]_{100\text{mm.}} = \frac{R_a}{R_u^2} \cdot \frac{100}{p_{\text{O}_2}} \cdot [\text{Hq}][\text{RH}]^2 \quad (7)$$

where $(\text{O}_2)_{100\text{mm.}}$ is the solubility of O_2 in ethyl linoleate at 100 mm. pressure. Values of K and K' based on data for initial rates of oxidation are included in Tables I and II. The constancy of K over these ranges of $[\text{Hq}]_0$, p_{O_2} , $[\text{RH}]_0$ and R_u shows that equation (4) correctly describes the kinetic characteristics of the oxidation of ethyl linoleate in presence of hydroquinone and initiated by either dibenzoyl peroxide or linoleate hydroperoxide. In contrast, the variation of K' with change in p_{O_2} and $[\text{RH}]$ is obvious. The conclusion therefore is that hydroquinone interferes in the oxidation in one way only, namely by removing the chain carrier RO_2- from the system. The chemical nature of the reaction is considered in a subsequent paper.⁹

The Energy of Activation of the Termination Reaction.—It is not possible from the above analysis to determine the energy of activation of the interaction between hydroquinone and the chain carrier, RO_2- ; it may, however, be estimated relative to that of the chain propagation reaction (R3). From equation (6)

$$E_k = E_6 - E_3 - E_9$$

where E_k is the apparent energy of activation corresponding to the temperature coefficient of the constant, K . Introducing the relation already found to hold for the uninhibited autoxidation of ethyl linoleate, that $2E_3 = E_6 + 8.4$ kcal./mole.

$$E_k = E_3 - E_9 - 8.4 \text{ kcal./mole.}$$

The values of K in Table I and Table II agree in indicating a value of 3 kcal./mole. for E_k . Hence $E_3 - E_9$ is estimated to be 5.4 kcal./mole.

Introducing the condition, which has now been justified experimentally, that $k_9 \gg k_{10}$ into equation (2)

$$\nu = k_3[\text{RH}]/k_9[\text{Hq}].$$

Making use of the estimated values of ν collected in Table I the mean value

⁹ Bolland and ten Have, *Trans. Faraday Soc.* (in press).

of k_9/k_3 at 45° c. is found to be 1,200; the corresponding value from Table II is 1,800. These figures, taken in conjunction with the experimental value for $E_3 - E_9$, suggest that the frequency factor of the reaction (R3) is 5.6 times greater (at 45° c.) than that of the reaction (R9). This calculation is to be interpreted as confirming the reliability of the above estimate for $E_3 - E_9$, since it would be expected from the close formal similarity of reactions (R3) and (R9) that their frequency factors would be of the same order.

Fate of Inhibitor Molecules.

As oxidation of ethyl linoleate proceeds in presence of hydroquinone, the rate of oxygen uptake increases in the manner shown in Fig. 1, until ultimately it attains an almost constant value. Apparently therefore hydroquinone is removed from the system during oxidation and the supposition that it is converted to benzoquinone is certainly supported by the yellow coloration assumed by samples of ethyl linoleate oxidising in presence of relatively large amounts of hydroquinone. It is apparent from Fig. 1 that the rate of oxidation to which each curve tends, is less than the corresponding uninhibited rate, R_u , and furthermore that it diminishes with increase in the initial hydroquinone concentration. This behaviour suggests that the product arising from hydroquinone itself possesses weak inhibitory properties, and is therefore not inconsistent with the formation of benzoquinone.¹⁰ This aspect of the oxidation will not, however, be pursued further here; it is, however, our purpose to present two lines of kinetic evidence which point in quantitative fashion to the destruction of hydroquinone during the chain termination process.

If it is supposed that each hydroquinone molecule is capable of terminating n oxidation chains before being converted to its final product

$$-\frac{d[\text{Hq}]}{dt} = \frac{R_1}{n} \quad \dots \quad (8)$$

Now, from equations (2), (4) and (8)

$$\frac{d[\text{O}_2]}{d[\text{Hq}]} = -\frac{d[\text{ROOH}]}{d[\text{Hq}]} = n \frac{k_3[\text{RH}]}{k_9[\text{Hq}]} \quad \dots \quad (9)$$

Integration of (9) gives

$$\ln [\text{Hq}]_0 - \ln [\text{Hq}] = \frac{k_9}{nk_3} \frac{[\text{ROOH}] - [\text{ROOH}]_0}{[\text{RH}]} \quad \dots \quad (10)$$

¹⁰ Calkins and Mattill, *J. Amer. Chem. Soc.*, 1944, 66, 239.

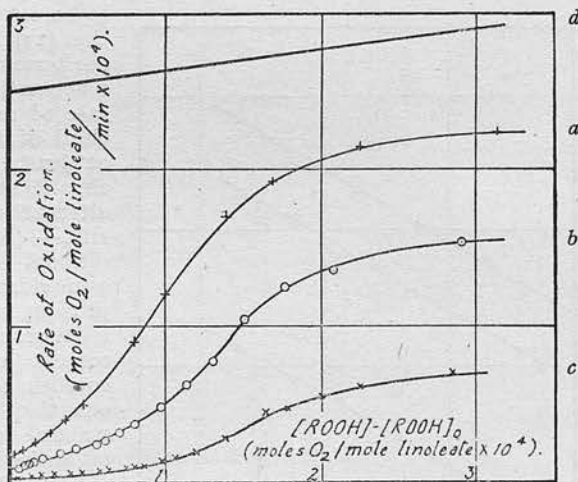


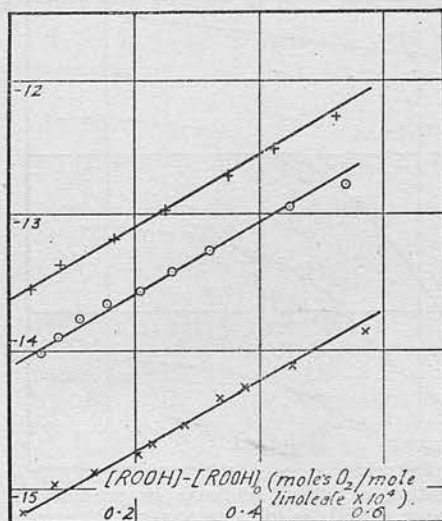
FIG. 1.—Oxidation of ethyl linoleate in presence of hydroquinone. $[\text{Hq}]_0$ is (a) 1.22×10^{-4} , (b) 2.75×10^{-4} , (c) 6.73×10^{-4} moles/mole linoleate and (d) $[\text{ROOH}]_0$ is 0.181 moles/mole linoleate.

$$\text{or } \ln R_a = \ln (R_a)_0 + \frac{1}{n} \cdot \frac{k_9}{k_3[\text{RH}]} \cdot [\text{ROOH}] - [\text{ROOH}]_0 \quad (11)$$

where $(R_a)_0$ and R_a are respectively the initial and current rates of oxidation.

The approximation is made in (10) that $[\text{RH}]$ remains constant and in (11) that the rate of chain initiation remains constant. Both approximations are in fact justified since over the limited extent of oxidation required to remove the small amounts of hydroquinone used in the present experiments the changes in $[\text{RH}]$ and R_1 were always less than 1% and 10% respectively.

In Fig. 2 the applicability of equation (11) is tested in the case of three experiments, in which the initial hydroquinone concentration is varied. Certainly in the earlier stages, the linearity of these three curves is satisfactory; deviations occur during the later phases of such runs and are



Ordinates: $\log_e R_a$

FIG. 2.

$$\text{Slope} = \frac{k_9}{n k_3[\text{RH}]} = \frac{\alpha}{n} \cdot \frac{R_D}{(R_a)_0} \cdot \frac{1}{[\text{Hq}]_0} \quad (12)$$

where R_D is the rate of decomposition of peroxide (as measured *in vacuo*, and equal to $k_7[\text{Bz}_2\text{O}_2]$ or $k_1[\text{ROOH}]^2$ according to whether the chain initiator is dibenzoyl peroxide¹¹ or linoleate hydroperoxide⁴). Values for the slope of a series of $\ln R_a/[\text{ROOH}] - [\text{ROOH}]_0$ curves are collected in Table III, together with the corresponding figures for n/α .

In the first place it is apparent that α/n is unaffected by considerable changes in the experimental conditions of oxidation. This provides strong evidence that the hydroquinone is destroyed in the course of the chain termination process and not by concurrent direct oxidation by peroxide or oxygen.

In these circumstances the divergence between the α/n values for the dibenzoyl peroxide and linoleate hydroperoxide initiated oxidations must be ascribed to different α values (α_7 and α_1 respectively) for the decomposition of these two peroxides. α_7/α_1 then becomes 5.0; giving n its most probable figure of two, α_7 and α_1 assume values of 1.0 and 0.2 re-

¹¹ McClure, Robertson and Cuthbertson, *Can. J. Research, B*, 1942, 20, 103.

to be expected since the equation (11) holds only so long as the termination occurs solely by reaction (R₉); thus when the rate of oxidation reaches one-third of the uninhibited value at least 10% of the chains should be terminated by the alternative reaction $\text{RO}_2\text{-} + \text{RO}_2\text{-}$, (R₆). Moreover the additional complication of the antioxidant activity of the final product from hydroquinone has to be reckoned with. A further respect in which these curves conform to the requirements of equation (11) lies in the substantial independence of slope on antioxidant concentration.

The factor n cannot be evaluated from the slope of curves in Fig. 2. The ratio n/α may, however, be determined, since at the peroxide concentrations here concerned

spectively. The former figure appears eminently reasonable; the latter on the other hand is quite consistent with two features of our earlier results which have at first sight appeared to suggest that the oxidation mechanisms of the oxidations initiated by dibenzoyl peroxide and ethyl linoleate hydroperoxide are not wholly identical. Thus in comparing the rates of oxidation (in absence of inhibitor at 45° c.) of ethyl linoleate when the concentrations of these two peroxides were adjusted to give equal rates of peroxide decomposition, it was found that oxidation in presence of dibenzoyl peroxide was about 2.2 times the faster. The difference may be explained in terms of different α values for the two peroxides provided $\alpha_7/\alpha_1 = (2.2)^2 = 4.8$. Furthermore the numerical values for K found in Table I and in Table II came to be of the same order, only because the assumption on which they were based was that

TABLE III

[Peroxide] ₀ (moles/mole ester) × 10 ² .	[H ₂] ₀ × 10 ⁴ .	p_{O_2} (mm.).	Temp. (°c.).	Slope.	n/α .
(a) Dibenzoyl peroxide initiated oxidation.					
7.30	2.60	100	45	0.69	1.5
6.18	1.46	100	45	0.46	2.1
2.84	1.34	100	45	0.55	2.1
3.26	0.776	100	45	0.46	2.1
2.76	0.286	100	45	0.46	2.8
3.02	1.47	30	45	0.69	1.8
3.18	1.48	7.5	45	0.74	1.8
3.10	0.150	100	52	0.41	2.3
2.86	0.616	100	52	0.46	2.0
1.03	0.660	100	52	0.40	2.1
(b) Ethyl linoleate hydroperoxide initiated oxidation.					
18.1	6.73	100	45	0.27	9.3
18.1	2.75	100	45	0.26	8.7
17.7	1.40	100	45	0.21	11.3
18.1	1.22	100	45	0.26	8.7
18.1	1.50	725	45	0.21	10.1
27.4	3.12	100	55	0.17	12.5
18.1	3.02	100	55	0.19	10.4
4.33	0.280	100	55	0.11	10.9

$R_1 = \text{const. } R_u^2$, where the constant was supposed to be independent of the nature of the initiating peroxide. If, however, conditions under which the decomposition of linoleate hydroperoxide or dibenzoyl peroxide represents the major mode of chain initiation, are considered, and R_1 is equated to the rate of peroxide decomposition, K becomes on the average about 3.2 times smaller for the ethyl linoleate hydroperoxide initiated oxidation runs, than for the corresponding runs with dibenzoyl peroxide. Again the discrepancy is explicable if $\alpha_7/\alpha_1 = 3.2$. The explanation of this variation in α from peroxide to peroxide must be intimately connected with the question of the precise mechanisms by which the thermal decomposition of peroxides occurs. As yet, insufficient evidence is available to provide a final solution to this problem.

The authors are greatly indebted to Dr. G. Gee for much helpful advice and criticism during the progress of the work, which forms part of the programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

Summary.

The kinetics of oxidation of ethyl linoleate in presence of hydroquinone have been investigated. It is shown that hydroquinone interferes in the oxidation chains in one way only, namely by interacting with peroxide radicals. Kinetic evidence is given that the hydroquinone undergoes chemical change during this termination reaction.

Résumé.

La cinétique de l'oxydation du linoléate d'éthyle en présence de hydroquinone a montré que celle-ci intervient dans les chaînes d'oxydation d'une seule façon—par interaction avec les radicaux peroxyde—et qu'elle subit un changement chimique durant la réaction de terminaison.

Zusammenfassung.

Die Kinetik der Oxydation von Äthyllinoleat in Gegenwart von Hydrochinon wurde untersucht. Es wird gezeigt, dass Hydrochinon die Oxydationsketten nur auf eine einzige Weise beeinflusst, u.zw. indem es mit RO_2 -Radikalen reagiert. Es werden kinetische Beweise dafür erbracht, dass das Hydrochinon in diesen Kettenabbruchsreaktionen chemisch verändert wird.

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SECTION 7

The Inhibitory Effect of Phenolic Compounds
on the Thermal Oxidation
of Ethyl Linoleate

KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS. V. THE INHIBITORY EFFECT OF PHENOLIC COMPOUNDS ON THE THERMAL OXIDATION OF ETHYL LINOLEATE

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In a previous paper in this series a kinetic study of the oxidation of ethyl linoleate in presence of a hydroperoxide phenol addition product was carried out in a range of conditions. The two main conclusions drawn were (a) that the hydroperoxide involvement in the oxidation process by increasing ethyl linoleate chain length, (b) — and (c) that the hydroperoxide was formed from the oxidizing chain in a way as an end-product. In a further paper in this series a kinetic study of the oxidation of ethyl linoleate in presence of a hydroperoxide phenol addition product was carried out in a range of conditions. The two main conclusions drawn were (a) that the hydroperoxide involvement in the oxidation process by increasing ethyl linoleate chain length, (b) — and (c) that the hydroperoxide was formed from the oxidizing chain in a way as an end-product.

Experimental

The experimental work was carried out in the laboratory of the B.I.R.A. The apparatus used was similar to that described in the previous paper. The reaction mixture was prepared by the method described in the previous paper. The reaction was carried out in a range of conditions. The two main conclusions drawn were (a) that the hydroperoxide involvement in the oxidation process by increasing ethyl linoleate chain length, (b) — and (c) that the hydroperoxide was formed from the oxidizing chain in a way as an end-product.

KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS.

V. THE INHIBITORY EFFECT OF PHENOLIC COMPOUNDS ON THE THERMAL OXIDATION OF ETHYL LINOLEATE.

BY J. L. BOLLAND AND P. TEN HAVE.*

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In a previous paper in this series¹ a kinetic analysis of the oxidation of ethyl linoleate in presence of a representative phenolic inhibitor, hydroquinone, was carried out in some detail. The two main conclusions drawn were (a) that the hydroquinone intervened in the oxidation chains by interacting with one chain carrier, RO_2- , and (b) that the hydroquinone was removed from the oxidising olefin in such a way as to correspond quantitatively to its chemical conversion (presumably to quinone) as a result of the termination reaction. In this paper, the choice of inhibitor is extended to other phenolic compounds, selected in such a way as to enable the chemical nature of the interaction with RO_2- to be identified by kinetic methods, and at the same time to bring to light additional ways in which diverse members of this group may interfere in the oxidation of olefins.

Some comparisons of the effectiveness of various phenols as inhibitors in different oxidation systems are available.²⁻⁶ These investigations almost invariably employ the length of induction period, which precedes the oxidation of peroxide-free hydrocarbon, as criterion for antioxidant efficiency: while this is obviously the type of measurement which is of most direct interest from the practical point of view, the oxidation mechanism under these conditions is undoubtedly complicated by the variety of ways in which oxidation may be initiated, and by the fact that in the course of the induction period the rate of chain initiation is by no means constant. Kinetically a far more satisfactory system is obtained by introducing peroxides into the hydrocarbon to be oxidised (either by preliminary autoxidation or by deliberate addition of pure simple peroxides): the oxidation chains are then initiated in one known way only and at a rate which is increased relatively little by the subsequent oxidation. In comparing a series of phenols, we have therefore concentrated attention on measuring the diminution in oxidation rate resulting from their addition to rapidly-oxidising ethyl linoleate and methyl oleate.

Experimental.

Materials: 1:4-Naphthohydroquinone was prepared by reduction of 1:4-naphthoquinone with $SnCl_2$,⁷ followed by recrystallisation from

* Seconded by the Netherlands Indies Govt. to the B.R.P.R.A.

¹ Bolland and ten Have, *Trans Faraday Soc.*, 1947, **43**, 201.

² Egloff, Lowry, Morrell and Dryer, *Ind. Eng. Chem.*, 1933, **25**, 804.

³ Jeu and Alyea, *J. Amer. Chem. Soc.*, 1933, **55**, 575.

⁴ Olcott, *ibid.*, 1934, **56**, 2492.

⁵ Bickoff, Williams and Sparks, *Oil and Soap*, 1944, **22**, 128.

⁶ Süllmann, *Helv. Chim. Acta*, 1943, **26**, 1114.

⁷ Russig, *J. prakt. Chem.*, 1900, **62**, 32.

benzene. The remaining phenols were commercial products,† carefully purified by repeated crystallisations. The methyl oleate was prepared (by Dr. D. A. Sutton) from olive oil; before use it was purified by molecular distillation⁸ (at 65° c.) and chromatographed on an alumina column.

Oxidation rates were normally measured by the technique described in Part IV. In a few experiments where the measurement of very small initial rates of oxidation was required, a simple constant-volume apparatus similar to the Warburg manometer was used. Octoil was used as manometric liquid.

The Relative Efficiency of Phenolic Antioxidants.—Initial rates of oxidation of ethyl linoleate containing dibenzoyl peroxide or linoleate hydroperoxide as oxidation initiator, and a phenol as inhibitor are collected in Table I. The kinetics of oxidation in presence of each of the phenols has not been studied in detail, though in each case the effect of antioxidant concentration has been sketched. The temperature used throughout was 45° c. and the oxygen pressure 30 mm.

TABLE I.

Antioxidant.	Peroxide.	[AH].	[Peroxide.]	R_U .	R_a .	K.
		(moles/mole ester)		(moles O ₂ /mole ester/min.)		
		× 10 ⁴	× 10 ²	× 10 ⁴ .		
Resorcinol . . .	Bz ₂ O ₂	4.14	3.20	2.30	1.48	116
		19.5	2.61	2.09	0.225	108
		302	2.69	2.13	0.020	—
β-Naphthol . . .	"	17.0	3.06	2.26	0.135	44.5
		81.4	2.50	2.04	0.023	43
		195	2.95	2.22	0.010	—
* p-Methoxyphenol . . .	"	1.86	3.18	2.29	0.550	19.4
		5.82	2.81	2.16	0.152	18.6
		16.0	2.86	2.18	0.066	20.2
α-Naphthol . . .	"	25.7	2.35	1.99	0.039	25
		2.36	2.85	2.18	0.118	5.8
		14.0	4.11	2.57	0.029	6.1
Catechol . . .	"	0.61	3.05	2.25	0.220	6.65
		2.02	2.67	2.11	0.064	2.84
		0.68	2.98	2.22	0.080	1.10
Pyrogallol . . .	"	1.98	2.85	2.18	0.029	1.24
		0.46	2.51	2.04	0.099	1.10
		0.88	2.56	2.06	0.058	1.20
Hydroquinone . . .	"	See Table I, Part IV.				1.70
		305°c	3.02	2.23	0.010	—
* Tri-methyl hydroquinone . . .	ROOH	See Table II, Part IV.				2.75
		0.89	17.7	2.30	0.032	0.48
1:4-Naphthohydroquinone . . .	"	3.65	17.7	2.30	0.008	0.5
		0.77	17.7	2.30	0.005	0.07

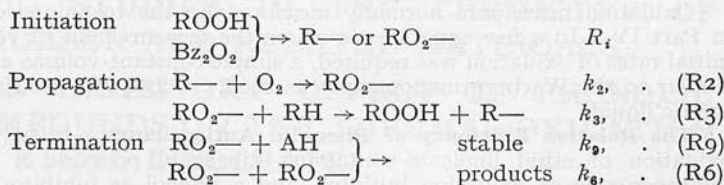
In Table I, R_U and R_a are respectively the initial rates of oxidation in absence and in presence of an inhibitor concentration of [AH]. The initial rates of oxidation in presence of hydroquinone were found experimentally¹ to conform to the relation

$$R_a = K \cdot \frac{R_U}{[RH][AH]} \quad (1)$$

† We are indebted to Messrs. Roche Products Ltd., for the gift of a sample of trimethylhydroquinone.

⁸ Farmer and Sutton, *J. Soc. Chem. Ind.*, 1946, 65, 164.

where [RH] represents the linoleate concentration, and K is a constant, which is practically independent of whether the oxidation is initiated by dibenzoyl peroxide or ethyl linoleate peroxide. The form of this kinetic equation is consistent with the following reaction scheme :



the reaction (R6) being only of importance when the antioxidant is absent. This kinetic analysis leads to the relation

$$K = \frac{k_6}{k_3 k_4} \quad (2)$$

Now k_6 is undoubtedly the most direct quantitative measure of the chain-breaking efficiency of an antioxidant. Since k_3 and k_4 depend only on the structure of the olefin, the relative efficiencies of a series of antioxidants, are given by the reciprocal of K —assuming that the mechanism by which the antioxidants act is in each case the same as for hydroquinone. While the assumption is not fully justified here, the data in Table I do indicate that the rate of oxidation is inversely proportional to [AH] in presence of at least 8 of the 9 phenols; in the case of 1:4-naphthohydroquinone, experimental difficulties outlined below precluded measurements over a range of [AH].

TABLE II

Antioxidant.	Relative Efficiency.	E_0 (v.).
(a) Phenols—		
Resorcinol	0.016	1.179
β -Naphthol	0.077	1.153
<i>p</i> -Methoxy-phenol	0.170	0.984
α -Naphthol	0.56	0.933
Pyrogallol	3.0	0.676
(b) Hydroquinones—		
Catechol	0.63	0.810
Hydroquinone	1.00	0.715
Tolhydroquinone	1.5	0.653
Trimethylhydroquinone	5.7	0.528
1:4-Naphthohydroquinone	40	0.482

Values of K calculated from (1) and quoted in Table I have been employed to calculate the chain-terminating efficiencies relative to that of hydroquinone. These are listed in Table II. Allowance has been made for the fact that whereas resorcinol and the 4 hydroquinones have two equivalent hydroxy groupings, the remainder have only one reactive group (in the case of pyrogallol reaction will presumably involve the 2-hydroxy group to the exclusion of the others).

The efficiency of an antioxidant is intimately related to its oxidisability and accordingly attempts have been made to correlate antioxidant efficiency with the oxidation-reduction potential of the antioxidant. Thus, Egloff, Lowry, Morrell and Dryer² examined the antioxidant effect of a wide range of phenolic and amino compounds on gasolene, and found

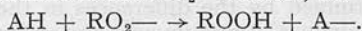
as a general trend, that antioxidant efficiency increased with diminishing oxidation-reduction potential. Elley⁹ gives a set of figures relating the oxidation-reduction potential of a series of amines and aminophenols to their anti-ageing influence on vulcanised rubber, though details of the method of measurement and conditions of test are lacking. The antioxidant efficiency of the members of the series having critical oxidation-reduction potentials greater than 0.8 v. increase regularly with decreasing reduction potential, but reduction of critical oxidation-reduction potential to 0.6 v. does not give any increase in efficiency, while those amines having still lower potentials are quite sharply less efficient.

The results of these authors, obtained as they are on systems where the

precise role of the antioxidant cannot be determined, are subject to extraneous complications, such as the volatility and direct oxidation of the antioxidant; on the other hand we have here identified the chemical reaction from which antioxidant activity results (i.e. $AH + RO_2 \rightarrow$) and estimated the efficiency with which each of our series of phenols reacts in this particular way.

