OLEFIN OXIDATION

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THE interaction of olefins with molecular oxygen is not only a subject of widespread industrial importance, but is one of the most thoroughly understood chemical processes. This Review attempts to give a broad picture of the main mechanistic features. An earlier article [1] has reviewed the historical background and has given details of the method of approach and of the earlier kinetic data which were largely responsible for opening up this field.

In Section (1) we present the generally accepted chain mechanism and the simpler rate expressions which are often obeyed. Certain quantitative comparisons of olefinic reactivity derivable on this basis are then discussed. Our main concern, however, is to show how comparatively small changes in certain mechanistic details can give rise to substantial differences in the observed kinetics—so much so that a profound change in mechanism might be imagined. Section (2) deals with rate measurements under nonstationary state conditions designed to determine the propagation- and termination-rate constants separately, and emphasises the inherent limitations to accuracy which oxidation systems present in this respect.

Sections (3), (4), and (5) are concerned with the initiation of the oxidation chain, and the part played in this by the hydroperoxide which is the primary reaction product. This behaviour of the hydroperoxide is responsible for the autocatalytic character of the oxidations, and the complexity and environmental sensitivity of its decomposition serves to complicate the kinetics of the oxidations as a whole. Attention is drawn to circumstances where the fraction of hydroperoxide undergoing decomposition is large compared with that being formed, so that the character and kinetics of the process are greatly altered despite the same fundamental reactions being involved. Section (6) describes efforts to analyse the initiation process quantitatively in order that the number of oxidation chains being started under given conditions can be specified.

Under mild conditions of oxidation, the chain is long and the fraction of the hydroperoxide which decomposes to initiate fresh chains is very small. The overall yield of hydroperoxide should thus be nearly quantitative. In Section (7) serious discrepancies are interpreted in terms of the dual reactivity of peroxy-radicals towards olefins, the consequence being that the measured rate constants are composite quantities relating to both hydrogen extraction and double-bond addition.
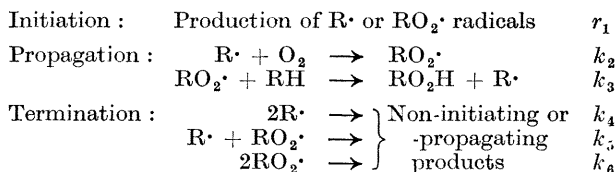
The allylic radicals formed on removal of an α-methylenic hydrogen atom from an olefin are mesomeric and hence the derived product may

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[1] Bolland, *Quart. Reviews*, 1949, **3**, 1.

consist of allylic isomerides. The behaviour of mono-olefins and $1:4$-diolefins in this respect is discussed in Section (8).

1. General Kinetic Behaviour

The following reaction scheme, where RH represents the olefin with an α-methylenic hydrogen atom H, r_i is the rate of chain initiation, and the k's are the velocity coefficients of the reactions indicated, accounts for the reaction characteristics with remarkable comprehensiveness.

$$
\begin{array}{lll}
\text{Initiation :} & \text{Production of R· or RO}_2\text{· radicals} & r_1 \\
\text{Propagation :} & \text{R· + O}_2 \longrightarrow \text{RO}_2\text{·} & k_2 \\
& \text{RO}_2\text{· + RH} \longrightarrow \text{RO}_2\text{H + R·} & k_3 \\
\text{Termination :} & 2\text{R·} \longrightarrow \left.\begin{array}{l}\text{Non-initiating or} \\ \text{-propagating} \\ \text{products}\end{array}\right. & k_4 \\
& \text{R· + RO}_2\text{·} \longrightarrow & k_5 \\
& 2\text{RO}_2\text{·} \longrightarrow & k_6
\end{array}
$$

The more obvious of these are : (i) high yields of the hydroperoxide, RO_2H (cf. p. 162) ; (ii) catalysis by light and by free-radical producing substances, indicating the free-radical nature of the reaction ; [2] (iii) quantum yields greater than one and a proportionality between rate and the square root of the light intensity in photo-oxidations, indicating a chain reaction with mutual destruction of two chain carriers in the termination step ; [3] (iv) a parallelism between oxidisability and the relative ease of rupture of the C–H bond in RH, indicating the importance of a hydrogen-exchange reaction such as (3) (cf. p. 149) ; (v) the formation of conjugated-diene hydroperoxides from $1:4$-dienes, in agreement with the generation of mesomeric R· radicals as in (2) (cf. p. 164) ; and (vi) the marked retardation in rate produced by phenolic compounds (among others), which interfere with the propagation process by providing an alternative and easier reaction for the RO_2· radicals that does not liberate a radical equivalent to R·.[4]

It being assumed that $k_5{}^2 = k_4 k_6$, the above mechanism yields the rate equation (for long chains)[5]

$$
r = r_1^{\frac{1}{2}} k_3 k_6^{-\frac{1}{2}} [\text{RH}] \frac{k_2 k_6^{-\frac{1}{2}}[\text{O}_2]}{k_3 k_4^{-\frac{1}{2}}[\text{RH}] + k_2 k_6^{-\frac{1}{2}}[\text{O}_2]} \qquad . \qquad . \quad (1)
$$

where r is the overall rate of oxidation and the square brackets signify concentration terms.

Oxidisability at " High " Oxygen Pressures.—When reaction (2) is so much faster than (3) that $[\text{R}] \ll [\text{RO}_2]$, termination can be assumed to occur entirely by reaction (6), and equation (1) simplifies to

$$
r_\infty = r_1^{\frac{1}{2}} k_3 k_6^{-\frac{1}{2}} [\text{RH}] \qquad . \qquad . \qquad . \qquad (2)
$$

Equation (2) accurately expresses the observed kinetics for most olefins at

[2] Bateman and Bolland, Proc. XIth International Congress of Pure and Applied Chem., 1947.

[3] Bateman and Gee, *Proc. Roy. Soc.*, 1948, A, **195**, 376.

[4] Bolland and ten Have, *Trans. Faraday Soc.*, 1947, **43**, 201 ; *Discuss. Faraday Soc.*, 1947, **2**, 252.

[5] Bolland, *Proc. Roy. Soc.*, 1946, A, **186**, 218.

oxygen pressures greater than 100 mm. (the " high " pressure region)—an interesting exception being discussed later.   At constant r_1, estimates of $k_3 k_6^{-\frac{1}{2}}$ are thus obtained from $r_\infty/[\text{RH}]$ and these measure the relative reactivities of different olefins in reaction (3), since k_6 is not very sensitive to changes in R (see p. 153).   Bolland [6] has in this way developed a correlation between olefinic structure and oxidisability.   Referring to propene, $CH_3 \cdot CH{:}CH_2$, at 45°, he concludes that :

   (a)   (b)   (c)

(i) Replacement of one or two hydrogen atoms at (a) and/or (c) by alkyl groups increases k_3 by $3 \cdot 3^n$, where n is the total number of substituents ; similar replacement at (b) is without effect.

(ii) Replacement of a hydrogen atom at (a) by a phenyl group increases k_3 23-fold.

(iii) Replacement of a hydrogen atom at (a) by an alk-1-enyl group increases k_3 107-fold.

(iv) The value of k_3 appropriate to an α-methylenic group contained in a cyclic structure is 1·7 times that of the group contained in an analogous acyclic structure.

