OLEFIN OXIDATION

By L. Bateman

(The British Rubber Producers' Research Association,
Welwyn Garden City, Herts.)

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 non-stationary 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.
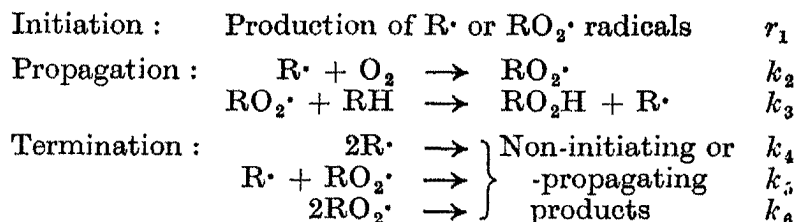
The allylic radicals formed on removal of an α-methylenic hydrogen atom from an olefin are mesomeric and hence the derived product may

[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.

Initiation :   Production of R· or RO$_2$· radicals r_1

Propagation : $R· + O_2 \rightarrow RO_2·$ k_2

$RO_2· + RH \rightarrow RO_2H + R·$ k_3

Termination : $2R· \rightarrow$ ⎤ Non-initiating or k_4

$R· + RO_2· \rightarrow$ ⎬ -propagating k_5

$2RO_2· \rightarrow$ ⎦ products k_6

The more obvious of these are : (i) high yields of the hydroperoxide, RO$_2$H (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]

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

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

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

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_i, estimates of $k_3 k_6^{-1}$ are thus obtained from $r_\infty/[RH]$ 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 :

$(a) \quad (b) \quad (c)$

(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-l-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]	$\Delta H_3 = E_3/0 \cdot 4$	$\Delta(\Delta H_3)$
$CH_2 : CH \cdot \overset{*}{C}H_3$	13·5	34	0
$CH_2 : CH \cdot \overset{*}{C}H_2 Alk$	11·5	29	5
$CHAlk : CH \cdot \overset{*}{C}H_2 Alk$	10·5	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
$CH : CH \cdot \overset{*}{C}H_2$ . . . . . . $\underset{Alk \text{---} Alk}{\vert \qquad \vert}$	9·5	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
(y) (x) (z)

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
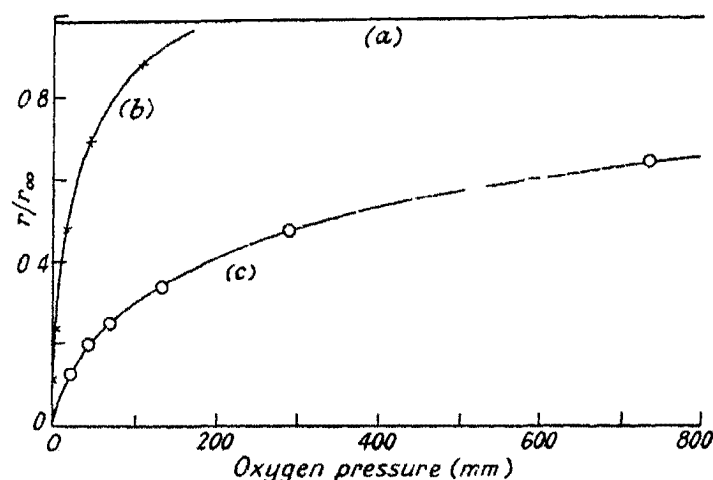

FIG. 1

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

[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.
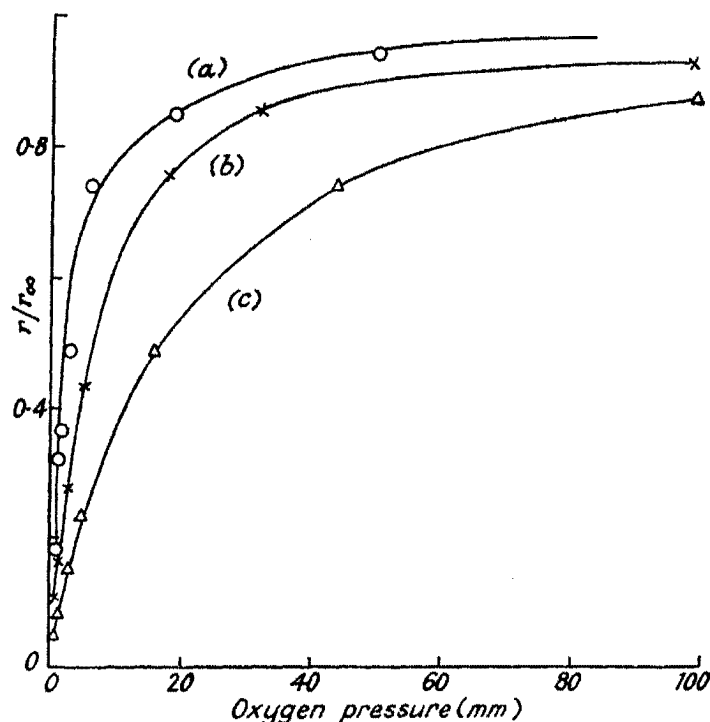

FIG. 2

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) :

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

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.

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