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KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS.

II. THE KINETICS OF OXIDATION OF UNCONJUGATED OLEFINS.

III. THERMOCHEMISTRY AND MECHANISMS OF OLEFIN OXIDATION.

KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS.

II. THE KINETICS OF OXIDATION OF UNCONJUGATED OLEFINS.

By J. L. Bolland and Geoffrey Gee.

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The oxidation of olefins generally leads to a complex mixture of products, in which the oxygen may be combined in a number of different ways.[1] Evidence has been accumulated in recent years [2] that in some cases at least the major primary product is an unsaturated hydroperoxide $RCH : CH . CH(O_2H) . R'$. Indeed conditions can be found in which certain olefins give a quantitative yield of this material. Under these circumstances we have found it possible to study this particular reaction by kinetic methods, and in this paper are summarised the results so far obtained; full experimental details are in course of publication elsewhere.[3]

Most of the work has been carried out on ethyl linoleate I, the other olefins studied being ethyl linolenate II, methyl oleate III, and squalene IV.

I. $CH_3(CH_2)_4CH=CH-CH_2-CH=CH-(CH_2)_7COO\ C_2H_5$

II. $CH_3 . CH_2 . CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_7COO\ C_2H_5$

III. $CH_3(CH_2)_7CH=CH(CH_2)_7COO\ CH_3$

IV. $(CH_3)_2C=CH . CH_2(CH_2 . C(CH_3)=CH . CH_2)_2(CH_2 . CH=C(CH_3)CH_2)_2$
$CH_2 . CH=C(CH_3)_2$.

It will be seen that I is a 1 : 4 diolefin; II may be considered as approximately equivalent to two 1 : 4 diolefins, III is a mono-olefin, while IV contains a repeating 1 : 5 diene unit analogous to that present in natural rubber. Rigorous purification was found necessary before

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[1] Hilton, *I.R.I. Trans.*, 1942, **17**, 319; Naylor, *ibid.*, 1944, **20**, 45.

[2] Crieger, Pilz and Flygare, *Ber.*, 1939, **72**, 1799; Farmer and Sundralingam, *J. Chem. Soc.*, 1942, 121.

[3] Bolland, *Proc. Roy. Soc.*, *in press.*

reproducible oxidation rates were obtained; this was generally accomplished by a combination of molecular distillation and chromatographic methods.

The peroxide contents of reaction products were determined by two methods: (*a*) by reaction with ferrous thiocyanate, using a colorimetric estimation of the ferric thiocyanate produced;[4] (*b*) by the modified iodine method of Dastur and Lea.[5] In general, the results of these methods were in good agreement, but in the case of oxidised ethyl linoleate the former method gave absurdly high values, equivalent to peroxide contents between 1 and 2 times higher than the total oxygen content. The origin of this discrepancy is unknown, and the iodine method has been assumed to give the correct result. Strong confirmation of this assumption is found in the close agreement of this value with (*a*) the total oxygen content, and (*b*) the active hydrogen value determined by a modified Zerewitinoff method.[6] Under the experimental conditions employed in the kinetic work, the first three olefins gave quantitative yields of hydroperoxide. The lower yield found in the case of squalene (see below) makes conclusions drawn from work on this olefin less certain.

Examination of the absorption spectra in the quartz U.V. region has shown [7] that oxidation of the linoleate and linolenate is accompanied by double bond displacement and the formation of conjugated materials. This displacement is confined to oxidised molecules, and it appears that the principal oxidation product of ethyl linoleate is a conjugated hydroperoxide (*e.g.* V).

V. $CH_3(CH_2)_4 . CH(OOH) . CH{=}CH . CH{=}CH . (CH_2)_7 . COO\ C_2H_5$.

Kinetic measurements were carried out on ca. 0·2 g. samples in small bulbs which were shaken sufficiently vigorously for the rate of oxidation to be independent of the rate of shaking. Oxygen uptake was measured by means of a thermostatted constant pressure gas burette, a pressure range of 5 to 750 mm. being employed. The reaction vessel was screened from light and separately thermostatted at 25°-75° C. Carefully purified ethyl stearate was employed as diluent when it was desired to examine the effect of olefin concentration.

(1) The Autoxidation of Ethyl Linoleate.

When pure ethyl linoleate was oxidised, the rate of reaction was found to be small initially and to increase linearly with the extent of oxidation as shown in the typical curves of Fig. 1. Neither the initial rate nor its dependence on extent of oxidation was significantly affected by (*a*) packing the pyrex reaction vessel with broken glass, (*b*) coating it completely with "polythene," or (*c*) replacing it by a silica vessel. It appears therefore that the overall oxidation is made up of two homogeneous reactions, of which the first depends only on olefin and oxygen, and the second involves catalysis by an oxidation product, which must almost certainly be the hydroperoxide. Except in the very early stages, only the catalytic oxidation is of importance, and we consider this first.

Systematic variation of the reactant concentrations showed that over a very wide range the rate of oxidation was represented by an equation of the form:

$$-\frac{d[O_2]}{dt} = k_3[RH][RO_2H]\phi(p) \quad . \quad . \quad . \quad (1)$$

where RH is written for the unoxidised olefin and RO_2H for the hydroperoxide. The form of the pressure variation $\phi(p)$ was less certainly

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[4] Bolland, Sundralingam, Sutton and Tristram, *I.R.I. Trans.*, 1941, **17**, 29.

[5] Dastur and Lea, *Analyst*, 1941, **66**, 90.

[6] Bolland, *I.R.I. Trans.*, 1941, **16**, 267.

[7] Bolland and Koch, *J. Chem. Soc.*, 1945, 445; Farmer, Koch and Sutton, *J. Chem. Soc.*, 1943, 541.

established, owing to the fact that oxygen pressure had scarcely any effect on the rate until pressures of less than 50 mm. were employed. The measured rates were consistent with the relationship :

$$\frac{1}{\phi(p)} = 1 + \lambda \frac{[RH]}{p} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The Mechanism of the Peroxide Catalysed Oxidation.

By analogy with other autoxidations [8] it was anticipated that this reaction would prove to be of chain character, and this has been shown to be the case by examination of the effects of inhibitors.[9] It is known that dibenzoyl peroxide readily decomposes thermally, producing free radical fragments which are able to initiate chain reactions.[10] A similar mechanism seemed likely to be responsible for the catalytic activity of the linoleate hydroperoxide, and confirmation of this view has been obtained in two ways : (a) by carrying out a parallel series of oxidations with benzoyl peroxide as catalyst (see below), and (b) by finding experimentally a correlation between the rate of autoxidation and the rate of decomposition of the hydroperoxide. The thermal decomposition of ethyl linoleate hydroperoxide has not yet been fully examined, but it has been shown that the reaction is of second order, *i.e.*