Now from Table II this efficiency increases progressively throughout the list of phenols arranged in order of diminishing normal oxidation-reduction potentials; the regularity of this correlation throughout the range of oxidation-reduction potentials 1.15 to 0.60 v. is apparent from Fig. 1 where a continuous plot is obtained between \log (relative efficiency) and the normal oxidation-reduction potential, E_0 .

The most obvious chemical interpretation of this quantitative dependence of antioxidant efficiency on the oxidisability of the antioxidant is that the termination reaction (R₀) involves the transfer of a hydrogen atom from the antioxidant to the RO_2 radical, i.e.



The efficiency of this reaction as we pass from one phenolic antioxidant to another would, because of its exchange character, be controlled entirely by the heat of reaction of the dissociation $AH \rightarrow A \cdot + H \cdot$. In deciding whether normal oxidation-reduction potentials should in fact give a quantitative measure of the free energy change associated with the dissociation reaction (and, therefore, the heat of reaction since entropy changes will be little altered by the identity of AH) difficulties are encountered: in order to cover a sufficiently wide range of antioxidant efficiency it was necessary to study the effect of examples of two distinct types of phenolic compound which differ essentially in their electrochemical behaviour. Thus Table II includes 5 hydroquinones, which give completely reversible oxidation-reduction systems with well-defined

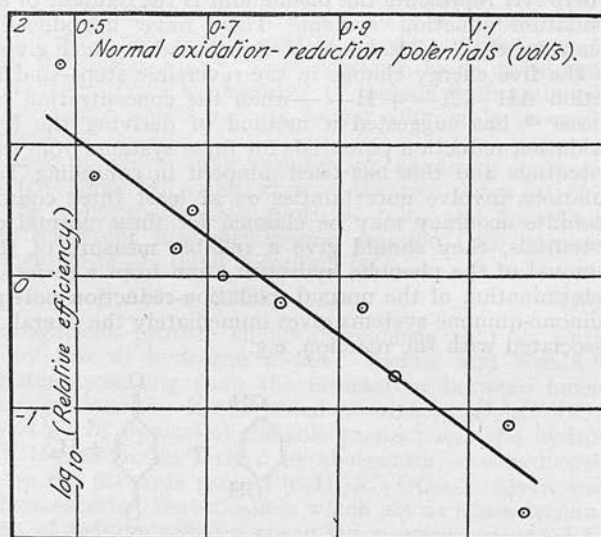


FIG. 1.

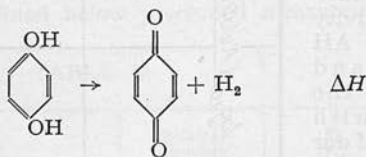
⁹ Elley, *Trans. Electrochem. Soc.*, 1935, 69, 239.

quinones as the completely oxidised state, and also 5 phenols for which the normal oxidation-reduction potential cannot be determined directly owing to the incomplete reversibility of the redox systems. Conant and Fieser^{15, 10, 16} have established that in the case of many phenols the following partly reversible system may be set up:

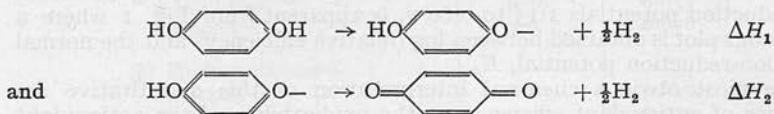


Final Products

where AH represents the phenol and B the oxidant of a suitable reversible oxidation-reduction system. They have introduced an experimental quantity, the "critical oxidation potential", which gives a relative measure of the free energy change in the reversible step—and therefore of the reaction $AH \rightarrow A + H$ —when the concentration of A is very small. Fieser¹⁰ has suggested a method of deriving the hypothetical normal oxidation-reduction potentials for these systems from the critical oxidation potentials and this has been adopted in compiling Table II: such calculations involve uncertainties on at least three counts, and while little absolute accuracy may be claimed for these normal oxidation-reduction potentials, they should give a reliable measure of the relative ease of removal of the phenolic hydrogen atom from a series of phenols. Direct determination of the normal oxidation-reduction potential for the hydroquinone-quinone systems gives immediately the overall free energy change associated with the reaction, e.g.



This in turn gives a relative measure of the corresponding heats of reaction (ΔH) for a series of hydroquinones if variations of entropy changes are neglected. There remains the problem of apportioning ΔH between the two successive steps



The relative values of ΔH , ΔH_1 and ΔH_2 within a series of hydroquinones will be determined by the differences in the resonance energies of the several hydroquinones, semiquinones and quinones, which may be represented by E_{HQ} , E_{SQ} and E_{Q} respectively. It may readily be shown that the necessary condition that ΔH_1 should decrease as ΔH decreases as we pass from one hydroquinone to another is that $\Delta E_{\text{Q}} > \Delta E_{\text{HQ}}$, $\Delta E_{\text{SQ}} > \Delta E_{\text{HQ}}$. If we consider a series of hydroquinones obtained by substitution of groups into the aromatic nucleus of the parent member, it becomes reasonable that such a relationship between ΔE_{HQ} , ΔE_{SQ} and

¹⁰ Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 5204.

¹¹ Fieser and Peters, *ibid.*, 1931, **53**, 793.

¹² Conant and Fieser, *ibid.*, 1924, **46**, 1858.

¹³ Conant and Fieser, *ibid.*, 1922, **44**, 2480.

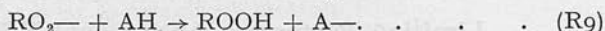
¹⁴ Conant, *Inter. Crit. Tables*, 1928, **6**, 333.

¹⁵ Conant, *Chem. Rev.*, 1929, **3**, 1.

¹⁶ See also Gershinowitz, *J. Chem. Physics*, 1936, **4**, 363.

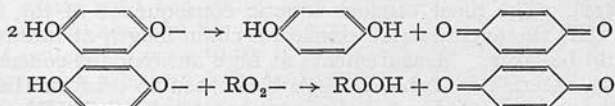
ΔE_Q should exist: the introduction for instance of an "acid-weakening" substituent (e.g. methyl) into an aromatic compound may be considered¹⁷ to have the effect of increasing the importance of any ionic canonical forms which have a positive charge situated in the aromatic nucleus; conversely, canonical forms having negative charges in the aromatic nucleus are in this particular case of reduced importance. Since the ionic canonical forms of quinones are of the former type and those of the hydroquinones of the latter—with the semiquinones including examples of both types—it becomes likely that here $\Delta E_Q > \Delta E_{SQ} > \Delta E_{HQ}$. The condition that ΔH_1 should decrease with decrease in ΔH is thus apparently reasonable, and accordingly it may be expected that within series of hydroquinones which are all substitutive derivatives of one member, the oxidation-reduction potential will give a relative measure of the ease of removal of a phenolic hydrogen atom.* It is, however, to be noted that if such a series of hydroquinones is extended to include hydroquinones containing different aromatic nuclei it is no longer admissible to apply the above simple argument.

The regular manner in which chain-terminating efficiency increases with decrease in E_0 (cf. Table II) within each of the two series (a) of 5 phenols and (b) of the 3 hydroquinones, *p*-benzo-, tolu- and trimethylhydroquinone, leaves no doubt that termination reaction (R9) involves the rupture of the phenolic O—H bond according to



Two earlier investigations provide chemical evidence that an anti-oxidant may react by loss of hydrogen atoms; Ziegler and Ewald¹⁹ showed that the product resulting from the interaction between hexaphenyl ethane and oxygen was the disubstituted peroxide $(C_6H_5)_3C \cdot OO \cdot C(C_6H_5)_3$ while in presence of pyrogallol the sole product was the hydroperoxide $(C_6H_5)_3 \cdot COOH$ presumably formed by abstraction of a hydrogen from the pyrogallol by the peroxide radical $(C_6H_5)_3C \cdot OO-$. Aleya and Bäckström²⁰ have demonstrated that alcohols which act as chain terminators in the oxidation of sodium sulphite are in the process converted to the corresponding aldehyde or ketone.

The essential requirement of the mechanism of inhibition by hydroquinone given earlier was the conversion of the chain carrier RO_2- to stable non-radical products. In the light of the chemical formulation of the interaction between RO_2- and AH now possible we may with some confidence suggest the following two ways in which the production of stable molecules may be completed:



¹⁷ Branch and Calvin, *The Theory of Organic Chemistry* (New York, 1941).

* The work of Dimroth¹⁸ is of interest in this connection. A study of the rate of dehydrogenation of certain dihydro compounds by different members of a series of *p*-benzoquinones showed that the rate of reaction increased smoothly with the normal oxidation-reduction potentials of the quinones, while in an example of the reverse type of reaction—between hydroquinones and hexanitroazobenzene—the rate diminished with increasing oxidation-reduction potential. While it is not possible to decide from Dimroth's data the identity of the rate-determining steps it is not unlikely that it involves in each case the formation of the semiquinone from the quinone or hydroquinone. On this assumption it follows that for substitution in *p*-benzoquinone

$$\Delta E_Q > \Delta E_{SQ} > \Delta E_{HQ}$$

¹⁸ Dimroth, *Z. angew. Chem.*, 1933, **46**, 571.

¹⁹ Ziegler and Ewald, *Annalen*, 1933, **504**, 162.

²⁰ Aleya and Bäckström, *J. Amer. Chem. Soc.*, 1929, **51**, 90.

It is not possible to differentiate between these two possibilities on kinetic grounds. In the case of antioxidants where ready conversion to quinonoid forms is not possible, other reactions such as combination of A— radicals are probably important.

The mechanism of the antioxidant action of phenols described above centres round the competition between antioxidant and hydrocarbon molecules for the chain carrier, RO_2 — according to (R9) or (R3) respectively. A consideration of the thermochemistry of these two reactions, based on the set of consistent bond energies already detailed²¹ has led to the conclusion that for all examples of AH here concerned (a) reaction (R9) is—like (R3)—exothermic and (b) it is unlikely that reaction (R9) is in fact more exothermic than (R3). Now the two main factors which determine the energy of activation of exothermic reactions appears to be the heat of reaction and the degree of resonance stabilisation in the transition state and Evans and Warhurst^{22, 23} have shown that in certain reactions at least the latter may be of predominant importance. It seems probable therefore that the deciding factor in making the energy of activation of (R9) smaller than that of (R3) is the resonance energy of the more highly symmetrical transition complex of reaction (R9) being greater than that associated with the transition complex of the competing reaction (R3).

Limiting Factors to Antioxidant Efficiency.

The dependence of the efficiency of the members of a series of phenolic antioxidants on the difference between the resonance energies of the A radical ($E_{A\cdot}$) and the AH molecule (E_{AH}) should hold only over a limited range since at both low and high values of ($E_{A\cdot} - E_{AH}$) additional complicating reactions would be expected to appear. Thus if ($E_{A\cdot} - E_{AH}$) is sufficiently small the possibility arises that the reaction



would become important.

This reaction would obviously limit the efficiency of an antioxidant by replacing one oxidation chain carrier destroyed by reaction (R9) with another. Looking at it in a qualitative way, it is apparent that whether this reaction will actually be important hinges on whether the minimum value of ($E_{A\cdot} - E_{AH}$) necessary for reaction (R9) to occur, is less than the maximum value of ($E_{A\cdot} - E_{AH}$) consistent with the ready occurrence of reaction (R11). The most obvious kinetic consequence of the intrusion of (R11) is that the extrapolated oxidation chain length at infinite values of AH should be large. Measurements at high antioxidant concentrations (marked with asterisk in Table I) have been used to confirm that for all 9 phenols the extrapolated rates of oxidation at infinite [AH] correspond to chain lengths certainly not greater than 2. In the case of these phenols therefore reaction (R11) may be left out of account. It may be noted that reaction (R11) would be expected to be still less efficient in the case of other nonconjugated olefins, where the difference between $E_{R\cdot}$ and E_{RH} is invariably smaller. Preliminary examination of *p*-hydroxy-biphenyl as an antioxidant has, however, revealed that in the case of this particular phenol reaction, (R11) may be of importance, since here the oxidation chain-length extrapolated to infinite [AH] is as high as 17 (in presence of 2.2 moles benzoyl peroxide/mole ester at 45° C.).

A second limiting factor to the efficiency of an antioxidant should appear when ($E_{A\cdot} - E_{AH}$) becomes sufficiently great: owing to the re-

²¹ Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42**, 244.

²² Evans and Warhurst, *ibid.*, 1938, **34**, 614.

²³ Evans, *ibid.*, 1939, **35**, 824.

sulting ease of dehydrogenation, molecular oxygen itself may attack the antioxidant, presumably according to



Our series of phenols has been extended to include examples of sufficiently low oxidation-reduction potential for this effect to be appreciable.

Readily-oxidisable Phenols as Antioxidants.

Egloff, Lowry, Morrell and Dryer³ have drawn attention to the possibility that antioxidants of sufficiently low oxidation-reduction potential may themselves interact directly with oxygen under the test conditions. Induction periods measured under such circumstances naturally fail to reflect the chain-terminating efficiency of the antioxidants. Doubtless this is the explanation of the apparently poor antioxidant properties observed by Elley for amino-compounds of critical oxidation potential less than 0.6 v. Under the mild temperature conditions used above the direct oxidation of hydroquinone was not appreciable, judging from the fact that the rate of removal of hydroquinone from the oxidising linoleate was independent of oxygen pressure: when, however, trimethyl-hydroquinone ($E_0 = 0.528$ v.) and 1:4-naphthohydroquinone ($E_0 = 0.482$ v.) were used as antioxidants, indications were obtained that their oxidisability was sufficiently great to complicate matters.

TABLE III.

Antioxidant.	[AH].	[ROOH].	p . (mm.)	R_U .	R_a .	t_{∞} . (min.)
	(moles/mole ester)			(moles O ₂ /mole ester/min.)		
	$\times 10^4$.	$\times 10^2$.		$\times 10^{-4}$.		
1:4-Naphtho- hydroquinone	0.76	17.7	10	2.30	0.006	100
	0.77	17.7	25	2.30	0.005	50
	0.80	17.7	50	2.30	0.005	32
Hydroquinone .	0.80	17.7	50	2.30	0.210	105

In the first place these two hydroquinones react with dibenzoyl peroxide *in vacuo* with the result that their concentration in the reaction mixture was diminished to an appreciable extent during the necessary period of evacuation prior to the introduction of oxygen into the apparatus. When, however, ethyl linoleate hydroperoxide is substituted for dibenzoyl peroxide as chain initiator this difficulty is removed. Accordingly in carrying out the comparison of the antioxidant efficiency of trimethyl-hydroquinone and 1:4-naphthohydroquinone with that of hydroquinone their retarding effect on the rate of oxidation of ethyl linoleate containing 1.7% peroxidic oxygen has been determined. The results of 3 such experiments with 1:4-naphthohydroquinone are summarised in Table III. The times required for complete removal of antioxidant quoted (t_{∞}) are estimated from the time taken for the rate of oxidation to reach its original uninhibited rate, and undoubtedly are liable to some uncertainty. For comparison, the time required for the removal of hydroquinone under rather similar experimental conditions is included. These figures demonstrate (a) that the 1:4-naphthohydroquinone is removed from the system more rapidly than hydroquinone, and (b) that in contrast to hydroquinone, the rate of removal definitely increases with increase in oxygen pressure. It is difficult to escape the conclusion that the antioxidant is itself destroyed by direct interaction with oxygen.

It has not been found practicable to measure the initial rates of oxidation over a wide range of 1:4-naphthohydroquinone concentration: at concentrations lower than those detailed in Table IV the rate of oxidation increases sufficiently rapidly with time to make extrapolation to zero time uncertain. The initial rates of oxidation observed with only 0.8×10^{-4} mole 1:4-naphthohydroquinone/mole ester correspond to only a fractional chain length and are some 40 times smaller than the rate of oxidation in presence of the same concentration of hydroquinone. The estimate of the relative chain-terminating efficiency of 1:4-naphthohydroquinone based on the ratio and quoted in Table II must be treated as approximate, since when the apparent chain length of oxidation is of the order of unity its reliability must be questioned as secondary effects, such as the evolution of volatile products may be of comparable magnitude to the rate of oxygen uptake.

The authors wish to express their thanks to Dr. G. Gee for his interest and advice during this work which forms part of the programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

Summary.

The effect of 10 phenolic antioxidants on the oxidation of ethyl linoleate has been investigated and the efficiencies with which they bring about the termination of the oxidation chains (by interacting with the peroxide-radical chain-carrier, RO_2^-) compared. The chain-terminating efficiency is shown to increase with decreasing oxidation-reduction potential (i.e. increasing oxidisability) of the antioxidant within two series of phenolic compounds, leading to the conclusion that the chain-termination reaction is $RO_2^- + AH \rightarrow ROOH + A-$ (where AH represents the phenol).

It is demonstrated that in the case of a sufficiently oxidisable phenol (normal oxidation-reduction potential $< ca. 0.6$ v.) destruction by direct reaction with oxygen becomes the most important factor in determining its practical utility as an antioxidant.

Résumé.

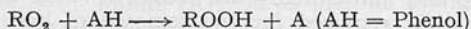
L'effet de 10 antioxydants phénoliques sur l'oxydation du linoléate d'éthyle a été étudié et leurs capacités respectives pour terminer les chaînes d'oxydation, comparées. Cette propriété augmente avec des potentiels d'oxydo-réduction croissants de l'antioxydant, pour deux séries de composés phénoliques, suggérant ainsi que la réaction de terminaison de chaîne est :



Quand le potentiel d'oxydo-réduction du phénol est inférieur à 0.6 v., le facteur dominant est la destruction par réaction directe avec l'oxygène.

Zusammenfassung.

Die Wirkung von 10 phenolischen Antioxydanten auf die Oxydation von Äthyllinoleat wurde untersucht und ihre Wirksamkeit für den Abbruch von Oxydationsketten verglichen. Diese Wirksamkeit wächst mit zunehmendem Redoxpotential des Antioxydanten innerhalb von zwei Reihen von Phenolverbindungen, was darauf hindeutet, dass der Kettenabbruch



ist. Wenn das Redoxpotential des Phenols geringer als 0.6 v. ist, wird die Zerstörung durch direkte Reaktion mit Sauerstoff der vorherrschende Faktor.

SECTION 8

The Mechanism of Chain Propagation in the Oxidation of Polyisoprenes

KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS

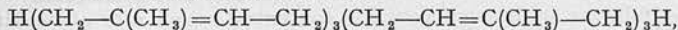
VII. THE MECHANISM OF CHAIN PROPAGATION IN THE OXIDATION OF POLYISOPRENES

BY J. L. BOLLAND AND P. TEN HAVE

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A kinetic investigation has been made of the interaction of the hexa-isoprene, squalene, with oxygen in presence of benzoyl peroxide, both in absence and presence of hydroquinone. The mechanism by which oxidation chains are propagated and terminated in these systems is identified and shown to be formally analogous to that already determined for the oxidation of mono-olefins and 1:4-dienes. The identity of the chain propagation reactions in the oxidation of polyisoprenes is discussed: the diperoxide type of primary oxidation product obtained with this class of olefin required the occurrence of a four-stage chain propagation cycle.

Recent work has established that the major primary autoxidation product of the hexa-isoprene,¹ squalene



and of the di-isoprene,² 2:6-dimethyl-octadiene-2:6, is in both cases a diperoxide in contrast to the mono-hydroperoxidic products formed by the autoxidation of mono-olefins and 1:4-dienes (e.g.^{3, 4, 5}). It should be emphasised that this diperoxide is formed even in the initial stages of autoxidation and is, therefore, to be regarded as formed in the propagation steps of the oxidation chains and not as a result of secondary reactions of a mono-hydroperoxidic primary product. In this paper we choose for kinetic study two oxidation systems involving squalene which give the most direct means of comparing the chain-propagation mechanism for the polyisoprene with those of the other (mono- and 1:4-di-) olefins already examined.^{6, 7, 8, 9} The first selected system is the benzoyl peroxide initiated oxidation of squalene, the second the same system in presence of certain phenolic antioxidants.

* Seconded by The Netherlands Indies Government to the B.R.P.R.A.

¹ Bolland and Hughes, *J. Chem. Soc.* (in press).

² Bolland and Hughes, unpublished work.

³ Farmer and Sundralingam, *J. Chem. Soc.*, 1942, 121.

⁴ Farmer and Sutton, *ibid.*, 1943, 119.

⁵ Bolland and Koch, *ibid.*, 1945, 445.

⁶ Bolland, *Proc. Roy. Soc. A*, 1946, 186, 218.

⁷ Bolland and Gee, *Trans. Faraday Soc.*, 1946, 42, 236.

⁸ Bolland, *Trans. Faraday Soc.*, 1948, 43, 669.

⁹ Bolland and ten Have, *ibid.*, 1947, 43, 201.

Experimental

The experimental technique of oxidation rate measurement was that already described.^{6, 9} Squalene was obtained from basking shark liver oil. After removal of saponifiable components, the oil was subjected to successive fractional molecular distillations in a still of the falling-film type.¹⁰ The squalene (2% solution in 40-60° petrol ether) was finally purified by passage through a 20 cm. alumina chromatographic column. The saturated hydrocarbon, used when required as diluent, was a normal paraffin mixture of setting point 38.9° C supplied by the Burma Oil Company.

2 : 6-dimethyl-octadiene-2 : 6, prepared by the reduction of purified geraniol with sodium in liquid ammonia, was kindly supplied by Dr. R. F. Naylor.

I. Benzoyl Peroxide Initiated Oxidations

(a) SQUALENE.—The manner in which the rate of oxidation of squalene depends on the concentration of benzoyl peroxide $[Bz_2O_2]$, oxygen pressure p and squalene concentration $[RH]$ is illustrated by Fig. 1 and 2 and Table I

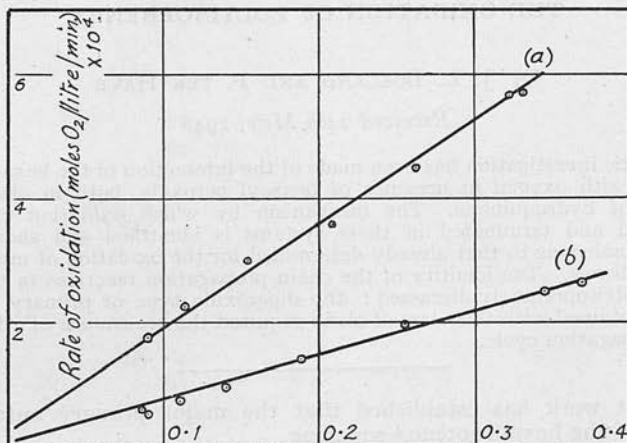


FIG. 1.—Influence of benzoyl peroxide concentration on rate of oxidation at 45° C and 100 mm Hg. oxygen pressure. (a) Squalene; (b) 2 : 6-Dimethyl-octadiene-2 : 6.