These rules relate to broad variations, as implied by the assumed equivalency of different alkyl groups.   The assumptions that k_6 is invariable and that benzoyl peroxide (used as a standard initiator) initiates throughout with equal efficiency also introduce second-order uncertainties.   More serious discrepancies occur in special cases.   Thus 2 : 4-dimethylpent-2-ene is at least 10 times less reactive than would be predicted,[7] presumably because of steric hindrance at C_3—behaviour simulated in a saturated

TABLE 1

Olefin, RH [a]	E_3 [b]	$\Delta H_3 = E_3/0\cdot4$	$\Delta(\Delta H_3)$
$CH_2{:}CH{\cdot}\overset{*}{C}H_3$	$13 \cdot_5$	34	0
$CH_2{:}CH{\cdot}\overset{*}{C}H_2 Alk$	$11 \cdot_5$	29	5
$CHAlk{:}CH{\cdot}\overset{*}{C}H_2 Alk$	$10 \cdot_5$	26	8
$CAlk_2{:}CH{\cdot}\overset{*}{C}H_2 Alk$	9	23	11
$CH_2{:}CH{\cdot}\overset{*}{C}H_2 Ph$	10	25	9
$CHAlk{:}CH{\cdot}\overset{*}{C}H_2{\cdot}CH{:}CHAlk$ . .	6	15	19
$CH{:}CH{\cdot}\overset{*}{C}H_2$ . . . . . . $\mid \qquad \mid$ $Alk{-}{-}{-}Alk$	$9 \cdot_5$	24	10

All values are in kcal./mole

Reactive α-methylenic group indicated by an asterisk.   [b] Calculated from $E_3 = E_0 - \frac{1}{2}E_1 + \frac{1}{2}E_6$, where E_0 designates the overall activation energy of oxidations catalysed by benzoyl peroxide. E_6 is taken as zero and E_1 as 30 kcal./mole (Bolland's published values are based on $E_1 = 31$ kcal./mole).

[6] Bolland, *Trans. Faraday Soc.*, 1950, **46**, 358.   [7] Morris, unpublished result.

hydrocarbon by the inertness of $2:2:4$-trimethylpentane.[8] In general, however, Bolland's rules rationalise the behaviour of different olefins and of different allylic systems in the same olefin. For example, in the isoprenic unit $\cdot CH_2 \cdot C(CH_3){:}CH \cdot CH_2 \cdot$, the relative α-methylenic activity at the three positions, $x : y : z$, is approximately $1 : 3 : 11$.

The numerical factors given for $45°$ become smaller at higher temperatures, since increased reactivity partly reflects a lower activation energy (E) for reaction (3).[6] Average values of E_3 for the systems considered in (i)—(iv) above are given in Table 1. E_3 may be related to the corresponding heat of reaction, ΔH_3,[6] whose variation, $\Delta(\Delta H_3)$, from olefin to olefin expresses differences in resonance energy and other stabilising influences in the different allylic radicals.

Oxygen-pressure Dependence.—Decreasing the oxygen pressure reduces the overall rate of oxidation only when reaction (2) is not incomparably faster than reaction (3), *i.e.*, when $[R\cdot]$ is not negligible compared with $[RO_2\cdot]$. The pressure at which this condition prevails depends on the reactivity of the olefin— the lower the reactivity, the slower is reaction (3), and the lower the value of $[O_2]$ necessary to reduce the rate of reaction (2) accordingly. This effect may be enhanced by the reactivity of R in reaction

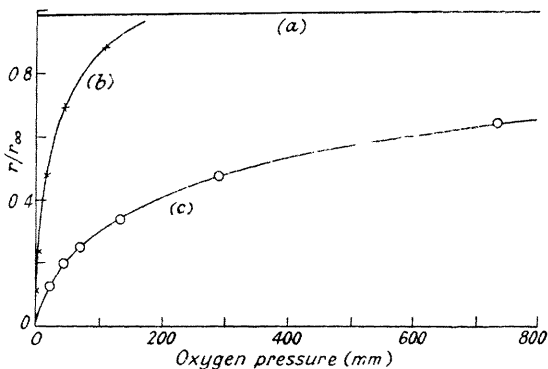Fig. 1

Variation of the rates of oxidation of (a) *hexadec*-1-*ene* $(45°)$, (b) *ethyl linolenate* $(45°)$ *and* (c) $2 : 6$-*dimethylhepta*-$2 : 5$-*diene* $(25°)$ *with oxygen pressure.*

(2) being qualitatively the inverse of that of RH in reaction (3), although the quasi radical–radical nature of (2) renders it far less responsive than (3) to changes in R. Some rate–pressure dependences are illustrated in Fig. 1. Hexadec-1-ene shows no dependence above 1 mm., but with increasing olefin reactivity the pressure at which the rate becomes insensitive also increases. With the intensely reactive $2 : 6$-dimethylhepta-$2 : 5$-diene, the rate at atmospheric pressure is well below r_∞. As only reaction (3) of the propagation and termination steps has an appreciable temperature

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[8] Wibaut and Strang, *Proc. K. Ned. Akad. Wet.*, 1951, **54**, *B*, 229.

coefficient, the dependence of rate on oxygen pressure extends to higher pressures at higher temperatures, as exemplified in Fig. 2.

Generalised Rate Equation.—For some olefins, equation (1) expresses exactly the observed kinetics over the whole range of oxygen pressures where accurate measurements are possible (down to about 1 mm.). In general, however, deviations are found which arise from departures from the assumption that $k_5{}^2 = k_4 k_6$ (p. 148), and which vary from olefin to olefin in an intelligible manner—in extreme cases being sufficient to modify the oxidation kinetics at pressures near atmospheric.
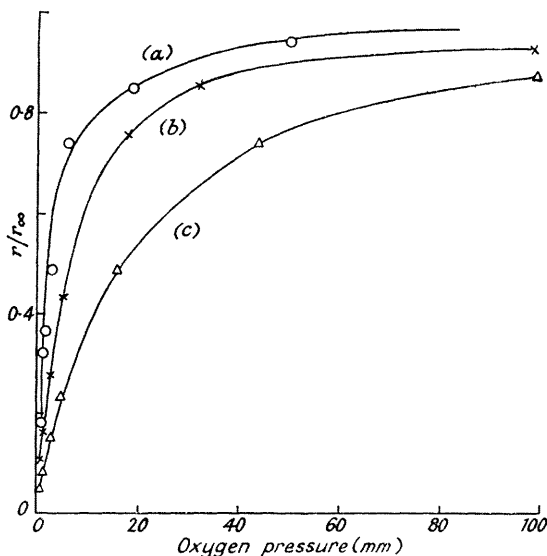
FIG. 2

Influence of temperature on the oxygen-pressure dependence of ethyl linolenate at (a) 25°, (b) 35°, *and* (c) 45°.

The completely general form of the rate equation (for long chains) is : [9]

$$r^{-2} = r_i{}^{-1}(k_2{}^{-2}k_4[O_2]^{-2} + 2k_2{}^{-1}k_3{}^{-1}k_5[RH]^{-1}[O_2]^{-1} + k_3{}^{-2}k_6[RH]^{-2}) \quad . \quad (3)$$

or, alternatively, by combination of (3) and (2) :

$$(r_\infty/r)^2 = 1 + 2\phi k_2{}^{-2}k_4{}^{\frac{1}{2}}k_3 k_6{}^{-\frac{1}{2}}[RH][O_2]^{-1} + k_2{}^{-2}k_4 k_3{}^2 k_6{}^{-1}[RH]^2[O_2]^{-2} \ . \ (4)$$

where $\phi = k_4{}^{-\frac{1}{2}}k_5 k_6{}^{-\frac{1}{2}}$ and r_∞ is defined by equation (2). Equation (4) requires a plot of (r_∞/r) against $[O_2]^{-1}$ to be linear if $\phi = 1$ [as assumed in deriving (1)], concave to the latter axis if $\phi < 1$, and convex if $\phi > 1$. Examples of all three conditions are known.[11] From the slope and ordinate intercept of the plot of $\{(r_\infty/r)^2 - 1\}[O_2]$ against $[O_2]^{-1}$ (see equation 4), ϕ and the composite coefficients $k_2 k_4{}^{-\frac{1}{2}}$ and $k_3 k_6{}^{-\frac{1}{2}}$ can be determined. The data listed in Table 2 show that the large variations in $k_3 k_6{}^{-\frac{1}{2}}$ with olefinic structure are not paralleled by any of comparable magnitude in $k_2 k_4{}^{-\frac{1}{2}}$.

[9] Bateman, Gee, Morris, and Watson, *Discuss. Faraday Soc.*, 1951, **10**, 250.