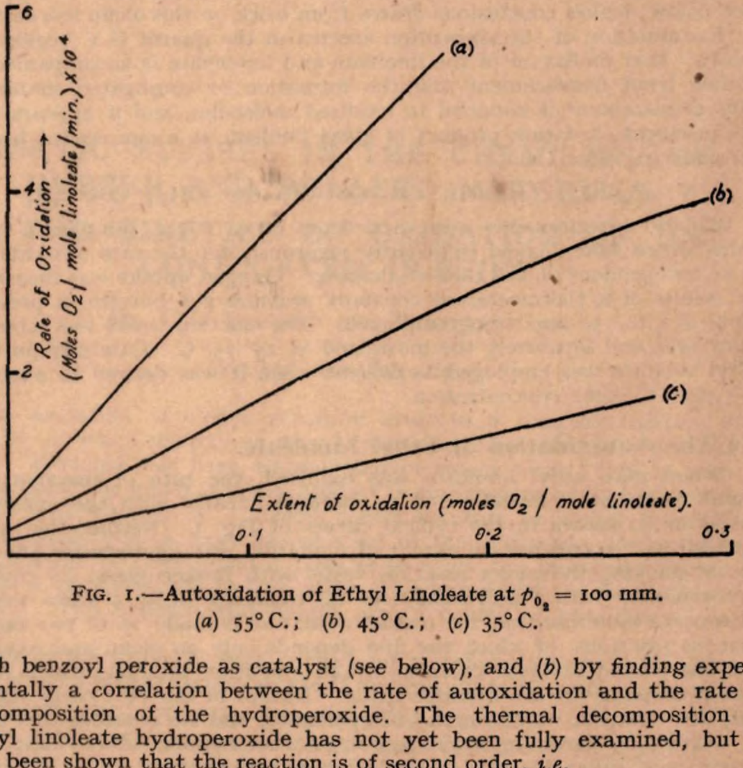

FIG. 1.—Autoxidation of Ethyl Linoleate at p_{O_2} = 100 mm.
(*a*) 55° C.; (*b*) 45° C.; (*c*) 35° C.

$$-\frac{d[RO_2H]}{dt} = k_1[RO_2H]^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The energy of activation E_1 calculated from the temperature dependence of k_1 is 26 k.cal.

Strong evidence as to the nature of the reaction chain is found in the observation already noted that oxidation of ethyl linoleate is accompanied

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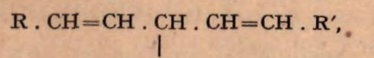
[8] *E.g.* Semenoff, *Chemical Kinetics of Chain Reactions*, Oxford, 1935.

[9] Bolland and ten Have, *unpublished work.*

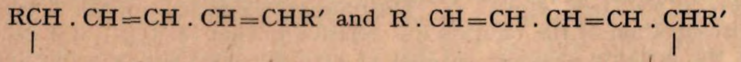
[10] Hey and Waters, *Chem. Rev.*, 1937, **21**, 169.

by double bond displacement. This is readily understood if one of the chain carriers is the free radical



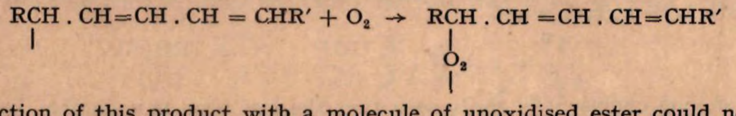
$$\mathrm{R\,.\,CH{=}CH\,.\,\underset{|}{CH}\,.\,CH{=}CH\,.\,R'},$$

since this radical will possess two other resonance hybrid configurations,



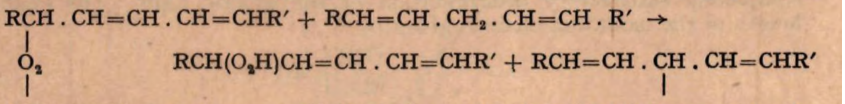
$$\mathrm{R\underset{|}{CH}\,.\,CH{=}CH\,.\,CH{=}CHR'} \text{ and } \mathrm{R\,.\,CH{=}CH\,.\,CH{=}CH\,.\,\underset{|}{C}HR'}$$

The existence of these three alternative forms gives rise to a large resonance stabilisation of this radical [11] and also permits the formation of isomeric peroxide radicals by attack of oxygen, *e.g.*



$$\mathrm{R\underset{|}{CH}\,.\,CH{=}CH\,.\,CH = CHR' + O_2 \rightarrow R\underset{\underset{|}{O_2}}{\underset{|}{CH}}\,.\,CH = CH\,.\,CH{=}CHR'}$$

Reaction of this product with a molecule of unoxidised ester could now give the observed hydroperoxide, with formation of a new free radical:



$$\mathrm{R\underset{\underset{|}{O_2}}{\underset{|}{CH}}\,.\,CH{=}CH\,.\,CH{=}CHR' + RCH{=}CH\,.\,CH_2\,.\,CH{=}CH\,.\,R' \rightarrow RCH(O_2H)CH{=}CH\,.\,CH{=}CHR' + RCH{=}CH\,.\,\underset{|}{CH}\,.\,CH{=}CHR'}$$

This reaction sequence, which is shown in the adjoining paper to be energetically reasonable, may be written formally:

$$\mathrm{R—} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{RO_2—}$$

$$\mathrm{RO_2—} + \mathrm{RH} \xrightarrow{k_3} \mathrm{RO_2H} + \mathrm{R—}$$

The initiation process, on this view, must be the production directly or indirectly of R— or RO_2— radicals by the decomposition of hydroperoxide. To conform with the results of the decomposition experiments this reaction must be of second order, with a velocity constant k_1:

$$2\mathrm{RO_2H} \xrightarrow{k_1} \mathrm{R—} + ?$$

In order to complete the reaction mechanism, we require to know how the chain carriers are destroyed. Since the overall rate is proportional to $[RO_2H]$ while the rate of initiation depends on $[RO_2H]^2$, it is easily seen that the termination must either involve (*a*) a hydroperoxide molecule and a free radical or (*b*) two free radicals. Of these alternatives the second is the one to be anticipated on chemical grounds, and is in fact the only one which is consistent with the results of benzoyl peroxide catalysed oxidation. There are three possible reactions of this type: *

$$2\mathrm{R—} \xrightarrow{k_4} \mathrm{R—R}$$

$$\mathrm{R—} + \mathrm{RO_2—} \xrightarrow{k_5} \mathrm{R—O—O—R}$$

$$2\mathrm{RO_2—} \xrightarrow{k_6} \mathrm{R—O—O—R} + \mathrm{O_2}$$

A complete kinetic analysis, allowing for all three termination reactions, gives no simple explicit rate equation. If (5) and (6) may be neglected. it is readily shown that

$$-\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = k_2(k_1/k_4)^{\frac{1}{2}}[\mathrm{RO_2H}]\,[\mathrm{O_2}] \quad . \quad . \quad . \quad (4)$$

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[11] Hückel, *Z. Elektrochem.*, 1937, 43, 841.

* The nature of the end products is of course not determinable by these experiments and may differ from that suggested here. Their concentration will in any case be very small if the chain length of the oxidation is long.

while if (4) and (5) are neglected, the rate equation is :

$$-\frac{d[O_2]}{dt} = k_3(k_1/k_6)^{\frac{1}{2}}[RO_2H]\,[RH] \quad . \quad . \quad . \quad (5)$$

Comparing the experimental equation (1) with (4) and (5) it will be observed that (1) reduces to (4) if p is small so that $\phi(p) \rightarrow p/\lambda[RH]$ and to (5) if p is large ($\phi(p) \rightarrow 1$). The physical significance of this is that the concentration of the radicals R— relative to that of RO_2— will decrease as the pressure increases, so that at high pressures the only termination reaction of any importance is that between two RO_2— radicals.

