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Mechanism of the Epoxidation of Alkenes by Molecular Oxygen

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Radical and molecular mechanisms of the formation of oxirans are examined in the oxidation of alkenes by molecular oxygen. The reactivities of various epoxidising agents are discussed. A list of 87 references is included.

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I. INTRODUCTION

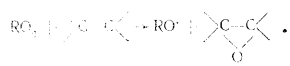
Direct oxidation of unsaturated compounds with molecular oxygen[1] is most promising for obtaining oxirans, which are used as monomers for the production of polyurethanes, stereospecific polymers, various additives, surface-active agents, and other important chemical products. The problem of establishing the mechanism of the epoxidation of alkenes by molecular oxygen therefore acquires great importance. It is now generally accepted that during direct oxidation alkene oxides are formed predominantly in the course of chain propagation by interaction between alkenes and various peroxy-radicals.

The present Review examines the structure of radical epoxidising agents, their reactivity, and the dependence of the selectivity of epoxidation on the structure of the initial alkene. Possible routes for epoxidation by molecular intermediate products are suggested. Catalytic epoxidation of alkenes by molecular oxygen and by hydroperoxides is not discussed here, since it has already been reviewed[2].

II. EPOXIDATION OF ALKENES BY ALKYLPEROXY-RADICALS

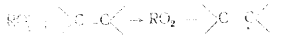
Most investigators accept that the main route to the formation of oxirans in the direct oxidation of alkenes is epoxidation of the latter by alkylperoxy-radicals[3-29].

The simplest reaction of this type occurs between a monomeric peroxy-radical and an alkene:



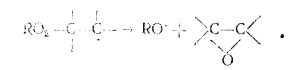
(1)

This takes place in two stages—addition of the peroxy-radical to the alkene to form a β-peroxyalkyl radical



(1′)

and breakdown of this radical into an oxiran and an alkoxy-radical



(1″)

The absence of stereospecificity in the epoxidation of alkenes by alkylperoxy-radicals[4,5,11,25] has been interpreted as evidence of intermediate formation of a β-peroxyalkyl radical. The probability of *cis–trans* isomerisation in this radical is determined by the relative rates of rotation about the C–C bond and of breakdown of the radical to form the oxiran.

The relative concentrations of *cis*- and *trans*-oxides of oct-4-ene among the reaction products depend[25] on the configuration of the alkene: more of the *cis*-oxide is obtained from *cis*-oct-4-ene, and more of the *trans*-oxide from the *trans*-alkene. This apparently indicates that the life of the β-peroxyalkyl radical is too short for the attainment of conformational equilibrium[25].

Effective activation energies for the overall reaction (1) have been determined for interaction of the methylperoxy-radical with substituted butenes in the gas phase at 100–130 °C[26] (Table 1). A similar value was obtained[87] for the gas-phase oxidation of ethylene: E_{eff} = 10 kcal mole^{-1}.

Table 1.

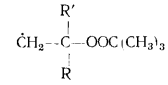
Alkene	2-Methylbut-1-ene	2-Methylbut-2-ene	2,3-Dimethylbut-2-ene
E_{eff}, kcal mole^{-1}	12.7±1.3	10.2±0.8	8.7±0.6

The addition of alkylperoxy-radicals to alkenes is reversible[28]. From the rate constants estimated from thermochemical data for the breakdown of β-peroxyalkyl radicals

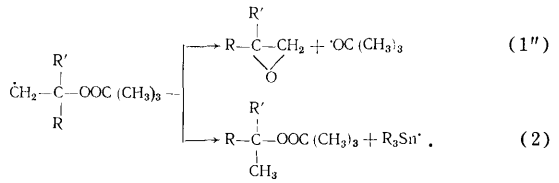
$$k_{1'}=10^{11.5}\exp(-14\,000/RT);\quad k_{-1'}=10^{13}\cdot\exp(-18\,000/RT)\quad (c^{-1}),$$

it can be concluded that the reverse reaction to (1′) begins to be significant only at high temperatures (above 300 °C)[28].

Rate constants for the decomposition of various β-peroxyalkyl radicals were determined experimentally[27]. The radicals were prepared independently by reaction between the corresponding brominated peroxides and hexamethyldistannane $(CH_3)_3Sn.Sn(CH_3)_3$ or a trialkylstannane R_3SnH in the presence of an initiator. Formation of the radicals was recorded by electron spin resonance at −70 °C. Further conversion of the β-peroxyalkyl radicals



was due to competition between two reactions—decomposition with formation of an oxiran (1″) and reduction in the presence of the trialkylstannane with formation of a dialkyl peroxide (2):



(1″)

(2)

The relative concentrations of the products—oxiran and dialkyl peroxide—gave the ratio of the rate constants of the two competing reactions k_1''/k_2. From the known value of k_2, rate constants were found[27] for the formation of oxirans in the decomposition at 25 °C of the β-peroxyalkyl radicals in Table 2.

Table 2.

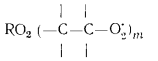
Radical*	$\dot{C}H_2-C(R)(R)-OOC(CH_3)_3$	$\dot{C}H_2-C(R')(R)-OOC(CH_3)_3$	$\dot{C}H_2-C(R')(R')-OOC(CH_3)_3$
10^3k, s^{-1}	700	40	2

* R = CH_3 and R′ = H.