TABLE 2*

Olefin	$10^3 k_3 k_6^{-\frac{1}{2}}(45°)$ (mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$)	$10^{-3} k_2 k_4^{-\frac{1}{2}}(45°)$ (mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$)	ϕ
Methyl oleate	1·53	0·5	0·3
Phytene	1·07	0·4	1·0
Digeranyl	3·82	0·9	3·1
Ethyl linoleate	20·7	1·6	2·5
Ethyl linolenate	41·4	1·3	3·3
2 : 6-Dimethylhepta-2 : 5-diene . .	130 (25°)	1·2 (25°)	6·5

* Absolute comparison requires the composite and individual rate constants in this and the following Tables to be multiplied by factors of $e^{\frac{1}{2}}_{B.P}$ and $e_{B.P}$, respectively, where $e_{B.P}$ denotes the initiating efficiency of benzoyl peroxide (see p. 161). As this quantity has been determined only for a few olefins and is variable, it is preferable here to base all the data on the value, $e_{B.P} = 1$.

ϕ **Values.**—Two points concerning the values of ϕ may be noted : (i) they are all rather small compared with some of the large values found for the equivalent quantity for cross-termination in copolymerisations ; and (ii) they increase with the reactivity of RH. These features probably have a common link in reflecting a large diminution in the resonance and polarity properties of the group R on relay through the O–O bond of the $RO_2\cdot$ radical. In copolymerisations, the analogous ϕ values relate to the interplay of structural effects in substituted alkyl radicals only ; in the oxidations, the $RO_2\cdot$ radical is essentially a common factor from system to system and tends to depress in reaction (5) any variation in reactivity in R· which is fully manifest in reaction (4).

Influence of ϕ on the Kinetic Form.—As the reactivity of RH increases, two factors enhance the kinetic importance of the R· radicals : (i) the lessening of the difference between k_2 and k_3 ; and (ii) the increase in ϕ. The practical repercussions are strikingly illustrated by comparing the variation in the relative importance of reactions (4), (5), and (6) at different oxygen pressures for different olefins (Fig. 3).[10] The displacement, broadening, and intensification of the R· + $RO_2\cdot$ curve on passing from phytene to 2 : 6-dimethylhepta-2 : 5-diene leads to such marked kinetic differences as to suggest that the oxidation mechanisms are fundamentally different. Even at pressures near atmospheric, equation (2) does not apply even approximately to the heptadiene ; the rate is neither directly proportional to [RH] nor independent of [O_2]. At pressures higher than 100 mm., termination by reaction (4) is negligible and the dependence of rate on [RH] is then given by equation (3) without the term $k_2^{-2} k_4 [O_2]^{-2}$.

The ability of the oxidation mechanism to account in so detailed and rational a manner for the kinetic behaviour of olefins of widely varying reactivity establishes its *formal* correctness. As discussed later (p. 162), it is sometimes necessary to modify or supplement the scheme given on p. 148 in order to obtain consistency with product data.

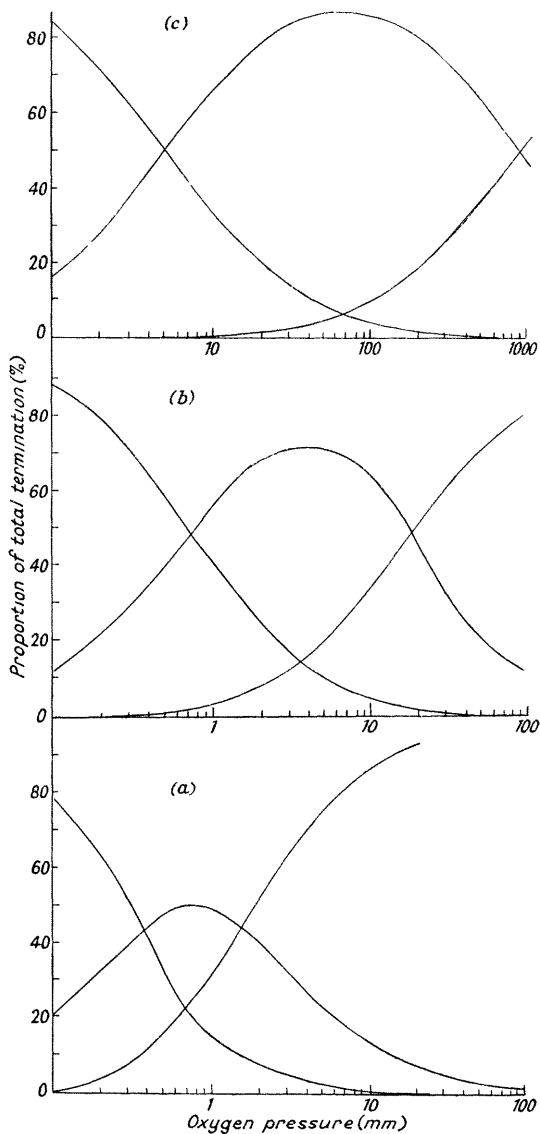[10] Bateman and Morris, *Trans. Faraday Soc.*, 1953, **49**, 1026.

Fig. 3

Termination characteristics of the oxidation of (a) *phytene* (45°), (b) *ethyl linoleate* (45°), *and* (c) 2 : 6-*dimethylhepta*-2 : 5-*diene* (25°) *at various oxygen pressures.*

2. Individual Rate Coefficients of the Propagation and Termination Reactions

For all chain reactions, measurements under stationary-state conditions permit only composite velocity coefficients (such as $k_3 k_6^{-\frac{1}{2}}$) to be determined.

Non-stationary-state measurements with oxidising olefins have been made by the rotating-sector technique [11], [12] and by following directly the photo-chemical pre- and after-effects, [9], [12], [13], [14] and absolute values of the several propagation and termination constants derived. However, severe limits to accuracy are imposed by certain inherent complications, which are common to similar measurements in all gas–liquid systems and deserve to be more widely known.

The principle of the photochemical pre- and after-effects is expressed in Fig. 4. If the oxidation is followed in the dark (rate $= r_D$) and then the light is switched on, a time interval elapses before the uniform
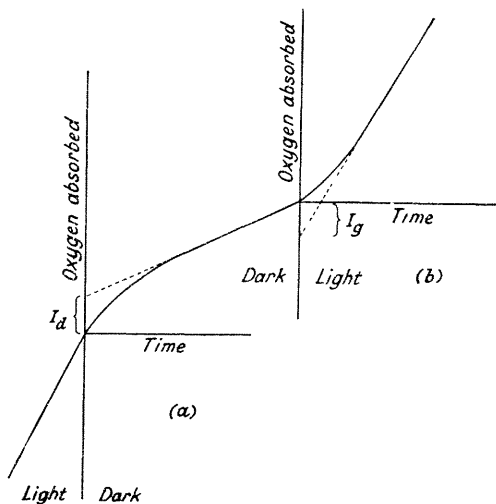
FIG. 4

Definition of (a) *the rate decay intercept,* I_d, *and* (b) *the rate growth intercept,* I_g.

light rate (r_L) is established, *i.e.*, while the increased concentration of chain carriers builds up. The inverse occurs when the light is switched off. The intercepts I_g and I_d represent amounts of oxygen absorbed during the non-stationary state conditions, and can be shown to be defined by $I_d = a \ln\{(r_L + r_D)/2r_D\}$ and $I_g = a \ln\{2r_L/(r_L + r_D)\}$, where a is a complex quantity containing the propagation and termination constants in different ratios from those in the stationary rate equations (under " high " pressure conditions, a reduces to $k_3 k_6^{-1}[\mathrm{RH}]$). The important complicating factor is that the oxygen concentration in the solution does not remain constant during the change from r_D to r_L. As oxygen is continually being removed by reaction, the actual value of $[O_2]$ is always lower than the satura-tion value. The extent of this difference depends on the speed by which

[11] Bateman and Gee, *Proc. Roy. Soc.*, 1948, *A*, **195**, 391.

[12] Bamford and Dewar, *ibid.*, 1949, *A*, **198**, 252.