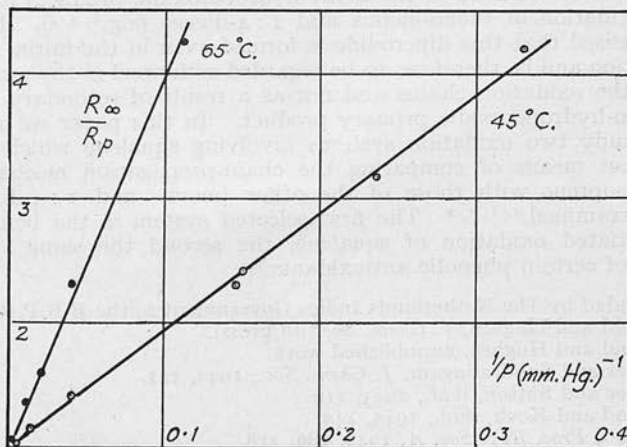


FIG. 2.—Influence of oxygen pressure on rate of oxidation (R_p) of squalene at 45° C ($[Bz_2O_2] = 0.0510$ moles/l.) and 65° C ($[Bz_2O_2] = 0.0372$ moles/l.). R_∞ represents the rate of oxidation at infinite oxygen pressure.

respectively. From the effect of these various parameters when varied individually the oxidation rate equation in the temperature range 45-65°C approximates closely to the form:

$$\text{Rate} = c [\text{Bz}_2\text{O}_2]^{\frac{1}{2}} [\text{RH}]^{\frac{1}{2}} \frac{p}{\lambda + p} + f([\text{RH}], p) \quad (1)$$

where c and λ are constants and p is the oxygen pressure. The function $f([\text{RH}], p)$, (i.e. $C [\text{Bz}_2\text{O}_2]$ etc.) attributable to the occurrence of oxidation chains not initiated

TABLE I.—INFLUENCE OF [RH] ON RATE OF OXIDATION AT 45°C

p (mm. Hg)	$[\text{Bz}_2\text{O}_2]$ Moles/l.	[RH]	Rate (moles/l./min.) $\times 10^4$.	Rate/[RH] * (min. ⁻¹). $\times 10^5$.
(a) Squalene 100	0.0682	12.6	4.45	3.60
		4.92	1.68	3.42
		2.05	0.70	3.41
		1.00	0.33	3.30
(b) 2 : 6-Dimethyl-octadiene-2 : 6 100	0.0642	11.2	1.94	1.73
		5.60	0.93	1.67
		3.10	0.52	1.68
		1.68	0.27	1.62
		0.98	0.170	1.73

by benzoyl peroxide, is of importance only at low $[\text{Bz}_2\text{O}_2]$. The values of c and λ required to define eqn. (1) at several temperatures are collected in Table II. The present data are incomplete in one minor respect: the dependence of λ on [RH] has not been determined.

(b) 2 : 6-DIMETHYL-OCTADIENE-2 : 6.—A parallel investigation of the oxidation kinetics of this di-isoprene led to precisely the same form of rate equation as (1). For example, the dependence of rate on $[\text{Bz}_2\text{O}_2]$ and [RH] is included in Fig. 1 and Table I respectively. Experimental determinations of c and λ are included in Table II.

The overall energies of activation (E_a) for the oxidation of these two hydrocarbons, based on the temperature coefficient of c , are 23.5 and 24.0 kcal./mole respectively. The temperature coefficient of λ corresponds to an energy term (E_λ) of 12 kcal./mole in the case of squalene.

Owing to the volatility of 2 : 6-dimethyl-octadiene-2 : 6, the limiting oxygen pressure below which reliable rate measurements could be made was too high for precise values of λ to be obtained. No attempt has therefore been made to measure the temperature coefficient in this case, and indeed the one figure quoted (at 45°C) may be subject to ca. 30% error.

Comparison with Kinetics for other Olefins.—(a) FORM OF RATE EQUATION.—Comparison of the rate equation (1) with those obtained for the benzoyl peroxide initiated oxidation of three such dissimilar olefins as ethyl linoleate,⁸ methyl oleate¹¹ and tetralin¹² reveals at once that the kinetic

TABLE II

Temp. (°C)	c (moles/l.) ⁻¹ min. ⁻¹ ($\times 10^4$)	λ mm. Hg
(a) Undiluted squalene		
35	0.44	3.8
45	1.47	9.6
55	4.35	—
65	13.0	30
(b) Undiluted 2 : 6-dimethyl-octadiene-2 : 6		
35	0.21	—
45	0.78	6
55	2.35	—
65	6.9	—

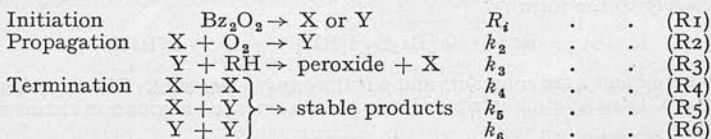
* [RH] is expressed in moles isoprene residues/l.

¹¹ Bolland, Part VIII of present series.

^{11a} Bolland, Part XI of present series.

¹² Bateman and Gee, *Proc. Roy. Soc. A* (in press).

characteristics are the same in all cases. The oxidation of the two polyisoprenes must therefore conform to a formal mechanism of the type :

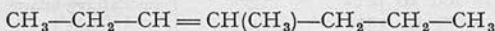


X and Y represent two chain carriers, R_i represents the rate of production of fresh chain carriers and k_2 - k_6 the velocity coefficients of the reactions (R2)-(R6). In the case of the other three olefins mentioned, X and Y are, of course, identified with R— and RO_2 — (where R represents an olefin with one α -methylene hydrogen removed) and the peroxidic product completed in reaction (R3) is an α -methylene hydroperoxide.

(b) VALUES OF VELOCITY COEFFICIENTS OF PROPAGATION STEPS.—The absence of compelling evidence as to the identity of the chain carriers in the present instance (in contrast to the case of ethyl linoleate⁶) renders important a quantitative comparison of the efficiencies of the elementary reactions (R2) and (R3) with those concerned in the oxidation of other olefins. The composite constant $k_3k_6^{-\frac{1}{2}}$ may be determined from the experimental constant, c , included in the rate equation (1), since

$$c = \alpha^{\frac{1}{2}} k_7^{\frac{1}{2}} [RH] k_3 k_6^{-\frac{1}{2}}, \quad \dots \quad (2)$$

where k_7 is the unimolecular velocity coefficient of the thermal decomposition of benzoyl peroxide, and α is the number of chains started by the decomposition of each benzoyl peroxide molecule. While the absolute value of $k_3k_6^{-\frac{1}{2}}$ may be in some doubt owing to uncertainty as to the value of α , reliable comparisons of $k_3k_6^{-\frac{1}{2}}$ may be made in this way for different olefins (always provided their oxidation chain mechanism follows the pattern R2-R6). Expressing [RH] in terms of moles isoprene residues/l. (six per molecule of squalene) and taking k_7 at 45° C as 3×10^{-5} min.⁻¹, $k_3k_6^{-\frac{1}{2}}$ at this temperature is calculated as 0.0268 for squalene and 0.0138 (mole/l. min.)⁻¹ for 2:6-dimethyl-octadiene-2:6. A mono-olefin in which the degree of substitution at the double bond reproduces that observed in the polyisoprenes—4-methyl-heptene-3,



—was found¹¹ to have a $k_3k_6^{-\frac{1}{2}}$ value of 0.0210 (mole/l. min.)⁻¹ at 45° C. By application of the rotating sector technique to the photo-oxidation of olefins, Bateman and Gee¹² have shown that the absolute values of k_6 for such diverse types of olefin as a 1:4-diene (ethyl linoleate) two mono-olefins (cyclohexene and methyl cyclohexene) and a di-isoprene (2:6-dimethyl-octadiene-2:6) are within experimental error identical. The efficiencies of reaction (R3) in the oxidation chain propagation of the two polyisoprenes and 4-methyl-heptene-3 must accordingly be very similar.

It is not possible to separate and evaluate the other propagation velocity constant, k_2 . The constant which defines the dependence of rate of oxidation on oxygen pressure is given, on the basis of the reaction mechanism R2-R6, by

$$\lambda = \frac{k_3}{k_2} \left(\frac{k_4}{k_6} \right)^{\frac{1}{2}} \times [RH]. \quad \dots \quad (3)$$

In conjunction with the value of $k_3k_6^{-\frac{1}{2}}$ and the solubility of oxygen (1.0×10^{-5} mole/l./mm Hg)^{12a}, this equation yields a figure for $k_2k_4^{-\frac{1}{2}}$. This is 3.5×10^3 (moles/l. min.)⁻¹ at 45° C for squalene. The corresponding data for a tri-substituted olefin like 4-methyl-heptene-3 is not available but $k_2k_4^{-\frac{1}{2}}$ values determined^{12a} for several dissimilar olefins—including mono-olefins, 1:4-dienes, and substituted aromatic hydrocarbons—are sufficiently concordant to show that this quantity is insensitive to olefinic structure and has a mean value of ca. 5×10^3 (moles/l. min.)⁻¹ at 45° C. While there is, at present, no direct experimental evidence on the point, it is safe to assume that k_4 remains sensibly constant for the various types of olefin mentioned, and therefore so also does the efficiency (k_2) of the interaction of the various R-radicals with oxygen.

There is thus convincing evidence that the three reaction constants k_6 , k_3

^{12a} Bolland, Part IX of present series.

and k_2 are each in close accord for the polyisoprenes and the most similar type of mono-olefin. The argument that the chain carriers concerned in the oxidation of squalene and 2:6-dimethyl-octadiene-2:6 are (as for the mono-olefin) of the R - and RO_2 -types is therefore undoubtedly strong.

II. Benzoyl Peroxide Initiated Oxidation of Squalene in Presence of Phenolic Inhibitors

(a) **Hydroquinone.**—A somewhat detailed examination of the kinetic characteristics of the oxidation of squalene, initiated by benzoyl peroxide, in presence of hydroquinone has been carried out in a similar manner to an earlier study of the corresponding ethyl linoleate system.⁹ Measurements of the initial rate of oxidation $(R_a)_0$ under a series of systematically varied conditions of benzoyl peroxide $[Bz_2O_2]_0$, hydroquinone $[Hq]_0$ and squalene $[RH]_0$ concentrations, oxygen pressure and temperature are recorded in Table III. These data may

TABLE III

$[Hq]_0$		$[Bz_2O_2]_0$	$[RH]_0$	p (mm)	Temp. (°C)	$(R_a)_0$		K	$t_{\frac{1}{2}}$ (min.)	n/α
$\times 10^4$	$\times 10^2$	mole per litre	$\times 10^4$			$\times 10^4$	mole/l./min.			
(a) Variation of $[Hq]_0$										
0.458	7.68	12.6	100	45	0.487	5.62	0.089	25	2.5	
0.783	7.29	12.6	100	45	0.309	5.50	0.100	44	2.4	
0.783	7.71	12.6	100	45	0.305	5.64	0.095	40	2.3	
1.85	7.06	12.6	100	45	0.121	5.40	0.097	85	2.0	
1.88	8.09	12.6	100	45	0.150	5.77	0.106	80	2.1	
3.77	8.55	12.6	100	45	0.074	5.90	0.100	—	—	
(b) Variation of $[Bz_2O_2]_0$										
0.937	0.86	12.6	100	45	0.042	2.22	0.101	—	—	
1.45	2.38	12.6	100	45	0.066	3.35	0.108	160	1.7	
1.57	10.7	12.6	100	45	0.237	6.56	0.107	53	2.2	
(c) Variation of $[RH]_0$										
0.95	7.20	4.80	100	45	0.090	2.07	0.095	—	—	
0.80	8.05	2.65	100	45	0.061	1.20	0.090	—	—	
(d) Variation of oxygen pressure										
1.65	7.52	12.6	11	45	0.108	538	0.080	90	2.4	
0.80	7.52	12.6	15	45	0.218	538	0.077	40	2.3	
(e) Variation of temperature										
3.57	7.14	12.6	100	52	0.240	11.7	0.078	65	2.2	
3.53	8.29	12.6	100	52	0.292	12.5	0.082	60	2.3	
0.353	6.22	12.6	100	38	0.151	2.38	0.119	70	2.7	
0.525	6.22	12.6	100	38	0.105	2.38	0.123	—	—	

be used to make four points of comparison between the effects of hydroquinone on the oxidation of squalene and ethyl linoleate respectively.

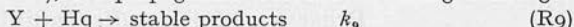
(i) **FORM OF RATE EQUATION.**—In presence of benzoyl peroxide and hydroquinone the rate of oxidation of ethyl linoleate conforms to the rate equation

$$(R_a)_0 = \text{const. } R_i \frac{[RH]_0}{[Hq]_0} \quad . \quad . \quad . \quad . \quad (4)$$

$$= K \times \frac{R_u^2}{[RH]_0[Hq]_0} \quad . \quad . \quad . \quad . \quad (5)$$

where R_i represents the rate of chain initiation (in presence of appreciable amounts of benzoyl peroxide, $k_1 [Bz_2O_2]$) and R_u the corresponding rate of oxidation in absence of hydroquinone: K is a constant. Application of this relation

to the data in Table III gives the values of K recorded therein. Apart from a slight dependence of K on oxygen pressure (which will, for the moment, be neglected) eqn. (5) accords well with the experimental facts. The mechanism of inhibition is thus formally analogous to that found for ethyl linoleate. The main chain-termination step may, therefore, be identified as interaction between a hydroquinone molecule and a chain carrier of the peroxide-radical type (Y in the formal scheme R1-R6), the propagation reactions remaining unchanged



(ii) EFFICIENCY OF TERMINATION REACTION, k_9 .—By application of stationary state methods to the reaction scheme (R1-R3, R9) the constant K may be evaluated in terms of the individual velocity coefficients:

$$K = k_6/k_3k_9 \quad \dots \quad (6)$$

In comparing the values of K obtained for ethyl linoleate and squalene, the olefin concentrations are best expressed in terms of moles reactive groups/l. (assuming the number in the ethyl linoleate and squalene molecules to be one and six respectively). The values of K at 45° C are then 0.100 for squalene and (using the rates of uninhibited oxidation given ref. ⁸) 0.032 (mole/l. min.) for ethyl linoleate. Utilising the known figures for $k_3k_6^{-\frac{1}{2}}$ — 0.0268 for squalene (cf. above) and 0.162 (mole/l. min.)^{-1/2} for ethyl linoleate—it is possible to estimate from (6) the quantity $k_9k_6^{-\frac{1}{2}}$. For squalene at 45° C then, $k_9k_6^{-\frac{1}{2}}$ is 373 compared with 194 (moles/l. min.)^{-1/2} for ethyl linoleate. Recalling Bateman and Gee's demonstration¹² that k_6 is very similar for ethyl linoleate and the di-isoprene 2 : 6-dimethyl-octadiene-2 : 6, the reactivity towards hydroquinone—and presumably therefore the essential chemical nature—of the peroxide radical chain carriers in the oxidation of ethyl linoleate and squalene are similar.

(iii) ACTIVATION ENERGIES.—A further—though much less sensitive—test of the quantitative correspondence between the oxidation of ethyl linoleate and squalene in presence of hydroquinone lies in the overall energy of activation (E_a). Since

$$(R_a)_0 = R_i \frac{k_3[RH]}{k_9[Hq]},$$

$$E_a = E_i + E_3 - E_9 \quad \dots \quad (7)$$

where E_i , E_3 and E_9 are the activation energies of the initiation process and the reactions (R3) and (R9) respectively. The experimental values of E_a are 38 and 42 kcal./mole respectively for ethyl linoleate and squalene. From the overall energies of activation of the uninhibited benzoyl peroxide initiated oxidation of these two olefins (cf. ref. ⁸ and above)

$$(E_3)_{\text{squalene}} - (E_3)_{\text{linoleate}} = 3.0 \text{ kcal./mole. Applying eqn. (7),}$$

$$(E_9)_{\text{squalene}} - (E_9)_{\text{linoleate}} = -1.0 \text{ kcal./mole.}$$

This energy difference must be regarded as not significant in view of the large activation energies on which its derivation is based.

(iv) REMOVAL OF INHIBITOR.—In the case of the oxidation of ethyl linoleate in presence of hydroquinone,⁹ the latter was apparently removed from the system as a result of participation in reaction (R9). A method was described for estimating the ratio n/α (where n is the number of oxidation chains terminated by one hydroquinone molecule and α is the number of chains initiated by the decomposition of one benzoyl peroxide molecule). Application of this method to the present set of data gave the values of n/α included in Table III. From their constancy over a wide range of experimental conditions, it follows that here also the major proportion of the hydroquinone is destroyed in the course of the termination reaction. The mean value of n/α is ca. 2.3, in excellent agreement with the figure (2.1) obtained from the earlier data on ethyl linoleate.

(b) Other Phenolic Inhibitors.—The chain-terminating efficiencies of seven other phenolic compounds have been determined by measurements of the type reported above for hydroquinone. A systematic study of the influence of the various concentration variables was not attempted. There was, however, every indication that in each case the initial rate of oxidation was inversely proportional to the concentration of antioxidant $[AH]_0$. The several values of K so obtained are collected in Table IV.

The increase in antioxidant efficiency with decreasing oxidation-reduction potential observed for the members of both types of phenolic compound parallels their inhibitory effect on the oxidation of ethyl linoleate.¹³ It is, however, noteworthy that the phenols are, on the average, some eight times more effective

¹³ Bolland and ten Have, *Faraday Soc. Discussions*, 1947, 2, 252.

in terminating oxidation chains in squalene than in ethyl linoleate, while the corresponding ratio in the case of the hydroquinone is no more than two. The explanation of this disparity is not apparent from these preliminary measurements.

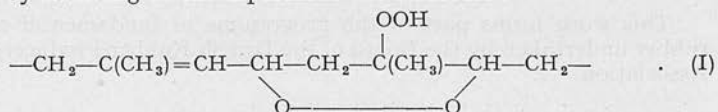
The influence of oxidation-reduction potential on inhibitor efficiency taken together with the measurements on the rate of removal of hydroquinone from the oxidising system (Table III) serves to emphasise that the terminating reactions operative in the two olefins are chemically very similar.

Discussion

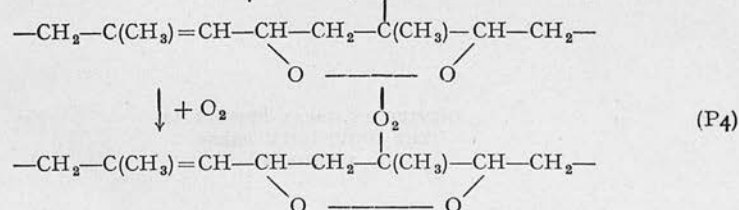
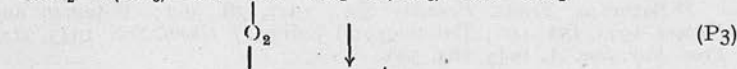
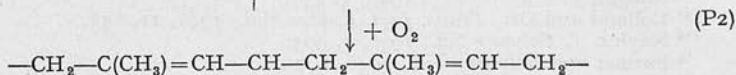
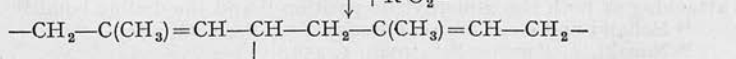
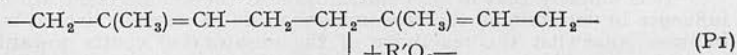
The complete identification of the main oxidation products of squalene and dihydromyrcene by standard organic chemical methods presents very real difficulties.¹⁴ The application of certain analytical methods to determine the number and type of the oxygen-containing chemical groupings in the oxidised hydrocarbons and their fully hydrogenated derivatives can, however, establish all but the finer structural details of the primary oxidation product. Thus it is found^{1,2} that in each oxidised polyisoprene molecule (*a*) four atoms of oxygen are present, (*b*) two of which form a hydroperoxide and (*c*) two a cyclic peroxide grouping, while (*d*) two oxygen atoms, one from each grouping, are attached to adjacent carbon atoms in the polyisoprene chain.

The kinetic investigations outlined in the previous two sections prove that the oxidation mechanism for polyisoprenes conform to the same formal pattern (R1-R6) as that for the various olefins and unsaturated esters which form α -mono-hydroperoxides as primary oxidation products. Moreover, the very similar rates found for the respective elementary reactions involved in the oxidation of squalene and comparable mono-olefins implies that the chain carriers concerned in the oxidation of these two types of olefins are chemically very similar.

These conclusions as to the chemical nature of the primary product and the chain carriers on the one hand, and the form of the elementary reactions by which it is formed on the other are most satisfactorily reconciled by ascribing to the diperoxide the structure :



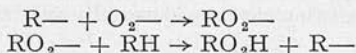
This formulation obviously embodies each of the four conclusions drawn from analytical investigation. The reasons for preferring this particular structure to others which also fulfil these same analytical requirements are detailed elsewhere.¹ The diperoxide is visualised as being formed by the following four-stage chain propagation cycle—



¹⁴ Farmer and Sutton, *J. Chem. Soc.*, 1942, 139.

This last peroxide radical then abstracts an α -methylene hydrogen from another isoprene residue to complete the diperoxide structure (I) and reproduce the first step (P₁) in the cycle.

The four-stage propagation cycle (P₁-P₄) will lead to kinetics indistinguishable from the two-stage propagation cycle :



appropriate to the oxidation of olefins giving mono-hydroperoxidic products only if the *intramolecular* process (P₃) is much more efficient than the alternative *intermolecular* reaction involving the transfer of an α -methylene hydrogen from another olefin molecule (analogous to step (P₁))—or indeed from the neighbouring α -methylene groups in the same molecule. One factor which may determine which reaction will preponderate is the exothermicity of the competing processes.¹⁵ In olefins containing more than one double bond, however, the relative positioning between unsaturated centres may be critical in so far as the possible formation of intramolecular cyclic products is concerned. The 1:5-diene structure found in polyisoprenes* would appear to be the most favourable in this respect since reaction (P₃) leads to formation of a six-membered ring. The formation of six- and five-membered cyclic products appears to be common in polyisoprenic systems: thus they appear as major products in the thermal depolymerisation of rubber¹⁷ (i.e. dipentene) and its interaction with H₂S¹⁸ and sulphur.¹⁹ In each case the most plausible mechanisms conform to the pattern suggested in the present instance: attack by the reagent at one unsaturated centre is followed by intramolecular reaction of the product so formed with the neighbouring unsaturated centre. It is not safe to conclude that the occurrence of the second intramolecular step is dictated entirely by the favourable steric conditions, until the role of the hyperconjugation effects suggested by Bateman and Jeffrey²⁰ has been more completely determined.

This work forms part of the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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* It is unlikely that methyl substitution at the double bond will have much influence in determining the predominant mode of reaction since it is known to increase somewhat the reactivity of the unsaturated centre towards radicals attacking at both the α -methylene position¹¹ and the double bond.¹⁶

¹⁵ Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42**, 244.

¹⁶ Nozaki, *J. Polymer Sci.*, 1946, **1**, 455.

¹⁷ Bolland and Orr, *Trans. Inst. Rubber Ind.*, 1946, **21**, 133.

¹⁸ Naylor, *J. Polymer Sci.*, 1946, **1**, 305.

¹⁹ Farmer and Shipley, *ibid.*, 1946, **1**, 293.

²⁰ Bateman, *Trans. Faraday Soc.*, 1942, **38**, 367; Bateman and Jeffrey, *Nature*, 1943, **152**, 446; Bateman and Jeffrey, *J. Chem. Soc.*, 1945, 211; Jeffrey, *Proc. Roy. Soc. A*, 1945, **183**, 388.

SECTION 9

The Primary Thermal Oxidation Product

of Squalene

111. *The Primary Thermal Oxidation Product of Squalene.*

By J. L. BOLLAND and HILDA HUGHES.

The product formed in the early stages of the thermal oxidation of squalene has been examined and found to consist substantially of a diperoxide in which four atoms of oxygen are combined with one squalene molecule. Two oxygen atoms are contained in a hydroperoxide group and two form an intramolecular peroxide ring; two oxygen atoms (one from each group) are attached to adjacent carbon atoms. The probable structure of this compound is suggested after consideration of certain kinetic data on the oxidation of polyisoprenes and related mono-olefins.

THE reaction of olefins with molecular oxygen forms primary products the nature of which depends upon the structure of the olefin. Mono-olefins and 1:4-dienes form α -methylene hydroperoxides, whereas the products from conjugated dienes are preponderantly disubstituted cyclic or polymeric peroxides. No similar characterisation has been made of the oxidation products of a further important type of unsaturated grouping, the 1:5-dienes, despite their obvious bearing on the problem of the oxidative ageing of natural rubber. We now report an examination of the product formed in the early stages of the oxidation of a representative of this class of olefin, namely the hexaisoprene, squalene.

The choice of this olefin was dictated partly by a desire to minimise any abnormal effects arising from the proximity of double bonds to the ends of the molecule (a possible objection to the use of the di-isoprene, dihydromyrcene) and partly because kinetic evidence (Bolland and ten Have, *Trans. Faraday Soc.*, 1949, 45, 93) makes it clear that in the thermal oxidation of this olefin the chain length exceeds 100. The product would thus contain almost 99% of the total combined oxygen in the form of the products from the chain propagation reactions (*i.e.*, the primary product).

