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KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS

1. THE THERMAL OXIDATION OF ETHYL LINOLEATE

By

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Kinetic studies in the chemistry of rubber and related materials

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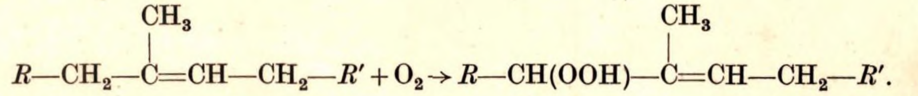
The kinetics of the initial stages of the thermal oxidation of ethyl linoleate (by molecular oxygen) have been investigated in the temperature range 35–75° C. From consideration of chemical and kinetic evidence the reaction mechanism has been established: oxidation chains are initiated by thermal decomposition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

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-methylenic 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:



$$R\text{—}CH_2\text{—}\overset{\displaystyle CH_3}{\overset{|}{C}}=CH\text{—}CH_2\text{—}R' + O_2 \rightarrow R\text{—}CH(OOH)\text{—}\overset{\displaystyle CH_3}{\overset{|}{C}}=CH\text{—}CH_2\text{—}R'. \qquad (1)$$

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):

$$CH_3(CH_2)_4 . CH=CH\text{—}CH_2\text{—}CH=CH\text{—}(CH_2)_7 . COOEt. \qquad (I)$$

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 ± 0·1° 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 $< 0{\cdot}01$ %, 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 ± 0·1° 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 ± 0·01° 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 ×), 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

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* 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 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.