[13] Bateman and Gee, *Trans. Faraday Soc.*, 1951, **47**, 155.

[14] Bateman, Bolland, and Gee, *ibid.*, p. 274.

the oxygen can be replenished from the gas phase by agitation. The intercepts actually measured are not in fact I_g and I_d but are given by [13] $I'_d = I_d + (r_L - r_D)/k_s$ and $I'_g = I_g + (r_L - r_D)/k_s$, where k_s represents the shaking efficiency. In principle, therefore, the change in oxygen concentration can be compensated for automatically by evaluating $I'_d - I'_g \ (= I_d - I_g = a \ \ln\{(r_L + r_D)^2/4r_Lr_D\})$. In practice, the term $(r_L - r_D)/k_s$, while often negligible compared with $[O_2]$, is large compared with I_d and I_g. For example, under favourable experimental conditions with ethyl linoleate at $15°$, an oxygen pressure of 550 mm., and a shaking frequency of 650 per minute, the values of $10^6I'_d$, $10^6I'_g$, and $10^6(r_L - r_D)/k_s$ were 27, 19, and 16 mole/l., respectively.

In the " low " pressure region, where r_L and r_D themselves vary with changes in $[O_2]$, an exceedingly complicated situation exists,[14] and derivations of the relevant constants are subject to much greater uncertainty.

Fairly reliable estimates of the several constants for ethyl linoleate and digeranyl are given in Table 3. The values of k_3 and k_6 are believed to be numerically significant, those of k_2, k_4, and k_5 express the order of magnitude.

TABLE 3. *Velocity coefficients at* $25°$ *(mole*$^{-1}$ *l. sec.*$^{-1}$*)*

	$10^{-6}k_2$	k_3	$10^{-6}k_4$	$10^{-6}k_5$	$10^{-6}k_6$
Ethyl linoleate . . .	10	50	20	50	20
Digeranyl	1	3	1	10	10

The rotating-sector technique involves measurements in circumstances where changes from r_L to r_D to r_L occur in rapid succession. The $(r_L - r_D)/k_s$ terms thus cancel out automatically. Even under high pressure conditions (as above, a complex situation prevails at " low " pressures), the advantage which this confers has not been realised owing to a lack of sensitivity in other respects, but practical improvements to remedy this appear feasible and worth developing.

3. Autocatalysis and Hydroperoxide Decomposition

Benzoyl peroxide and azo*iso*butyronitrile undergo unimolecular thermal dissociation into free radicals and catalyse the oxidation of olefins proportionally to the square root of their concentration. This affords critical evidence, in conjunction with photocatalysis (p. 148), for the form of r_i in equation (3) and its simplified versions.

Bimolecular Hydroperoxide Decomposition.—The autocatalytic character of the oxidation is illustrated in Fig. 5. The overall rate is proportional to the hydroperoxide produced during the earlier stages of the reaction, and thus from equation (3) $r_i \propto [RO_2H]^2$, *i.e.*, chain initiation ensues from a bimolecular decomposition of the hydroperoxide. This result was unexpected when first encountered because saturated and arylated hydroperoxides had previously been said to undergo a unimolecular primary scission. The self-consistency of the kinetic data on oxidation catalysis and a direct study
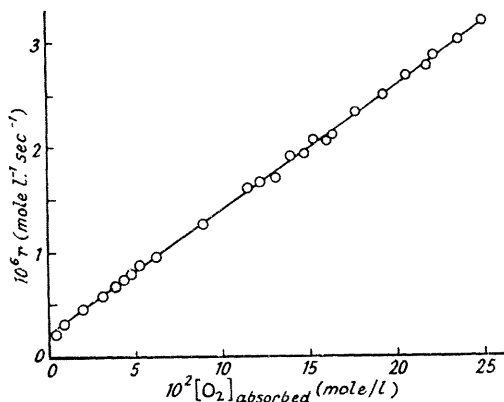
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FIG. 5

Autoxidation of cyclo*hexene at 45° and 728 mm.*

of the decomposition of an olefinic hydroperoxide,[15] however, combine to establish its validity. As mentioned later, differences concerning the order of peroxide decomposition may not be antagonistic.

For the above catalytic form in the " high " pressure region, we have

$$r = \{ek''[\mathrm{RO_2H}]^2\}^{\frac{1}{2}}k_3k_6^{-\frac{1}{2}}[\mathrm{RH}] \qquad . \qquad . \qquad . \quad (5)$$

where k'' is the bimolecular velocity coefficient for the hydroperoxide decomposition and e represents the efficiency with which the liberated radicals produce $\mathrm{R}\cdot$ or $\mathrm{RO_2}\cdot$ radicals. From benzoyl-catalysed oxidations,

TABLE 4

Olefin	Hydroperoxide-type, %			$10^4 k_3 k_6^{-\frac{1}{2}}$ * (mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$)	$10^6 ek''$ * (mole^{-1} l. sec.$^{-1}$)
	prim.	*sec.*	*tert.*		
Allylbenzene	100			14·4	0·28
Oct-1-ene	70	30		3·6	0·29
Methyl oleate		100		21·5	0·46
cycloHexene		100		37·0	0·54
Ethyl linoleate . . .		100		278·	0·47
4-Methylhept-3-ene . .		70	30	32·4	1·72
1-Methylcyclohexene . . .		70	30	65·1	1·14
1 : 3 : 5-Trimethylcyclohexene		15	85	150	3·25
Dicyclohex-2-enyl		25	75	200	2·48
Squalene			~100	39·7	2·97
Digeranyl			~100	49·4	2·62

* At 55°.

[15] Bateman and (Mrs.) Hughes, *J.*, 1952, 4594.

and determination of the appropriate value of e for this system,[16] $k_3 k_6^{-\frac{1}{2}}$ can be determined and thus (ek'') from (5).   In Table 4,[17] the olefins are grouped according to the structural type of hydroperoxide involved, as deduced from the relative susceptibility of non-equivalent α-methylenic C–H bonds to attack by $RO_2\cdot$ radicals (p. 149) and from the tendency of allylic systems to form isomeric products (p. 166).

No parallelism is apparent between the differences in ek'' and the oxidisabilities of the olefin $(k_3 k_6^{-\frac{1}{2}})$, but a clear correlation exists with hydroperoxide type in the sense $ek''_{\text{prim.}} : ek''_{\text{sec.}} : ek''_{\text{tert.}} = 1 : 2 : 14$.   For reasons unknown, this order is the reverse of the commonly recognised stability of analogous saturated hydroperoxides.
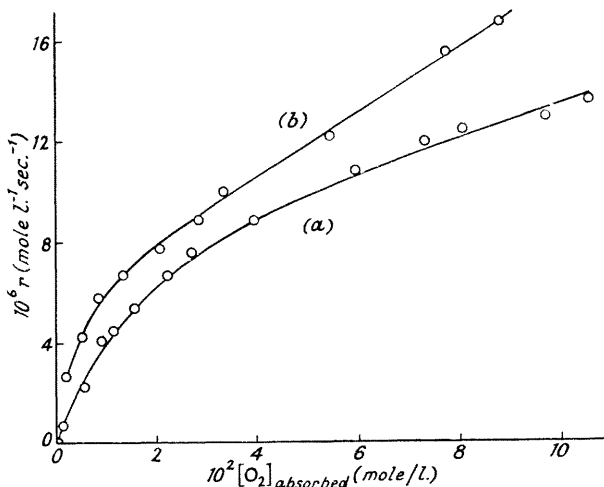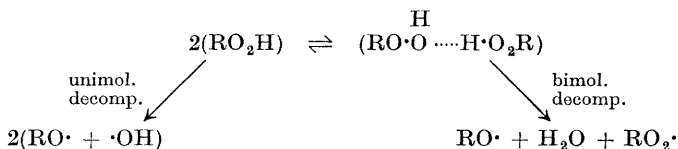

FIG. 6

Autoxidation of (a) *tetralin at* 75° *and* 180 *mm. and* (b) 1-*methylcyclohexene at* 65° *and* 350 *mm. at low extents of oxidation.*