An approximate complete treatment is possible by assuming $k_5{}^2 \simeq k_4 k_6$ when it may be shown that an equation of the same form as (1) is found, with $k_a = k_3(k_1/k_6)^{\frac{1}{2}}$ and

$$\frac{1}{\phi(p)} = 1 + \frac{k_3}{k_2}\sqrt{\frac{k_4}{k_6}}\,\frac{[RH]}{[O_2]} + \frac{\sqrt{k_1 k_4}}{k_2}\,\frac{[RO_2H]}{[O_2]} \quad . \quad . \quad (6)$$

For long chains, it is easily seen that the last term is negligible, so that (6) is equivalent to (2). In other words, this reaction scheme leads to a completely satisfactory interpretation of the kinetic data. The chain length of the oxidation chain is given by

$$\nu = \frac{k_3}{\sqrt{k_1 k_6}}\,\frac{[RH]}{[RO_2H]}\,\phi(p) \quad . \quad . \quad . \quad . \quad (7)$$

With $[RH]/[RO_2H] = 10$, $\phi(p) = 1$, this gives $\nu \simeq 100$ at 45° C. Values calculated from this equation agree reasonably well with those obtained from the study of the effect of inhibitors.[9] No other sequence of reactions has been found which accounts satisfactorily for all the kinetic and chemical observations, and we therefore feel considerable confidence in employing this analysis to discuss the rates and energies of the elementary reactions.

Energies of Activation.

From the temperature dependence of the overall velocity constant k_a (at $p \rightarrow \infty$) we find an energy of activation $E_a = 17{\cdot}2$ k.cal. which, according to (5) is equal to $E_3 + \frac{1}{2}(E_1 - E_6)$. We have already noted that E_1, measured directly, is 26 k.cal., so that

$$E_3 - \tfrac{1}{2}E_6 = 4{\cdot}2 \text{ k.cal.} \quad . \quad . \quad . \quad . \quad (8)$$

Similarly, from the temperature dependence of λ, assuming a negligible heat of solution of oxygen, we find

$$E_\lambda = E_3 - E_2 + \tfrac{1}{2}(E_4 - E_6) \simeq 8{\cdot}7 \text{ k.cal.} \quad . \quad . \quad (9)$$

Combining (8) and (9) :

$$\tfrac{1}{2}E_4 - E_2 \simeq 4{\cdot}5 \text{ k.cal.} \quad . \quad . \quad . \quad . \quad (10)$$

Since reaction (4) involves two free radicals, E_4 must be small (say < 10), so that, even allowing for a rather large experimental error in E_λ, it is clear that $E_2 \sim 0$. The chemistry of reaction (6) is less clear, so that we can only conclude from (8) that $E_3 > 4$ k.cal.

(2) The Autoxidation of Ethyl Linolenate.

Much less complete data are available for ethyl linolenate, but they suffice to show that the general course of the reaction is identical with that found for ethyl linoleate. The overall energy of activation for the autocatalysed reaction is almost identical (17·5 k.cal.) and it appears unlikely that any serious differences between the two systems would be revealed by a more detailed analysis.

(3) Benzoyl Peroxide Catalysed Oxidations.

The rate of oxidation of all the olefins studied was found to be markedly increased in the presence of benzoyl peroxide. In order to study the kinetics of this reaction separately, it was necessary to deduct the contributions of the uncatalysed and autocatalysed reactions. The latter was readily eliminated by measuring the rate in presence of peroxide as a function of extent of oxidation, and extrapolating back to zero. In the case of methyl oleate, this gave at once the rate of the catalysed reaction, since the uncatalysed oxidation was negligibly slow under the conditions employed. The rate of the catalysed reaction was then found to be proportional to the square root of the benzoyl peroxide concentration, and almost independent of oxygen pressure down to 10 mm. Determination of the dependence on olefin concentration presented a slight difficulty, since the rate of oxidation of the solvent (ethyl stearate) was found to be not quite negligible in dilute solution ; the rate was, however, very nearly proportional to olefin concentration, so that we have

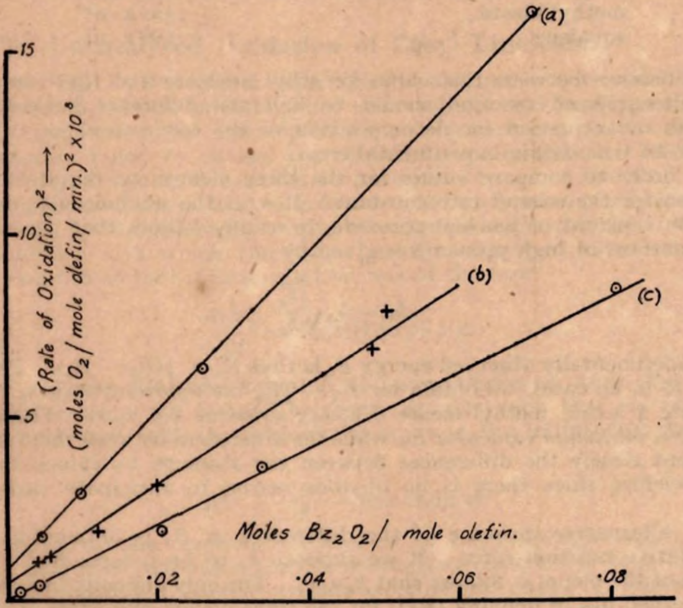

FIG. 2.—Benzoyl Peroxide Catalysed Oxidation of (*a*) ethyl linoleate at 45° C. ; (*b*) squalene at 45° C. ; (*c*) methyl oleate at 65° C. $p_{O_2} = 100$ mm.

$$-\frac{d[O_2]}{dt} = k_c[RH]\,[Bz_2O_2]^{\frac{1}{2}}\,\phi(p) \quad . \quad . \quad . \quad (11)$$

where $\phi(p) \simeq 1$ for methyl oleate.

In the other olefins, the uncatalysed rate was in general not negligible, and it was necessary to allow for it by means of a linear plot of $(\text{rate})^2$ against $[Bz_2O_2]$, *e.g.* in Fig. 2. The square root of the slope of this line gave the rate of the catalysed reaction, which was found to conform closely to equation (11).* For ethyl linoleate, $\phi(p)$ had the same form as in the autocatalysed reaction.

It is evident from a comparison of equations (1) and (11) that the rate equations of the autocatalysed and benzoyl peroxide catalysed

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* It is of interest to note that the benzoyl peroxide catalysed oxidation of cyclohexene has been studied by Medvedev (*Acta Physico Chimica U.R.S.S.*, 1938, **9**, 395). His results show the rate of oxidation to be very similar to that of methyl oleate under equivalent conditions. It appears probable from the fragmentary data available that the reaction is also kinetically similar to those we have studied, although Medvedev advances a different interpretation.

reactions differ only in the dependence on peroxide content. This difference finds a ready interpretation in the observation that the thermal decomposition of benzoyl peroxide is unimolecular, with an energy of activation of 30 k.cal.[12] Strong evidence of the identity of the chain sequences in the autocatalysed and benzoyl peroxide catalysed oxidations is found in the close agreement between the rates of oxidation of two samples of ethyl linoleate (*a*) autocatalysed, and (*b*) benzoyl peroxide catalysed, when the concentration of the two peroxides were such as to make their decomposition rates equal (at the same temperature).