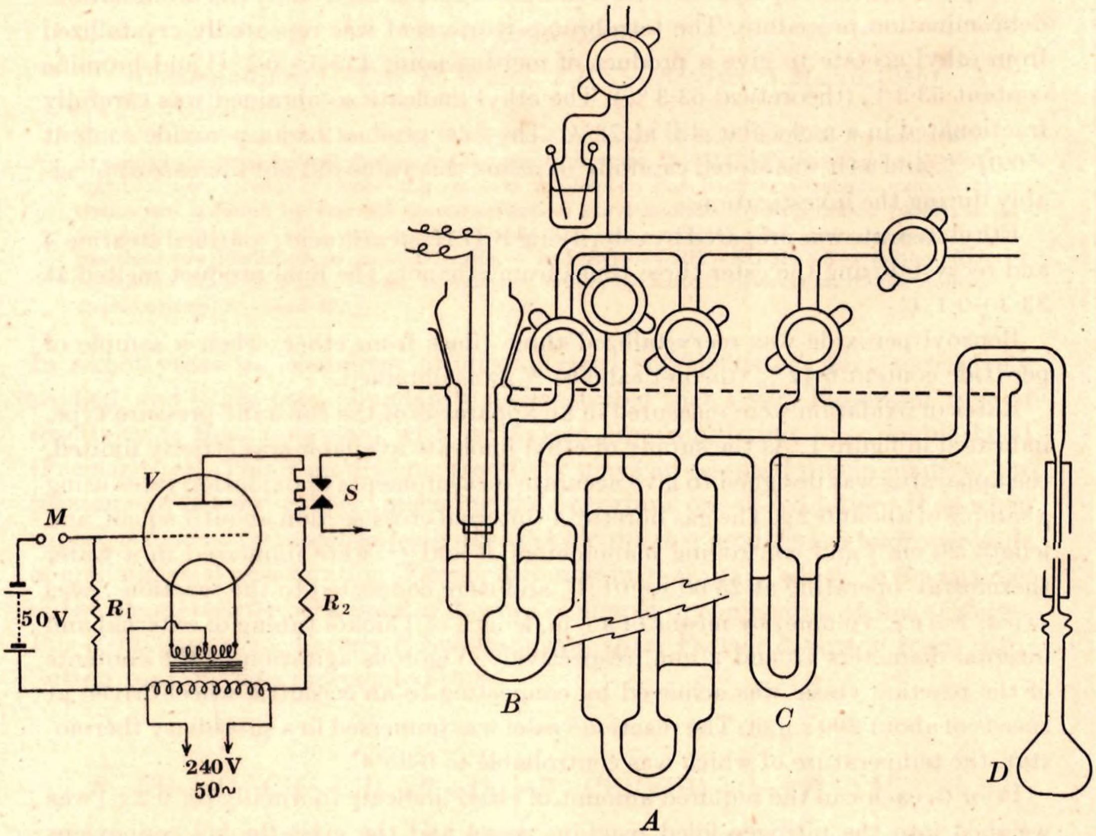


FIGURE 1. Apparatus for measuring rates of oxidation and circuit of electronic relay. V represents a PX4 valve, S a Sunvic hot-wire vacuum switch (type 602V), M the contacts in the manometer, C and R_1 and R_2 resistances of 5 megohms and 5000 ohms respectively.

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.

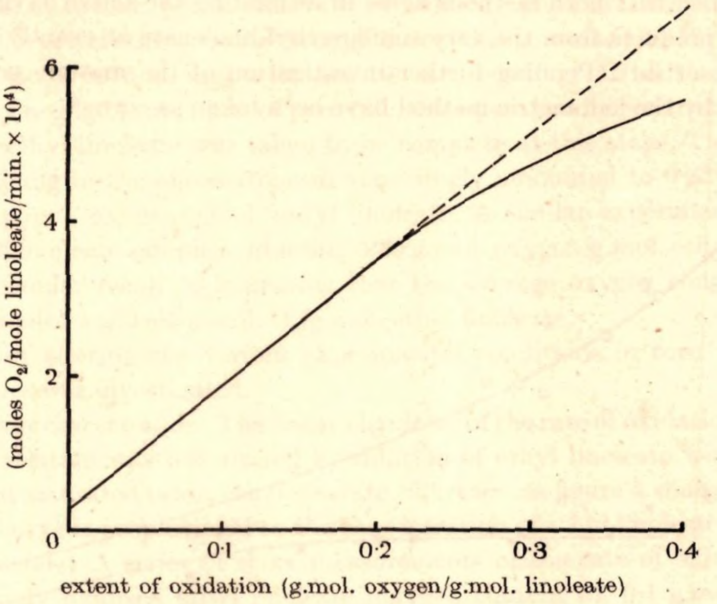


FIGURE 2. Oxidation of ethyl linoleate at 25° C and 100 mm. oxygen pressure.

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 correspond 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.