In view of the polymeric nature of the hydrocarbon, it is obvious that, even if the oxygen reacts uniquely with the unsaturated centres, the oxidation product itself, and any of its derivatives, must contain a sufficient variety of species to preclude their separate isolation and identification by normally used experimental techniques. The present work has therefore of necessity been limited to the application of analytical methods which give quantitative estimates of chemical groupings in the oxidation product and certain of its derivatives. Certain finer details of the molecular structure of oxidised squalene cannot be established by this approach; it is, however, possible to demonstrate that the primary oxidation product combines certain of the structural characteristics of products derived from conjugated and mono-olefins in a manner which might have been anticipated from the particular spacing of double bonds in 1:5-polyenes.

Chemical Examination of Oxidised Squalene.—Earlier work on the oxidation of polyisoprenes (Farmer and Sutton, *J.*, 1942, 139) suggested that, although the oxygen combined in the initial stages of the reaction was converted quantitatively into hydroperoxide groups, yet the yield of hydroperoxide diminished as oxidation progressed. These observations were accounted for in terms of an α -hydroperoxidic primary product which was so thermally unstable as to reduce appreciably the overall yield in which it was obtained. This view requires modification, since careful measurement has now shown that the nature of the oxidised squalene is unchanged over a substantial range of oxidation.

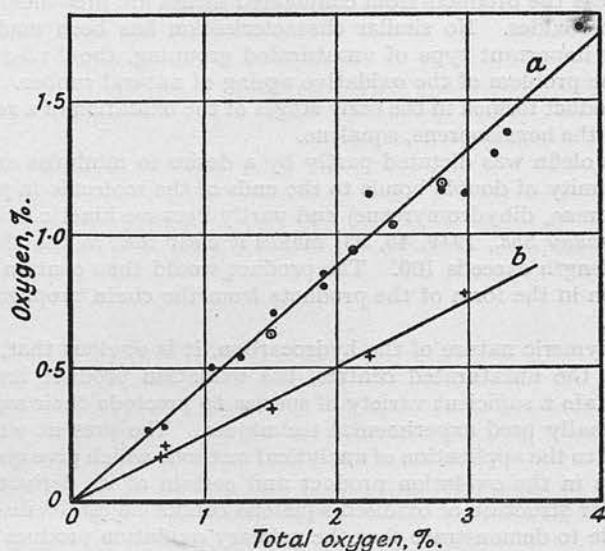
This point has been established by following three analytical characteristics over a series of oxidised squalene samples containing up to 3% of combined oxygen (0.4 mole per mole of squalene): (a) peroxide content, (b) active-hydrogen content, and (c) average total oxygen content of the fraction of squalene which has been oxidised. Peroxide contents, measured iodometrically and with ferrous thiocyanate reagent, and active-hydrogen contents are presented in the figure. Throughout the introduction of the first 3% of oxygen, each molecule of oxygen incorporated in the squalene introduces 0.90 atom of peroxidic oxygen (reactive towards the above two analytical reagents) and 0.50 atom of active hydrogen. The obvious implication is that one hydroperoxidic group is present in each oxidised molecule. A simple form of chromatographic technique achieves quantitative separation of the oxidised material

from the unoxidised squalene. Determination of the amount of unattacked olefin recoverable from a known weight of oxidised squalene of known oxygen content gives at once the average oxygen content of the oxidised squalene (cf. Bolland and Koch, *J.*, 1945, 445). In this way it was found that throughout the total oxygen content range of 0.58 to 2.98%, each molecule of oxidised product contained just over four atoms of oxygen :

Total oxygen (%)	Atoms of oxygen/mole oxidised squalene :		Total oxygen (%)	Atoms of oxygen/mole oxidised squalene :	
	Found.	Calc.		Found.	Calc.
0.58	4.4	4.07	2.3	4.1	4.25
1.65	4.4	4.18	2.95	4.4	4.33
1.9	4.1	4.21	2.98	4.3	4.33

The calculated oxygen content of the oxidised squalene is derived on the suppositions that each time a squalene molecule is oxidised, four oxygen atoms are introduced, and that oxidation proceeds with equal facility at oxidised and unoxidised molecules.

Examination of the Separated Oxidation Product.—Analyses carried out on the oxidised fraction separated chromatographically agreed well with the indications obtained from analyses of the unfractionated oxidised samples as quoted above. The total oxygen content corresponded



Relationship between total oxygen content and (a) peroxidic and (b) hydroxylic oxygen contents in autoxidised squalene. Peroxide contents measured iodometrically and with ferrous thiocyanate reagent are indicated by \odot and \bullet respectively. The curves correspond to yields of (a) 0.90 atom of peroxidic oxygen and (b) 0.50 atom of hydroxylic oxygen per molecule of oxygen incorporated in the squalene.

fairly well to the presence of four oxygen atoms per molecule, while peroxide and active hydrogen analyses indicated the presence of two peroxidic oxygen atoms and one active hydrogen atom per molecule. Cryoscopic determinations of the molecular weight of the oxidised material gave a mean value of 490. Since the molecular weight of the squalene molecule oxidised to contain four oxygen atoms is 474, there is little evidence of intermolecular bridging by oxygen. Nevertheless, traces of gel were on occasion observed adhering to the reaction vessel at the end of experiments. This product which might well owe its insolubility to polymeric peroxidation was ignored in all the analyses quoted here.

Nature of Unreactive Oxygen.—Examination of the infra-red spectrum of oxidised squalene at the Department of Colloid Science, Cambridge, has revealed the presence of only trivial amounts of carbonyl oxygen. The two oxygen atoms per oxidised squalene molecule not reactive toward peroxide reagents do not therefore reside in ketonic, aldehydic, acidic, or ester groupings. Application of the method of Swern, Findley, Billen, and Scanlan (*Ind. Eng. Chem. Anal.*, 1947, 19, 414) for the estimation of epoxide oxygen revealed the presence of only a fractional amount of this grouping (0.06 epoxide group per oxidised molecule). The remaining possible groups—ether or cyclic peroxide—are sufficiently unreactive to analytical reagents to

and $\text{RO}_2\cdot$ by addition of an oxygen molecule to $\text{R}\cdot$ in an α -methylene position and the main primary oxidation product is an α -methylene hydroperoxide.

The critical point at which these two types of oxidation-chain cycle diverge lies in reaction (C): in the case of squalene the peroxido-radical cyclises by interaction with the neighbouring double bond more efficiently than it abstracts a hydrogen atom from another squalene molecule. The nature of the elementary reaction ($\text{RO}_2\cdot + \text{olefinic centre}$) undoubtedly determines the type of oxidation product which any olefin forms. Since, in general, the interaction of a peroxide radical with either a double bond or an α -methylene group appears to be of comparable efficiency, the balance in favour of one or the other mode of reaction may be altered by differences in the type of olefinic system. Thus the formation of α -methylene hydroperoxides from mono-olefins and 1:4-dienes on the one hand and mainly polymeric peroxides from conjugated olefins on the other can be correlated with variations in the exothermicity of the reactions of the respective peroxide radicals with either the appropriate α -methylene groups or double bonds (Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42**, 244). In the present case the determining factor appears to be predominantly a steric one: the particular spacing of the double bonds must be sufficiently favourable for cyclisation of the peroxide radical to replace the normal hydrogen atom extraction process of peroxide radicals disposed next to a trisubstituted ethylenic bond—as exemplified by 1-methylcyclohexene (Farmer and Sundralingam, *J.*, 1942, 121). It is significant, however, that the chain propagation steps (A) and (B), in which the influence of the neighbouring double bonds should be small, may be shown to occur at almost precisely the same rates as the corresponding reactions in the oxidation of a methyl-substituted mono-olefin like 4-methylhept-3-ene (Bolland and ten Have, *loc. cit.*).

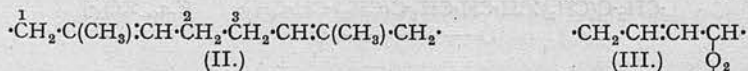
Owing to the unsymmetrical nature of the unsaturated centres in squalene, the three propagation steps (A)—(C) may each be formulated in two ways, which differ only in the side of the double bond involved in the reactions. The alternatives given above were chosen as the more probable on the following grounds.

(A) The relative efficiencies of the analogous reaction $\text{RO}_2\cdot + \text{RH} \longrightarrow \text{RO}_2\text{H} + \text{R}\cdot$ for a series of olefins (Bolland, *Trans. Faraday Soc.*, in the press) lead to the conclusion that in the unsaturated system $\cdot\overset{1}{\text{C}}\text{H}_2\text{C}(\text{CH}_3)\overset{2}{\text{C}}\text{H}\cdot\overset{3}{\text{C}}\text{H}_2\cdot$ hydrogen abstraction from the α -methylene group (2) occurs some three times more readily than from α -methylene group (1).

(B) The attachment of the oxygen molecule in this reaction to the resonating hydrocarbon radical so that the double bond retains its original position is preferred on infra-red spectral evidence (obtained at Cambridge): oxidised squalene did not apparently contain the symmetrically disubstituted type of double bond which would necessarily result from oxygen addition at the tertiary carbon atom. It is, however, unlikely that differentiation between the two possibilities is clear-cut, since ample evidence of the insensitivity of this type of addition reaction to the structure of the hydrocarbon radical has been obtained (*idem, ibid.*).

(C) The accepted mechanisms of abnormal (peroxide initiated) addition to ethylenic bonds (Mayo and Walling, *Chem. Reviews*, 1940, **27**, 351) and formation of head-to-tail polymers (*e.g.*, Flory, *J. Polymer Sci.*, 1947, **2**, 36) require that radical addition should be more facile at the less highly substituted carbon atom in the double bond.

It is to be emphasised that the structure (I) represents only the most frequently occurring diperoxide structure: the alternative ways in which reactions (A) and (B) can proceed are sufficiently efficient to assure the presence of an appreciable proportion of other species in the oxidation product. Provided, however, that formation of six-membered peroxide rings by step (C) can proceed at either side of a trisubstituted double bond more efficiently than the competing intermolecular reactions involving a double bond or α -methylene group of another squalene molecule, the reaction product will be a diperoxide of the same type as (I). This situation arises with special force in the case of the central $\Delta^{1:5}$ -system in the squalene molecule



(II). In reactions (A) and (B) the attachment of a peroxide radical group at carbon atom 2 or 3 will be favoured. Addition of this radical at the mono-substituted end of either of the neighbouring double bonds is unlikely, on the grounds that ring-closure of the radical (III) in the oxidation of mono-olefins (to give four- or five-membered rings) is not observed. The condition of diperoxide formation is thus again that addition of the peroxide radical at even the less favoured side of the neighbouring double bond should be more efficient than reaction with other olefin molecules.

EXPERIMENTAL.

Crude squalene obtained from basking shark liver oil was freed from saponifiable material and purified by repeated molecular distillation. Before use samples, in the form of a 2% solution in light petroleum (b. p. 40–60°), were passed through a 12-cm. alumina column.

Thermal oxidation of squalene was carried out in a constant-pressure apparatus of the type already described (Bolland, *Proc. Roy. Soc.*, 1946, *A*, **186**, 218; Bolland and ten Have, *Trans. Faraday Soc.*, 1947, **43**, 201). The temperature employed was 55° and the oxygen pressure *ca.* 760 mm. Hg.

Separation of Oxidised Product.—The oxidised material was quantitatively removed from known weights of oxidised squalene by passing the latter in the form of a 2% solution in light petroleum (b. p. 40–60°) through a 12-cm. alumina column. From the weight of squalene recovered from the solution, the oxygen content of the oxidised portion was calculated: elementary analyses on the recovered squalene demonstrated the absence of oxygenated groups (*e.g.*, C, 87.6%; H, 12.3. Calc. for $C_{30}H_{50}$: C, 87.75; H, 12.25%). The oxidised product was eluted from the column with 150 ml. of acetone. Recovery yields averaged 90%. Evaporation of the acetone solution in a vacuum at room temperature left a slightly yellow liquid of viscosity similar to that of the original squalene. Analyses on different samples gave: (a) C, 76.7₅; H, 10.8; O (by diff.), 12.4₅; (b) C, 76.5₅; H, 10.6₅; O, 12.8; (c) C, 76.0; H, 10.6₅; O, 13.3₅; (d) C, 75.5; H, 10.6; O, 13.9%. The molecular weight, determined cryoscopically in benzene, was (a) 454, (b) 533 ($C_{30}H_{50}O_4$ requires C, 75.9; H, 10.62; O, 13.48%; *M*, 474). The peroxidic oxygen contents of three separated oxidised products measured colorimetrically were 5.75, 6.5, and 5.1%, showing that no marked decomposition had taken place during the chromatographic treatment.

Peroxide Determination.—Two distinct methods were used: (a) Dastur and Lea's iodometric procedure (*Analyst*, 1941, **66**, 90) and (b) the oxidation of ferrous to ferric thiocyanate, measured colorimetrically. In the latter case the effect of varying the concentration of the various constituents of the reagent was studied systematically. It was found that the total acid concentration could be varied between 0.1N and 1.1N with no appreciable change in estimated peroxide content, but below certain critical concentrations the apparent peroxide content decreased with decreasing ferrous salt concentration, but increased with decreasing thiocyanate concentration. Increase in concentration of these three reagent constituents above these critical values had no appreciable effect on the colour developed. The reagent finally adopted varied slightly from that of Bolland *et al.* (*Trans. India Rubber Inst.*, 1941, **17**, 29) and consisted of 0.5 g. of ammonium thiocyanate in 100 ml. of 94% methanol/water, 0.5 ml. of 36N-sulphuric acid, and 0.04 g. of ferrous ammonium sulphate (dissolved in *ca.* 0.3 ml. water to ensure complete solubility when mixed with the methanol-rich reagent). The methanol was redistilled over ferric alum before use to remove oxidisable impurities. The reagent was used immediately after being made up.

Active-hydrogen Determinations.—These were carried out by the modified Zerewitinoff method described by Bolland (*ibid.*, 1941, **16**, 267).

Hydrogenations.—These were carried out in the conventional constant-pressure type of apparatus of 200-ml. capacity. Weighed samples were dissolved in 15–20 ml. of redistilled ethanol, and *ca.* 3 g. of Raney nickel added. Hydrogenation was usually complete in 7–10 hours. The catalyst was separated off by filtration through a wad of "Hyflo Super-cel" which was then washed with either petrol or ethanol, depending on whether unoxidised squalene was present in the hydrogenated sample or not. The filtrate, which was shown to be entirely free from hydroperoxide, was made up to known volume. Aliquots were pipetted into the active-hydrogen apparatus, and the solvent evaporated off in a vacuum at room temperature. The remainder was evaporated down and weighed. Losses during the above procedure were thus shown to be less than 2%. The reduced material was dissolved in 46% or 90% methanol-benzene mixture, depending on whether the starting material contained considerable amounts of squalene or not, before treatment with lead tetra-acetate.

Reaction with Lead Tetra-acetate.—This process was carried out according to Criegee's method (*Ber.*, 1931, **64**, 260). Aliquots of the reduced product were left for various periods in contact with 0.1N-lead tetra-acetate in anhydrous acetic acid. Maximum reaction was reached after about 6 hours. Compared with the reduced oxidation product, reduced squalene showed only slight reactivity toward lead tetra-acetate.

The following results were obtained with hydrogenated samples of separated and unseparated oxidation products. In each case the total number of hydroxyl groups and the number contained in 1 : 2-diol groupings per oxidised squalene molecule are calculated.

Total oxygen (%).	Active H (%).	No. of OH groups per oxidised mol. :	
		Total.	As 1 : 2-diol.
(a) Unseparated oxidised squalene.			
2.93	0.113	2.66	1.5
2.98	0.113	2.62	1.5 ₅
(b) Separated oxidation product.			
—	0.491	2.31	1.5
—	0.428, 0.433	2.03	1.5 ₅
—	0.407, 0.412	1.93	—
—	—	—	1.6

These active-hydrogen values (b) should be regarded as minimum values: condensation between hydroxyl groups during the necessary drying treatment of the sample before active-hydrogen determination must inevitably be favoured by the relatively high hydroxyl content of the reduced separated oxidation product.

The total oxygen content of two samples of separated oxidation product after reduction averaged 10.4% [C, 76.0; H, 13.6; O (by diff.), 10.4; and C, 76.3, 76.4; H, 13.1, 13.1; O (by diff.), 10.5%].

The hydrogenation product of (I) would be $C_{30}H_{62}O_3$ (oxygen content, 10.2%) and would contain three hydroxyl groups (Found, *ca.* 2.6) and one 1 : 2-diol group (Found, 0.78).

This paper forms part of the programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association. The authors are indebted to Dr. G. Gee for advice and criticism during the progress of the work, to Dr. G. B. M. Sutherland for the infra-red examination of oxidised squalene samples, and to Dr. W. T. Chambers for carrying out the elementary analyses.

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[Received, June 5th, 1948.]

SECTION 10

The Influence of Chemical Structure

on the α -methylene Reactivity

of Olefins

KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS

VII.—INFLUENCE OF CHEMICAL STRUCTURE ON THE α -METHYLENIC REACTIVITY OF OLEFINS

[The following text is extremely faint and largely illegible due to the quality of the scan. It appears to be the beginning of the main body of the paper, containing introductory text and possibly the start of a reaction scheme or list of compounds.]

* *Journal of Polymer Science*, Vol. 5, 1950, p. 105.
† *Journal of Polymer Science*, Vol. 5, 1950, p. 107.
‡ *Journal of Polymer Science*, Vol. 5, 1950, p. 109.
§ *Journal of Polymer Science*, Vol. 5, 1950, p. 111.
|| *Journal of Polymer Science*, Vol. 5, 1950, p. 113.

KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS

VII.—INFLUENCE OF CHEMICAL STRUCTURE ON THE α -METHYLENIC REACTIVITY OF OLEFINS

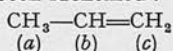
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The efficiency of the radical reaction



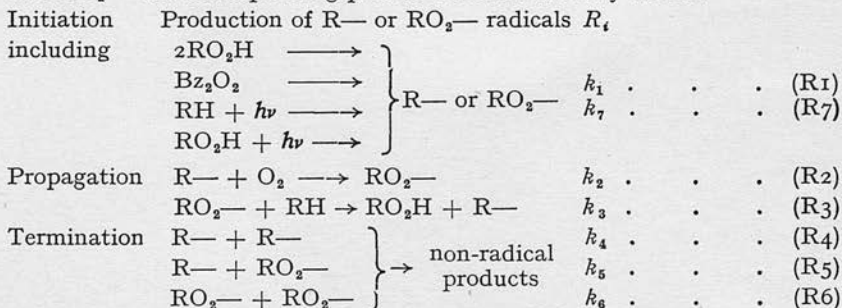
(representing the exchange of a hydrogen atom between an α -group of an olefin RH and a peroxide radical $\text{RO}_2\text{—}$) has been determined for the members of a series of twenty-four unsaturated hydrocarbons. The influence of certain structural features of olefinic groupings in determining the ease of α -methylene hydrocarbon abstraction (and hence on the dissociation energy of α - β carbon-hydrogen bonds) have been identified: thus in the olefinic system



the α -methylene reactivity of the group (a) (as measured by the above exchange reaction) is unaffected by alkyl substitution at (b), but is increased by alkyl substitution at (a) and (c) (at 45° C by a factor of $3 \cdot 3^n$, where n is the total number of substituents introduced).

Olefins are attacked by oxygen at rates which are markedly dependent on the detailed chemical structure of the unsaturated grouping. In general such reaction rate differences could result from variations in the actual mechanism by which various olefins oxidize or could on the other hand reflect the influences of olefinic structure on one or more of the elementary reactions in a mechanism common to all olefins.

The former factor may be ruled out for the interaction of oxygen with a wide range of non-conjugated unsaturated hydrocarbons, as evidenced by the common mechanism carefully established for representative 1:4-dienic,^{1, 2, 3} mono-olefinic (cf. ref. 4 and the Appendix to this paper) and hydroaromatic⁵ molecules. The chain mechanism which holds⁶ alike for oxidations initiated photochemically, by dissociable molecules (e.g. benzoyl peroxide) or by the α -hydroperoxidic oxidation product is reproduced here for convenience. If R— represents the radical obtained by abstraction of an α -methylene hydrogen atom from an olefin (RH) and $\text{RO}_2\text{—}$ the corresponding peroxide radical we may write:



¹ Bolland, *Proc. Roy. Soc. A*, 1946, **186**, 218.

² Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42**, 230.

³ Bolland, *ibid.*, 1948, **44**, 669.

⁴ Bateman and Gee, *Proc. Roy. Soc. A*, 1948, **195**, 376.

⁵ Bolland (in press).

⁶ Bateman and Bolland, *Proc. XIth Int. Cong. Pure Appl. Chem.*, 1947.

R_i represents the rate of the initiation step and k_1-k_7 the velocity constants of the elementary steps (R1)-(R7)

A systematic attempt to determine the effect of variations in RH on these various elementary reactions is made in this and two subsequent papers. Here the influence of structural factors on the propagation step (R3) is traced: in the second we deal with the other propagation process



the third paper considers the type of chain initiation most likely to be intimately dependent on olefinic structure, namely hydroperoxide decomposition (R1).

Non-conjugated olefins undergo a variety of reactions in which the replacement of a hydrogen atom situated in an α -methylene group occurs. One of the major factors controlling the rates with which individual olefins partake in this type of reaction will undoubtedly be the strength with which the replaceable α - β hydrogen atoms are attached to the α -carbon atoms. The reaction



affords an excellent opportunity of separating and studying this factor since here the α - β hydrogen atom is attacked by a radical the essential character and reactivity of which may safely be assumed insensitive to the identity of R. Variations in k_3 and the energy of activation of the reaction E_3 may thus be used to give quantitative information regarding α -methylene reactivity in general and its relation to the architecture of olefins.

Determination of the relative efficiency of (R3) for different olefins rests on the following argument. Of the various possible oxidation conditions those best calculated to show up changes in k_3 require the presence of benzoyl peroxide as chain initiator and the use of high oxygen pressures: the former condition gives the best authenticated method of providing a rate of chain initiation which is independent of the nature of the olefin, while at high oxygen pressures the rate of oxidation consistent with the above mechanism assumes the simple form,³

$$\text{Rate} = k_7^{\frac{1}{2}} [Bz_2O_2]^{\frac{1}{2}} [RH] \left(1 + \frac{1}{\nu} \right) \cdot k_3 k_6^{-\frac{1}{2}} \quad (1)$$

The inclusion of ν , the chain length of oxidation, is of significance only in the case of the least oxidizable olefins. $k_3 k_6^{-\frac{1}{2}}$ may thus be determined if the rate of chain initiation is assumed (a) equal to the rate of decomposition of benzoyl peroxide and (b) independent of the nature of the olefin. Bartlett and Nozaki's⁷ extensive kinetic measurements on the thermal decomposition of benzoyl peroxide indicate that these assumptions are unlikely to introduce any large uncertainty; these authors show that the unimolecular dissociation of peroxide molecules (into radicals) accounts for a large proportion of the observed peroxide decomposition. For example, even at the highest concentration of benzoyl peroxide here used in cyclohexene (Fig. 1) the rate of unimolecular dissociation accounts for some 60% of the total peroxide decomposition observed at 80°C.

By application of the rotating-sector technique to the photo-oxidation of olefins, Bateman and Gee⁸ have recently obtained absolute values for the efficiency k_6 and the activation energy E_6 of the chain terminating step (R6). The values of k_6 so obtained for four dissimilar olefins are sufficiently concordant to justify the assumption that k_6 is in fact independent of the nature of the olefin. On this basis the composite term $k_3 k_6^{-\frac{1}{2}}$ can be separated into individual k_3 and k_6 values. From measurements of the temperature dependence of k_6 Bateman and Gee suggest

⁷ *J. Amer. Chem. Soc.*, 1946, **68**, 1686.