Unimolecular Hydroperoxide Decomposition.—A curious feature of the plots of r against $[O_2]_{\text{absorbed}}$ (such as in Fig. 5) is that extrapolation of the linear portion to $[O_2]_{\text{absorbed}} = 0$ gives a small but real intercept on the r-axis.   This was first thought to represent the rate of the direct reaction between the olefin and oxygen ($RH + O_2 \rightarrow$).[1]   In fact, the basis of performing the extrapolation has proved fallacious.   The true behaviour is shown for two olefins in Fig. 6.   The curvature towards the origin in the very early stages of the reaction denotes catalysis of the form $r \propto [RO_2H]^{\frac{1}{2}}$, instead of the commonly observed $r \propto [RO_2H]$.   This in turn implies that the hydroperoxide at low concentrations ($< 10^{-2}$ mole/l. in the temperature range studied) yields radicals by a first-order decomposition, which is superseded by a second-order decomposition at a higher concentration.   This unique change in decomposition order with concentration

[16] Bateman and Morris, *Trans. Faraday Soc.*, 1952, **48**, 1149.
[17] Morris, Ph.D. Thesis, London, 1952.

appears to be associated with the state of molecular association of the hydroperoxide :

$$2(RO_2H) \quad \rightleftharpoons \quad (RO \cdot O \cdots H \cdot O_2 R)$$

H (above right species)

unimol. decomp. (lower left branch)

bimol. decomp. (lower right branch)

$$2(RO \cdot + \cdot OH) \qquad\qquad\qquad RO \cdot + H_2O + RO_2 \cdot$$

Infra-red spectroscopy provides clear-cut evidence that the intense association in the neat hydroperoxide becomes progressively less with dilution.[15]   In general, conditions conducive to a low degree of association would be expected to emphasise the first-order decomposition.   Consistently, the catalytic form $r' \propto [RO_2H]^{\frac{1}{2}}$ persists to higher concentrations at higher temperatures,[17] and the addition of more strongly bonding substances than the peroxide itself suffices to change the observed catalysis from $r \propto [RO_2H]$ to $r \propto [RO_2H]^{\frac{1}{2}}$.[15, 17]   The effect of temperature is significant in providing a probable explanation of the differences in hydroperoxide decomposition reported by different workers (cf. p. 155).   The inference from the oxidation kinetics of a bimolecular mechanism relates to temperatures lower than about 80°, while the direct decompositions have mostly been studied at above 130° where the first-order dissociation will be greatly favoured.

TABLE 5

Olefin	Temp.	$10^7 e'k'$ (sec.$^{-1}$)	Olefin	Temp.	$10^7 e'k'$ (sec.$^{-1}$)
Allylbenzene . . .	75°	2·9	Dicyclohex-2-enyl . .	45°	0·7
cycloHexene	55	0·1$_5$	,,	65	6·9
Ethyl linoleate . . .	55	0·2$_0$	2-Methyloct-2-ene . .	55	0·5$_0$
1-Methylcyclohex-1-ene	45	0·4$_5$	2-Methyl-4-phenyl-	55	1·6
,,	65	3·9	but-2-ene		
1 : 3 : 5-Trimethyl-cyclohex-1-ene	65	3·7	Digeranyl	45	0·5$_4$

The quantity $e'k'$, analogous to ek'', can likewise be determined for the first-order hydroperoxide initiation process (Table 5).[17]   For the limited data available, no well-defined correlation with hydroperoxide type as in the case of ek'' can be recognised, but the predominantly tertiary derivatives again seem to be the more reactive.

4. The Direct Reaction between an Olefin and Oxygen

A natural consequence of the free-radical character of oxygen is that it should display in some measure the reactivity of $RO_2 \cdot$ radicals towards olefins.   It is actually so much less reactive that direct olefin–oxygen inter-action ($RH + O_2 \rightarrow$) has so far proved impossible to measure.   As described in section (3), instead of being able to define this rate relatively easily by extrapolating the plot of r against $[O_2]_{absorbed}$ (as Fig. 5) to $[O_2]_{absorbed} = 0$ (e.g., 6×10^{-6} mole l.$^{-1}$ sec.$^{-1}$ for tetralin at 75°), the true value is so many times smaller that it is difficult to observe (see Fig. 6).   The absorption of

as little as 0·02—0·05 ml. (N.T.P.) of oxygen per ml. produces a degree of hydroperoxide catalysis sufficient to obscure any possible initiation by direct olefin–oxygen interaction.[17, 18] The latter clearly cannot be an observable component of the overall oxidation reaction at moderate temperatures. The initiation step as a whole accounts for only $1/n$th of the total products, where n is the chain length, and hydroperoxide decomposition accounts for nearly all of this fraction.

Obviously no examination of the oxidation product can hope to provide information on any non-hydroperoxidic initiation. In fact it would appear that the only means of obtaining critical evidence on the direct olefin–oxygen reaction is to study the system in the presence of a highly efficient inhibitor which would prevent any primary peroxy-intermediate from becoming a hydroperoxide (therefore not a phenolic-type inhibitor).

Hydroperoxide initiation is likewise predominant in photochemical oxidations. The formation of a very small amount of hydroperoxide has been shown quantitatively to establish $RO_2H + h\nu \rightarrow$ rather than $RH + h\nu \rightarrow$ as the primary activation process.[3]

5. Metallic-ion Catalysis

The intense activity of certain metallic compounds (notably those of iron, cobalt, nickel, copper, and manganese) as oxidation catalysts is a matter of immense technological interest. The consequences can be both highly undesirable and advantageous. Thus the comparatively rapid oxidative deterioration induced in rubber or lubricating oils calls for strict preventive measures ; while the use of cobalt compounds as " driers " to promote the rapid oxidative hardening of unsaturated esters is all-important in paint technology. Although knowledge of how these compounds act remains obscure in many details, the general picture is fairly clear. Of particular interest in the present context are certain distinctive kinetic characteristics.

The active metals are those having two or more valency states, clearly suggesting that an oxidation–reduction process is involved. They function *via* their ions, as is evident from the industrial practice of using the so-called sequestering (complex-forming) agents (*e.g.* ethylenediaminetetra-acetic acid) to counteract metallic contamination—the metal is converted from an ionic into a chelated form and thereby rendered innocuous. Obtaining of a suitable homogeneous reaction system for mechanistic studies is thus a difficulty. The solvent employed so far has been acetic acid, which is a catalyst for hydroperoxide decomposition and therefore might be expected to create confusion in any direct comparison of results with those obtained for oxidation in hydrocarbon solvents. Whether this is so or not remains to be proved, but fortunately the catalysis by active metal salts is so great that the reaction can be studied under conditions where oxidation in acetic acid alone is negligible.

Working with cobaltous acetate in acetic acid, Bawn and his

[18] Bateman, (Mrs.) Hughes, and Morris, *Discuss. Faraday Soc.*, 1953, **14**, 190.

co-workers [19, 20] conclude that the rate-determining initiation process is

$$RO_2H + M^{3+} \longrightarrow RO_2\cdot + M^{2+} + H^+ \ldots r_i(M)$$
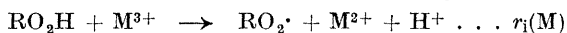
where M^{3+} represents a complex tervalent cobaltic ion. The cobaltous ion produced is immediately reconverted into M^{3+} by the much faster reaction :

$$RO_2H + M^{2+} \longrightarrow RO\cdot + M^{3+} + OH^-$$
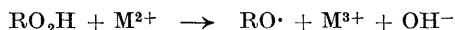
The sum of these consecutive reactions is seen to be exactly the bimolecular decomposition pattern proposed for the hydroperoxide by itself :

$$2RO_2H \longrightarrow RO_2\cdot + RO\cdot + H_2O$$
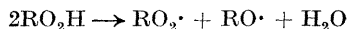
cf. p. 158, and the truly catalytic role of the metal salt is readily apparent.