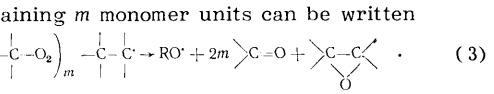
Thus the rate constant of reaction (1″) increases sharply with the number of substituent groups in the β-peroxyalkyl radical. The decomposition rate constants of such radicals are surprisingly large in absolute magnitude: the values obtained[27] exceed by many orders of magnitude those for the corresponding dialkyl peroxides (e.g. 10^{-6} s^{-1} for di-t-butyl peroxide in benzene at 80 °C[31]).

Indirect confirmation of the possibility that β-peroxyalkyl radicals decompose with the formation of oxirans was obtained as early as 1950[30]. Isobutene oxide (30 mole % based on the peroxide that had reacted) was detected in the thermal (100 °C) and photochemical decomposition of di-t-butyl peroxide, as a result of breakdown of the radical $(CH_3)_3COOC.(CH_3)_2CH_2$, formed in chain propagation[30].

Peroxy-radicals involved in epoxidation can react in either monomeric (RO_2·) or polymeric

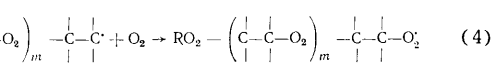


form[6,7,13-16,29]. Breakdown of the latter results in formation of an oxiran and a carbonyl compound in a single step, which for a radical containing m monomer units can be written



(3)

The length m of the carbon chain is determined by the relative rates of decomposition of the β-peroxyalkyl radicals (1″) or (3) and of reaction with oxygen



(4)

and depends on the structure of the initial alkene and the reaction conditions (Section IV).

Competition between reactions (1″) or (3) and (4) should lead to an inversely proportional dependence of the yield of oxiran on the concentration of molecular oxygen[10]:

$$\frac{w_{Ox}}{w_{Eth}} = \frac{1}{(A + B[O_2])} \qquad (4a)$$

where w_{Ox} is the rate of formation of the oxiran, w_{Eth} is the rate of consumption of the initial ethylenic compound, and A and B are constants containing the ratios of the rate constants of the primary stages. Decrease in yield (and rate of formation) of alkene oxides with increase in oxygen concentration over a certain range has been observed experimentally in the oxidation of a substituted norbornene (Fig. 1, curve *1*),[46] propene[59], and other alkenes[10,22,23], and is regarded as kinetic evidence of the formation of oxirans in the decomposition of β-peroxyalkyl radicals.

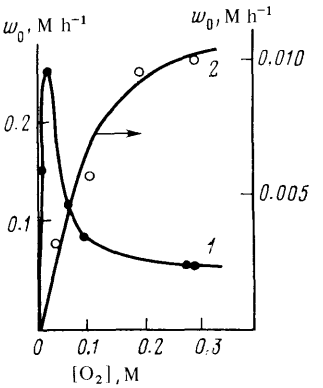
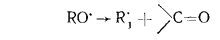


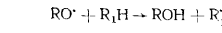
Figure 1. Dependence of initial rate of accumulation of alkene oxide on concentration of oxygen in the oxidation of methyl *exo*-2-methylbicyclo[2,2,1]hept-5-*endo*-carboxylate (a substituted norbornene) by molecular oxygen (50 atm) in benzene at 70 °C[46] in the presence of: 1) 0.01 M azoisobutyronitrile; 2) acetaldehyde (concerted oxidation).

Epoxidation (1″) should lead to the formation of equimolecular quantities of oxirans and monomeric or polymeric conversion products of alkoxy-radicals. Therefore some information on the course of such reactions in the complicated multistage oxidation of alkenes can be obtained by tracing the fate of such radicals formed in the epoxidation step. Three possible types of conversion are considered—(i) unimolecular decomposition with formation of an aldehyde and an alkyl radical[2,4,8,67]



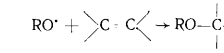
(5)

(ii) detachment of a hydrogen atom with formation of an unsaturated alcohol (in the case of an allylic alkoxy-radical) or a polymer containing a terminal hydroxy-group[4,8-10,20,32,67]



(6)

and (iii) addition at the double bond of the initial alkene[8-10,32]



(7)

In some cases (when epoxidation of alkenes is the main source of alkoxy-radicals) equivalence has been established

between the quantities of oxirans and conversion products of the radicals[3,8,9]. However, attempts to draw up such a balance have not always been successful. Thus decomposition should not be the only conversion undergone by alkoxy-radicals: in the presence of hydrocarbons containing reactive carbon–hydrogen or ethylenic bonds reaction (6) or (7) can compete successfully with unimolecular decomposition (5)[6,7] (especially in the case of primary and secondary alkoxy-radicals). In most work on the oxidation of alkenes however, unsaturated alcohols have been either detected in insignificant quantities or completely absent from the reaction products (Table 3).

Table 3. Oxidation of alkenes at 60–70 °C[8,9]*.

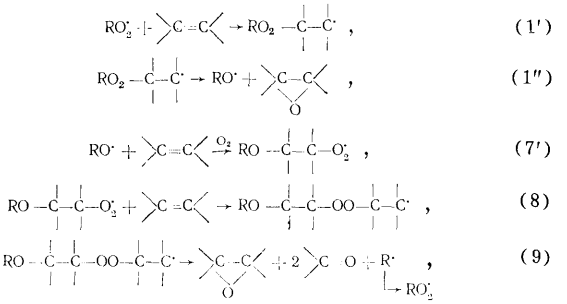
Alkene	β, %	10^3[Ox], moles	10^3[Alc], mole	10^3[Ke], moles	j	k	l
But-2-ene	4.5	2.31	0	3.27	4.00	7.78	2.18
2-Methylbut-2-ene	4.2	1.94	0.63	3.36	5.00	9.72	2.18
2,3-Dimethylbut-2-ene	4.7	3.06	0.58	4.31	6.00	11.66	2.26
Isobutene	4.5	3.39	0	2.82	4.00	6.98	1.60
Hex-1-ene	3.7	0.86	0.59		6.00	11.76	2.37
Cycloheptene (Ref.73)	5.5	2.04	1.55	0	7.00	13.81	2.00

* Here β represents the degree of conversion, Ox the alkene oxide, Alc an unsaturated alcohol, and Ke carbonyl compounds containing fewer carbon atoms than in the initial alkene. The composition of the macromolecular products $(C_jH_kO_l)_{m_i}$ was determined from elementary analysis; m_i is the number of monomer units in the polymer molecule.