⁸ *Proc. Roy. Soc. A*, 1948, **195**, 391.

maximum and minimum figures for E_6 of 5 and 0 kcal. We have here arbitrarily taken E_6 as zero and have allotted k_6 Bateman and Gee's mean value of 6×10^5 mole⁻¹ l. sec.⁻¹ to all olefins considered in this paper.* Hence, taking k_7 at 45° C as 5×10^{-7} sec.⁻¹, k_3 at this temperature is given by

$$k_3 = 1.10 \times 10^6 \cdot \frac{\text{Rate}}{[\text{Bz}_2\text{O}_2]^{\frac{1}{2}} \cdot [\text{RH}]} \quad (1a)$$

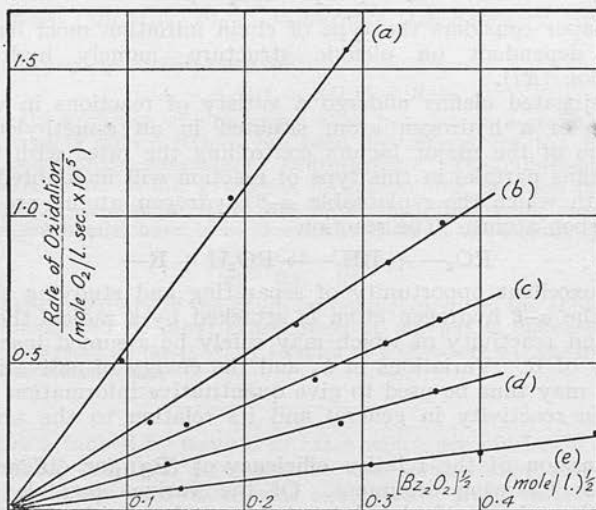


FIG. 1.—Variation of initial rate of oxidation with benzoyl peroxide at 45° C and 760 mm. oxygen pressure: (a) 1 : 3 : 5-trimethyl-cyclohexene; (b) 1-methyl-cyclohexene; (c) cyclohexene; (d) 4-methyl-heptene-3; and (e) allyl benzene.

Experimental

Rate Measurements.—Apart from substitution of a quill tubing glass spiral for the flexible connection between reaction vessel and gas burette system, the general method of oxidation rate measurement was that already outlined.¹ When dealing with relatively volatile olefins, the stem of the reaction vessel formed the inside wall of a condenser through which tap water (temperature *ca.* 10° C) was circulated. Where necessary the preliminary pumping out of the reaction vessel and gas burette system was carried out with the former maintained (by immersion in a CO₂-acetone bath) at a temperature sufficiently low to reduce the vapour pressure of the olefin to 10⁻⁴ mm. Measurements were carried out at oxygen pressures of approximately 760 mm. Hg.

Materials.—The methyl oleate, and ethyl linoleate samples were those used previously.^{1, 3} The 2 : 4 : 4-trimethyl-pentene-1 was kindly provided by Dr. A. G. Evans of Manchester University. Fourteen of the other olefins used were drawn from pure samples prepared for other purposes in these laboratories: cyclohexene and 1-methyl cyclohexene (Dr. L. Bateman), 2-methyl-pentene-2 (Dr. J. I. Cuneen), diallyl (Mr. A. W. Kenchington), allyl benzene (Dr. H. P. Koch), crotyl benzene and γ -methyl crotyl benzene (Mr. J. A. Lyons), heptene-1, heptene-3 and 4-methyl-heptene-3 (Dr. C. G. Moore), 1 : 3 : 5-trimethyl-cyclohexene, and 2-methyl hepten-3-yl benzoate (Mr. A. L. Morris), 1 : 2-dimethyl cyclohexene-1 and ethyl linolenate (Dr. D. A. Sutton). Octene-1, hexadecene-1 and decane were commercial samples which were carefully fractionated on a

* We may note that the photo-oxidation chain lengths required in Bateman and Gee's deductions are derived from estimates of the chain length of the benzoyl peroxide initiated oxidation. It is readily shown that the individual rate constants deduced in this way are in fact αk_3 and αk_6 , where α is the number of chains started by the decomposition of each benzoyl peroxide molecule.

15-plate column, small middle fractions being taken. 2:3:3-Trimethylbutene-1 was synthesized via pinacolone and 2:3:3-trimethyl butanol-2. The hexene-2 sample was obtained by careful fractionation of the dehydration product of hexanol-2.

The purity of the various olefins was examined by infra-red and ultra-violet spectrographic analyses (kindly carried out by Dr. H. P. Koch). Impurities were detected in only two cases: the hexene-2 and 4-methyl-heptene-3 samples contained not more than 10% of their much less reactive isomers, hexene-1 and 2-propyl-pentene-1 respectively.

Results

The dependence of oxidation rate on the concentration of added benzoyl peroxide was found to conform for each olefin to a linear initial rate against

TABLE I

Olefin	[RH] Mole/l.	Rate/[Bz ₂ O ₂] ^½					E _g
		(Mole/l.) ^½ sec. ⁻¹ × 10 ⁵					
		35°	45°	55°	65°	75°	
1 2:3:3-Trimethyl butene-1	7.20	—	0.030	—	—	—	—
2 Heptene-1 . . .	7.12	—	0.085	0.275	—	—	(24.6)
3 Octene-1 . . .	6.40	—	0.079	0.333	1.40	—	26.8
4 Hexadecene-1 . . .	3.50	0.011 ₅	0.045	0.175	0.60 ₂	—	27.6
5 Diallyl . . .	8.42	—	0.20 ₁ (a)	—	—	—	(27.9)
6 2:4:4-Trimethyl- pentene-1 . . .	6.40	—	0.078	0.305	1.08	—	28.0
7 Hexene-2 . . .	8.00	—	0.49	—	—	—	—
8 Methyl oleate . . .	2.96	—	0.32	0.95	2.83	8.0	23.5
9 Heptene-3 . . .	7.20	—	0.60	—	—	—	—
10 3-Methyl-pentene-2	8.33	—	0.75	—	—	—	—
11 Tetramethyl ethylene . . .	8.40	—	3.20	—	—	—	—
12 2-Methyl-pentene-2	8.25	—	1.70	—	—	—	—
13 2-Me-heptenyl- benzoate . . .	3.90	—	0.80	0.242	7.36	—	23.3
14 4-Methyl heptene-3	6.55	—	1.12	3.18	9.7	—	23.6
15 Allyl benzene . . .	7.65	—	0.51	1.60	4.83	14.1	24.5
16 Crotyl benzene . . .	6.67	0.74	2.33	6.83	—	—	22.3
17 γ-Methyl crotyl benzene . . .	6.12	2.57	7.21	21.0	—	—	21.5
18 Ethyl linolenate . . .	2.89	1.55	4.23	12.0	28.3	—	20.5
19 Ethyl linolenate . . .	2.91	—	8.2	—	—	—	—
20 Cyclohexene . . .	9.86	0.51	1.80	5.55	—	—	24.0
21 1-Methyl-cyclo- hexene . . .	8.45	0.78	2.62	8.16	—	—	23.5
22 1:2-Dimethyl cyclohexene . . .	7.47	1.41	4.58	13.7	—	—	23.0
23 1:3:5-Trimethyl cyclohexene . . .	6.48	(b)	5.5	16.2	—	—	22.4
24 Tetralin . . .	7.35	0.282	1.02	3.33	10.6	—	24.8
25 n-Decane . . .	5.14	—	0.006	—	—	—	—

(a) Extrapolated value from 0.0167 at 28° C and 0.074 at 38° C.

(b) 0.49 at 25° C.

[Bz₂O₂]^½ relation. Fig. 1 and data quoted elsewhere illustrate the accuracy with which the relation is obeyed. Values of the slope of the linear rate against [Bz₂O₂]^½ curves obtained for 24 olefins are collected in Table I. In most cases the slope was determined at at least three temperatures to give an accurate

estimate of the overall energy of activation E_a . The oxygen pressure to which these data refer may be taken as infinite: the necessary small corrections have been applied to the slopes obtained at about atmospheric pressure.

Evaluation of k_3 for Individual α -Groups.—The presence of more than one α -methylene site of reaction in many of the olefins examined implies that the observed k_3 [RH] is a composite factor which may be resolved into a number of such terms each expressing the efficiency with which a particular α -group

TABLE II

No	Type	Substitution*	Olefin	Reactive Grouping	$k_3 \times 10 \text{ mole}^{-1} \text{ l. sec.}^{-1}$				
					Calculated			Obs.	
					(a)	(b)	(c)	Total	Total
A. Acyclic Olefins									
1	I	None	2 : 3 : 3-Tri-Me-butene-1	$\text{CH}_2 : \text{C} - \text{CH}_3$ (a)	0.42	—	—	0.42	0.46
2	II	1 Alkyl	Heptene-1	$\text{CH}_2 : \text{CH} : \text{CH}_2$ Alk. (a)	1.40	—	—	1.40	1.26
3	"	"	Octene-1	"	1.40	—	—	1.40	1.35
4	"	"	Hexadecene-1	"	1.40	—	—	1.40	1.41
5	"	"	Diallyl	"	1.40	—	—	2.80	2.63
6	"	"	2 : 4 : 4-Tri-Me-pentene-1	$\text{CH}_2 : \text{C}(\text{CH}_3) : \text{CH}_2$ Alk. (b) (a)	1.40	0.42	—	1.82	1.34
7	III	2 Alkyl	Hexene-2	$\text{CH}_3 : \text{CH} : \text{CH} : \text{CH}_2$ Alk. (b) (a)	4.6	1.4	—	6.0	6.7
8	"	"	Methyl oleate	Alk. $\text{CH}_2\text{CH} : \text{CH} : \text{CH}_2$ Alk. (a) (a)	4.6	—	—	9.2	11.9
9	"	"	Heptene-3	"	4.6	—	—	9.2	9.2
10	"	"	3-Methyl-pentene-2	$\text{CH}_3 : \text{CH} : \text{C}(\text{CH}_3)\text{CH}_2$ Alk. (a) (b) (a)	4.6	1.4	—	10.6	9.8
11	"	"	Tetramethyl-ethylene	$(\text{CH}_3)_2\text{C} : \text{C}(\text{CH}_3)_2$	4.6	—	—	18.4	42
12	IV	3 Alkyl	2-Me-pentene-2	$(\text{CH}_3)_2\text{C} : \text{CH} : \text{CH}_3$ Alk. (b) (a)	15.2	1.4	—	18.0	22.6
13	"	"	2-Me-heptenyl benzoate	"	15.2	1.4	—	18.0	22.5
14	"	"	4-Me-heptene-3	Alk. $\text{CH}_2\text{C}(\text{CH}_3) : \text{CHCH}_2$ Alk. (b) (c) (a)	15.2	4.6	1.4	21.2	18.7
—	V	4 Alkyl	—	—	—	—	—	—	—
15	VI	1 Phenyl	Allyl benzene	Ph. $\text{CH}_2\text{CH} : \text{CH}_2$ (a)	10.0	—	—	10.0	7.3
16	"	"	Crotyl benzene	Ph. $\text{CH}_2 : \text{CH} : \text{CH} : \text{CH}_3$ (a) (b)	33	1.4	—	34.4	38.3
17	"	"	γ -Me-Crotyl benzene	Ph. $\text{CH}_2 : \text{CH} : \text{C} : (\text{CH}_3)_2$ (a) (b)	109	1.4	—	112	129
18	VII	1 Vinyl	Ethyl linolenate	Alk. $\text{CH}_2\text{CH} : \text{CH} : \text{CH}_2 : \text{CH} : \text{CH} : \text{CH}_2$ Alk. (b) (a) (b)	150	4.6	—	159	160
19	"	"	Ethyl linolenate	" " " " " "	150	4.6	—	309	310
B. Cyclic Olefins									
20	III	2 Alkyl	Cyclohexene	Alk. $\text{CH}_2\text{CH} : \text{CH} : \text{CH}_2$ Alk. (a) (a)	7.8	—	—	15.6	19.9
21	IV	3 Alkyl	1-Me-Cyclohexene	Alk. $\text{CH}_2 : \text{C}(\text{CH}_3) : \text{CH} : \text{CH}_2$ Alk. (b) (c) (a)	25.7	7.8	2.4	35.9	34.0
22	"	"	1 : 2-Di-Me-Cyclohexene	Alk. $\text{CH}_2\text{C}(\text{CH}_3) : \text{C}(\text{CH}_3)\text{CH}_2$ Alk. (a) (b)	25.7	7.8	—	67.0	67.2
23	V	4 Alkyl	1 : 3 : 5-Tri-Me-Cyclohexene	Alk. $\text{CH}(\text{CH}_3)\text{CH} : \text{C}(\text{CH}_3)\text{CH}_2$ Alk. (a) (c) (b)	84.8	7.8	2.4	95	93.1
24	"	—	Tetralin	Ph. CH_2 Alk.	—	—	—	—	15.2

* I.e., total substitution with reference to the most reactive α -group in the olefin (i.e. (a)) at the α -group itself and at the "far" end of the olefinic double bond.

reacts with RO_2 -radicals. The olefins listed in Table I contain a wide variety of α -groupings each of which is distinguishable from the remainder by some feature of the unsaturated environment in which it occurs. All (apart from tetralin) can however be derived from the simplest possible type of α -group that encountered in propylene $CH_3 \cdot CH=CH_2$ (I) by substitution of methyl, (a) (b) (c) alkyl, Alk. $CH=CH_2$ - or phenyl groups at the three carbon atoms (Alk. = alkyl group). Such substitution may be expected to influence the reactivity (as measured by k_3) of the α -group (a) to a degree which is dependent on the identity of the substituting group and also on the particular carbon atom (a), (b), or (c) to which it is attached. Among the olefins examined the gradations from (I) in type and degree of substitution are sufficiently small and regular to allow quantitative evaluation of the specific influence of alkyl substitution at each of the three carbon atoms, and of substitution of Alk. $CH=CH$ - and phenyl groups at the α -group (a). The conclusions may be summarized in the form of four rules, which refer to a temperature of 45° C.

- (i) Effect of replacing one or two hydrogen atoms at (a) and/or (c) by methyl or other alkyl groups increases k_3 of α -group by $3 \cdot 3^n$, where n is the total number of alkyl groups introduced at (a) and/or (c). Replacement of the hydrogen atom at (b) has no effect.
- (ii) Replacement of a hydrogen atom at (a) by a phenyl group increases k_3 23 times.
- (iii) Replacement of a hydrogen atom at (a) by an Alk. $CH=CH$ - group increases k_3 107-fold.
- (iv) The k_3 value appropriate to an α -group contained in a cyclic structure is 1.7 times greater than that contained in the analogous acyclic olefinic group.

The applicability of these rules is tested in Table II, by using them to calculate the overall k_3 values for the complete range of olefins and making comparison with the figures actually found experimentally at 45° C. Taking k_3 for the standard propylene type of grouping as 0.042 the calculated k_3 values for individual α -groups (up to three in some cases) are inserted in columns 6-8, Table II. On the whole satisfactory agreement between calculated and observed overall k_3 data is obtained (though the deviation with tetra-methyl ethylene is to be noted). Closer agreement could of course be obtained⁹ by introducing additional rules in which minor differences in the types of alkyl substitution are taken into account (e.g. as between methyl and other alkyl groups, between substitution at carbon atoms (a) and (c) and between substitution of the first and second hydrogen atoms at either of these two sites). An insufficient number of olefins has as yet been examined to identify such second-order effects with certainty.

We may note that the experimental justification for the conclusion that methyl substitution at the double bond has no influence on the reactivity of the "nearer" α -group rests on comparison of the k_3 values for 2:4:4-trimethyl-pentene-1 and 3-methyl-pentene-2 with those for the Δ^1 -olefins (No. 2-5) and hexene-2 respectively.

Discussion

It seems in the first place advisable to make it clear that the observed differences in the efficiency of (R3) arise primarily from variations in the energy of activation and not, for example, from random variations in the frequency factor, of a type not intimately connected with the structure of the unsaturated grouping. This point is made by the correlation between E_3 and $\log_{10} k_3$ shown in Fig. 2. E_3 is derived simply from the overall energy of activation of the oxidation E_0 , since

$$E_0 = E_3 + \frac{1}{2}E_4 - \frac{1}{2}E_6$$

(cf. eqn. (1)) and E_4 and E_6 may be taken as 31 kcal./mole¹⁰ and zero respectively. Departures from a linear relationship between E_3 and

⁹ Bolland, *Quart. Rev.*, 1949, 3, 1.

¹⁰ This figure represents the mean of several determinations. McClure, Robertson and Cuthbertson, *Can. J. Res. B*, 1942, 20, 103; Kamenskaya and Medvedev, *Acta Physicochim.*, 1940, 13, 565; Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, 68, 1690.

$\log k_3$ do not exceed the estimated experimental error involved in the experimental determination of E_a .

The frequency factor does, however, show systematic variation as the energy of activation alters. From the Arrhenius equation, $k_3 = PZ e^{-E_3/RT}$ the slope of the $\log_{10} k_3$ against E_3 would be $(2.3 RT)^{-1}$ (equal to 6.83×10^{-4} at 45°C) if PZ remained constant throughout the series. The observed slope of 3.3×10^{-4} is only about half this value, indicating that PZ changes smoothly from 3×10^4 for the most reactive olefin (ethyl linoleate) to *ca.* 10^7 for the least reactive. A similar effect has been noted for several types of ionic reaction¹¹ and also for one other reaction involving radicals.¹² An explanation composed in general terms and so presumably applicable here also has been given by Fairclough and Hinshelwood¹¹ in which the importance of the time interval required for the necessary redistribution of energy accompanying chemical reaction is stressed. It should also be noted that the entire range of PZ found for (R_3) lies well below the value (*ca.* 10^{11}) calculated from simple collisional kinetic theory and

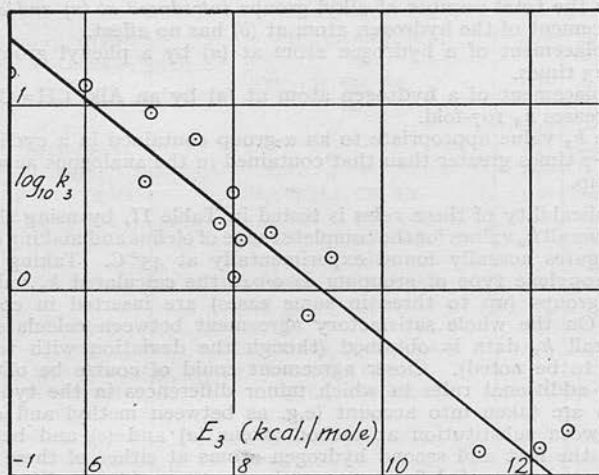
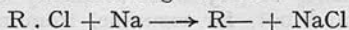


FIG. 2.—Relation between the velocity coefficients k_3 and the energies of activation E_3 of the reaction $\text{RO}_2 + \text{RH} \rightarrow \text{RO}_2\text{H} + \text{R}$ — based on data for fifteen olefins.

found to hold for numerous bimolecular reactions involving molecules and ions.¹³

α -Methylene Carbon-Hydrogen Dissociation Energies.—Within a series of similar reactions, the members of which are all exothermic, a close relationship is to be expected between the heat of reaction and the energy of activation. The exchange reaction



(where variations in the hydrocarbon residue R in the alkyl chloride may be introduced) has been studied from this point of view. Evans and Polanyi¹⁴ suggested on theoretical grounds that a simple linear relation

$$\Delta E = \alpha \Delta H \quad (3)$$

(where α is a constant having a value between zero and one) might exist between variations in energy of activation ΔE and corresponding variations in reaction heat ΔH . Using the dissociation energy of the alkyl iodides as a measure of ΔH , Butler and Polanyi¹⁵ have provided an

¹¹ Fairclough and Hinshelwood, *J. Chem. Soc.*, 1937, 538.

¹² Gregg and Mayo, *Faraday Soc. Discussion*, 1947, 2, 329.


¹³ Moelwyn-Hughes, *The Kinetics of Reactions in Solution*, 2nd Edn., Chap. 3.

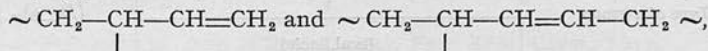
¹⁴ *Trans. Faraday Soc.*, 1938, 34, 11.

¹⁵ *Ibid.*, 1943, 39, 19.

experimental basis for (3), finding a value of α of 0.27 for this particular reaction. Eqn. (3) was derived for reactions involving very small resonance energies in the transition state and it is to be expected that the reactions studied by Butler and Polanyi fulfil this requirement. Indications that the relation may also apply to exchange reactions involving appreciable transition state resonance have been obtained by Steiner and Watson¹⁶ in their treatment of the substitutive reaction of chlorine with hydrocarbons.

A similar approach is possible with the general reaction, (R₃). Here also the individual reactions are exothermic and variations in the heat of reaction can be directly related to differences in the dissociation energy of one bond—the α - β carbon-hydrogen bond severed in the course of reaction (R₃). In the absence of an experimental study of the strengths of these α - β bonds in various unsaturated environments, we must turn to estimates of the dissociation energies based on calculations of resonance energies of various R— type radicals. Self-consistent calculations¹⁷ for the radicals, which are derived from three main types of olefin examined here, —CH—CH=CH_2 , —CH=CH—CH—CH=CH— and

—CH₂— give resonance energies of 18.7, 40.4 and 16.2 * kcal./mole respectively. These calculations are insufficiently refined to distinguish between, e.g., the radicals



though judging from the relative rates of oxidation of say the Δ^1 olefins and methyl oleate these two radicals have significantly different resonance energies. We have chosen to take the calculated resonance energies as corresponding to the latter radical. The differences in activation energy of reaction (R₃) involving olefins from which these three radicals can be derived are best estimated from the linear $\log k_3 - E_3$ relation in Fig. 2, taking for each type of olefin a k_3 value suggested by the rules given above. On this basis ΔE_3 as between linoleyl and allyl systems is 4.9 kcal./mole and that between linoleyl and benzyl systems 5.0 kcal./mole. The respective α values are thus 0.42 and 0.35 (mean 0.39).

Eqn. (3) may be used to estimate in approximate fashion the relatively small differences in heat of reaction for olefins which differ from these three basic types in methyl substitution only. Again ΔE is estimated from the linear $\log k_3 - E_3$ relation in Fig. 2. Values of ΔH calculated from (3) taking $\alpha = 0.39$ throughout and given in Table III, measure directly differences in the resonance energies E_{res} of the various radicals and in the dissociation energies (D_{C-H}) $_{\alpha-\beta}$ of the various types of carbon-hydrogen bond. (The latter are taken simply as (D_{C-H}) $_{\alpha-\beta} = (D_{C-H})_{\text{methane}} - E_{res}$).

The generalization has been made above that k_3 for an α -group is increased 3.3-fold for each methyl substituent introduced into either of two alternative positions [(a) and (c) in (I)]. Where the α -group becomes alkyl substituted, the frequency factor contained in k_3 must be reduced in sympathy with the reduction in replaceable β -hydrogen atoms. It is doubtful whether the frequency factor for any α -group will in fact be proportional to the number of β -hydrogen atoms contained therein. If

¹⁶ Steiner and Watson, *Faraday Soc. Discussion*, 1947, 2, 88.

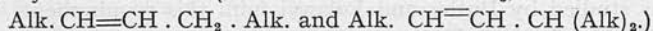
¹⁷ Orr, quoted by Bolland and Gee, *Trans. Faraday Soc.*, 1946, 42, 246.

* A recent estimate¹⁸ of the resonance energy of the benzyl radical based on a study of the pyrolysis of toluene¹⁹ suggests the rather higher value of 24.5 kcal./mole. The calculated resonance energies are employed here as giving the best comparative data for all three types of unsaturated systems in which we are interested.

¹⁸ Swarc, *Faraday Soc. Discussion*, 1947, 2, 39.

¹⁹ Swarc, *J. Chem. Physics*, 1948, 16, 138.

however this (maximum) correction is applied, the relative ease of removal (by RO_2 —radicals) of a hydrogen atom from primary, secondary and tertiary carbon atoms (as in Alk. $\text{CH}=\text{CH} \cdot \text{CH}_3$,



is in the ratio 1/4.8/32.7 (at 35° C). This suggests that an α - β carbon-hydrogen bond involving a primary carbon atom is 5.5 and 12.2 kcal. greater than that of similar bonds involving secondary and tertiary carbon atoms respectively.