Oxidation subsequently proceeds by the ordinary mechanism, *i.e.*, involving reactions (2), (3), and (6) under the conditions employed. In conformity with this, the reaction shows autocatalysis in the earlier stages and hydroperoxide is steadily formed. However, since the catalyst promotes the decomposition of the hydroperoxide so strongly, $r_i(M)$ will rapidly increase, the chain length $\{r/r_i(M)\}$ will decrease correspondingly, and we should expect the reaction soon to lose its chain character. For these circumstances, the formation and decomposition of the hydroperoxide become equal. This can arise, of course, independently of the mode of initiation, and the generalised kinetic changes and their detection experimentally have been discussed in detail by Tobolsky and his co-workers.[21] Under these conditions, the products of hydroperoxide decomposition and of inter-radical reactions, essentially (6), form a major part of the total products.

The maximum limiting rate of oxidation at a given temperature when the chain length tends to one follows from eqn. (2) as $r_{lim.} = k_3^2 k_6^{-1}[RH]^2$. It can also be shown that the stationary hydroperoxide concentration is given [21] by $[RO_2H]_{lim.} = k_3^2 k_6^{-1}[RH]^2 k_1^{-1}[catalyst]^{-1}$ where k_1 is the rate constant for the initiating reaction.

The cobalt-catalysed oxidation of tetralin in acetic acid solution exhibits these relationships.[22] The oxidation proceeds at an increasing rate to a limit which depends on $[RH]^2$ and is independent of catalyst concentration, while the maximum hydroperoxide concentration is proportional to $[RH]^2$ and inversely proportional to [catalyst].

The mechanism of metal ion–hydroperoxide interaction follows no simple pattern. Thus, in the tetralin reaction referred to above, two cobalt ions (in complex form) appear to participate in this reaction, but there are indications that such behaviour varies from one peroxide to another and even with different concentrations of the same peroxide.[20]

It is conceivable that the olefin itself could react directly with the catalyst by a process expressed in skeletal form as $RH + M^{3+} \longrightarrow R\cdot + M^{2+} + H^+$. No evidence for this initiation reaction has yet been advanced, and in fact

[19] Bawn, Pennington, and Tipper, *Discuss. Faraday Soc.*, 1951, **10**, 282.

[20] Bawn, *ibid.*, 1953, **14**, 181.

[21] Tobolsky, Metz, and Mesrobian, *J. Amer. Chem. Soc.*, 1950, **72**, 1942.

[22] Woodward and Mesrobian, *ibid.*, 1953, **75**, 6189.

the common circumstance prevails that whatever the reactivity of the olefin in such respects the reactivity of the hydroperoxide is very much greater (cf. p. 159).

6. Initiation Efficiencies

In order to specify absolutely the constants in the rate equations, r_i must be qualified by a numerical factor to express the ability of the primary radicals to initiate oxidation chains rather than undergo other reactions [cf. equation (5)]. Determination of this factor invariably involves measurements on inhibited systems.

Bolland and ten Have [4] studied the system ethyl linoleate–benzoyl peroxide–quinol and showed first that the inhibitor acts solely by removal of $RO_2\cdot$ radicals. Then, on the assumption that each molecule of quinol reacts with two of these radicals, they deduced that each molecule of benzoyl peroxide decomposing starts one chain. Bamford and Dewar [12] later studied the inhibition of photo-sensitised oxidations of tetralin and reported an efficiency of only about one-fifth of the above value, the important assumption involved being that the inhibitor does not interfere in the photo-initiation process.

A more extensive investigation [16] supports these indications of a variation in initiation efficiency from olefin to olefin. With azo*iso*butyronitrile

TABLE 6

Olefin	$k_3k_6^{-\frac{1}{2}}$ *	Efficiency	Olefin	$k_3k_6^{-\frac{1}{2}}$ *	Efficiency
2 : 6-Dimethyl-hepta-2 : 5-diene	200	2	Tetralin	12·0	1·0
			Methyl oleate . . .	1·5	0·7
Ethyl linoleate . . .	20·7	1·5	Ethyl undec-10-oate .	0·17	1·3
Digeranyl	3·8	1·3	Ethyl stearate . . .	0·01	0·4

* At 45° ; units, mole $^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec. $^{-\frac{1}{2}}$.

as initiator in strongly inhibited systems, the efficiencies given in Table 6 have been found. There is a steady decrease in efficiency with decreased α-methylenic reactivity, except for ethyl undecenoate. It has therefore been suggested that the initiating radicals act both by removing hydrogen atoms (this being the dominant mode in the more reactive olefins and of course in the saturated ester) and by attacking the double bond (this being appreciable only in the Δ^1-ester). The second mode is analogous to the presumed function of the catalyst in vinyl polymerisations, and its occurrence is consistent with other features of the oxidation of Δ^1-olefins (p. 163). Further information about the detailed chemistry of these processes is needed to check the validity of these ideas, since unfavourable evidence can be quoted (*e.g.*, Bickel and Waters [23] failed to detect the reaction of $CN\cdot CMe_2\cdot$ and related radicals with toluene).

Translation of these results to systems initiated by benzoyl peroxide

[23] Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 312.

leads to efficiency values for this catalyst some 50% higher than for the azo-compound. In the case of ethyl linoleate, there is a minor anomaly in that a value slightly greater than 2 is obtained. In systems initiated by hydroperoxide, more serious anomalies of the same kind appear. No adequate explanation of these effects is yet apparent, although it seems significant that similar anomalies have been recognised in peroxide-catalysed polymerisations.[24, 25]

7. Hydroperoxide Yields

Determination of the hydroperoxide yield has long presented a problem, partly because of the delayed development of efficient techniques for isolating and purifying these compounds and more especially because of the unreliability of analytical methods for the O_2H group. The indefinite stoicheiometry of the common methods employing iodide and ferrous ions may be inferred from the numerous variants that have been advocated for different purposes. For any particular conditions, these methods can generally be adapted to give the " right " answer, but their sensitivity to procedural variations obscures their absolute validity.

Barnard and Hargrave [26] have recently developed a standard method, based on stannous chloride as reductant, which permits the vagaries of other procedures to be ascertained. For example, a convenient modification of the Dastu–Lea iodometric method gives approximately correct results with *cyclo*hexenyl hydroperoxide in an atmosphere of nitrogen, but only 80% of the theoretical when oxygen is rigorously removed by vacuum technique. Under ordinary aerobic conditions, 114% of the theoretical value is found, and for tetralin and 1-methyl*cyclo*hexene hydroperoxides the corresponding figures are 126 and 147%. Since the high sensitivity, as well as the accurate relative estimates obtained under standard conditions for a given olefin, confer a valuable practical advantage on the iodometric and certain other methods, their absolute calibration represents an important advance. Moreover, polarographic analysis of peroxides has recently come to the fore,[27] and here again an absolute chemical standard is necessary for calibration purposes.

The peroxide yields of several olefins oxidised to oxygen contents of approximately 2% by weight have been determined by the stannous chloride method (Table 7).[28] Conditions were chosen to ensure that the chain lengths were never less than about 30, and were mostly much greater. No appreciable variation in peroxide yield with extent of reaction (to that stated above) was found.

The virtually quantitative yields obtained with the 1 : 4-dienes and equivalent phenyl-substituted olefins point to the reaction scheme on p. 148 being closely followed. The small decrease observed on passing to the

[24] Mayo, Gregg, and Matheson, *J. Amer. Chem. Soc.*, 1951, **73**, 1691.

[25] Johnson and Tobolsky, *ibid.*, 1952, **74**, 938.

[26] Barnard and Hargrave, *Anal. Chim. Acta*, 1951, **5**, 476.

[27] Willits, Ricciuti, Knight, and Swern, *Anal. Chem.*, 1952, **24**, 785.
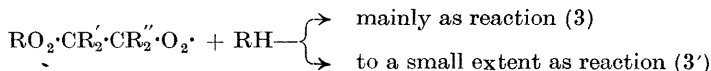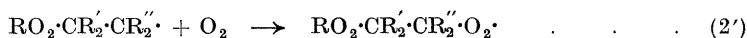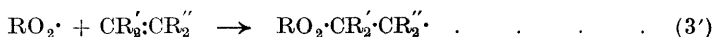
[28] Hargrave and Morris, in the press.