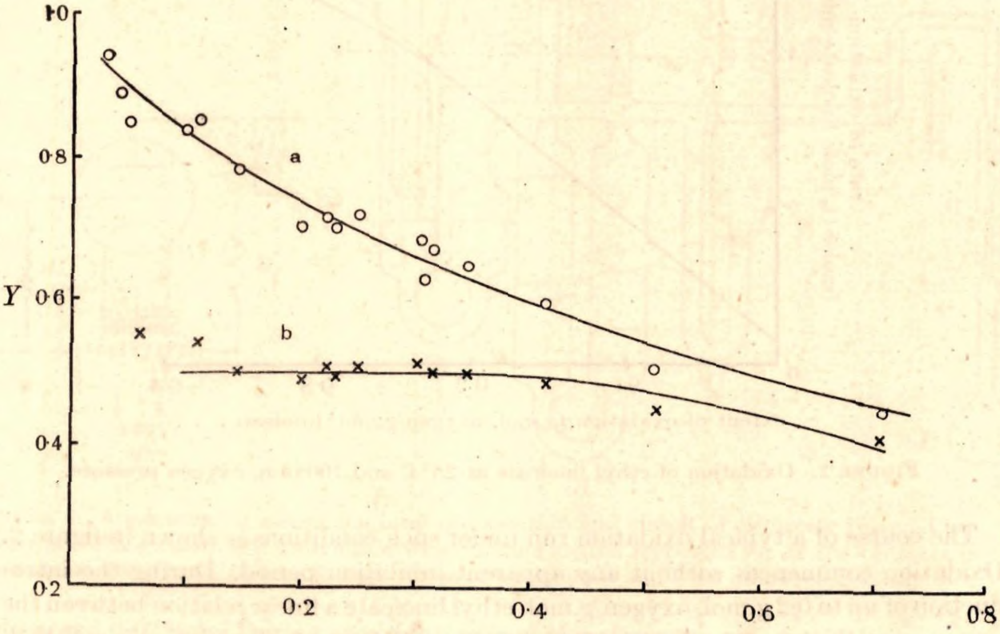


FIGURE 3. Determination of peroxide content of oxidized ethyl linoleate. Y represents the fraction of oxygen atoms in oxidation products active in oxidation of ferrous ion (curve a) and KI (curve b).

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. O_2/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

$$(\text{Rate})_0 = 1{\cdot}20 \times 10^{-3}[C]^{\frac{1}{2}} + 0{\cdot}30 \times 10^{-4}, \tag{2}$$

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

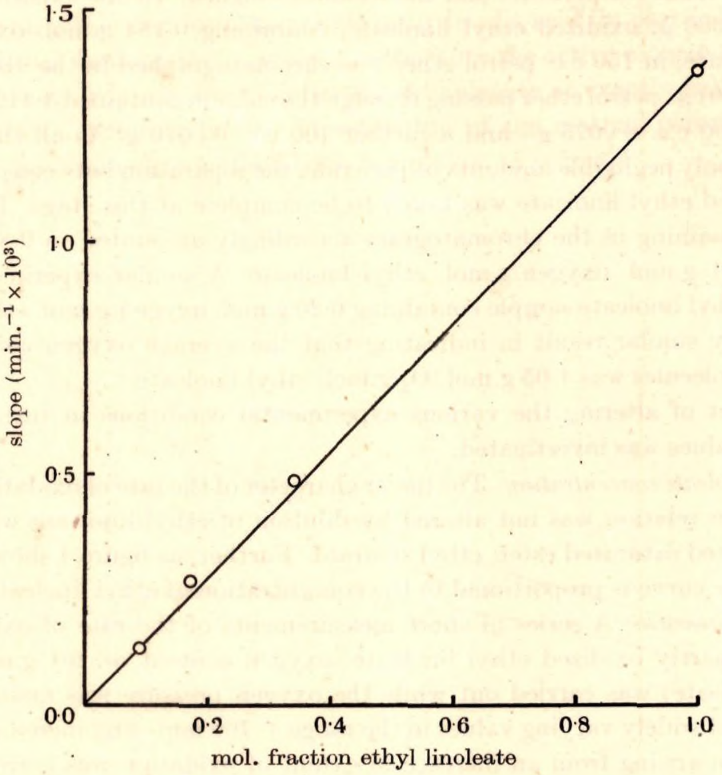


FIGURE 4. Dependence of rate of oxidation on concentration of ethyl linoleate at 45° C and 100 mm. oxygen pressure.

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 $1{\cdot}50 \times 10^{-4}$ (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.