The hypothesis that alkoxy-radicals are consumed mainly by addition to the double bond of the alkene is contradicted by the experimental observation that the rate of abstraction of a hydrogen atom from propene, determined for the t-butoxy-radical, exceeds about thirtyfold the rate of addition of this radical to propene[32] and other alkenes[31]. Furthermore, elementary analysis[8,9] indicates that the composition of the macromolecular products from several alkenes approximates to the empirical formula $C_nH_{2n}O_2$ (Table 3), which indicates that monomeric groups of peroxide character predominate in the polymer.

From the stoichiometry of the epoxidations (1) and (3) it may be expected that equimolecular quantities of alkene oxide and total conversion products of the epoxidising agent will be formed. This imposes a limit on the yield of oxiran, which theoretically should not exceed 50% based on the alkene consumed. In several cases, however, e.g. in the oxidation of cyclo-octene[34], norbornene derivatives[35–37,24], hexafluoropropene[38], "di-isobutene" (2,4,4-trimethylpent-1-ene)[39], and 2-methylpent-1-ene[33], the yield of alkene oxide exceeds the total yield of products formed from alkoxy-radicals, and reaches 70–80% based on the alkene that has reacted.

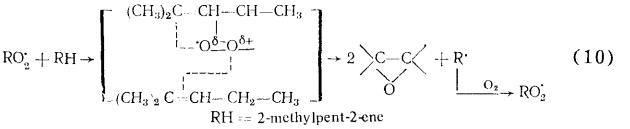
Except in the early work, in which direct incorporation of an oxygen molecule at the double bond of the alkene was assumed, as e.g. for di-isobutene[39], the observed regularities are mostly explained in terms of various radical epoxidation reactions having one fundamental common feature: regeneration of the R· (or RO_2·) radical carrying the chain oxidation is postulated in the epoxidation step. Thus the sequence of reactions



(1′) (1″) (7′) (8) (9)

provides a description of the kinetics of the oxidation of styrene derivatives[6,13], and gives theoretical maximum yields of alkene oxides up to 66%. This scheme of oxidation is applicable only to alkenes containing no reactive hydrogen atoms, for which chain propagation involves mainly addition of radicals at the double bond of the alkene and breakdown of the resulting polymeric radicals.

The composition of the oxidation products of 2-methylpent-2-ene, which is characterised by reactions involving abstraction of a hydrogen atom[33], can be explained by introducing into the scheme another epoxidation reaction

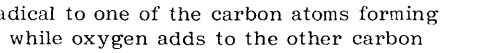


RH = 2-methylpent-2-ene (10)

which like reaction (9) leads to regeneration of the peroxy-radical. Scheme (10) involves polarisation of the dioxy-bond in an allylic peroxy-radical by interaction of the electron of the latter with the π-electrons of the double bond. This facilitates migration of the oxygen atom to the double bond and detachment of the second oxygen atom by an adjacent alkene molecule.

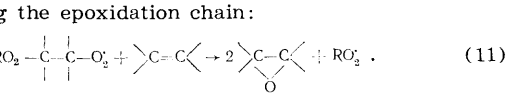
The high yield of oxides of norbornene derivatives, in particular of cyanonorbornene (~ 70% based on the alkene consumed)[35–37], cannot be explained by the above reactions (9) and (10), since structural features of norbornene make formation of allylic peroxy-radicals improbable[24,35,41] (the usual delocalisation of electron density in the radical formed by detachment of an α-hydrogen atom is difficult). Furthermore, the carbonyl compounds whose formation is implied by reaction (9) do not exceed 10% of the alkene that has reacted in the oxidation of norbornene derivatives.

We have suggested a mechanism[35,42] in which the epoxidising agent is a peroxy-radical formed by addition of a chain-carrying radical to one of the carbon atoms forming the double bond, while oxygen adds to the other carbon atom:



(1‴)

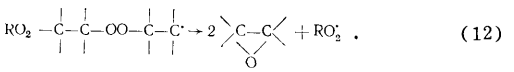
Such a radical reacts with the initial cyanobornene to form two molecules of the alkene oxide and regenerate the peroxy-radical carrying the epoxidation chain:



(11)

Overall, reaction (11) is energetically advantageous[42]. It

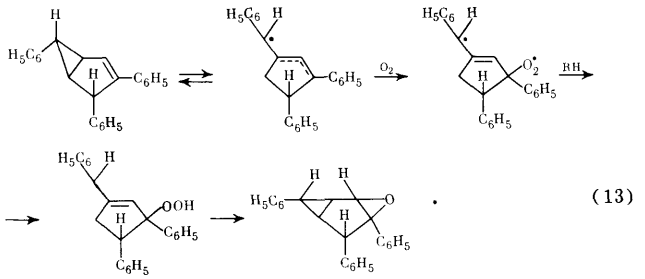
may take place not in a single stage but by formation and subsequent breakdown of a β-peroxyalkyl radical:



(12)

The mechanism of epoxidation suggested for derivatives of norbornene is also the most probable mode of formation of hexafluoropropene oxide[38], the yield of which reaches 80% based on the alkene that has reacted.