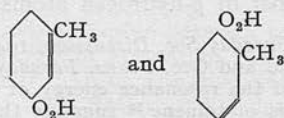
The conclusion reached that a methyl substituent on an ethylenic bond activates the "far" rather than the "near" α -methylene group does not receive unanimous support from published chemical evidence. On the one hand are the observations of Cook,²⁰ Blumann and Zietschel,²¹ and Hock and Lang²² who identified products resulting from attack by oxygen at the α -methylene group *farther* from the alkyl substituent in methyl cyclohexene, α -pinene and *p*-menthene respectively. On the other hand, Dupont,²³ and Blumann and Zietschel²⁴ have isolated products from the auto-oxidation of methyl cyclohexene and limonene respectively, explicable only in terms of reaction occurring at the "near"

TABLE III

Type of α -group	E_3	E_{res}	$(D_{O_2})_{\alpha,\beta}$
	(kcal./mole)		
I	12.2	10.3	88.2
II	10.6	14.5	84.0
III	9.0	18.7	79.8
IV	7.4	22.9	75.6
V	5.8	27.1	71.4

α -methylene group. Farmer and Sundralingam²⁵ recognized the formation of hydroperoxides at both the 6- and the 3- α -methylene groups in 1-methyl cyclohexene and expressed the opinion that the former (corresponding to attack at the nearer α -methylene group) predominated. In these various investigations, however, no serious attempt was made to account for all the reacted oxygen so that the products reported may well be those which are most readily recognized in a complex mixture of oxidation products and not necessarily those arising from the major cause of reaction.

Complexity of Oxidation Products.—The k_3 values deduced for the three types of α -group in 1-methyl cyclohexene (Table II) may be used to illustrate the complexity of the primary oxidation product which may on occasion be encountered: in all, six α -hydroperoxides are to be expected, three corresponding to addition of oxygen to the allylic radical (eqn. (R2)) at the three original α -groups and three to the other end of the allylic systems with accompanying double bond shift. Since oxygen addition appears to occur in these two senses with equal ease, the two major products are



²⁰ *J. Amer. Chem. Soc.*, 1938, **60**, 1774.

²¹ *Ber.*, 1913, **46**, 1178.

²² *Bull. Soc. Chim. Belg.*, 1936, **55**, 57.

²³ *Ber.*, 1914, **47**, 2623.

²⁴ *Ber.*, 1942, **75B**, 300.

²⁵ *J. Chem. Soc.*, 1942, 121.

each in only 32 % yield. 14% and 4 % yields of the two analogous isomers resulting from initial attack at the 6-position, and the methyl group respectively complete the primary oxidation product.

Despite certain qualifications regarding their absolute accuracy the α - β -carbon-hydrogen dissociation energies listed in Table III do represent an advance toward a quantitative understanding of α -methylene reactivity of olefins. The mechanisms by which olefins undergo other reactions resulting in substitution at α -groupings have not been determined in detail. Exceptions lie in the peroxidation reaction and the addition of certain maleic anhydride derivatives.²⁶ In so far as any general pattern can be distinguished, one step in the various schemes must involve removal of a hydrogen atom from the α -group concerned in the reaction ((R₃) in the peroxidation mechanism). Provided this step has a determining influence on the overall rate of any given α -methylene reaction, the structural effects outlined above will be of material importance.

The author wishes to express his gratitude to his colleagues who provided pure samples of olefins (as indicated in the test), to Dr. H. P. Koch for performing infra-red spectroscopic analyses, and to Dr. L. Bateman and Dr. G. Gee for valuable discussions during the course of the work. This work forms part of a programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

²⁶ Delalande, *Proc. XIth Int. Cong. Pure Appl. Chem.*, 1947.

APPENDIX

Benzoyl Peroxide Initiated Oxidation of Methyl Oleate.—The dependence of oxidation rate on the three concentration variables, [Bz₂O₂], [RH] and oxygen pressure was found to conform to the following pattern:

(a) **BENZOYL PEROXIDE CONCENTRATION.**—Fig. 2 of Part II of the present series² contained data which showed that below the concentration limit imposed by the solubility of benzoyl peroxide in methyl oleate at 65° C, the rate of oxidation is proportional to [Bz₂O₂]^{1/2}.

(b) **OLEFIN CONCENTRATION.**—Oxidation rate data obtained with ethyl stearate as diluent are reproduced in Table IV. Over a ten-fold range of olefin concentration the ratio Rate/[RH] varies by only 40 %.

TABLE IV

Mole Fraction		Rate $\times 10^6$	Rate/oleate $\times 10^6$	Rate - $f_{R'H}$ · Rate _{R'H} f_{RH}
Oleate	Stearate			
100	0	10.8	1.08	1.08
32.5	67.5	3.94	1.22	1.14
19.7	80.3	2.63	1.34	1.18
9.5	90.5	1.43	1.50	1.16
0	100	0.36	—	—

Rates are expressed in moles O₂ per l. per sec.

(c) **OXYGEN PRESSURE.**—The rate of oxidation of methyl oleate is insufficiently sensitive to variations in the oxygen pressure to permit an unequivocal decision as to the form the relation between these two quantities assumes. The data presented in Fig. 3 can however be regarded as being at least

consistent with the relation established with much greater precision in the case of ethyl linoleate, viz. :

$$\text{Rate} = \text{const.} \frac{p}{p + \lambda}$$

The kinetic evidence detailed above leads to the conclusion that the rate of oxidation of methyl oleate in presence of benzoyl peroxide may be represented by an equation equivalent in all respects to that obtained for ethyl linoleate.³ An oxidation chain mechanism analogous to (R2)-(R6) must be considered as established with this mono-olefin also.

The relatively minor deviation from proportionality between oxidation rate and [RH] ((b) above) may be satisfactorily accounted for: the rate of oxidation of pure ethyl stearate itself is too great to justify treating it as an inert solvent at low methyl oleate concentrations. On the assumption that the reaction of oxygen with ethyl stearate occurs through reaction steps analogous to (R2) and (R3) ethyl stearate may be involved in the oxidation chain occurring in oleate-stearate mixtures without introducing any striking kinetic complication. The rate of such a coupled oxidation may be expressed in the simple form of eqn. (4) if the assumption is made that analogous reactions

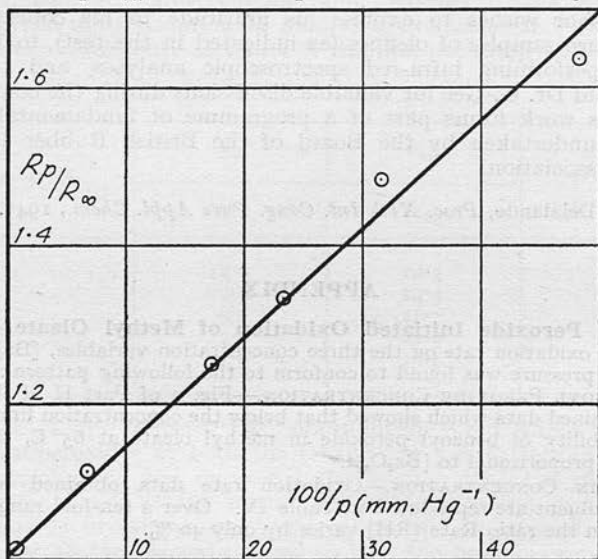


FIG. 3.—Variation of initial rate of oxidation of methyl oleate R_p with oxygen pressure p . Temperature 65° C. Concentration of benzoyl peroxide 0.02 mole/l. R_∞ represents the rate of oxidation at infinite oxygen pressure.

differing only in the peroxide radical involved (i.e. RO_2- and $R'O_2-$, if oleate and stearate are represented by RH and R'H) occur with equal efficiency.

$$\text{Rate} = \frac{R_i^{\frac{1}{2}}}{\sqrt{k_6}} \cdot (k_3[RH] + k_3'[R'H]) \quad (4)$$

R_i is the rate of chain initiation and k_3' the velocity coefficient of the reaction between R'H and $R'O_2-$ (or RO_2-).

From eqn. (4)

$$\begin{aligned} \frac{R_i^{\frac{1}{2}}}{\sqrt{k_6}} k_3 \cdot [RH] &= \text{Rate} - \frac{R_i^{\frac{1}{2}}}{\sqrt{k_6}} k_3' \cdot [R'H] \\ &= \text{Rate} - f_{R'H} \text{Rate}_{R'H} \end{aligned}$$

where $f_{R'H}$ is the mole fraction of stearate and $\text{Rate}_{R'H}$ the rate of oxidation of pure stearate under similar conditions of chain initiation.

The constancy of the figures contained in the fifth column of Table IV show that the variation in $\text{Rate}/[RH]$ (column 4) can be accounted for adequately in this way.

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SECTION 11

The Oxidation Chain-initiating Efficiency of

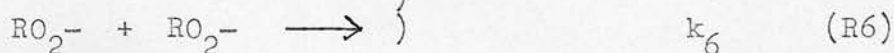
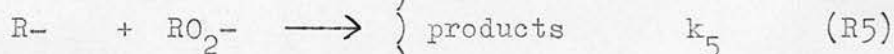
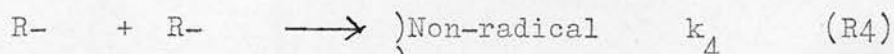
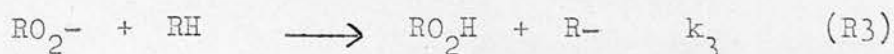
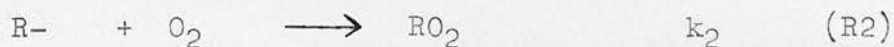
α -Methylenic Hydroperoxides.

The interaction of molecular oxygen with olefins is an autocatalytic - or more correctly auto-accelerating - reaction. Oxidation of a peroxide-free olefin commences at a small but definite rate which increases regularly during the progress of the reaction. The rate of oxidation at any point in the initial stages may in fact be resolved into two parts, one attributable to the initial "uncatalysed" rate of oxidation, the second to the accumulation of the primary oxidation products in the system.

A kinetic analysis (see Section 3) of the autooxidation of ethyl linoleate has shown clearly that the acceleration in oxidation rate arises from the initiation of additional oxidation chains by thermal decomposition of the α -hydroperoxide oxidation product. The formation of fresh chain carriers was identified as a bimolecular process, which may be written in general terms



(where, as before, R represents the linoleyl acid residue, and $\text{R}\cdot$ and $\text{RO}_2\cdot$ are the corresponding hydrocarbon and peroxy-free radicals). Chain propagation and termination followed this course



We are here concerned to show that the mechanism is applicable to a range of olefins, and also to use the quantitative characteristics of the autocatalytic effect to compare the efficiencies with which α -hydroperoxides of significantly different types generate radicals (according to (R1)) capable of initiating oxidation chains.

Experimental

Details of preparation and purification of the olefins used in this investigation are contained in Section 10.

The experimental method for measurement of rate of oxygen uptake was essentially that described in Sections 3 and 6. Increased precision was obtained by introducing two minor alterations: the flexible Pyrex quill-tubing spiral connecting the reaction vessel and gas burette was immersed in the thermostat used to maintain the reaction vessel at the desired temperature. The water condenser inserted between the reaction vessel and the spiral (to minimise diffusion of relatively volatile olefins into the remainder of the apparatus) was supplied with tap water at a constant rate of flow from a constant-head gravity ~~flow~~

flow device. This modified apparatus permits measurements of an accuracy comparable with those previously obtained with non-volatile olefins, such as ethyl linoleate.

Mechanism of Autoxidation

1. Mono-olefins

The rate of oxidation of ethyl linoleate containing significant amounts of α -hydroperoxide is consistent with the relation

$$\text{Rate} = \frac{k_1}{\sqrt{k_6}} \cdot k_3 [\text{RH}] [\text{RO}_2\text{H}] \cdot \frac{k_2 \sqrt{k_6} [\text{O}_2]}{k_2 \sqrt{k_6} [\text{O}_2] + k_3 \sqrt{k_4} [\text{RH}]} \quad (1)$$

deduced on the basis of the chain mechanism (R1)-(R6).

Tests of proportionality between rate of oxidation and $[\text{RO}_2\text{H}]$ and $[\text{RH}]$ respectively, in the case of other non-conjugated olefins, are relatively straightforward.

Typical autoxidation curves are presented in Figure 1.

During the initial stages of these and all other non-conjugated olefins examined, the rate was a linear function of the extent of oxidation and hence (since in all cases the yield of hydroperoxide was close to 100%) of hydroperoxide concentration, $[\text{RO}_2\text{H}]$. The proportionality between the slope of the autoxidation curves (equal to $k_1^{\frac{1}{2}} k_3 k_6^{-\frac{1}{2}} [\text{RH}]$ at high oxygen pressures, according to equation (1)) and olefin concentration is illustrated in Figure 2.

In contrast, detailed characterisation of the term in (1) describing the dependence of oxidation rate on oxygen

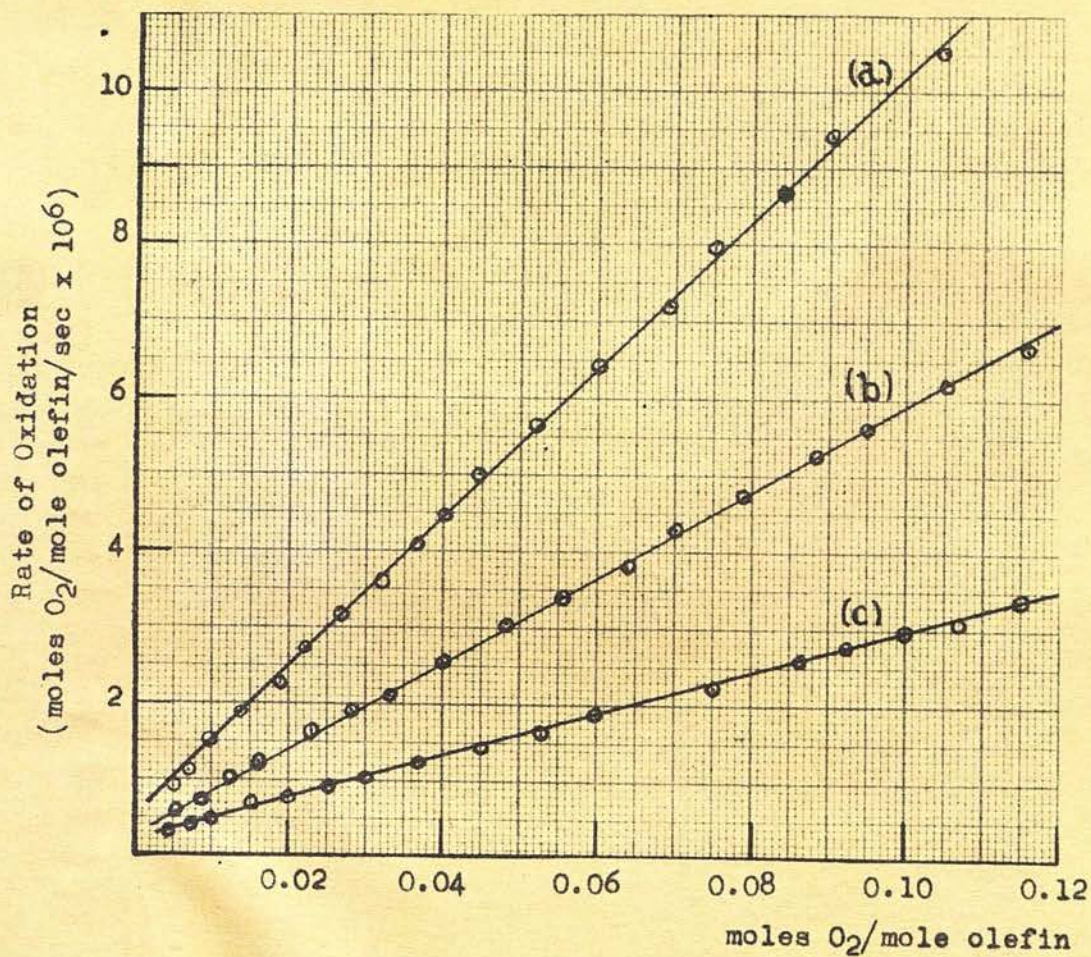


Fig. 1. Course of autoxidation of (a) squalene (b) ethyl linoleate (c) cyclo-hexene at 45°C; oxygen pressure c.a. 760 mm.

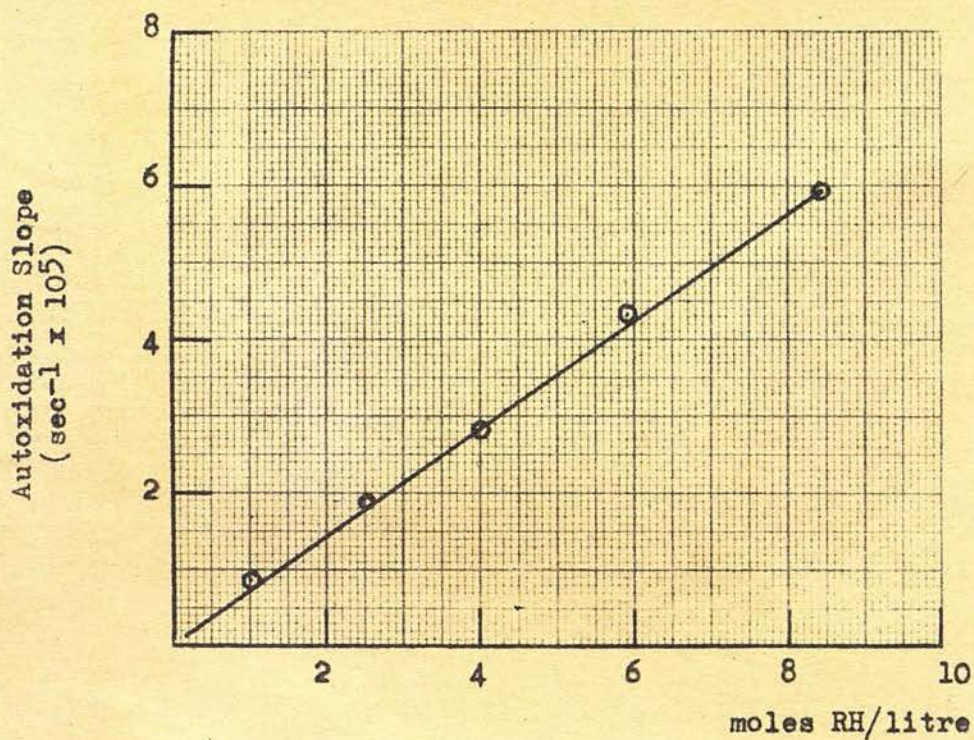


Fig. 2. Proportionality between autoxidation slope and [RH], in the case of methyl cyclo-hexene diluted with n-decane at 45°C.

pressure presents very real difficulties: with the low-molecular olefins employed here, the range of oxygen pressures which may be used without encountering difficulties from the volatility of the olefin is too restricted to allow unequivocal identification of the form this term assumes. Nonetheless all measurements of the autocatalytic slope carried out at oxygen pressures above about 100 mm. agreed in demonstrating its marked insensitivity in this high pressure range; such variations as were noted were in each instance consistent with those found in the case of the oxidation of the same olefin in the presence of benzoyl peroxide. Since the more precise estimations of pressure dependence possible in the latter system conform to the requirements of equation (1) (see Sections 5, 8, 10 and 12) for a range of olefins we may with some confidence assume that this relationship extends to the autocatalytic oxidation.

On this basis, then, we conclude that the mechanism (R1)-(R6) does in fact hold for the initial stages of the autoxidation of mono-olefins.

2. Polyisoprenes

Kinetic examination of the autoxidation of these typical liquid polyisoprenes 2,6-dimethyl octadiene-2,6 ("dihydromyrcene") digeranyl and squalene shows that this class of olefin conforms to the pattern set by the 1,4-dienes and mono-olefins: the rate of autoxidation is in

the initial stages proportional to the extent of oxidation, and the olefin concentration, $[RH]$, while linear plots between reciprocal rate and reciprocal oxygen pressure are obtained for each polyisoprene.

The primary product resulting from the interaction of oxygen and polyisoprenes differs radically from those obtained from 1,4-dienes and mono-olefins, in that it is a diperoxide: thus, each isoprene residue oxidised contains four atoms of oxygen, two of which are contained in a hydroperoxide group and two in a ring peroxide (see Section 9). In the case of oxidation initiated by benzoyl peroxide this difference in structure of the oxidation products does not lead to any novel features in the kinetics of oxidation (see Section 8), and it is in fact readily shown that the above diperoxide formulation would not in fact give grounds for any such expectation. The results now reported enable us to carry one stage further the analogy between the oxidation of polyisoprenes and mono-hydroperoxide-forming olefins: the major mode of decomposition of the polyisoprene diperoxides which results in the initiation of fresh oxidation chains is - as in the earlier cases (cf. (R1)) - bimolecular. This result is of course in keeping with the suggested structure of polyisoprene peroxides since it is unlikely that the stable peroxide ring adjacent to the hydroperoxide group would materially influence their mode of thermal decomposition.

Efficiency of Hydroperoxides as Chain Initiators

At high oxygen pressures the relation (1) reduces to the simple form

$$\text{Rate} = k_1^{\frac{1}{2}} k_3 k_6^{-\frac{1}{2}} [\text{RH}][\text{RO}_2\text{H}]$$

The bimolecular velocity coefficients, k_1 , for the production of chain carriers from a range of hydroperoxides have been calculated from this equation using the data contained in Table 1. Values of $k_3 k_6^{-\frac{1}{2}}$ based on measurement of the benzoyl peroxide catalysed oxidation are drawn almost entirely from Section 10.

Such calculations of the absolute value of k_1 are subject to some uncertainty: any error in the earlier estimates of $k_3 k_6^{-\frac{1}{2}}$ will be reflected in these figures, and all the more so because of the occurrence of k_1 in equation (1) as a square root term. In addition, the significance in absolute terms of these coefficients is limited by the basic assumption that the chain length of the thermal decomposition is unity: if in fact this chain length is α the values of $k_3 k_6^{-\frac{1}{2}}$ and k_1 in Table 1 require multiplication by $\alpha^{\frac{1}{2}}$ and α respectively. It is however unlikely that α is greatly in excess of unity.

Influence of Hydrocarbon Structure on Chain-Initiating Efficiency of Hydroperoxides

Notwithstanding these reservations regarding their absolute accuracy, the k_1 values in Table 1 do serve to

Table I

Olefin	Autoxidation Slope $\text{sec}^{-1} \times 10^5$ (45°C)	[RH] moles/l.	$k_3 k_6^{-\frac{1}{2}} \times 10^4$ (45°C)	$k_1 \times 10^6$ (45°C)
(a) Heptene-1	0.09	7.12	2.61	0.24
Octene-1	0.12	6.40	3.59	0.29
(b) Ethyl linoleate	5.50	2.89	278	0.47
Ethyl linolenate	10.8	2.91	546	0.46
Methyl oleate	0.5	2.96	21.5	0.64
Cyclo-hexene	2.7	9.86	37.0	0.54
(c) Methyl heptenyl benzoate	1.5	3.90	37.8	1.1
2-methyl-pentene-2	3.6	8.25	42.1	1.1
Methyl cyclo-hexene	5.9	8.45	65.1	1.14
4-methyl-heptene-3	2.8	6.55	32.4	1.72
2-cyclo-hexenyl cyclo-hexene-2'	18.0	5.47	200	2.48
1,3,5-trimethyl cyclo-hexene	8.0	6.47	151	3.25
(d) Digeranyl	9.8	12.2*	49.4	2.63
Squalene	8.7	12.6*	39.7	2.97

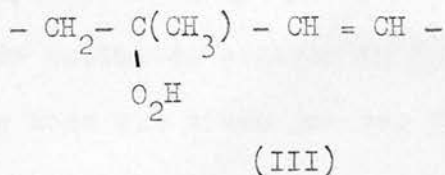
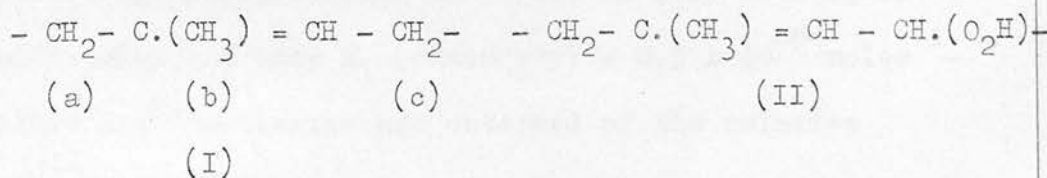
k_1 , k_3 and k_6 are expressed in moles⁻¹-litre-sec⁻¹ units.