TABLE 7

Olefin	Hydroperoxide yield, %	Olefin	Hydroperoxide yield, %
2 : 6-Dimethylhepta-2 : 5-diene	100	Methyl oleate	81
Ethyl linoleate	98	Hept-2-ene	79
2-Methyl-4-phenylbut-2-ene .	99	Allylbenzene	82
Dicyclohex-2-enyl	98	3 : 7-Dimethyloct-1-ene . .	74
1 : 3 : 5-Trimethylcyclohexene.	97	Oct-1-ene.	69
1-Methylcyclohexene . . .	90	Squalene *	46
cycloHexene	96	Digeranyl *	47
2-Methyloct-2-ene	61		

* Theoretical yield = 50%.[31]

1 : 2-disubstituted ethylenes is attributed either to some molecular scission occurring simultaneously with hydroperoxide formation or to partial attack of the $RO_2 \cdot$ radicals at the double bonds as an alternative to reaction 3 :

$$RO_2 \cdot + CR_2':CR_2'' \longrightarrow RO_2 \cdot CR_2' \cdot CR_2'' \cdot \qquad . \qquad . \qquad . \qquad . \qquad (3')$$

$$RO_2 \cdot CR_2' \cdot CR_2'' \cdot + O_2 \longrightarrow RO_2 \cdot CR_2' \cdot CR_2'' \cdot O_2 \cdot \qquad . \qquad . \qquad . \qquad (2')$$

$$RO_2 \cdot CR_2' \cdot CR_2'' \cdot O_2 \cdot + RH \left\{ \begin{array}{l} \text{mainly as reaction (3)} \\ \text{to a small extent as reaction (3')} \end{array} \right.$$

The oxygen in the disubstituted peroxide groupings is undetected in the hydroperoxide estimation.

This second possibility is believed to be encountered in enhanced form with Δ^1-olefins, the results lending experimental support to Bolland and Gee's arguments [29] concerning the relative tendencies towards (3)- and (3')-type reactions in different olefins.*   Thermochemical calculations indicate that these reactions have roughly comparable heats of reactions, but a comparison of different olefins shows that the high lability of the reactive methylene group in 1 : 4-dienes strongly favours reaction (3), whereas the additive function of conjugated dienes acts reversely.   In mono-olefins the balance is even enough for fairly small structural variations to be reflected in changes in product composition.   In particular, reaction (3') would be expected to be favoured in Δ^1-olefins owing to their low α-methylenic reactivity and the exposure of $CH_2:CHR$ molecules to direct attack. $RO_2 \cdot$ radicals generated by the action of cobalt salts on hydroperoxides readily react with Δ^1-olefins in this way.[30]

The 1 : 5-dienes provide a unique example of the dual reactivity of $RO_2 \cdot$ radicals being fully displayed in the same molecule.   The reaction

[29] Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42,** 294.

[30] Kharasch, Pauson, and Nudenberg, *J. Org. Chem.*, 1953, **18,** 323.

* The departure from 100% yield of hydroperoxide being assumed to be due entirely to the occurrence of reactions (2') and (3') with (2) and (3), the measured propagation-rate constant at high oxygen pressures can readily be expressed in terms of k_3 and k'_3, which may then be evaluated separately if the actual yield is known.[28]

sequence envisaged is : [31]

(A)
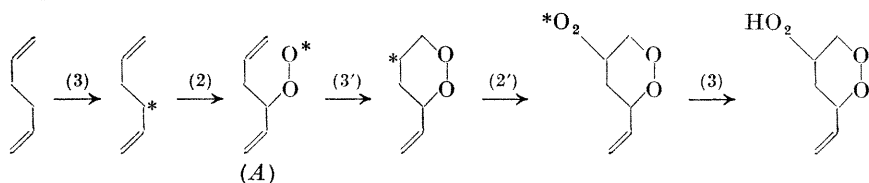
The special steric conditions evidently induce the peroxy-radical (A) to engage so efficiently in the intramolecular 3′ reaction.

The effect of additional methyl substitution in reducing the yield in 2-methyloct-2-ene compared with the corresponding unsubstituted olefins is more difficult to explain, but is thought to reflect an increase in the molecular scission which is a well-recognised phenomenon accompanying certain oxidations. This is particularly manifest in high polymeric olefins, where it leads to deterioration in their valuable physical properties, although little is yet known of its detailed chemistry. Kinetic studies [17] suggest that it connotes independent reactions of $R\cdot$ and/or $RO_2\cdot$ radicals, and in compounds of low molecular weight is associated with the appearance of carbonyl-containing products from the earliest stages of oxidation. The suggested effect of methyl groups is well-developed in phenyl-substituted analogues, benzaldehyde being formed in quantity from the compounds $CHPh:CH\cdot CH_2R$.[32]

8. Oxidative Isomerisations

1 : 4-*Dienes*.—The development of diene conjugation during the oxidation of ethyl linoleate was first observed by Farmer, Koch, and Sutton,[33] who recognised its importance as evidence, supplementary to kinetic data, for the participation of pentadienyl radicals in the reaction. Bolland and Koch [34] proved later that the conjugated units reside only in the monohydroperoxide, which is derived from these radicals and is virtually the sole reaction product under the conditions employed. Estimation of the extent of conjugation presented difficulties. The molecular extinction coefficient (ε) of the product at 2315 Å was found to be *ca.* 23,000, a value much lower than determined for the known $\Delta^{9:11}$- and $\Delta^{10:12}$-linoleic esters (*ca.* 32,000). This difference was thought to indicate that the hydroperoxide was a mixture of conjugated and non-conjugated isomers, roughly in the proportion 3 : 1. The theoretical implication is that oxygen combines with almost equal ease at the $C_{(9)}$, $C_{(11)}$, and $C_{(13)}$ in the resonating pentadienyl unit.

These findings have been confirmed by numerous workers and are typical of chemically-catalysed oxidations of various linoleic acid derivatives under a variety of conditions. The conclusion on the isomeric heterogeneity of the hydroperoxide also received wide acceptance, although other evidence

[31] Bolland and (Mrs.) Hughes, *J.*, 1949, 492.

[32] Barnard and Watson, unpublished results.

[33] Farmer, Koch, and Sutton, *J.*, 1943, 541.

[34] Bolland and Koch, *J.*, 1945, 445.

on this point was not entirely favourable. In particular, Bergström [35] hydrogenated the product from methyl linoleate and proved the formation of 9- and 13-hydroxystearic acid, but failed to detect the 11-hydroxy-isomer. This implies the absence of a non-conjugated component in the oxidation product, but the possibility that isomerisation proceeded during the catalytic hydrogenation impairs its decisiveness.
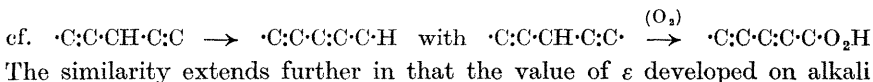
A striking result is obtained from the lipoxidase-catalysed oxidation of sodium linoleate in aqueous solution.[36] Again, the product is a mono-hydroperoxide, and, when formed during oxidations at 37°, has similar ultra-violet absorption characteristics to those above ($\lambda_{max.}$ 2340 Å, $\varepsilon = 23,000$). At lower reaction temperatures, however, the value of ε increases ; at 8° to 27,800, at 0° to 31,400. The fully conjugated nature of the last material can hardly be doubted, and some subtle factor evidently intrudes to produce the intensity differences.