Yet another scheme of epoxidation was suggested in work[40] on the thermal oxidation of a bicyclo[3,1,0]hex-2-ene:



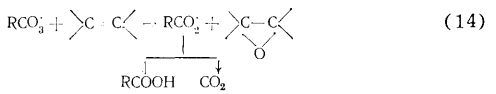
(13)

In this case the alkene oxide is formed by the breakdown and rearrangement of a hydroperoxyalkyl radical. The reaction sequence (13) was assumed by analogy with the published mechanism of thermal *exo–endo* isomerisation of bicyclo-compounds. However, oxidation of this bicyclo[3,1,0]hex-2-ene was conducted in xylene at temperatures above 100 °C, so that peroxy-radicals of xylene could have been the epoxidising agents, a possibility that was not considered[40]. Later other workers[19] published a study of the oxidation of conjugated dienones in cumene and in xylene at 120–130 °C, in which results were obtained indicating that under these conditions epoxidation involved peroxy-radicals of these solvents.

It must be noted that decomposition of hydroperoxyalkyl radicals has been assumed as the mode of formation of alkene oxides in the high-temperature (~ 400 °C) oxidation of alkenes in the gas phase[70–72].

III. EPOXIDATION OF ALKENES BY ACYLPEROXY-RADICALS

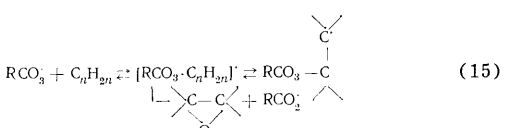
The epoxidation of alkenes by acylperoxy-radicals



(14)

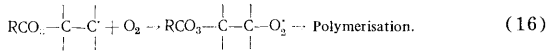
has an important role in systems in which aldehydes are formed as reactive intermediates. Reaction (14) has been studied in detail on the concerted oxidation of alkenes and aldehydes, a relatively simple process in which acylperoxy-radicals are the sole radical epoxidising agents[43–47,49,50,54]. The effective rate constant of reaction (14) determined for the concerted oxidation of nonene and benzaldehyde is 18000 M^{-1} s^{-1} at 90 °C[47]. The first stage of this reaction is assumed to be addition of acylperoxy-radicals at the double bond of the alkene.

One of the two views held concerning the structure of the radical adduct is that[43–45] reaction between acylperoxy-radicals and alkenes involves intermediate formation of a π-complex radical (as in the interaction of peracetic acid with propene[48]). The suggested general scheme of epoxidation[46]



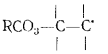
(15)

indicates that the initially formed π-complex $[RCO_3.C_nH_{2n}]^{\cdot}$ can react in two ways: it can decompose with formation of an oxiran or rearrange with fission of the π-bond. The latter process leads to subsequent formation of polymeric products:

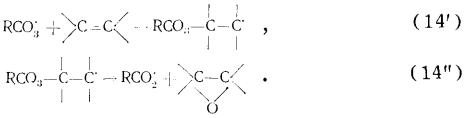


(16)

The alternative view[47] does not exclude the possibility of initial formation of a π-complex between radical and alkene. However, its concentration is considered[47] to be far lower than that of acylperoxy-radicals: a π-complex, even if formed, would rearrange rapidly into a β-peroxyalkyl radical



Thus formation of a complex is not a stage determining the macrokinetics of the process, and the mechanism of epoxidation by acylperoxy-radicals is assumed to resemble that by alkylperoxy-radicals:



(14′)

(14″)

The kinetics of the concerted oxidation of alkenes and aldehydes can be described on both views.

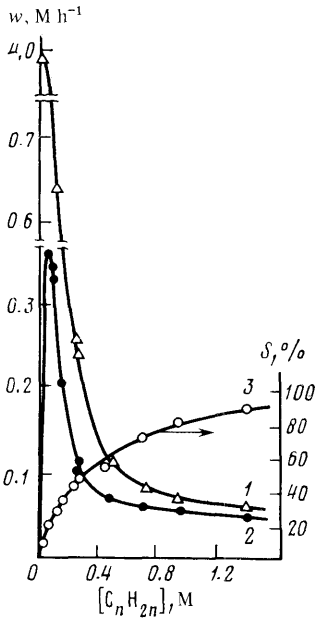


Figure 2. Effect of concentration of non-1-ene in chlorobenzene at 90 °C[47] on: 1) rate of consumption of benzaldehyde; 2) rate of accumulation of nonene oxide; 3) variation in yield of nonene oxide based on the benzaldehyde that has reacted.

Above a certain limiting value the alkene concentration ceases to affect the rate of accumulation of oxiran. Such a relation has been observed in the concerted oxidation of propene[45] and of nonene[47] with aldehydes (Fig.2). In terms of

the hypothetical formation of an intermediate complex radical the explanation is that at a certain alkene concentration all acylperoxy-radicals are bound in the complex, and further increase in the alkene concentration leads to no increase in the concentration of the intermediate complex and hence in the rate of formation of the oxiran[45].