The overall energies of activation found for the benzoyl peroxide catalysed oxidation (at $p \rightarrow \infty$) were :

ethyl linoleate	19·0 k.cal.
methyl oleate	23·0 k.cal.
squalene	21·8 k.cal.

The difference between this value for ethyl linoleate and that found for the autocatalysed reaction should be half the difference between the energies of activation for decomposition of the two peroxides ; this is seen to be true within experimental error.

In order to compare values for the three olefins, we require an expression for the overall rate constant. If k_7 is the unimolecular decomposition constant of benzoyl peroxide, it readily follows that the overall rate constant at high pressures is given by

$$k_c = k_3\sqrt{\frac{k_7}{k_6}} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The experimentally observed energy E_c is thus $E_3 + \frac{1}{2}(E_7 - E_6)$. Putting $E_7 = 30$ in all cases, we obtain for $E_3 - \frac{1}{2}E_6$ the following values : ethyl linoleate 4 k.cal., methyl oleate 8 k.cal., squalene 6·8 k.cal. These are, of course, *minimum* values for E_3, while the differences between them should represent closely the differences between the absolute E_3 values for the three olefins, since there is no obvious reason to anticipate variations in E_6.

An alternative estimate of the differences in E_3 is obtainable from the relative reaction rates. If we suppose k_6 to be independent of the nature of the olefin, it follows that $k_c \propto k_3$. The only difficulty in applying this method lies in defining [RH] for the three olefins, since this quantity is actually the concentration of readily removable hydrogen atoms. Assuming that the number of reactive methylene groups per molecule is 1 in ethyl linoleate,† 2 in methyl oleate and 12 in squalene, we find for the relative values of k_3 at 55° C. : methyl oleate 1, squalene 2·1, ethyl linoleate 24. If these differences arise solely from differences in E_3, we find

$$E_3 \text{ (oleate)} - E_3 \text{ (squalene)} = 0{\cdot}4$$
$$E_3 \text{ (oleate)} - E_3 \text{ (linoleate)} = 2{\cdot}2.$$

The significance of these energy differences will be discussed in the next paper.

(4) Nature of the Oxidation Product of Squalene.

The above discussion is based on the assumption of a quantitative yield of hydroperoxide, which does not appear to hold in the case of squalene. The peroxide yield found experimentally was of the order of 40 % and substantially independent of the extent of oxidation in the

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[12] McClure, Robertson and Cuthbertson, *Can. J. Res.*, *B*, 1942, **20**, 103.

† Only the most reactive are of course counted ; the effect of the less reactive groups flanking the diene system will be negligible.

range 0·7 % to 3 % oxygen by weight. This figure was confirmed by both methods of peroxide determination, but preliminary active hydrogen estimations suggest a value of the order of one active hydrogen per oxygen molecule introduced. This discrepancy might arise from a decomposition of hydroperoxide during the reaction, but two considerations make this rather unlikely: (1) the failure to find substantially higher peroxide yields at small extents of oxidation, and (2) the observation that the stability of the peroxide on heating in vacuum is of the same order as that of ethyl linoleate hydroperoxide. This difficulty remains to be resolved in the light of further experiment. The close parallelism between the kinetics of benzoyl peroxide catalysed oxidation of all the olefins studied, makes it appear extremely probable that the essential chain mechanism is formally the same for squalene as for the other olefins.

(5) The Uncatalysed Oxidation of Ethyl Linoleate.

Great difficulty was at first experienced in obtaining reproducible values for the initial rate of oxidation, but eventually it was found possible to purify a specimen of the ester by fractional chromatography until further fractionation failed to change the initial rate of oxidation. The main cause of the difficulty is believed to have been traces of free acid, since small additions of stearic acid were found to have a marked catalytic effect, apparently by accelerating the rate of peroxide decomposition. Within the accuracy with which the rather small uncatalysed rates could be measured, the empirical rate equation was of the form

$$-\frac{\mathrm{d}[\mathrm{O}_2]}{\mathrm{d}t} = k_u[\mathrm{RH}]^{3/2} p^{\frac{1}{2}} \phi(p), \quad . \quad . \quad . \quad (13)$$

where $\phi(p)$ was the same function of oxygen pressure as in the autocatalytic reaction. It is hard to resist the conclusion that we are concerned once more with the same chain sequence, but initiated in this case by

$$\mathrm{RH} + \mathrm{O}_2 \xrightarrow{k_8} \text{free radicals}$$

(the nature of this reaction is discussed in the following paper). The overall energy of activation for the uncatalysed reaction is equal to that of the autocatalysed reaction, within experimental error. It follows that $E_8 \simeq E_1 = 26$ k.cal.

Summary.

A brief review is given of kinetic work on the oxidation of representative mono, 1 : 4 and 1 : 5 olefins. The essential process in each case is identified as a chain reaction in which hydrocarbon radicals are formed, absorb oxygen, and then react with another molecule of olefin to give a hydroperoxide and a new free radical. Three methods of chain initiation are considered: (*a*) direct attack of oxygen on the olefin, (*b*) thermal decomposition of the hydroperoxide, (*c*) thermal decomposition of added benzoyl peroxide. Chain termination results from interaction of two free radicals; except at low oxygen pressures, these are both peroxidic.

KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS.

III. THERMOCHEMISTRY AND MECHANISMS OF OLEFIN OXIDATION.

By J. L. Bolland and Geoffrey Gee.

Received 28th July, 1945.

In the preceding paper we have considered the kinetics of oxidation of olefins under conditions such that a substantially quantitative yield of hydroperoxide is obtained, and have advanced a mechanism which accords satisfactorily with the experimental data. Part of our purpose in this paper is to show that all the elementary reactions involved in this scheme are thermochemically reasonable. Arising out of this discussion, an attempt is made to define the conditions under which such a reaction sequence will be abandoned in favour of alternatives leading to cyclic or polymeric peroxides, or to hydrocarbon polymers. The chemical evidence [1] suggests strongly that such alternative products are indeed formed in the oxidation of certain olefins, and that they appear to be primary products, and not merely the result of secondary changes of hydroperoxides. That secondary reactions do occur, and are of great importance as oxidation advances, is beyond question, but a consideration of the way in which these take place is outside the scope of the present paper.

The general method of argument followed in this paper is as follows. Suppose we have a series of structurally different olefins, A, B, . . . and that alternative reactions, α, β . . . are possible. For each alternative reaction of each olefin, the heat of reaction may be estimated: suppose these to be $\Delta H_{A\alpha}$, $\Delta H_{A\beta}$, $\Delta H_{B\alpha}$ . . . . These heats of reaction may be used in two ways: (i) If the energy of activation E is known from kinetic data, it is clear that we can exclude any mechanism for which $\Delta H > E$. (ii) In the absence of any kinetic evidence, it is not possible to argue that because $\Delta H_\alpha > \Delta H_\beta$, reaction β will necessarily be preferred to α. If, however, we compare the values of ΔH_α for a series of olefins, there is good reason to expect that the energies of activation for path α will lie in the same order as the heats of reaction, so that the absolute rates of reaction should be in the reverse order. Similarly the reactivities by path β can be arranged in order. If the actual order of reactivities of the series is known experimentally, comparison with the theory provides evidence as to the actual reaction mechanisms.