Bolland and Koch had considered whether their product could be fully conjugated material having an unusual configuration of the substituents at the double bonds, but decided against this on the grounds that steric factors of this kind would not be expected to affect the intensity so markedly. In view of the much larger differences between the stereoisomeric 1 : 4-diphenylbutadienes (the cis-cis-, cis-trans-, and trans-trans-isomers have $\varepsilon_{max.} = 29,500$, 30,600, and 56,200, respectively) [37] and the comparable differences in the related methyl muconates ($\varepsilon_{2590\text{Å}} = 26,400$, 29,800, and 36,700 for the cis-cis-, cis-trans-, and trans-trans-forms, respectively),[38] this reasoning has now lost its force. This is especially so since the same phenomenon has been recognised more recently in the linoleate system itself.[39] In fact, there is now little doubt that the hydroperoxide in question consists almost wholly of conjugated structures, which probably have mainly the cis-trans-configuration.

Four lines of evidence may be considered :

(i) The first is Bergström's findings on the composition of the hydroxy-stearic acid mixture produced on catalytic reduction of the hydroperoxide (see above). A more rigorous and detailed investigation fully confirms these findings.[40]

(ii) An exactly parallel problem is encountered in the alkali-isomerization of linoleates.[41, 42] Hydrogen displacement occurs here in a manner having formal similarity to the displacement during oxidation :

cf. ·C:C·CH·C:C $\longrightarrow$ ·C:C·C:C·C·H with ·C:C·CH·C:C· $\xrightarrow{(O_2)}$ ·C:C·C:C·C·O$_2$H

The similarity extends further in that the value of ε developed on alkali

[35] Bergström, *Arkiv Kemi. Min. Geol.*, 1945, *A*, **21**, 1 ; *Nature*, 1945, **156**, 717.

[36] Holman, *Arch. Biochem.*, 1947, **15**, 403 ; Bergström and Holman, *Nature*, 1948, **161**, 55.

[37] Pinkard, Wille, and Zechmeister, *J. Amer. Chem. Soc.*, 1948, **70**, 1938.

[38] Elvidge, Linstead, Sims and Orkin, *J.*, 1950, 2235.

[39] Nichols, Herb, and Riemenschneider, *J. Amer. Chem. Soc.*, 1951, **73**, 247.

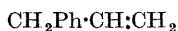[40] Sephton and Sutton, *Chem. and Ind.*, 1953, 667.

[41] See, *e.g.*, Holman and Burr, *Arch. Biochem.*, 1948, **19**, 474.

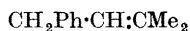[42] Brice and Swain, *J. Opt. Soc. Amer.*, 1945, **35**, 532.

treatment is also *ca.* 24,000. Unlike certain related styryl compounds,[43] the latter acids are themselves unchanged by alkali treatment [44] and hence there is no question of conjugated and non-conjugated acids existing in equilibrium. The resolution of this problem follows some outstanding work by Nichols, Herb, and Riemenschneider.[39] They isolated the products of isomerisation and identified them as two previously unknown acids which were separately converted into the known $\Delta^{9:11}$- and $\Delta^{10:12}$-linoleic acids under conditions inducing *cis-trans*-conversions. The *neo*-$\Delta^{9:11}$- and *neo*-$\Delta^{10:12}$-acids were found to have $\varepsilon_{max.} = 24,400$ and $26,600$, respectively (the former was thought to be slightly impure). The two pairs of acids are obviously related stereochemically, and Nichols *et al.* presented convincing arguments that the older acids have the *trans-trans*-configuration as generally supposed and the newer the *cis*-9-*trans*-11- and *trans*-10-*cis*-12-arrangements.

(iii) Two groups of American workers have recently attempted to determine the double-bond configurations in the hydroperoxide directly by analysis of infra-red absorption spectra.[44, 45] This cannot be done simply because correlation rules for distinguishing absorption by different types of double bond in conjugated units have yet to be established. Comparison was therefore restricted to the isomeric linoleic acids discussed immediately above, and apparently showed that hydroperoxide samples obtained from oxidations at 25° and 0° consist principally of *trans-trans* and *cis-trans* conjugated isomers, the former type predominating at 25°, the latter at 0°. These conclusions are not easily reconciled with the ultra-violet spectral data. Thus, if the *trans-trans*-forms, having $\varepsilon \sim 32,000$, predominate in the product obtained at 25° (having $\varepsilon \sim 23,000$), the accompanying *cis-trans*-forms must have $\varepsilon < 14,000$, which seems impossibly low (cf. p. 165). Further, if this should be so, it is difficult to explain the higher value of ε of the product obtained at 0° (which is said to be more *cis-trans* than *trans-trans*). It appears therefore that this work is qualitatively significant but quantitatively suspect.

(iv) A study of oxidative isomerisations in similar but simpler systems, more amenable to comparison with appropriate standards, shows that complete, or nearly complete, conjugation is generally developed.[46] The

$$\text{CH}_2\text{Ph·CH:CH}_2 \qquad \text{CH}_2\text{Ph·CH:CMe}_2 \qquad \text{CMe}_2\text{:CH·CH}_2\text{·CH:CMe}_2$$
$$\text{(I)} \qquad\qquad\qquad \text{(II)} \qquad\qquad\qquad\qquad \text{(III)}$$

hydroperoxide from (I) can be shown unequivocally to be completely conjugated (absence of CHR:CH$_2$ groups by infra-red absorption). The same is essentially true for the hydroperoxides derived from (II) and (III) as shown by their ultra-violet absorptions (an important simplification compared with the linoleate system is that *cis-trans*-isomerism is restricted to one double bond in these examples). Since the *iso*propylidene groups in (II) and (III) do not suffice to restrain the displacement of the double

[43] Bateman and Cunneen, *J.*, 1951, 2283.
[44] Cannon, Zilch, Burket, and Dutton, *J. Amer. Oil Chem. Soc.*, 1952, **29**, 447.
[45] Privett, Lundberg, Khan, Tolberg, and Wheeler, *ibid.*, 1953, **30**, 61.
[46] Bateman, Morris, and Waight, to be published.

bonds into conjugation, then *a fortiori* the substituted ethylidene groups in the linoleate system will not do so (cf. ref. 43).

Theoretical Considerations.—The formation of fully conjugated hydroperoxides is consistent with the theory that reactivity in mesomeric pentadienyl radicals is mainly concentrated at the terminal carbon atoms,[47] but does not amount to proof. If the non-conjugated peroxy-radical were formed initially, intramolecular rearrangement into the thermodynamically favoured conjugated form could proceed very easily (cf. the fate of the primary $RO_2·$ radicals in 1 : 5-dienes ; p. 164) :
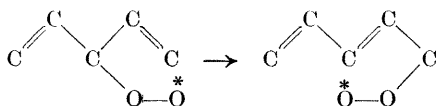
The few data on the behaviour of free pentadienyl and equivalent radicals when presumed to be formed otherwise tend to support this possibility. Thus, the dehydro-dimer produced when (I) reacts with acetyl peroxide consists mainly of *iso*dicinnamyl ; [48] and that from methyl linoleate on treatment with di-*tert.*-butyl peroxide contains roughly equal proportions of conjugated and non-conjugated diene units.[49]

Mono-olefins. In substituted ethylenes, allyl radical mesomerism allows two hydroperoxides to be formed for each unsymmetrical allylic system present :

$$CHR:CH·CH_2R \longrightarrow CHR:CH·CHR'·O_2H + CHR(O_2H)·CH:CHR'$$
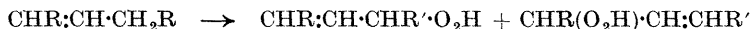
Attempts to establish the composite nature of these hydroperoxides by degradation and similar procedures have met with fair success,[50] but the non-quantitative conversion into identifiable products and the possibility of secondary rearrangements detract from the value of such evidence. Infra-red measurements yield more decisive data, and reveal that the structural types $CH_2:CH·CH_2R$, $CH_2:CH·CHMeR$, and $CMe_2:CH·CH_2R$ undergo double-bond displacement to the extents of about 50, 80, and 30%, respectively.[46] As with the 1 : 4-dienes, configurational changes at the double bonds accompany these isomerisations. Thus, oleic esters having *cis*-ethylenic units yield a hydroperoxide with predominantly *trans*-substituted double bonds.[51]

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