However, attainment of a limiting rate of epoxidation is not unequivocal evidence of existence of the complex $[RCO_3.C_nH_{2n}]_\infty$. This relation can be explained by compensation of the increase in rate of epoxidation due to increase in alkene concentration by decrease in the steady-state concentration of $RCO_{3\infty}$ radicals as a consequence of reaction (14')[47]. Thus this reaction produces a linear loss of such radicals. The dimeric (polymeric) peroxy-radical $MO_{2\infty}$ thus formed does not undergo the exchange reaction during development of the primary chain:

$$MO_{2\infty}^{\cdot} + RCHO \xrightarrow{O_2} RCO_{3\infty}^{\cdot} + MOOH. \qquad (17)$$

In the concerted oxidation of alkenes and aldehydes the dependence of rate of epoxidation (and yield of oxiran) on the oxygen concentration is similar to that observed for the oxidation of saturated compounds. Thus the rates of formation of the oxides of propene[45] and of a substituted norbornene[46] in the concerted oxidation of these alkenes with acetaldehyde increase continuously with the concentration of molecular oxygen up to a certain value, after which they cease to depend on this concentration (Fig. 1, curve 2).

Thus the dependence of rate of epoxidation on oxygen concentration changes qualitatively with the nature of the epoxidising agent (as mentioned above, a fall in rate with increase in oxygen concentration over a certain range has been observed for reactions of alkylperoxy-radicals[10,46]). One explanation for this difference is that reaction (16) with oxygen is improbable for a π-complex radical devoid of a free valency localised on a carbon atom[45]. Hence the epoxidation of alkenes by acylperoxy-radicals does not involve the competition between breakdown of a π-complex and its interaction with oxygen that can produce a fall in yield of alkene oxide with increase in oxygen concentration.

If the direct precursor of the oxiran is a σ-bound not a π-complex radical, the near independence of the yield (and rate of formation) of the oxiran from the oxygen concentration is interpreted as due to the rate of reaction (14") exceeding the rate of reaction (16) in the competition for radicals of type RCO_3-C-C_{∞}[49].

The ratio of the rate constants $k_{16}/k_{14''}$ estimated for the concerted oxidation of valeraldehyde and cyclohexene[49] supports the hypothetical rapidity of unimolecular decomposition (14"). However, it was admitted[49] that the accuracy of such an estimate was low, since the ratio was determined from constants *A* and *B* in Eqn.(4a), although the yield of the cyclohexene oxide varied very little with the oxygen concentration.

The stereochemical consequences of epoxidation by acylperoxy-radicals also support the concept of formation of the oxiran in decomposition of a σ-bound radical (14") having a carbon–carbon single bond. The concerted oxidation of benzaldehyde separately with *cis*- and *trans*-but-2-ene[50] and also the oxidation of isobutyraldehyde with the stereoisomers of oct-2-ene[54] yield mixtures of the *cis*- and *trans*-oxirans. Two trends were distinguished[50,54] in this process—stereospecific epoxidation of alkenes by peroxy-acids[51–53] and non-stereospecific epoxidation by acylperoxy-radicals.

Reaction (14) is accepted as the main path to formation of the oxides of propene[55–57,59], unbranched nonene[58], and hexene[60] in the direct oxidation of these alkenes by molecular oxygen. Involvement of acetylperoxy-radicals in the epoxidation step in the oxidation of propene is confirmed by experiments on the concerted oxidation of propene with acetaldehyde in the presence of iminoxyl radicals at 150 °C[57,59]. Under these conditions oxidation of propene is inhibited by iminoxyl radicals, and the only processes that occur are the oxidation of acetaldehyde and the epoxidation of propene by acylperoxy-radicals.

Table 4.

$[O_2]$, vol.%	21	12	8.0	2.5
Propene	0.8	—	2.0	—
Isobutene	1.1	—	2.1	2.2
Propene / Acetaldehyde	0.51	0.51	0.52	—

* Oxidation was conducted in the presence of stable iminoxyl radicals.

If acylperoxy-radicals are the sole epoxidising agents, the stoichiometry of reaction (14) requires that the rates of formation of the oxidation products should satisfy the relation†

$$\alpha = w_{Ox}/(w_A + w_{CO_2}) \leqslant 1,$$

in which w_{Ox} and w_A are the rates of formation of oxide and acid respectively. Such a relation has indeed been observed in the concerted oxidation of alkenes and aldehydes[43–47,59]. In the direct oxidation of alkenes, however, e.g. of propene[59] and isobutene[23], the parameter α increases to ~ 2–2.2 with decrease in the oxygen concentration of the oxidising gas. Table 4 gives the values obtained for α.

These results indicate that epoxidation of alkenes when oxidised by molecular oxygen has a complicated mechanism and that several epoxidising agents are involved in the formation of alkene oxides (e.g. alkylperoxy-radicals, which exhibit an increase in yield of alkene oxides with fall in oxygen concentration).

IV. INFLUENCE OF STRUCTURE OF ALKENES AND PEROXY-RADICALS ON RATE OF EPOXIDATION

The relative rates of epoxidation of alkenes by peroxy-radicals depend on the structure of the initial alkenes and on the reactivity of the double bond towards different epoxidising agents, as well as on the conditions of oxidation. We shall examine specific examples of the formation of alkene oxides involving various types of peroxy-radicals. Unfortunately, rigorous quantitative comparison of reaction rate constants is impossible because of the lack of appropriate data (different workers conducted oxidation under conditions that could not be compared, in several cases rates of initiation and chain-termination rate constants were not determined, etc.).