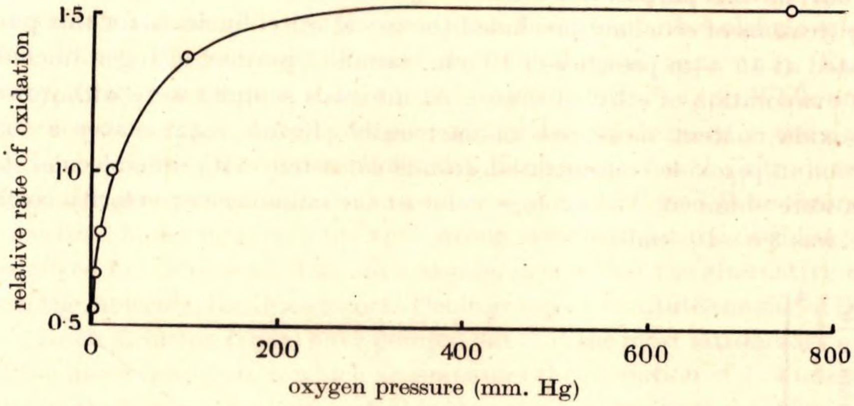


FIGURE 5

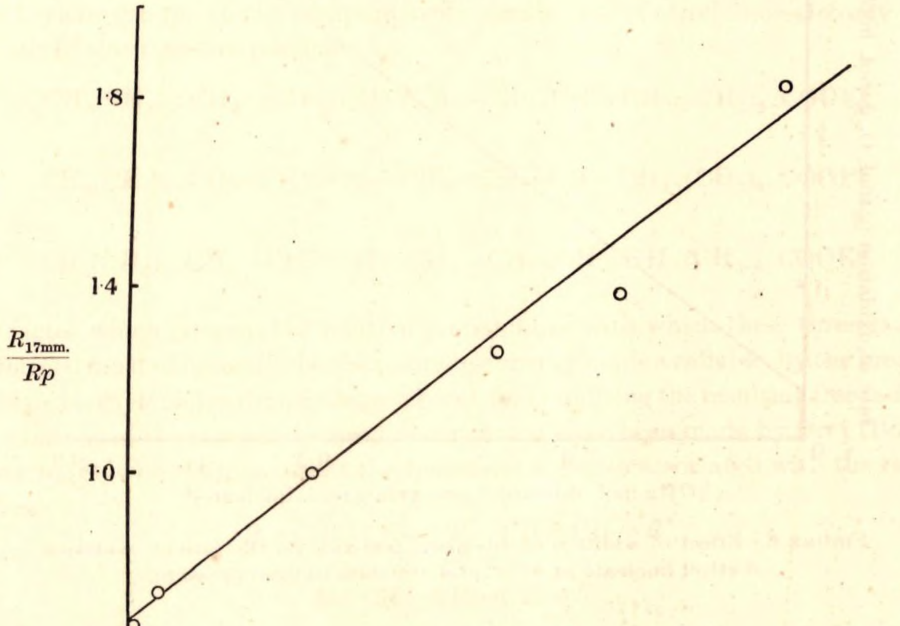


FIGURE 5A

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 $3{\cdot}0 \times 10^{-5}$ min.$^{-1}$.

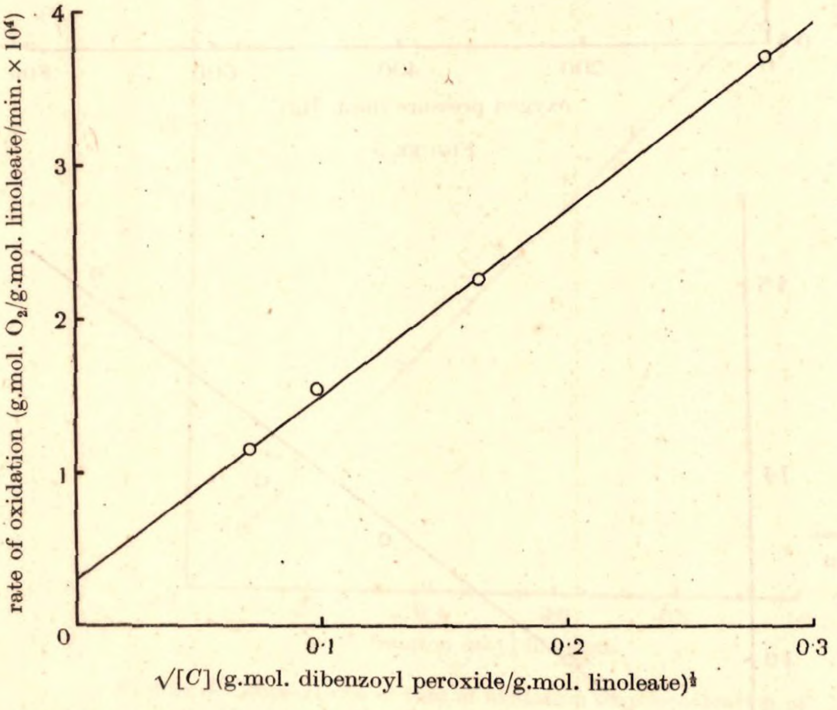
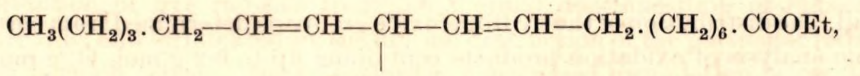
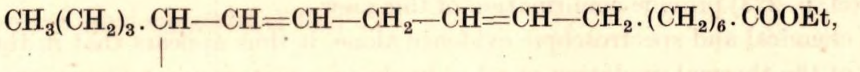