* moles isoprene residue/litre.

identify certain significant trends in the efficiency of radical production by α -hydroperoxides of different types. In the first place, the four olefins - ethyl linoleate, ethyl linolenate, methyl oleate and cyclohexene - which give oxidation products in which the α -hydroperoxide groups must be attached exclusively to secondary carbon atoms, give values of k_1 which are identical to within experimental error. This at once emphasises the insensitivity of the radical-producing step to the nature of the unsaturated hydrocarbon system to which the hydroperoxide is attached: we may contrast the 26-fold variation in the efficiencies with which these four olefins partake in the typical α -methylene reaction (R3) $RO_2 + RH \longrightarrow RO_2H + R\cdot$. When the k_1 values for these four secondary hydroperoxides are compared with those for α -hydroperoxides, attached to primary and tertiary carbon atoms, an undoubted trend becomes apparent.

Tertiary α -hydroperoxides. The members of group (c) in Table 1 are to be expected to give α -hydroperoxidic oxidation products containing both secondary and tertiary constituents. Thus, of the three α -groups at which olefins containing the grouping (I) may suffer hydrogen abstraction (by $RO_2\cdot$), the one marked (c) will finally give rise to one of two types of RO_2H molecules ((II) and (III) depending on the point at which the oxygen molecule combines with the R-type radical (in chain propagation reaction (R2)); peroxide

(III) is a



tertiary hydroperoxide involving shifting of the double bond from its original position. In an earlier discussion of this point (Section 10, p.366) it was suggested that this tertiary hydroperoxide would constitute some 32% of the oxidation product from 1-methyl-cyclohexene. Similar arguments applied to the members of group (c) in Table I suggest yields of tertiary α -hydroperoxides as given in Table II. Comparison of the k_1 data for the second and

Table II

Olefin	% tertiary hydroperoxides	k_1 (tert.) k_1 (sec.)
Me-heptenyl benzoate	44	3.7
2-me-pentene-2	44	3.7
1-me-cyclohexene	32	5.0
4-me-heptene-3	32	8.6
2-cyclohexenyl-cyclohexene-2'	84	6.6
1,3,5-tri-me-cyclohexene	76	7.5

third groups of olefins in Table I shows that qualitatively the presence of the tertiary hydroperoxides have an undoubted effect in increasing the chain-initiating

efficiency. If we adopt the simplifying assumption that all secondary hydroperoxides take part in (R1) with equal efficiency and take k_1 (secondary) = 0.5×10^{-6} moles⁻¹-litre-sec.⁻¹ estimates are obtained of the relative efficiency with which secondary and tertiary hydroperoxides initiate chains at 55°C. These estimates are given in Table II - suggest k_1 (tertiary) to be some six times greater than k_1 (secondary).

Primary α -hydroperoxides. -olefins of the type contained in the first group of Table I may be expected to contain up to 50% hydroperoxide attached to primary carbon atoms. The measured values of k_1 for heptene-1 and octene-1 are about half those obtained for the four olefins (group (b)) giving 100% secondary α -hydroperoxides. While the accuracy of these figures is insufficient to justify an estimate of the relative k_1 for primary and secondary hydroperoxides, they are at least consistent with the trend.

$$k_1 \text{ (tertiary)} > k_1 \text{ (secondary)} > k_1 \text{ (primary)}.$$

Since reaction (R1) will always be endothermic the relative rates for the three types of α -hydroperoxides may be expected to reflect in full any changes in endothermicity. On this basis the heat of reaction, and energy of activation, of (R1) is estimated as being about one k.cal/mole greater for a secondary than for a tertiary α -hydroperoxide.

SECTION 12

Determination of Absolute Rate Constants
for Olefinic Oxidations by Measurements of
Photochemical Pre- and After-Effects

**DETERMINATION OF ABSOLUTE RATE CON-
STANTS FOR OLEFINIC OXIDATIONS BY
MEASUREMENT OF PHOTOCHEMICAL
PRE- AND AFTER-EFFECTS**

PART II.—AT "LOW" OXYGEN PRESSURES

BY L. BATEMAN, J. L. BOLLAND AND G. GEE

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The aim of this investigation was to supplement the results given in a preceding paper* by determining the absolute rate constants of the reactions $R + O_2 \rightarrow$ and $2R \rightarrow$ (k_2 and k_4 , respectively). However, the application of the technique therein described to oxidations at low oxygen pressure is seriously

* Part I, *Trans. Faraday Soc.*, 1951, **47**, 155.

impeded by the rate control exerted by oxygen diffusion. Termination reactions involving RO_2 —radicals only become negligible at pressures so low that, under our experimental conditions, diffusion is completely rate controlling.

Approximate values of the ratio $k_2k_4^{-1}$ have been determined for ethyl linoleate and digeranyl, and these, taken in conjunction with the more accurately determinable $k_2k_4^{-1}$ values (data for nine olefins being reported), permit approximate evaluation of the separate rate constants. The significance of the results is discussed, particularly in relation to other comparable radical reactions.

In a preceding paper* we discuss the determination of the propagation and termination rate constants of oxidation designated respectively k_3 and k_6 for a number of olefins of different structural type. This involves measurements at sufficiently high oxygen pressures so that the overall rate of oxidation r is related to the rate of chain initiation r_i to a very close approximation by

$$r = k_3k_6^{-\frac{1}{2}}[\text{RH}]r_i^{\frac{1}{2}} \quad (1)$$

In this paper, we describe corresponding determinations at a lower oxygen pressure where reactions (2), (4) and (5) (this vol., p. 156) become rate determining.

At very low oxygen pressures where termination reactions involving RO_2 —radicals (reactions (5) and (6)) are negligible, the rate of oxidation is given by

$$r = k_2k_4^{-\frac{1}{2}}[\text{O}_2]r_i^{\frac{1}{2}} \quad (2)$$

Unfortunately it appears virtually impossible to work in this pressure region owing to the experimental considerations (i) that the vapour pressure of the olefin must be substantially less than the overall pressure, and (ii) that at reasonably measurable rates of oxidation the rate of solution of oxygen must not become rate-determining.

At slightly higher pressures (1 to 5 mm.), the termination reaction $\text{R} + \text{RO}_2$ — becomes important, and it is then necessary to consider the complete kinetic system. In order to deduce k_4 from measurements in this pressure region, it is necessary to know or assume some relationship between k_4 , k_5 and k_6 . Bolland¹ has suggested that it is reasonable to assume the relationship $k_5^2 = k_4k_6$, and other workers² have reported data consistent with this assumption. The appropriate rate equation, valid when the chain length is not too small, is then

$$r^{-1}r_i^{\frac{1}{2}} = k_3^{-1}k_6^{\frac{1}{2}}[\text{RH}]^{-1} + k_2^{-1}k_4^{\frac{1}{2}}[\text{O}_2]^{-1} \quad (3)$$

Denoting the limiting rate at high oxygen pressures by r_∞ , we have

$$r^{-1}r_\infty = 1 + k_2^{-1}k_3k_4^{\frac{1}{2}}k_6^{-\frac{1}{2}}[\text{RH}][\text{O}_2]^{-1} \quad (4)$$

Thus, at constant r_i and $[\text{RH}]$, a plot of $r^{-1}r_\infty$ against $[\text{O}_2]^{-1}$ should be linear.

In practice, it has been usual to plot $r^{-1}r_\infty$ against p^{-1} , assuming $[\text{O}_2] = \beta p$, where β is a constant, thus obtaining a slope

$$k_2^{-1}k_3k_4^{\frac{1}{2}}k_6^{-\frac{1}{2}}[\text{RH}]\beta^{-1}.$$

It must be remembered that this involves the assumption that the liquid remains effectively saturated with oxygen under all experimental conditions. It is clear from the evidence advanced in the previous paper* that this may not necessarily be true, especially if high rates are observed at low pressures. It was shown there that the decrease in oxygen concentration Δc from its saturation value c_0 is proportional to the oxidation rate. Writing $\Delta c = \alpha r$, with Δc in mole l^{-1} and r in mole $\text{l}^{-1} \text{sec}^{-1}$, the value of α for the experimental conditions described in the previous paper was 5.2 sec. Since this method of estimation was rather indirect and the value obtained depends on the precise experimental arrangements, it is desirable to estimate α directly for the particular arrangement used.

¹ *Proc. Roy. Soc. A*, 1946, **186**, 218.

² Bamford and Dewar, *Proc. Roy. Soc. A*, 1949, **198**, 252.

This is possible from a series of experiments at constant p , in which r_i is increased until the rate begins to approach a constant value independent of further increases in r_i . If we substitute $[O_2] = \beta p - \alpha r$ in eqn. (3) it is easily seen that the limiting rate at high values of r_i is $\alpha^{-1}\beta p$. Consideration of the form of the rate equation as this limit is approached suggests that extrapolation to $r_i = \infty$ should be based on a linear plot of r^{-1} against $r_i^{-\frac{1}{2}}$. Our experimental procedure for determining α thus consisted of a series of measurements of the rate of oxidation at $p = 1$ mm. in presence of varying concentrations of benzoyl peroxide. Fig. 1 records two sets of data for digeranyl, plotted in the form r^{-1} against $[Bz_2O_2]^{-\frac{1}{2}}$. It is not easy to measure accurately the large rates observed under these conditions, but both plots are seen to be reasonably linear. The upper (determined at 45°) refers to the experimental conditions used in the previous paper, and the value of $\alpha = 5.0$ sec. is in

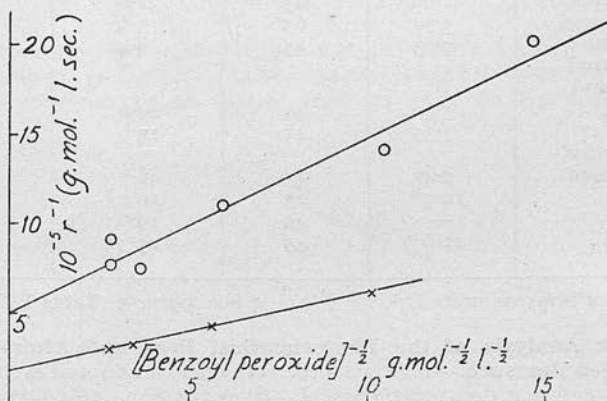


FIG. 1.—Determination of limiting value of r as $r_i \rightarrow \infty$ at $p_{O_2} = 1$ mm. for digeranyl.

excellent agreement with the previous estimate. The lower plot (determined at 55°) is for data obtained under conditions similar to those employed by Bolland in the work from which our values of $k_2 k_4^{-\frac{1}{2}}$ were calculated. The lower value of α ($= 1.8$ sec.) shows that no correction for reduced oxygen concentration is needed for most of his data; where one is required it has been based on the equation

$$[O_2] = \beta p - 1.8 r.$$

Table I summarizes values of $k_3 k_6^{-\frac{1}{2}}$ and $k_2 k_4^{-\frac{1}{2}}$ for a number of olefins. It must be stressed that the values of the latter were not measured directly under conditions where it would be legitimate to neglect termination processes other than that involving two R— radicals. They rest on the assumption that $k_5^2 = k_4 k_6$, justification for which is to be found in the observed linearity of the plot of r^{-1} against $[O_2]^{-1}$. Even at the lowest pressure at which we have been able to work, approximately one-third of the termination reactions involve R— + RO₂—. This consideration has to be recognized as limiting the accuracy of our analysis of the data now to be presented, the object of which is to determine k_2 and k_4 separately.

The isolation of k_2 and k_4 requires the above data to be supplemented by a study of either the rate of photo-oxidation under intermittent illumination or the photochemical pre- and after-effects. At low oxygen pressures both present difficulties of experiment and interpretation, but the latter technique has seemed to us preferable and has therefore been adopted. In the next section, a kinetic analysis is made of the pre- and after-effects at low pressures. Full correction is made for changes

in oxygen concentration, but it has not been found feasible at the same time to allow for more than one termination process. The equations derived are not therefore rigorously applicable to our experimental data, but it is believed that any error thus introduced is unlikely to exceed the rather large experimental uncertainty.

TABLE I

Olefin	[RH] (mole l. ⁻¹)	Temp. (°C)	$10^{-4}k_2k_6^{-\frac{1}{2}}$ (mole ⁻¹ l. ^{1/2} sec. ^{-1/2})	$10^{-2}k_2k_4^{-\frac{1}{2}}$ (mole ⁻¹ l. ^{1/2} sec. ^{-1/2})
Ethyl linoleate .	2.89	25	121	13.0
	—	45	207	7.8
	—	65	330	5.3
Methyl oleate .	2.96	65	31.6	4.7
Hexadec-1-ene .	3.50	65	5.6	6.5
Allylbenzene .	7.65	45	9.4	3.5
2 : 6-Dimethyl- hexa-2-enyl benzoate. .	3.90	45	29.0	3.2
Tetralin .	7.35	45	19.6	7.2
1 : 2-Dimethyl- cyclohexene .	7.47	45	86.7	4.3
Digeranyl .	12.3 *	25	10.7 †	9.0 †
	—	45	19.6 †	5.0 †
Squalene .	12.6 *	45	17.3 †	2.3 †

* Mole of isoprene units l.⁻¹.

† See footnote, Table I, Part I.

Kinetic Analysis of the Photochemical Pre- and After-Effects at Low Oxygen Pressure.—Following the conventions adopted in the previous paper, we define a decay intercept I_d , from the time $t = 0$ at which the light is switched on, by the expression

$$I_d \equiv \int_0^{\infty} (r - r_D) dt, \quad . \quad . \quad . \quad (5)$$

where

$$r_D = k_2k_4^{-\frac{1}{2}}[O_2]_D r_i^{\frac{1}{2}}. \quad . \quad . \quad . \quad (6)$$

If r is the overall rate at any time t , we have

$$r = k_2[R-][O_2]. \quad . \quad . \quad . \quad (7)$$

During the non-stationary period, $[R-]$ and $[O_2]$ are both changing, and it is therefore convenient to define a new variable

$$x \equiv r/[O_2] = k_2[R-]. \quad . \quad . \quad . \quad (8)$$

At sufficiently low pressures, substantially all the radicals present in the system are $R-$, in which case

$$d[R-]/dt = r_i - k_4[R-]^2. \quad . \quad . \quad . \quad (9)$$

Combining eqn. (7) to (9) it is easily shown that if

$$x_D \equiv r_D/[O_2]_D,$$

$$\frac{dx}{dt} = \frac{k_4}{k_2}(x^2 - x_D^2) \quad . \quad . \quad . \quad (10)$$

which can be integrated at once to give x as a function of t .

To obtain the time dependence of $[O_2]$ we write, following the argument of the previous paper,

$$\frac{d[O_2]}{dt} = k_8c_0 - k_8[O_2] - r,$$

$$= k_8c_0 - [O_2](k_8 + x). \quad . \quad . \quad . \quad (11)$$

Eqn. (5), (8), (10) and (11) contain a complete mathematical formulation of the problem of calculating I_d as a function of the ratio $k_2^{-1}k_4$, which it is the purpose of this investigation to determine.

As in the previous paper, the experimental decay intercept I_d' is not identical with the calculated value I_d , so that again we have considered it best to calculate also a growth intercept I_g , and to use the relationship $I_d - I_g = I_d' - I_g'$. I_g is defined by

$$I_g = \int_0^\infty (r_L - r) dt, \quad \dots \quad (5')$$

where t is measured from the instant at which the light is switched on. Repetition of the analysis outlined above leads again to eqn. (8) and (11), but (10) is replaced by

$$\frac{dx}{dt} = \frac{k_4}{k_2} (x_L^2 - x^2). \quad \dots \quad (10')$$

Unfortunately the equations are not in a form leading to a simple explicit solution, and it becomes necessary to resort to numerical methods. This procedure has to be carried through with an assumed value of

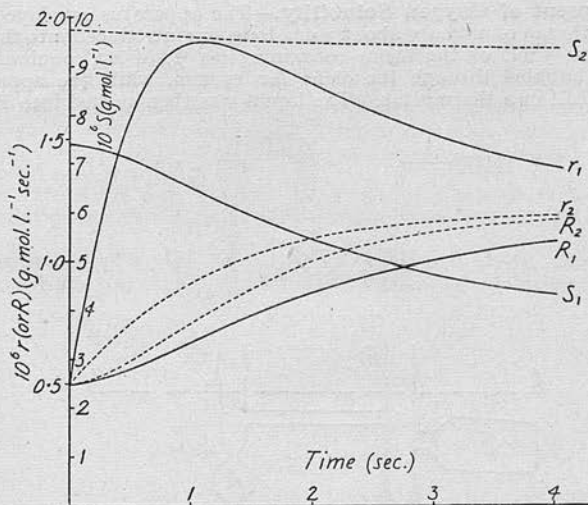


FIG 2.—Calculated oxidation rates and oxygen concentrations. Full curves, $k_2^{-1} = 5.2 \text{ sec.}$, $k_2 k_4^{-1} = 0.24$. Broken curves, $k_2^{-1} = 0.52 \text{ sec.}$, $k_2 k_4^{-1} = 0.24$. r = true oxidation rate (in solution); R = apparent oxidation rate (= rate of loss of oxygen from gas phase); s = oxygen concentration in solution.

$k_2^{-1}k_4$ and repeated so as to give $I_d - I_g$ as a function of the value taken for $k_2^{-1}k_4$. A suitable mathematical technique has been worked out by Miss K. Britten, and is outlined in the appendix.

It is not immediately apparent from this analysis how greatly this situation is complicated as compared with that discussed in the previous paper by the fact that the reaction rate depends on the oxygen concentration. Fig. 2 is illustrative of the behaviour of the system revealed by numerical computation. Two sets of curves are shown, the full lines are calculated from the constants found in one of our experiments with ethyl linoleate, and the broken lines represent hypothetical conditions for a ten-fold increase in shaking efficiency. With the experimental values, it will be seen that although the apparent rate increases smoothly during the growth period, the true rate passes through a maximum before falling to its final value. The reason for this is that in the early stages

of the growth period the oxygen concentration is still fairly high and the free radical concentration $[R\cdot]$ builds up by the photo-catalyzed sequence of reactions much faster than the oxygen concentration falls. Even with the much higher shaking efficiency assumed in calculating the broken curves, the apparent rate lags quite seriously behind the true one, due to failure of the oxygen concentration to keep in step with the oxidation rate. Bamford and Dewar³ claim to have avoided this difficulty even at pressures considerably lower than we have used, arguing that in their experiments the concentration of oxygen in solution during the time of the after-effect remained substantially constant and equal to its value in the light. This condition could be satisfied if either (i) shaking was extremely efficient, or (ii) the after-effect removed only a small fraction of the dissolved oxygen. The latter is apparently not so (and in any case would make the after-effect almost unobservable), and our analysis of Bamford and Dewar's data indicates a shaking efficiency comparable with that in our experiments.

Experimental

Olefins.—The source and purity of the olefins examined have been described elsewhere.^{1, 3, 4, 5}

Measurement of Oxygen Solubility.—The apparatus employed is shown in Fig. 3. A thread of mercury about 3 cm. long was introduced into the capillary U-tube B, and 5 ml. of the olefin containing 0.1% of hydroquinone into A. Oxygen was bubbled through the olefin for 15 min. while the apparatus was immersed to LL' in a thermostat. The liquid was then sucked into B, C and D

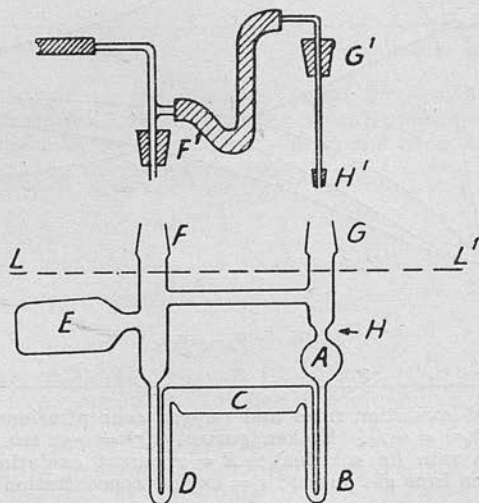


FIG. 3.—Apparatus for measuring the solubility of oxygen in olefins.

by means of the attachment possessing rubber bungs F' , G' and H' which fitted the ground glass joints F and G and the constriction H respectively. The liquid in the bulb C was isolated by the introduction of mercury threads (ca. 6 cm. long) into B and D , and the excess liquid above the mercury pipetted off. The apparatus was then attached to a vacuum line through a detachable tap at G (F being closed with a ground-glass cap), liquid oxygen applied at B and D to form solid mercury gas-tight seals, thorough pumping out effected, and the apparatus (with the tap) removed from the line. After the mercury had melted, the olefin was allowed to flow into E , and the apparatus again attached (with E vertical) to a calibrated McLeod gauge system. The evolved gas was measured in successive doses, the last traces being extracted from the olefin

³ Bolland, *Trans. Faraday Soc.*, 1950, 46, 358.

⁴ Bateman and Gee *Proc. Roy. Soc. A*, 1948, 195, 376.

⁵ Part I.

by the usual degassing procedure. An accurate estimate of the volume of the isolated liquid was obtained from the predetermined volume of C and the cross sections of B and D.

TABLE II

Olefin	Temp. (° C)	Volume (ml.)	p_{O_2} (mm. Hg.)	Volume of Dissolved O_2 (ml.)	Bunsen Coefficient	$10^6 [O_2] \phi^{-1}$ (mole l^{-1} mm. ⁻¹)
Ethyl linoleate	11	3.47	748	0.758	0.212	1.26
	35	3.40	748	0.650	0.191	1.14
	55	3.45	748	0.535	0.161	0.96
Methyl oleate	10	3.44	745	0.685	0.199	1.19
	50	3.45	745	0.570	0.171	1.03
1-Methylcyclohexene	35	3.42	750	0.598	0.175	1.04
Tetralin	10	3.40	758	0.571	0.168	0.99
	40	3.45	755	0.586	0.170	1.01
	65	3.30	760	0.570	0.173	1.02
Ethyl stearate	55	3.45	745	0.620	0.180	1.08

Two points of interest are that the solubility of oxygen within the temperature range investigated is only slightly dependent upon the type of ethylenic bond and its concentration, and that the temperature coefficient of the solubility is almost negligible.

Determination of k_2/k_4 .—The apparatus and procedure for measuring rates of oxidation for this purpose have already been detailed (ref. (1), and see p. 159).

Determination of $k_2^{-1}k_4$.—For reasons mentioned above, these determinations were restricted to the more involatile olefins, ethyl linoleate and digeryl.

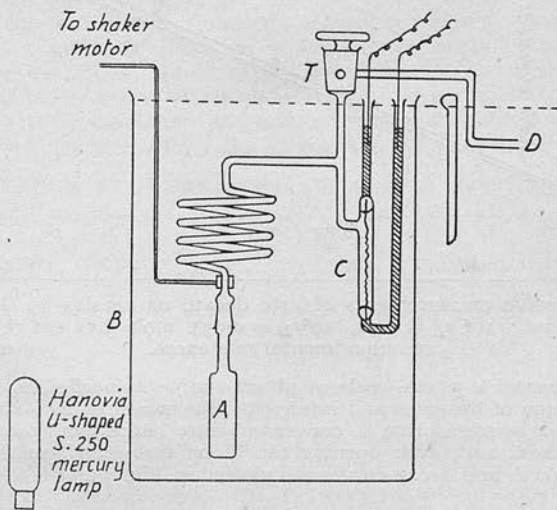


FIG. 4.—Experimental arrangement for measuring photochemical pre- and after-effects at low oxygen pressure. A represents a plane-faced silica reaction cell (5 ml. capacity); B a Pyrex beaker containing thermostated water to the level shown; C a Pirani gauge (vol. \sim 5 ml.; resistance 95 ohms) with mercury contact limbs; and T a two-way tap. Connection at D is to the apparatus shown in *Proc. Roy. Soc. A*, 1946, 186, 220. Intensity reduction screens were sometimes interposed between the lamp and the beaker.