† The acid and carbon dioxide are products of further conversion of the alkylperoxy-radical, and are formed also in parallel chain oxidation reactions of aldehydes, e.g.

$$RCO_3^{\cdot} + RH \rightarrow \begin{cases} RCO_3H \\ \rightarrow RCO_2H. \end{cases}$$

The epoxidation of propene by peroxy-radicals formed in the oxidation of various compounds—aldehydes, butan-2-one, alkylated arenes, and saturated hydrocarbons—exhibits (Table 5)[43] clear selectivity of propene towards the epoxidising agents: the yield of methyloxiran is several times higher in the presence of acylperoxy-radicals than in epoxidation by peroxy-radicals e.g. of cumene or ethylbenzene. These results are consistent with experiments showing[62] that at 90 °C propene undergoes hardly any epoxidation by peroxy-radicals of ethylbenzene, whereas cyanoisopropylperoxy-radicals under the same conditions give only ~ 1% yield of methyloxiran calculated on the epoxidising compound.

Epoxidation by acyl- and alkyl-peroxy-radicals has been compared[46] in the oxidation of methyl *exo*-2-methylbicyclo.[2,2,1]hept-5-ene-*endo*-carboxylate by molecular oxygen in the presence of an initiator and in the concerted oxidation of this ester with acetaldehyde. The rate of formation of the alkene oxide via acylperoxy-radicals exceeded that via alkylperoxy-radicals by factors of ~ 30–40. Similar results have been obtained for the direct and concerted oxidation of cyclohexene[8,49]: whereas the former leads mainly to the formation of cyclohexenyl hydroperoxide (negligible quantities of cyclohexene oxide were detected), in the concerted oxidation of this alkene with valeraldehyde the oxiran becomes the main oxidation product.

Table 5. Yield S of alkene oxides calculated as a percentage of compound consumed.

Compound	t, °C	S, %	Compound	t, °C	S, %
Acetaldehyde	55—80	30.0—70.0	Butane	145	11.0
Propionaldehyde	70	50.0	Cumene	130	13.4
Butan-2-one	145	96.0	Ethylbenzene	120—140	15.0

The greater epoxidising power of acylperoxy- than of alkylperoxy-radicals can be explained in terms of the relative rates of the two competing reactions[49]—addition of peroxy-radicals to the ethylenic double bond

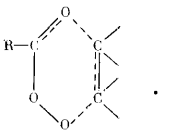
$$RCO_3^{\cdot}\ (\text{or}\ RO_2^{\cdot}) + \rangle C{=}C\langle \rightarrow RCO_3{-}\overset{|}{C}{-}\overset{|}{C}^{\cdot}\ (\text{or}\ RO_2{-}\overset{|}{C}{-}\overset{|}{C}^{\cdot}) \qquad (14')$$

and abstraction of an α-hydrogen atom relative to this bond

$$RCO_3^{\cdot}\ (\text{or}\ RO_2^{\cdot}) + RH \rightarrow R^{\cdot} + RCO_3H\ (\text{or}\ RO_2H)\ . \qquad (18)$$

The ratio of the rate constants of reactions (14′) and (18) for the interaction of the acetylperoxy-radical with cyclohexene exceeds the ratio for that of the cyclohexenylperoxy-radical by a factor of 30. This was attributed[49] to better stabilisation of the partial positive charge induced on the alkene in the transition state corresponding to addition of acylperoxy-radicals than in that arising on abstraction of a hydrogen atom. Such behaviour of acylperoxy-radicals will explain the high yields of alkene oxide obtained with respect not only to the alkene consumed but also to the organic compound introduced (Table 5).

In terms of scheme (15), which involves formation of π-complex radicals, the higher rates of epoxidation of alkenes by acylperoxy-radicals are explained[46] by stabilisation of π-complexes of alkenes with the latter radicals due to formation of six-membered structures of the type



Because of the relatively greater stability of such a complex with acylperoxy-radicals the equilibrium (15) will be displaced to the left, and it appears that only breakdown of the complex into the alkene oxide and the $RCOO_2^{\cdot}$ radical will take place[46].

Hypotheses[46,49] advanced to explain the great epoxidising power of acylperoxy-radicals are not inconsistent, since they concern different primary stages in the oxidation of alkenes. However, the epoxidation of alkenes by such radicals is not effective in all cases. Thus chloromethyloxiran could not be obtained at all by the concerted oxidation of acetaldehyde and allyl chloride (at 70–100 °C)[64]. Comparison of the reactivities of several hydrocarbons towards acetylperoxy-radicals shows that the rate of epoxidation depends significantly on the nature of the substituent adjacent to the double bond in the alkene[63,64]. This is illustrated by Table 6, in which w_0 is the initial rate of formation of the oxiran; the rate of chain initiation is in all cases 0.039 mM s^{-1} at 90 °C and 50 atm.

Table 6.

Alkene	Propene	Styrene	Cyclohexene
$10^5 w_0$, M s^{-1}	47	2.6	6.4
$10^2 k_2/k_6^{1/2}$, $M^{3/2}$ $s^{-3/2}$	24	1.3	3.3

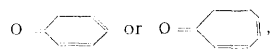
Table 7. Rates of formation w and yields S (based on alkene that has reacted) of alkene oxides in the action of isobutylperoxy-radicals on alkenes at 120 °C.[20]

Alkene	$10^6 w_0$, M s^{-1} (120° C)	S, %
α-Methylstyrene	16	86.5
Styrene	29	86
Propene	1.65	30
2,3-Dimethylbut-2-ene	1.55	38
Hex-1-ene	0.42	11.5

The epoxidising power of alkylperoxy-radical also is strongly dependent on the structure of the alkene and the conditions of oxidation. Thus epoxidation of cyanonorbornene—an alkene containing a reactive double bond (due to deformation of bond angles at the carbon atoms forming the double bond[65])—by peroxy-radicals of alkylarenes is observed even at 80 °C.[42] Under these conditions, however, the peroxy-radicals of ethylbenzene, as noted above, cause hardly any epoxidation of propene, an alkene containing a less reactive terminal double bond[43,62]. Epoxidation of propene by peroxy-radicals of alkyl groups—t-butyl[20] and apparently allyl[59]—begins to occur at an appreciable rate only at higher temperatures (120–150 °C—Table 7). Similarly, in the gas-phase oxidation of propene epoxidation by alkylperoxy-radicals becomes the predominant mode of formation

of methyloxiran only at high temperatures (above 350 °C). Under these conditions methyloxiran and acetaldehyde are formed simultaneously[66] (not consecutively, as would have been observed in epoxidation by acylperoxy-radicals).