The estimation of heats of reaction involves the algebraic summation of the formal strengths of the bonds broken and formed, with corrections for the estimated resonance energies of reactants and products. Except in the final section, we have made no attempt to introduce the effects of hyperconjugation and we consider in the main only three types of olefin: mono-, 1 : 3 di-, and 1 : 4 di-olefins. To this approximation, double bonds separated by more than one saturated carbon are regarded as isolated. The effects of substituents are only referred to in the last section. The following bond strengths have been employed: C—C, 81 k.cal.; [2] C=C, 145 k.cal.; [2] C—O, 87 k.cal.; [3] C=O, 174 k.cal.; [2]

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[1] Farmer, *I.R.I. Trans.*, *in press*; paper contributed to this meeting.

[2] Values from Pauling, *Nature of the Chemical Bond*, recalculated on the basis of Kynch and Penney's value of 168·6 k.cal. for the sublimation energy of carbon (*Proc. Roy. Soc., A*, 1941, **179**, 214).

[3] Baughan, Evans and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377.

C—H, 99 k.cal. ;[4] O=O (oxygen molecule), 118 k.cal. ; O—O (peroxide), 66 k.cal. ; O—H, 110 k.cal. The only one of these calling for comment is the O—O bond strength in peroxides, for which data in the literature are extremely inconsistent, ranging from 32 k.cal. (from the activation energy of diethyl peroxide decomposition[5]) to ca. 57 k.cal. (from the heats of combustion of ethyl and propyl hydroperoxide and diethyl peroxide[6]). In order to obtain a more direct estimate of the O—O bond strength in hydroperoxides, the heats of oxidation of ethyl linoleate and linolenate have been measured calorimetrically. The experimental data set out in the next section lead to the figure (66 k.cal.) used in this paper.

The Heats of Oxidation of Ethyl Linoleate and Linolenate.

The adiabatic calorimeter constructed of pyrex to the design indicated in Fig 1 consisted of a 15 c.c. vacuum-jacketed bulb connected through a length of Thiokol tubing to a pumping system and a constant pressure gas burette. Single copper-constantan (32 SWG) thermocouples in series with a Tinsley taut suspension galvanometer (resistance 10 ohms, sensitivity 180 mm. per microamp.) served to indicate any difference in temperature between the contents of the calorimeter and the surrounding water bath. Heat losses along the leads of the resistance heater (ca. 30 ohms), *H*, were prevented by means of the mercury contact cups, *C*.

About 7 c.c. ester was used for each determination. A suitable rate of oxygen uptake (here, 0·1 to 1×10^{-5} mole. O_2/min.) was arranged for by preliminary autoxidation or addition of benzoyl peroxide. After thermal equilibrium (as indicated by the galvanometer) had been established between the inside and outside of the calorimeter at about 40° C. oxygen at about atmospheric pressure was admitted ; rapid mechanical shaking of the calorimeter ensured mixing of ester and oxygen ; isothermal conditions inside and outside the calorimeter were maintained (to within 0i·02° C.) by means of manually-controlled resistance heaters immersed in the outer bath. Concurrent measurements were made of the temperature of the outer bath (using a Beckmann thermometer) and the oxygen uptake. Satisfactorily linear plots of these two measured quantities were in every case obtained throughout a temperature rise of at least 5° C. The apparent heat capacity of the calorimeter in this temperature range was determined from the energy which had to be passed through *H* to give a very similar rate of temperature rise in the calorimeter. While this procedure

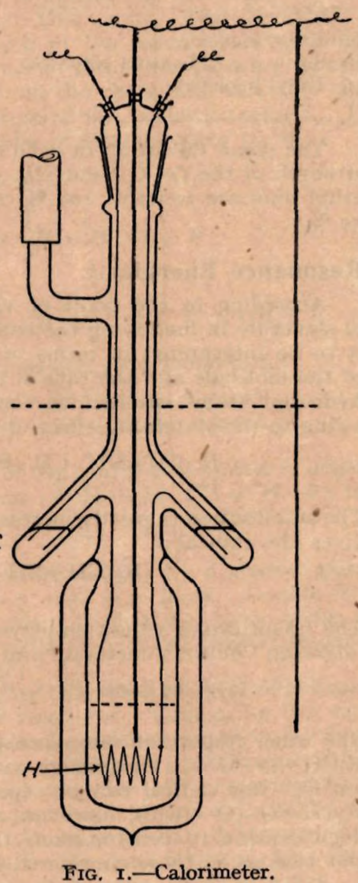

FIG. 1.—Calorimeter.

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[4] Baughan, *Nature*, 1941, **147**, 542.

[5] Harris and Egerton, *Proc. Roy. Soc.*, *A*, 1938, **168**, 1.

[6] Stathis and Egerton, *Trans. Faraday Soc.*, 1940, **35**, 606.

should eliminate errors due to conduction heat losses, it may be noted that even for this unrefined design of calorimeter direct experimental determination of the total heat losses showed that they were in any case less than 1 % of the heat evolved by the oxidation.

The final results obtained for the heat of oxidation of ethyl linoleate and linolenate are summarised below.

	No. of Determinations.	Mean $-\Delta H$ k.cal.	D_{O-O} k.cal.
(*a*) Ethyl linoleate . . .	5	53·3	66
(*b*) do. + 0·4 % benzoyl peroxide .	2	52·5	65
(*c*) Ethyl linolenate . . .	3	52·0	68

The mean deviation in each series was of the order of 1 k.cal. The strength of the O—O bond (D_{O-O}) is calculated * on the assumption that ethyl linoleate contains 100 % conjugated isomers [7] and ethyl linolenate 50 %.[8]

Resonance Energies.†

According to the point of view developed in this paper, the effect of structure in modifying the reactivities of a series of related compounds is to be interpreted in terms of its effect on the resonance possibilities of the molecule and the radical derived from it. Thus in a mono-olefin, hydrogen atoms situated on the α-carbon atom are particularly labile, owing to the stabilising effect of the resonance energy in the allyl radical

$$\mathrm{R\,.\,CH{=}CH\,.\,\underset{|}{CH}\,.\,R'} \rightleftharpoons \mathrm{R\,.\,\underset{|}{CH}{-}CH{=}CH\,.\,R'}$$

The stabilisation is greatly increased in a 1 : 3 or 1 : 4 diene, either of which gives the radical :

$$\mathrm{R\,.\,CH{=}CH\,.\,CH{=}CH\,.\,\underset{|}{CH}\,.\,R'}.$$

The quantitative values employed here have been re-calculated by Orr, following Coulson's method,[9] and are as follows :—

$$\mathrm{C{=}C{-}C{=}C}\ 6{\cdot}9\ \text{k.cal.},\quad \mathrm{C{=}C{-}\underset{|}{C}}\ 18{\cdot}7\ \text{k.cal.},\quad \mathrm{C{=}C{-}\underset{|}{C}{-}C{=}C}\ 30{\cdot}4\ \text{k.cal.}$$

The other important resonance possibility is that in a peroxide radical $R_2CH—O—O—$. By analogy with Pauling's treatment [10] of the peroxide ion O_2^- this radical can be represented with a three electron bond, as $R_2CH—O—O—$ with, however, a charge displacement. In view of this displacement, it seems unlikely that the bond can be nearly so strong in this case as in those considered by Pauling, in which the three electron

[7] Bolland and Koch, *J. Chem. Soc.*, 1945, 445.