FIGURE 6. Effect of addition of dibenzoyl peroxide on the rate of oxidation of ethyl linoleate at 45° C and 100 mm. oxygen pressure.

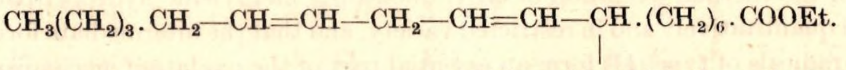
DISCUSSION

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-methylenic 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:

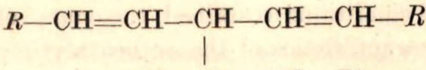

$$CH_3(CH_2)_3.CH_2{-}CH{=}CH{-}\underset{|}{CH}{-}CH{=}CH{-}CH_2.(CH_2)_6.COOEt, \qquad (II)$$


$$CH_3(CH_2)_3.\underset{|}{CH}{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2.(CH_2)_6.COOEt, \qquad (III)$$

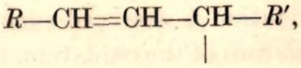
and


$$CH_3(CH_2)_3.CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}\underset{|}{CH}.(CH_2)_6.COOEt. \qquad (IV)$$

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-methylenic) 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


$$R{-}CH{=}CH{-}\underset{|}{CH}{-}CH{=}CH{-}R', \qquad (V)$$

and


$$R{-}CH{=}CH{-}\underset{|}{CH}{-}R', \qquad (VI)$$

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

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* Thus if rubber is oxidized in the temperature range 25–100° C, about 0·05 g.mol. H_2O and 0·02 g.mol. CO_2 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:

$$\mathrm{CH_3(CH_2)_4.CH{=}CH{-}CH{=}CH{-}CH(OOH){-}(CH_2)_7.COOEt}, \qquad \text{(VII)}$$

$$\mathrm{CH_3(CH_2)_4.CH(OOH){-}CH{=}CH{-}CH{=}CH{-}(CH_2)_7.COOEt}, \qquad \text{(VIII)}$$

$$\mathrm{CH_3(CH_2)_4.CH{=}CH{-}CH(OOH){-}CH{=}CH{-}(CH_2)_7.COOEt}. \qquad \text{(IX)}$$

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.

$$\mathrm{CH_3(CH_2)_3CH(OOH).CH{=}CH{-}CH{=}CH{-}CH(OOH).(CH_2)_7COOEt} \qquad \text{(X)}$$

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-methylenic 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:

$$\text{rate of oxidation} = \frac{d[R\mathrm{OOH}]}{dt} = K.[R\mathrm{OOH}]\,[R\mathrm{H}].f([\mathrm{O_2}]) + f'([R\mathrm{H}], [\mathrm{O_2}]), \qquad (3)$$

where $[R\mathrm{H}]$, $[R\mathrm{OOH}]$ and $[\mathrm{O}_2]$ 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 $f'([R\mathrm{H}], [\mathrm{O}_2])$ 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 ($R\,1$–$R\,6$) 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:

$$\begin{array}{llll}
\text{Initiation:} & 2R\mathrm{OOH} \rightarrow X \text{ or } Y & k_1,\ E_1, & (R1) \\
\text{Propagation:} & X + \mathrm{O}_2 \rightarrow Y + & k_2,\ E_2, & (R2) \\
 & Y + R\mathrm{H} \rightarrow X + R\mathrm{OOH} & k_3,\ E_3, & (R3) \\
\text{Termination:} & \left.\begin{array}{l} X + X \rightarrow \\ X + Y \rightarrow \\ Y + Y \rightarrow \end{array}\right\} \text{end-products} & \begin{array}{l} k_4,\ E_4, \\ k_5,\ E_5, \\ k_6,\ E_6, \end{array} & \begin{array}{l} (R4) \\ (R5) \\ (R6) \end{array}
\end{array}$$

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 ($R\,1$) to ($R\,6$) 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 ($R\,3$) and the rate at which it is destroyed by termination

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* 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 $[R\mathrm{H}]$ (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

$$d[R\mathrm{OOH}]/dt = k_3\sqrt{(k_1/k_6)}\,[R\mathrm{OOH}]\,[R\mathrm{H}]. \tag{4}$$

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

$$d[R\mathrm{OOH}]/dt = k_2\sqrt{(k_1/k_4)}\,[R\mathrm{OOH}]\,[O_2]. \tag{5}$$

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 $k_5^2 = k_4 k_6$:

$$\frac{d[R\mathrm{OOH}]}{dt} = k_3\sqrt{\frac{k_1}{k_6}}\,[R\mathrm{OOH}]\,[R\mathrm{H}]\,\frac{k_2\sqrt{k_6}\,[O_2]}{k_2\sqrt{k_6}\,[O_2] + k_3\sqrt{k_4}\,[R\mathrm{H}] + \sqrt{(k_1k_4k_6)}\,[R\mathrm{OOH}]}. \tag{6}$$

When the oxidation chain length is large—as is shown below to be the case in the present system—the term $\sqrt{(k_1k_4k_6)}\,[R\mathrm{OOH}]$ 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

$$\nu = \frac{R}{\alpha R_D} = \frac{1}{\alpha}\,\frac{k_3}{\sqrt{(k_1k_6)}}\,\frac{[R\mathrm{H}]}{[R\mathrm{OOH}]}\,\frac{k_2\sqrt{k_6}\,[O_2]}{k_2\sqrt{k_6}\,[O_2] + k_3\sqrt{k_4}\,[R\mathrm{H}]}, \tag{7}$$

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

$$\nu = \frac{9{\cdot}6}{\alpha[R\mathrm{OOH}]}, \tag{8}$$

when $[R\mathrm{OOH}]$ 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 C_6H_5- and benzoate C_6H_5COO- 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

$$\frac{d[R\mathrm{OOH}]}{dt} = k_3\sqrt{\frac{k_7}{k_6}}\sqrt{[C]}\,[R\mathrm{H}]\,\frac{k_2\sqrt{k_6}\,[\mathrm{O}_2]}{k_2\sqrt{k_6}\,[\mathrm{O}_2]+k_3\sqrt{k_4}\,[R\mathrm{H}]}, \tag{9}$$

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 ($\sqrt{k_1}\,[R\mathrm{OOH}]$ 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 ($1{\cdot}5\times10^{-6}$ 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 $3{\cdot}2\times10^{-4}$ and

$1{\cdot}4\times10^{-4}$ 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

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

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 × 10^3 min.$^{-1}$ 100 mm.	slope × 10^3 min.$^{-1}$ $p = \infty$
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

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

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

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

and

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

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)

$$E_3 - E_2 + \tfrac{1}{2}(E_4 - E_6) \approx 8\cdot7 \text{ kcal./g.mol.} \tag{14}$$