Another illustration of the selectivity of epoxidation by alkylperoxy-radicals is the oxidation of conjugated dienones and diene ethers in cumene or xylene at 120–130 °C, when peroxy-radicals of the solvents act as epoxidising agents[19]. Cumenylperoxy-radicals react with conjugated alkenes, e.g.



to give oxides of the alkenes in high (50–95%) yields. However, these radicals do not epoxidise molecules containing isolated double bonds or cross-conjugated systems such as



Two factors govern selectivity according to the above mechanisms of epoxidation of alkenes by alkylperoxy-radicals. The first is the ratio of the rate constants of the two reactions between these species—addition at the double bond (1′) and (14′) and detachment of a hydrogen atom (18)—the kinetic consequences of competition between reactions (1′) and (18) having been examined first in 1958[63] and also subsequently[7–10,20,49]. Selectivity of epoxidation of various alkenes by t-butylperoxy-radicals in an inert atmosphere at 120 °C (Table 7) has in particular been related[20] to three factors—(*a*) the reactivity of the double bond (which varies with the substituents attached to the ethylenic carbon atoms), (*b*) the number of hydrogen atoms located α to the double bond (the greater the number of allylic hydrogen atoms the more rapid the detachment of a hydrogen atom (18), which competes with addition), and (*c*) characteristics of the allylic hydrogen atoms (whether primary, secondary, etc.). Table 7 shows that the maximum yield of alkene oxide is obtained with styrene derivatives, which interact with t-butylperoxy-radicals almost solely by addition of the latter at the double bond.

Table 8. Ratios $k_{1'}/k_r^{1/2}$ and $k_{18}/k_r^{1/2}$ $M^{-1/2}$ $h^{-1/2}$ at 70 °C.[9]

Alkene	$k_{1'}/k_r^{1/2}$	$k_{18}/k_r^{1/2}$	Alkene	$k_{1'}/k_r^{1/2}$	$k_{18}/k_r^{1/2}$
Propene	0.014	0.013	Isobutene	0.051	0.012
But-1-ene	0.017	0.019	2-Methylbut-2-ene	0.111	0.102
trans-But-2-ene	0.033	0.040	2,3-Dimethylbut-2-ene	0.25	0.67

Published results[9] also permit comparison of the ratios $k_{1'}/k_r^{1/2}$ and $k_{18}/k_r^{1/2}$ (in which k_r is the rate constant of quadratic recombination of peroxy-radicals) for the interaction of alkenes with allylic peroxy-radicals of the same structure as the initial alkene. Comparison was based on the postulate that variation of these parameters was due mainly to change in $k_{1'}$ and k_{18}. Although this approximation is not entirely accurate (as was admitted[9]), a general tendency for the reactivity of alkenes to vary with their structure can be quite definitely traced (Table 8). Maximum values of $k_{18}/k_r^{1/2}$ were obtained for alkenes having the largest number of allylic hydrogen atoms; the ratio $k_{1'}/k_r^{1/2}$ increases with the number of substituents attached to the ethylenic carbon atoms in the alkenes investigated.

Data on the influence of temperature on competition between reactions (18) and (1′) are few and disconnected. An example is provided by chain-propagation rate constants obtained for the oxidation of cyclohexene[68]:

$$k_{18} = 4.8 \cdot 10^6 \exp[(-6300 \pm 300)/RT] \ (M^{-1} s^{-1})$$
$$k_{1'} = 1.2 \cdot 10^8 \exp[(-14000 \pm 600)/RT] \ (M^{-1} s^{-1}).$$

These results show that rise in temperature should lead to a relative increase in the rate of addition of peroxy-radicals to the double bond in cyclohexene.

Table 9.

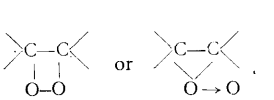
Alkene	*t*, °C	$k_4/k_{1''}$, M^{-1}	Alkene	*t*, °C	$k_4/k_{1''}$, M^{-1}
2,3-Dimethylbut-2-ene	50	32	But-2-ene	70	110
Cycloheptene	60	34	2-Methylbut-2-ene	60	150
Cycloheptene (*in benzene*)	90	25	α-Methylstyrene	50	5.9–11.0
2-Methylpent-1-ene	70	110	Styrene	50	53–154

The second factor governing selectivity of epoxidation is the ratio of the rates of the two conversions undergone by β-peroxyalkyl radicals—decomposition with formation of alkene oxide (1″) and reaction with oxygen (copolymerisation of alkene with oxygen) (4)—competition between which has already been discussed in connection with the influence of oxygen concentration on the yield of alkene oxides (Section II). Table 9 shows that the ratios of the rate constants $k_4/k_{1''}$ for various alkenes differ more than tenfold (cf. styrene and ethylene derivatives)[10]. This is due to variation in both k_4[31] and $k_{1''}$, the latter of which increases[27] from 2000 to 700000 s^{-1} with the number of methyl groups in the β-peroxyalkyl radical. It is noteworthy also that values of $k_{1''}$, estimated from the ratio $k_4/k_{1''}$ (using values of k_4 from Ref. 31) lie in the range 10^4–10^6 s^{-1}. This is consistent with results obtained for the decomposition of β-peroxyalkyl radicals prepared from the corresponding bromo-peroxides[27].