[8] Farmer, Koch and Sutton, *ibid.*, 1943, 541.

[9] Coulson, *Proc. Roy. Soc.*, *A*, 1938, **164**, 323.

[10] Pauling, *Nature of the Chemical Bond*, Cornell, 1940.

* If $D_{\alpha-\beta}$ is the strength of the bond $\alpha-\beta$, the heat of oxidation is given by

$$\Delta H = D_{C-H} + D_{O_2}\ \text{molecule} + \Delta H_S - D_{C-O} - D_{O-O} - D_{O-H} - E_{res.}$$

where ΔH_S is the heat of solution of oxygen and $E_{res.}$ is the increased resonance energy of the hydrocarbon resulting from any double bond displacement, *e.g.* for ethyl linoleate we have :

$$-53 = 99 + 118 + 0 - 87 - D_{O-O} - 110 - 7$$

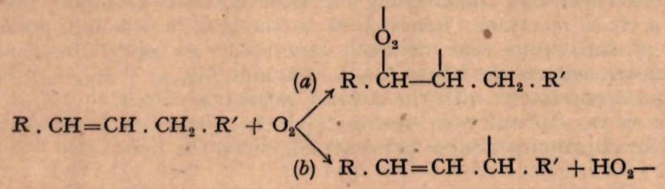
whence $D_{O-O} = 66$ k.cal.

† We are indebted to Dr. W. J. C. Orr for helpful suggestions concerning this section, and for permission to employ his revised figures.

bond is taken to make a contribution equal to one-half the single bond strength. Thus, instead of assuming a resonance stabilisation of the radical of some 30 k.cal., we have quite arbitrarily taken 15 k.cal. as a more probable estimate. In point of fact, none of the conclusions drawn below are seriously influenced by the value chosen.

The Point of Oxidative Attack in Olefins.

There are two possible sites for oxidative attack; the double bond, and an active methylene group. In cases where a very high yield of α-methylenic hydroperoxide is obtained, it appears at first sight that the primary attack of oxygen must be at this point. This argument is certainly invalid unless the chain length of the oxidation is extremely short. Where a chain length of the order of 100 is found (as *e.g.* in ethyl linoleate) 99 % of the peroxide arises from the chain, and therefore gives no indication whatsoever as to the nature of the primary product. The most likely formulations of the two modes of attack appear to be



$$\mathrm{R\,.\,CH{=}CH\,.\,CH_2\,.\,R' + O_2} \begin{cases} (a)\ \mathrm{R\,.\,\overset{\overset{|}{O_2}}{\overset{|}{C}}H{-}\overset{|}{C}H\,.\,CH_2\,.\,R'} \\ (b)\ \mathrm{R\,.\,CH{=}CH\,.\,\overset{|}{C}H\,.\,R' + HO_2{-}} \end{cases}$$

The estimated heats of these two reactions are, for a mono-olefin :

$$\Delta H_a = 145 + 118 - 81 - 87 - 66 - 15 = 14 \text{ k.cal.}$$
$$\Delta H_b = 99 + 118 - 19 - 110 - 66 - 15 = 7 \text{ k.cal.}$$

For a 1 : 3 di-olefin, attack at one end of the conjugated system is assisted by the development of allyl resonance $-\underset{\underset{|}{O_2}}{\underset{|}{C}H}-\underset{|}{C}H\,.\,CH{=}CH-$so that $\Delta H_a = 14 - 19 + 7 = 2$ k.cal.

The alternative path is also somewhat assisted by a greater gain of resonance energy: $\Delta H_b = 7 + 19 + 7 - 30 = 3$ k.cal. Double bond attack in a 1 : 4 di-olefin will be equivalent to that in a mono-olefin, but α-methylenic attack will be easier by virtue of 11 k.cal. greater resonance energy in the radical ($\Delta H_b = -4$ k.cal.).

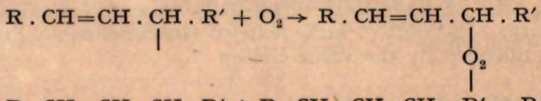
All of these reactions have heats lying below the energies of activation found experimentally, so none can be ruled out. Comparing the values found for the various olefins we note that the order of reactivity by double bond attack is 1 : 3 > mono- or 1 : 4; while for α-methylenic attack, 1 : 4 > 1 : 3 > mono. These two reaction paths are not mutually exclusive and in principle we should expect both to proceed side by side, with one more or less predominant. An experimental determination of the absolute rates of the primary steps for the three types of olefin should throw light on the relative importance of the two reaction paths. Experimental work on this problem is now in progress, but is rendered very difficult by the smallness of the rates to be observed, and the relatively large disturbing influence of even small amounts of impurity.

The Nature of the Peroxides.

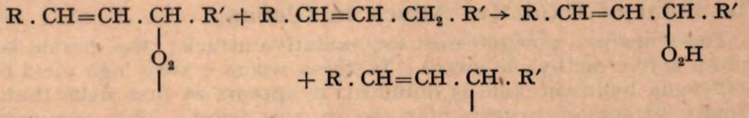
In addition to α-methylenic hydroperoxides, oxidation frequently leads to peroxides of polymeric character,[1] whose structure is less certain, but which appear to be relatively stable. Cyclic peroxides are also known, *e.g.* ascaridol, and are apparently formed directly in the oxidation of anthracenes.[11] We have therefore to consider how the various forms of peroxide can arise during the course of the oxidative chain reaction.

[11] Dufraisse, *Bull. Soc. Chim. France*, 1939, [5], **6**, 422.

The kinetic evidence of the previous paper led to the view that hydroperoxides arise from the following chain cycle :

(c) 

$$\mathrm{R\,.\,CH{=}CH\,.\,\underset{|}{CH}\,.\,R' + O_2 \rightarrow R\,.\,CH{=}CH\,.\,\underset{\underset{\underset{|}{O_2}}{|}}{CH}\,.\,R'}$$

(d) 

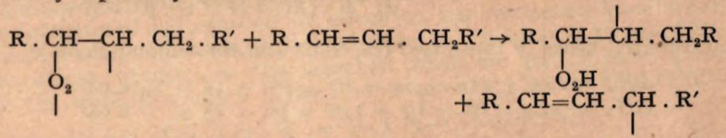
$$\mathrm{R\,.\,CH{=}CH\,.\,\underset{\underset{\underset{|}{O_2}}{|}}{CH}\,.\,R' + R\,.\,CH{=}CH\,.\,CH_2\,.\,R' \rightarrow R\,.\,CH{=}CH\,.\,\underset{\underset{O_2H}{|}}{CH}\,.\,R' + R\,.\,CH{=}CH\,.\,\underset{|}{CH}\,.\,R'}$$

Estimation of the heats of these reactions for the three types of olefins gives :

	mono-	1 : 3	1 : 4
ΔH_c	-31	-27*	-27*
ΔH_d	-15	-19	-26

These steps are clearly all so strongly exothermic as to be highly probable steps in a chain reaction. Reaction (*d*) is the one for which approximate energies of activation were deduced kinetically for ethyl linoleate and methyl oleate, the results being $E_{\mathrm{lin}} > 4{\cdot}2$, and $E_{\mathrm{oleate}} - E_{\mathrm{lin}} \simeq 4$, which appear quite consistent with the present estimates of ΔH.