The experimental arrangement is shown in Fig. 4. Comparative measurements of r_L and r_D and of I_d' and I_g' were made at constant volume with tap T shut (cf. Part I) in terms of the deflection of a galvanometer (critically damped: period 1 sec.) incorporated with the Pirani gauge in a conventional Wheatstone bridge circuit. Delay in galvanometer response was found to be inappreciable by the same type of test as applied to the octoil manometer in the high pressure experiments (this vol., p. 160). The pressure drop during the maximum extent of any of the rate measurements (transverse of the reflected light beam from the

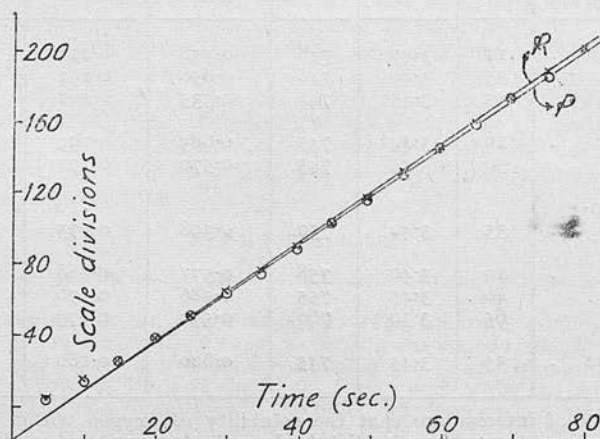


FIG. 5.—Successive measurements of rate growth on commencing to illuminate at $t = 0$. Digeranyl; $10^6 r_L = 0.71$, $10^6 r_D = 0.055$ mole l.⁻¹ sec.⁻¹. P and R are experimental references.

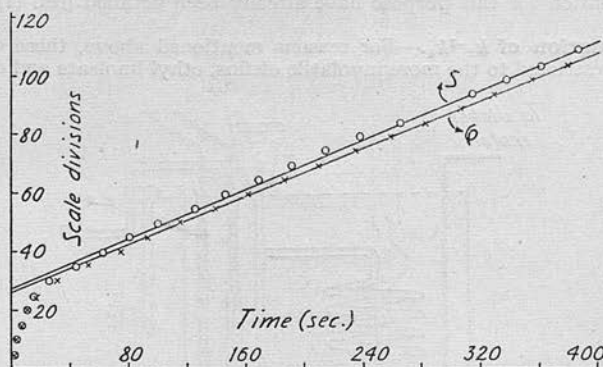


FIG. 6.—Successive measurements of rate decay, on ceasing to illuminate at $t = 0$. Digeranyl; $10^6 r_L = 0.71$, $10^6 r_D = 0.055$ mole l.⁻¹ sec.⁻¹. Q and S are experimental references.

galvanometer across a 50 cm. scale at about 1 m.) was negligible. The factor for the conversion of the rates and intercepts thus measured into absolute units was determined by measuring a convenient rate successively on the Pirani gauge arrangement and, after opening tap T, on the usual apparatus. Some typical rate growth and decay curves are plotted in Fig. 5 and 6.

Discussion

The experimental data and the values of $k_2^{-1}k_4$ calculated in accordance with the procedure described on page 163 are presented in Table III. The values obtained, however, are rather sensitive to the values of $I_d' - I_g'$, and the figures in parentheses following the tabulated values of $k_2^{-1}k_4$ represent the limits within which this quantity could lie if the

uncertainty in $I_d' - I_g'$ is assumed to be ± 2 galvanometer scale divisions. While the observed variations in $k_2^{-1}k_4$ are very much smaller, it would clearly be unwise to assume that the results do much more than indicate the order of magnitude of the constants, particularly in view of the neglect of termination processes involving RO_2 - radicals.

TABLE III

Olefin	Volume (ml.)	Temp. (°C)	s_0 (10^6 mole l. ⁻¹)	k_2^{-1} (sec.)	rL	rD	I_d'	I_g'	$k_2^{-1}k_4$
					(10 ⁶ mole l. ⁻¹ sec. ⁻¹)		10 ⁶ mole		
Ethyl linoleate	1.6	25	1	5.2	0.70	0.30	3.2	1.6	2 (4, 1)
	—	—	—	—	1.20	0.50	6.0	3.8	4 (35, 2)
Digeranyl	2.0	25	1	5.2	0.34	0.050	3.5	2.5	22 (80, 12)
	—	—	—	—	0.98	0.049	8.6	3.9	10 (14, 8)
	—	—	—	—	0.71	0.055	7.3	5.1	18 (30, 14)
	—	—	—	—	0.27	0.045	2.9	2.1	18 (400, 10)

Bearing in mind the above considerations, it is of interest to evaluate k_2 and k_4 separately and to compare them with the related k_3 and k_6 values (Table IV). A notable feature is then apparent, viz., that whereas the rate of interaction of two RO_2 - radicals is independent of the olefinic character of RH (cf. this vol., p. 160), the rates of reaction of an R- radical with oxygen and with another similar R- radical vary greatly and in a reasonable manner. The characteristics of olefinic structure which enhance the reactivity of RH towards RO_2 - obviously confer enhanced stability on the derived radical R-, thus leading to the inverse relationship between the k_2 's and the k_4 's on the one hand and the k_3 's on the other on passing from digeranyl to ethyl linoleate. Furthermore, the fact that both k_2 and k_4 are sensitive to the nature of R- is seen to result in the composite quantity $k_2k_4^{-1}$ remaining sensibly constant throughout a series of olefins in which the oxidizability at high oxygen pressure varies about 60-fold (Table I). This feature finds a parallel in polymerization systems, where different R- type radicals combine with the corresponding monomers and interact with their kind at widely different rates and yet the rates of $k_{\text{propagation}}/k_{\text{termination}}^{-1}$ show little variation.⁶

TABLE IV.—RATE CONSTANTS AT 25° C (mole⁻¹ l. sec.⁻¹)

Olefin	k_2	k_3	k_4	k_6
Digeranyl *	15×10^6	0.5	260×10^6	0.3×10^6
Ethyl linoleate	5×10^6	7.0	15×10^6	0.3×10^6

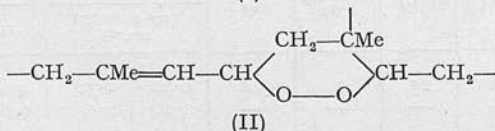
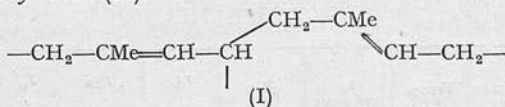
* See footnote, Table I, Part I.

Although the lower reactivity of the R- radical derived from ethyl linoleate accords with the large resonance stabilization of the pentadienyl radical,⁷ the extent to which energy factors are responsible for the rate differences from olefin to olefin is uncertain owing to the very small activation energies of the relevant reactions. Assuming, however, that the so-called steric factors are the same for ethyl linoleate and digeranyl, the rate constants quoted correspond to activation energy differences

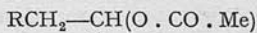
⁶ Melville and Valentine, *Trans. Faraday Soc.*, 1950, 46, 210.

⁷ Bolland and Orr, *I.R.I. Trans.*, 1945, 21, 133.

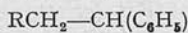
of 0.65 and 1.7 kcal. for reactions (2) and (4) respectively. These differences appear reasonable both relatively and absolutely if the absolute values for digeranyl are near to zero. Concerning the latter point, it must be remembered that in polyisoprene systems two R— type radicals are involved,^{8*} namely, the ordinary allylic type (I) and the cyclo peroxido-substituted *alkyl* unit (II).



It does not appear possible at present to decide which of these radicals is involved in the rate-determining propagation and termination reactions, although it must be the same one in each reaction. If the radical involved is (II), the above condition will certainly be satisfied; if (I), any departure is likely to be small. It is noteworthy that the activation energy differences considered may be correlated with similar differences reported for termination processes in polymerizations. Thus, the activation energy for the interaction of two substituted acetoxymethyl radicals (III) derived from vinyl acetate is indistinguishable from zero, whereas



(III)



(IV)

that for the similar phenylmethyl radicals (IV) derived from styrene is of the order² of 3 kcal.—this reflecting the stabilization resulting from the allylic-type resonance within the benzyl unit.

Appendix

By K. H. V. BRITTEN

The problem is to determine a value of $k_2^{-1}k_4$ by means of eqn. (5), (5'), (8), (10), (10') and (11) so that agreement exists between the calculated and experimental values of $I_d - I_g$.

For purposes of computation, it is convenient to use eqn. (11) to convert the expression for $I_d - I_g$ into the form

$$I_d - I_g = k_2 \left\{ \int_0^\infty ([\text{O}_2]_D - [\text{O}_2]) dt - \int_0^\infty ([\text{O}_2] - [\text{O}_2]_L) dt \right\}, \quad (12)$$

where the first integral is taken over the decay period, the second over the growth.

INTEGRATION OF GROWTH INTERCEPT TERM.—Eqn. (10) can be integrated immediately giving

$$x = x_L \left\{ \frac{A - e^{-\alpha_1 t}}{A + e^{-\alpha_1 t}} \right\}, \quad (13)$$

where $\alpha_1 = 2Kx_L$, $K = k_2^{-1}k_4$ and $A = \frac{x_L + x_D}{x_L - x_D}$.

Introduction of a new variable $\tau = e^{-\alpha_1 t}$ yields eqn. (13) in the simple form

$$x = x_L \left\{ \frac{A - \tau}{A + \tau} \right\}.$$

⁸ Bolland and ten Have, *Trans. Faraday Soc.*, 1949, **45**, 93. Bolland and (Mrs.) Hughes, *J. Chem. Soc.*, 1949, 492.

* Mr. A. L. Morris has confirmed that the yield of hydroperoxide remains about 50% when oxidation proceeds at oxygen pressures as low as 3 mm.

Substituting into eqn. (11) and changing variables we have

$$\frac{d[\text{O}_2]}{d\tau} - [\text{O}_2] \left\{ \frac{A(k_s + x_L) + \tau(k_s - x_L)}{\alpha_1 \tau(A + \tau)} \right\} + \frac{k_s c_0}{\alpha_1 \tau} = 0.$$

This equation has an integrating factor $\frac{(A + \tau)^{\alpha_1}}{\tau b_1}$, where $a_1 = \frac{2x_L}{\alpha_1}$ and

$b_1 = \frac{k_s + x_L}{\alpha_1}$ and the solution takes the form

$$[\text{O}_2] = \frac{\tau^{b_1}}{(A + \tau)^{a_1}} \left\{ [\text{O}_2]_D (A + 1)^{a_1} - \frac{k_s c_0}{\alpha_1} \int_1^\tau \frac{(A + \tau)^{a_1}}{\tau^{b_1 + 1}} d\tau \right\} \quad (14)$$

As the coefficients a_1 and b_1 are not, in general, integers, the integral in this solution cannot be evaluated analytically. Moreover, difficulty is encountered on attempting a numerical solution since at one end of the range of integration ($t = \infty, \tau = 0$) the integral becomes infinite. Some readjustment is therefore necessary.

It follows from (12) that $[\text{O}_2] - [\text{O}_2]_L$ is required finally, and this can be obtained at once from (14) by an integration in parts, giving

$$[\text{O}_2] - [\text{O}_2]_L = \frac{\tau^{b_1}}{(A + \tau)^{a_1}} \left\{ (A + 1)^{a_1} ([\text{O}_2]_D - [\text{O}_2]_L) - \frac{k_s c_0 a_1}{\alpha_1 b_1} \int_1^\tau \frac{(A + \tau)^{a_1 - 1}}{\tau^{b_1}} d\tau \right\}.$$

The integrand $\frac{(A + \tau)^{a_1 - 1}}{\tau^{b_1}}$ is now expanded as a series in τ and the integral obtained in the form

$$\begin{aligned} \int_1^\tau \frac{(A + \tau)^{a_1 - 1}}{\tau^{b_1}} d\tau &= \frac{A^{a_1}}{\tau^{b_1}} \left\{ \frac{1}{1 - b_1} \left(\frac{\tau}{A} \right) + \frac{a_1 - 1}{2 - b_1} \left(\frac{\tau}{A} \right)^2 + \frac{1}{2} \frac{(a_1 - 1)(a_1 - 2)}{3 - b_1} \left(\frac{\tau}{A} \right)^3 \right. \\ &\quad \left. + \frac{1}{6} \frac{(a_1 - 1)(a_1 - 2)(a_1 - 3)}{4 - b_1} \left(\frac{\tau}{A} \right)^4 + \dots \right\} \\ &\quad - A^{a_1} \left\{ \frac{1}{1 - b_1} \frac{1}{A} + \frac{a_1 - 1}{2 - b_1} \cdot \frac{1}{A^2} + \frac{1}{2} \frac{(a_1 - 1)(a_1 - 2)}{3 - b_1} \frac{1}{A^3} \right. \\ &\quad \left. + \frac{1}{6} \frac{(a_1 - 1)(a_1 - 2)(a_1 - 3)}{4 - b_1} \frac{1}{A^4} + \dots \right\}, \end{aligned}$$

whence we obtain

$$\begin{aligned} [\text{O}_2] - [\text{O}_2]_L &= \frac{\tau^{b_1}}{(A + \tau)^{a_1}} \left\{ (A + 1)^{a_1} ([\text{O}_2]_D - [\text{O}_2]_L) + \frac{k_s c_0 a_1}{\alpha_1 b_1} A^{a_1} \left(\frac{1}{1 - b_1} \frac{1}{A} \right. \right. \\ &\quad \left. \left. + \frac{a_1 - 1}{2 - b_1} \frac{1}{A^2} + \dots \right) \right\} - \frac{1}{(A + \tau)^{a_1}} \frac{k_s c_0 a_1}{\alpha_1 b_1} A^{a_1} \left\{ \frac{1}{1 - b_1} \frac{\tau}{A} \right. \\ &\quad \left. + \frac{a_1 - 1}{2 - b_1} \left(\frac{\tau}{A} \right)^2 + \dots \right\} \quad (15) \end{aligned}$$

INTEGRATION OF DECAY INTERCEPT TERM.—By an exactly similar procedure as the above, we obtain

$$\begin{aligned} [\text{O}_2] - [\text{O}_2]_D &= \frac{\tau^{b_2}}{(A - \tau)^{a_2}} \left\{ (A - 1)^{a_2} ([\text{O}_2]_L - [\text{O}_2]_D) + \frac{k_s c_0 a_2}{\alpha_2 b_2} A^{a_2} \left(\frac{1}{1 - b_2} \frac{1}{A} \right. \right. \\ &\quad \left. \left. - \frac{a_2 - 1}{2 - b_2} \frac{1}{A^2} + \dots \right) \right\} - \frac{1}{(A - \tau)^{a_2}} \frac{k_s c_0 a_2}{\alpha_2 b_2} A^{a_2} \\ &\quad \left\{ \frac{1}{1 - b_2} \frac{\tau}{A} - \frac{a_2 - 1}{2 - b_2} \left(\frac{\tau}{A} \right)^2 + \dots \right\}, \quad (16) \end{aligned}$$

where $\alpha_2 = 2Kx_D, a_2 = \frac{2x_D}{\alpha_2}$ and $b_2 = \frac{k_s + x_D}{\alpha_2}$.

It should be noted that the signs in the power series in this case are alternatively positive and negative.

DETAILS OF COMPUTATION.—The convergence of the power series in (15) and (16) depends of course on the values of a_1, a_2 , etc. Actually, they were found

to be fairly rapidly convergent: in the worst region (near $\tau = 1$) it was sometimes necessary to use eight terms, but near to $\tau = 0$ one or two were sufficient. A check on the accuracy was available at $\tau = 1$ since the value at this point is known.

Values of $([O_2] - [O_2]_L)$ and $([O_2]_D - [O_2])$ were calculated from (15) and (16) using an assumed value of $k_2^{-1}k_4$,

and the values of $\int_0^\infty ([O_2]_D - [O_2]) dt$

and $\int_0^\infty ([O_2] - [O_2]_L) dt$ deduced

numerically. These were then substituted into (12) to give $I_d - I_g$. In practice, it proved sufficient to confine the limits of integration to $t = 0$ and $t = 40$ in the worse case. This process was repeated for a series of $k_2^{-1}k_4$ values and the value giving agreement with the experimental $I_d' - I_g'$ value determined by graphical interpolation, the form of the relationship between $I_d - I_g$ and $k_2^{-1}k_4$ being shown in Fig. 7.

Unfortunately the interpolations usually occurred on the steeply inclined left-hand side of the curve, and hence a small experimental error in $I_d' - I_g'$ results in a disproportionately

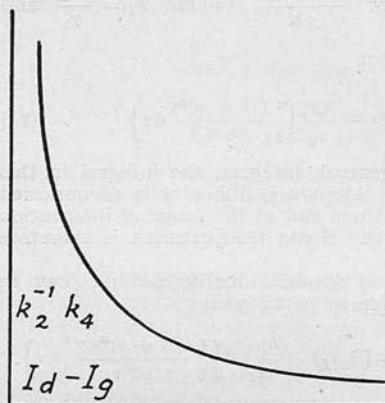


FIG. 7.—Relationship between $k_2^{-1}k_4$ and $I_d - I_g$ for a given value of k_2 .

large error in $k_2^{-1}k_4$.

We thank Mr. A. L. Morris for performing the experiments to determine the shaking constant, and for certain measurements on digeranyl and gutta-percha recorded in this and the previous paper, Miss X. Sweeting for the computations necessary to derive $k_2k_4^{-1}$ as described in the Appendix, and Dr. W. F. Watson for valuable advice and criticism.

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SECTION 13

The Photosensitised Oxidation of Alcohols

Recent investigations of the photo-oxidation of alcohols, sensitised by benzophenone¹ and by azo-dyes², while providing valuable information regarding the general form of the reaction, do not enable its detailed mechanism to be specified. Using anthraquinonoid sensitisers, however, it has been possible to obtain diagnostic evidence as to the nature of the individual processes concerned.

Aqueous neutral or acid solutions of the alcohol containing small quantities (10^{-3} - 10^{-4} M) of anthraquinone 2:6-disodium sulphonate were irradiated (λ ca. 3650 Å) in presence of oxygen at a shaking speed of 600 cycles/min.

The chief features of the photosensitised oxidation of ethanol are:

(a) The rate of oxygen uptake at constant pressure is virtually independent of the reactant concentrations but is proportional to the first power of the rate of light absorption. Also the quantum yield ~ 1 and is independent of temperature (0-40°C). Hence a non-chain mechanism is in operation.

(b) The reaction products consist simply of acetaldehyde, acetic acid and peroxide (almost entirely hydrogen peroxide). It has been demonstrated conclusively that, except at low alcohol concentrations, acetic acid

arises directly from the ethanol; it is not the result of secondary oxidation of the acetaldehyde.

(c) Product yields based on the oxygen absorbed by the system are independent of light intensity and alcohol concentration but vary significantly with oxygen pressure and sensitiser concentration. The limiting conditions are:

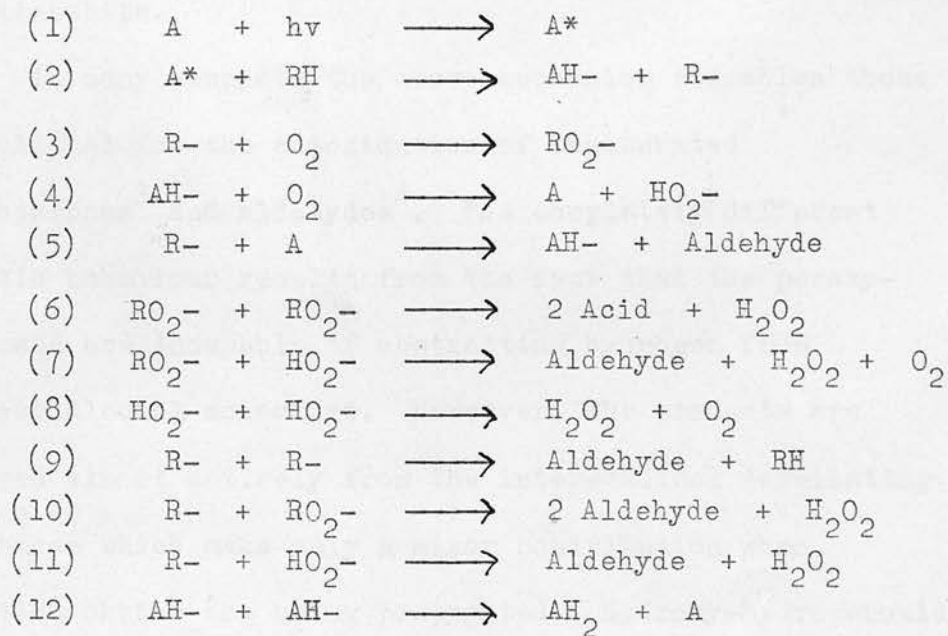
Oxygen Pressure	Low	High
Sensitiser Concentration	High	Low
Acid Yield	0%	55%
Aldehyde Yield	100%	18%
Peroxide Yield	100%	70%

(d) The reaction rate and product yields are independent of pH under non-alkaline conditions. This, together with other evidence, suggests that the photo-oxidation occurs by a free-radical mechanism.

(e) The anthraquinonoid sensitiser operates by a cyclic mechanism; its concentration remains unchanged after the absorption of many times the equivalent amount of oxygen. At low oxygen pressures, measurable quantities of the corresponding anthrahydroquinone are produced, indicating that the initial attack by the photo-excited sensitiser molecule involves abstraction of hydrogen from its surroundings. Since this does not occur in absence of the substrate, it follows that the hydrogen is removed from the alcohol, with the simultaneous production of a semi-quinone radical. At high oxygen pressure, this is

rapidly re-oxidised to the anthraquinone form; at low oxygen pressure further reduction to the anthrahydroquinone can occur.

These observations may all be interpreted in terms of the following reaction scheme:-



RH represents the alcohol, R- the radical R.C -
 $\begin{matrix} \text{H} \\ | \\ \text{R.C} \\ | \\ \text{OH} \end{matrix}$
 while RO_2^- corresponds to R.C -OO- and AH^- to the semi-
 $\begin{matrix} \text{H} \\ | \\ \text{R.C} \\ | \\ \text{OH} \end{matrix}$
 quinone radical. When acid production is favoured, reactions (1)-(4) and (6)-(8) predominate.

Applying stationary state conditions to this scheme it can be shown that:

(a) to a first approximation over the whole range of oxygen pressure and sensitiser concentration:

$$\frac{1}{(\text{Acid Yield})^{\frac{1}{2}}} = C' + C'' \frac{[A]}{[O_2]}$$

where C' and C'' are constants.

(b) at high $[O_2]$ and low $[A]$

$$\text{Acid Yield} \times \frac{3}{2} + \text{Aldehyde Yield} = 100\%$$

$$\text{Acid Yield} + \text{Aldehyde Yield} = \text{Peroxide Yield}$$

(c) at low $[O_2]$ and high $[A]$

$$\text{Aldehyde Yield} = \text{Peroxide Yield} = 100\%$$

The experimental data are in accordance with these relationships.

In many respects the above mechanism resembles those established for the autoxidation of unsaturated hydrocarbons³ and aldehydes⁴. The completely different kinetic behaviour results from the fact that the peroxy-radicals are incapable of abstracting hydrogen from further alcohol molecules. Moreover, the products are derived almost entirely from the inter-radical terminating processes which make only a minor contribution when reaction chains are being propagated. Hydroxy-hydroperoxide and hydroxy-peroxides do not figure significantly among the products because they readily break down to aldehyde and hydrogen peroxide⁵.

Photo-oxidations conducted in absence of water using anthraquinone as sensitiser and also in aqueous solution using hydrogen peroxide agree with the above picture. Similar considerations have been applied to secondary alcohols and α -glycols. Isopropanol, for example, gives the expected 100% yields of acetone and hydrogen peroxide at all oxygen pressure and sensitiser concentrations. 2:3-butylene glycol, however, exhibits the additional feature of carbon-carbon bond fission.

This mechanism has a direct bearing on the phototendering of cellulosic textiles, in so far as it shows how the action of light may lead to the introduction of carbonyl groups into the material. The mild alkaline conditions of washing are then sufficient to bring about degradative reactions of the type indicated by Davidson⁶ and recently interpreted by Corbett, Kenner and Richards⁷. It is important to emphasise, however, that this represents only one aspect of the complex tendering process.

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