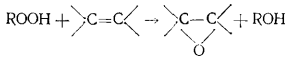
The ratio $k_4/k_{1''}$ diminishes with rise in temperature, since estimated[26] activation energies of decomposition of β-peroxyalkyl radicals are 14–15 kcal $mole^{-1}$, whereas addition of R_2 radicals to oxygen takes place with almost zero activation energy[4]. As a consequence, oxidative polymerisation predominates at low temperatures[61,69], but rise in temperature produces an increase in yield of monomeric decomposition products of the radicals—carbonyl compounds and alkene oxides[13,61].

V. EPOXIDATION OF ALKENES BY INTERMEDIATE MOLECULAR OXIDATION PRODUCTS

We have hitherto examined known routes to the formation of alkene oxides involving free radicals. An alternative view found in the literature (the earliest idea on the mechanism of epoxidation) regards the process as involving intermediate molecular oxidation products—hydroperoxides[73–75] and cyclic peroxides having the structure[39,76,77]



However, later work showed[4] that alkene oxide and hydroperoxide are formed in parallel in the oxidation of cyclohexene, and the rate of formation of the oxiran far exceeds the rate of epoxidation by the hydroperoxide

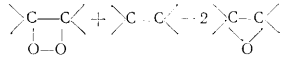


(19)

in the absence of a catalyst. Nor were alkene oxides detected in the thermal decomposition of hydroperoxides in the presence of alkenes[78,79].

The role of cyclic peroxides (dioxetans) in the mechanism of the oxidation of alkenes, and in epoxidation in particular, has recently been the subject of renewed attention[80], for experimental results have been obtained indicating the possibility of their formation in the oxidation of certain alkenes by molecular oxygen[81]. The chemiluminescence method suggests[81] that dioxetans are formed by a radical process in chain-propagation reactions, not by direct addition of oxygen at the double bond of the alkene, as had earlier been postulated[76]. Chain formation of dioxetans has been assumed[82] also in the oxidation of pent-1-ene.

An epoxidising role of dioxetans



(20)

has been postulated for the oxidation of norbornene[83] and of 7,7-binorbornylidene[84] by singlet oxygen under conditions such that the rate of radical oxidation by triplet molecular oxygen is negligible. However, the hypothetical involvement of dioxetans in epoxidation has not yet found direct experimental confirmation. Detailed investigation of the dependence of the yield of alkene oxide on the nature and concentration of the sensitiser used and also on additions of inhibitors of free-radical reactions in the oxidation of biadamantylidene[85] indicated the occurrence of two independent processes—(i) formation of a dioxetan by a molecular process and (ii) radical epoxidation involving sensitiser molecules.

Results have been obtained recently[80] indicating a molecular mechanism of epoxidation in the oxidation of alkenes. A solution of styrene in chlorobenzene with additions of a polymeric product (of the copolymerisation of styrene with oxygen) when oxidised gives a nearly 100% yield of styrene oxide calculated on the styrene that has reacted (Fig.3)#. Additions of an inhibitor of free-radical reactions do not halt epoxidation. Table 10 shows the changes in concentration (molarity) of styrene, benzaldehyde, and styrene oxide 20 min after addition of the inhibitor (0.01 M 1-naphthol) to the reaction mixture in the oxidation of styrene§. It is evident that the oxide accumulates as the sole reaction product under the inhibited conditions of oxidation.

It has been shown also[80,86] that such molecular epoxidising agents as hydroperoxides and peroxy-acids are absent from the reaction mixture, and that the polymeric product is a precursor of styrene oxide in the sequence of primary oxidation stages. These results suggest that oxygen transfers from the polymer molecule, the "matrix", to the double bond of the alkene. The structure of the oxygen-containing polymer is being further investigated. Perhaps the active agent in epoxidation is the dioxetan group



on the polymer matrix[80].

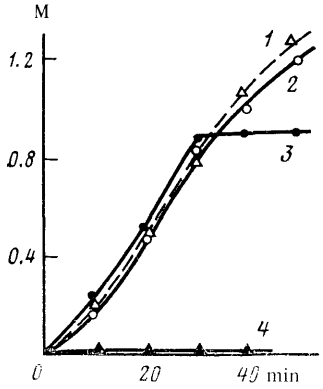


Figure 3. Rate curves for the oxidation of styrene in chlorobenzene solution with addition of 30 vol.% of a styrene–oxygen copolymer[80] at 120 °C: 1) consumption of styrene ($[RH]_0-[RH]_{inst}$); 2) accumulation of styrene oxide; 3) accumulation of benzaldehyde; 4) accumulation of polymeric product.

Table 10.

Styrene	oxide Styrene	Benzaldehyde
1.25 — 1.00	0.42 — 0.62	0.30 — 0.32

Thus the above results[80,81,86] indicate that formation of alkene oxides involving peroxy-radicals is not the sole mode of epoxidation. Under certain conditions a molecular mechanism makes a contribution to epoxidation. Its inclusion provides an explanation of facts that are not covered in generally accepted schemes of epoxidation.

Benzaldehyde is formed by decomposition of the polymeric product.

§ The initial concentration of styrene was 1.8 M, and that of the polymeric product 30 vol.%; the solvent was chlorobenzene, and the temperature 120 °C.

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