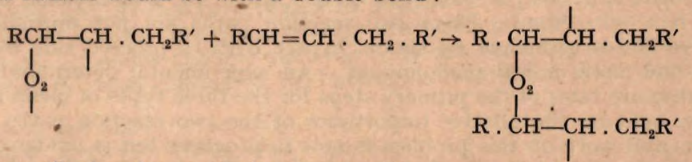
There is no difficulty in seeing how the chain (*c*) + (*d*) could be initiated by a primary double bond attack, since the reaction

(e) 

$$\mathrm{R\,.\,\underset{\underset{\underset{|}{O_2}}{|}}{CH}{—}\underset{|}{CH}\,.\,CH_2\,.\,R' + R\,.\,CH{=}CH\,.\,CH_2R' \rightarrow R\,.\,\underset{\underset{O_2H}{|}}{CH}{—}\overset{|}{CH}\,.\,CH_2R + R\,.\,CH{=}CH\,.\,\underset{|}{CH}\,.\,R'}$$

would have the same heat of reaction as (*d*). Thus the reaction scheme put forward in the previous paper is completely satisfactory thermochemically. Taken in conjunction with its complete agreement with the chemical, spectroscopic and kinetic evidence, this affords valuable confirmation of its probable correctness.

We now wish to show how alternative reactions of the radicals which participate in this scheme can lead to different final products. Except at low pressures, the chain length of all the oxidation chains discussed in the previous paper is determined by the relative rates at which $\mathrm{RO_2}$— radicals react (*a*) with a molecule of olefin and (*b*) with other $\mathrm{RO_2}$— radicals. Just as oxygen might attack either a double bond or an active methylene group, so it is to be anticipated that a further possible reaction of a peroxide radical would be with a double bond :

(f) 

$$\mathrm{R\underset{\underset{\underset{|}{O_2}}{|}}{CH}{—}\underset{|}{CH}\,.\,CH_2R' + RCH{=}CH\,.\,CH_2\,.\,R' \rightarrow R\,.\,\underset{\underset{\underset{\underset{R\,.\,CH—\underset{|}{CH}\,.\,CH_2R'}{|}}{O_2}}{|}}{CH}{—}\overset{|}{CH}\,.\,CH_2R'}$$

The free radical ends would then react with oxygen (as in (*c*)) producing further peroxide radicals which could again add olefin, thus building up a polymeric chain in which the repeating unit is

$$\mathrm{—CH(CH_2R')\,.\,\underset{|}{C}HR\,.\,O_2—}$$

In the case of a conjugated olefin, addition could also take place across the terminal carbons of the system, giving

$$\mathrm{—[CHR\,.\,CH{=}CH\,.\,CHR'\,.\,O_2]_n—}$$

Estimation of the heat of reaction ΔH_f for various olefins gives : mono-, -8 ; 1 : 3, -20 ; 1 : 4, -8. This step is alternative to (*e*) and

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* Assuming the peroxide radical to be conjugated.

it is clear that the probability of a polymeric chain will be highest for conjugated olefins and least for 1 : 4 dienes : it is in very satisfactory agreement with this conclusion that it is in fact conjugated olefins which display a high tendency to yield polymeric peroxides, while ethyl linoleate and methyl oleate have been found to give quantitatively hydroperoxide.

Reaction (*f*) represents the formation of polymer from a peroxide radical derived by double bond attack, but it is clear that a similar reaction could occur, with the same ΔH, with an α-methylenic peroxide radical. Hence, even in a reaction chain leading normally to hydroperoxide, occasional linking of two or more molecules can occur by this mechanism. Conversely, at any stage of the polymerisation, growth of the polymer can be terminated by the intervention of reaction (*e*). It is important to note that this would not constitute a termination reaction in the kinetic sense, since the number of free radicals remains unchanged. Reaction (*e*) in this way would function as a " transfer " reaction,[12] and the kinetic chain length could be considerably greater than the average degree of polymerisation. Although we have at present no kinetic data for conjugated systems, the relatively low molecular nature of the polymers reported [1] suggests that this may well be the case.

It is interesting to compare the kinetics of a chain leading to hydroperoxide with those of a polymeric chain of the type suggested here. This kinetic problem can be treated very simply on the assumption that the reactivities of radicals are independent of the size of polymer to which they are attached. Formally the reaction sequence may then be written (with RH for the olefin, R— for any hydrocarbon radical and RO_2— for any peroxide radical) :

$$\mathrm{RH} + \mathrm{O_2} \xrightarrow{k_8} \mathrm{R}\text{—} + \mathrm{RO_2}\text{—}\ (i.e.\ \text{—}\mathrm{RHO_2}\text{—})$$

$$\mathrm{R}\text{—} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{RO_2}\text{—}$$

$$\mathrm{RO_2}\text{—} + \mathrm{RH} \xrightarrow{k_9} \mathrm{R}\text{—}$$

$$2\mathrm{RO_2}\text{—} \xrightarrow{k_6} \text{stable products}$$

. . . .

$$\mathrm{RO_2}\text{—} + \mathrm{RH} \xrightarrow{k_3} \mathrm{RO_2H} + \mathrm{R}\text{—}.$$

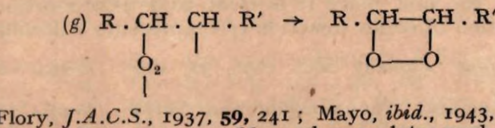
Reactions (8), (2), (9) and (6) form the polymerisation chain ; (3) a reaction, alternative at any stage to (9), which yields hydroperoxide. By writing down stationary state equations for the total concentration of the two types of free radicals, it is readily shown that,

$$-\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = (k_3 + k_9)(2k_8/k_4)^{1/2}[\mathrm{RH}]^{3/2}[\mathrm{O_2}]^{1/2}$$

$$\frac{\mathrm{d}[\mathrm{RO_2H}]}{\mathrm{d}t} = k_3(2k_8/k_4)^{1/2}[\mathrm{RH}]^{3/2}[\mathrm{O_2}]^{1/2}.$$

The conclusion is that reactions leading to hydroperoxide and to polymer would be kinetically indistinguishable.

One other type of peroxide which should be considered is a cyclic structure, forming a ring of either 4 or 6 members. The former, which has been widely suggested [13] could readily arise from cyclisation of the primary peroxide radical :

(*g*)


$$\underset{\substack{|\\ \mathrm{O_2}\\ |}}{\mathrm{R\,.\,CH}}\,.\,\underset{|}{\mathrm{CH}}\,.\,\mathrm{R'} \rightarrow \mathrm{R\,.\,CH}\text{—}\mathrm{CH\,.\,R'}\ (\text{O—O ring})$$

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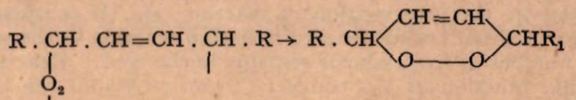
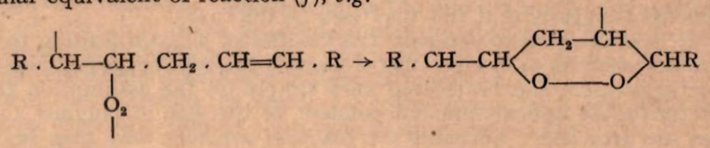
[12] Flory, *J.A.C.S.*, 1937, **59**, 241 ; Mayo, *ibid.*, 1943, **65**, 2324.