We also have $E_3 + \tfrac{1}{2}(E_1 - E_6) = 17\cdot2$ 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,

$$E_3 - \tfrac{1}{2}E_6 = 4\cdot2 \text{ kcal./g.mol.} \tag{15}$$

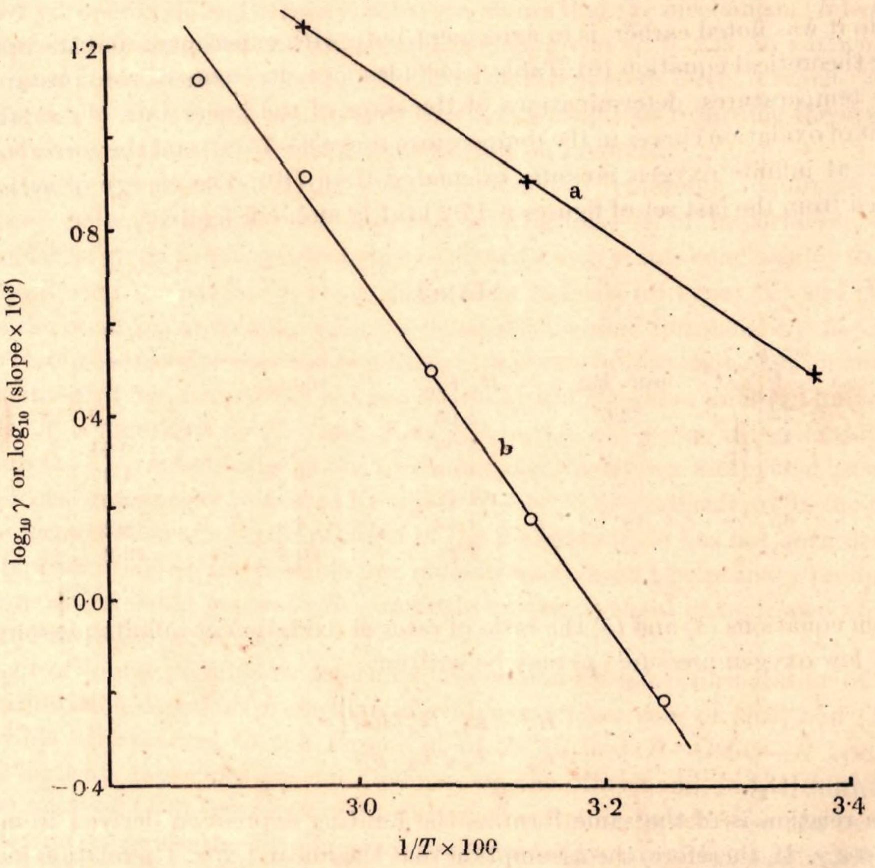

FIGURE 7. Dependence on temperature of γ (curve *a*) and the slope of the rate of oxidation *v.* extent of oxidation relation (curve *b*).

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 $-1\cdot5$ 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_γ 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

$$RO_2\text{—} + RH \rightarrow ROOH + R\text{—} \qquad (R3')$$

is significantly in excess of that for

$$R\text{—} + O_2 \rightarrow RO_2\text{—}. \qquad (R2')$$

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 ($D_{\text{O—O}}$) 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 $D'_{\text{O—O}} > 54$ kcal., where $D'_{\text{O—O}}$ represents the oxygen-oxygen bond energy in the peroxide radical, RO_2. This requirement will obviously be fulfilled provided $D'_{\text{O—O}}$ is not significantly less than $D_{\text{O—O}}$. $D'_{\text{O—O}}$ does in fact exceed $D_{\text{O—O}}$ 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 $R\text{—}O\overset{\cdots}{\text{—}}O$, the three-electron bond serving to make $D'_{\text{O—O}} > D_{\text{O—O}}$; Pauling's quantitative interpretation of the three-electron bond would suggest that $D'_{\text{O—O}} \sim \frac{3}{2} D_{\text{O—O}}$.

Since it is unlikely that $D'_{\text{O—O}}$ will exceed $D_{\text{O—O}}$ 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.

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