[13] Engler, *Ber.*, 1897, **30**, 1669, and many later workers.

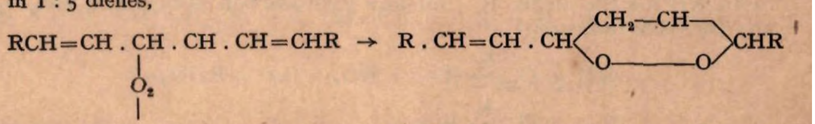
Although this reaction would be strongly exothermic ($\Delta H_g \simeq -70$) at least two factors militate against its importance (i) the geometrical improbability of 4 membered rings [14] and (ii) the great ease with which the hydrocarbon radical reacts with oxygen. It is doubtful whether peroxides of this structure would be isolable, even if formed, since it is easily shown that the simultaneous rupture of C—C and O—O bonds to give RCHO + R′CHO would be exothermic by some 27 k.cal. Scission reactions based on the breakdown of such rings have been suggested.[15] Stable six membered rings might well be formed by this process from conjugated di-olefins, particularly at low oxygen pressures and in dilute solution, so that competing reactions are retarded :

(h)  ($\Delta H_h = -53$)

Less facile ring closure reactions are also to be expected from an intramolecular equivalent of reaction (*f*), *e.g.*

(*i*) 

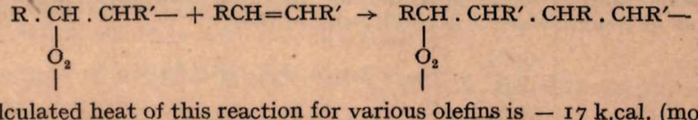
or, in 1 : 5 dienes,

(*j*) 

The relative importance of these various processes is at present completely unknown.

Hydrocarbon Polymers.

Another possibility to be borne in mind in considering the oxidation of olefins is that of the production of hydrocarbon polymers, for which oxygen is known to be a catalyst. Hitherto, we have in effect assumed that every hydrocarbon free radical produced reacts with oxygen. Clearly an alternative to this is an addition of the radical at a double bond, the typical chain propagation step in olefin polymerisation, *e.g.*

(*k*) 

$$\underset{\substack{|\\O_2\\|}}{\mathrm{R\,.\,CH}}\mathrm{\,.\,CHR'—} + \mathrm{RCH{=}CHR'} \rightarrow \underset{\substack{|\\O_2\\|}}{\mathrm{RCH}}\mathrm{\,.\,CHR'\,.\,CHR\,.\,CHR'—}$$

The calculated heat of this reaction for various olefins is − 17 k.cal. (mono- or 1 : 4), − 10 k.cal. (1 : 3). Its exothermic character means that it will always be a possibility to be seriously considered, particularly at low oxygen pressures.

It is to be noted that an α-methylenic free radical is much less likely to promote polymerisation, the estimated heats of reaction for addition to a double bond being 2 k.cal. (mono-), 1 k.cal. (1 : 3) and 6 k.cal. (1 : 4).

The inter-relation between the chain processes leading respectively to polymeric peroxide and to hydrocarbon polymer suggests some interesting possibilities. In the first place it is clear that incorporation of oxygen followed by addition of olefin (reaction (*f*)) represents a double step which

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[14] Salamon, *Trans. Faraday Soc.*, 1936, **32**, 160 ; Treolar, *Proc. Physic. Soc.*, 1943, **55**, 345.

[15] Farmer, Bloomfield, Sundralingam and Sutton, *Trans. Faraday Soc.*, 1942, **38**, 348. *Cf.* also refs. 1 and 16.

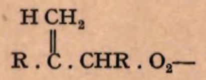
is substantially equivalent to reaction (*k*) and gives a similar free radical. It follows that the two alternative processes can proceed consecutively, giving rise to a range of polymers whose oxygen content will be determined by the oxygen pressure. This dual polymerisation will be interrupted if at any stage the peroxide radical reacts by path (*e*), thus terminating the polymer growth by the formation of a hydroperoxide end. The possibilities thus envisaged do not appear to have been seriously investigated. Although Medvedev and Zeitlin[16] have shown the production of a considerable amount of high polymer to accompany the thermal oxidation of styrene, they unfortunately do not report the effect of oxygen pressure on either the yield or oxygen content of the polymer.

The Oxidation of Polyisoprenes.

To the approximation employed above, polyisoprenes are treated as assemblies of isolated double bonds. Since the ultimate objective of our work is the understanding of polyisoprene oxidation, it is desirable to discuss this system in a little more detail. The essential reactive system is a methyl substituted 1 : 5 diene unit :

$$\mathrm{RCH_2\,.\,C(CH_3)\,:\,CH\,.\,(CH_2)_2\,C(CH_3)\,:\,CH\,.\,CH_2R.}$$

The reactivity to oxygen or peroxide radicals of the double bonds in any olefin will be enhanced by methyl substitution on the double bond, owing to stabilisation of the resulting radicals by the contribution of such forms as :



$$\mathrm{R\,.\,\overset{\overset{H\,CH_2}{\|}}{C}\,.\,CHR\,.\,O_2—}$$

Two consequences may be expected to follow : (i) an increased rate of oxidation, and (ii) a greater tendency to polymer formation, as compared with the unsubstituted olefin. We have at present no experimental data bearing directly on this point.

Strong evidence has also been advanced[17] in support of the view that the central bond in 1 : 5 diene systems is considerably strengthened by a hyperconjugation involving the two methylene groups. This would tend to reduce the α-methylenic reactivity of the molecule, but since similar possibilities exist in the α-methylenic radicals, it is difficult to predict the resultant effects.

Comparing squalene with a typical mono-olefin, methyl oleate, there is some indication both of increased oxidisability and of greater ease of polymerisation.

Summary.

A new estimate of the O—O bond strength in hydroperoxides is reported, based on a determination of the heats of oxidation of ethyl linoleate and linolenate.

This value is employed, together with other known bond strengths and resonance energies, to estimate the heats of a number of alternative oxidation reactions of olefins. By considering the effects of the olefin structure on these heats of reaction, it is possible to see how structural differences can lead to the formation of different oxidation products. The discussion is confined to primary products of the oxidation chain, but even so a considerable diversity of behaviour is shown to be possible. The final material may include simple monomeric hydroperoxides, polymers

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[16] Medvedev and Zeitlin, *Acta Physicochimico U.R.S.S.*, 1945, **20**, 3.

[17] 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. Jeffrey, *Nature*, 1945, **156**, 82.

with varying amounts of oxygen incorporated in the chain, cyclic peroxides, and scission products. The very limited experimental evidence available falls generally into line with expectation.

The work described in this and the preceding paper 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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