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Reaction Mechanisms of the Direct Epoxidation of Alkenes in the Liquid Phase

D.I.Metelitsa

Reaction mechanisms for the liquid-phase epoxidation of alkenes are reviewed critically: the classical Prilezhaev reaction, catalytic epoxidation with participation of hydrogen peroxide and of organic hydroperoxides, reactions for the production of alkene oxides in the oxidation of unsaturated hydrocarbons, reaction of a combined oxidation of alkenes with aldehydes. The mechanism and prospects of the catalysed oxidation with oxygen of alkenes to epoxides are discussed in detail. 150 references.

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1. INTRODUCTION

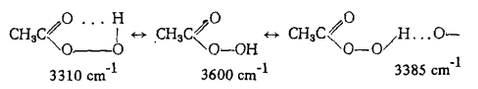
Alkene oxides are important intermediates in industrial organic synthesis. In addition to traditional uses—the production of antifreezes, solvents, and plasticisers for plastics and explosives—new ways of using them have appeared: the production of non-ionogenic surface-active substances, polyethers, polyurethanes, etc. In this connection the direct oxidation of alkenes now has a permanent place in the organic synthesis industry with an extremely promising future[1]. Processes for the oxidation of alkenic hydrocarbons are displacing such traditional and well-accepted processes as the synthesis of ethylene oxide through 2-chloroethanol. Almost all the ethylene oxide is obtained by the direct vapour-phase oxidation of ethylene on a silver catalyst. Monographs and reviews have dealt with this important process and the mechanism of the reactions on which it is based[2-5]. Although the direct vapour-phase oxidation of alkenes is used in all the works built in the last 10–15 years, there is a continuous search for new paths of liquid-phase oxidation of alkenes, since this allows the temperature at which the processes are conducted to be reduced and (especially important) their selectivity to be increased. For example, in addition to the classical method of epoxidising propene with peracids a new method of epoxidation with the hydroperoxides of such organic compounds which are readily oxidised by molecular oxygen has appeared. The combined oxidation of propene plus aldehydes lies at the basis of processes developed by the Institute of Chemical Physics of the

Academy of Sciences of the USSR and by the Institut francais du Pétrole. Very recently there have been extensive searches for catalytic systems activated by oxygen in the epoxidation of unsaturated compounds. Complexes of metals of variable valency (Mo, V, W, Ir, and Rh) with various ligands form such systems. An investigation of liquid-phase epoxidation processes is continuing and being extended. A special part is played by the study of the mechanisms of these reactions, which are of practical importance. The task of the present review is a critical examination of papers dealing with the reaction mechanisms of liquid-phase epoxidation—from the classical Prilezhaev reaction to the most recent investigations into the activation of molecular oxygen in the epoxidation of alkenes.

2. THE PRILEZHAEV REACTION

The Prilezhaev reaction[6,7] between a per-acid and an alkene is now reliable and has been studied in detail: methods of preparation of the per-acids and the reactions of many unsaturated compounds have been examined in detail[8,9]. However, the search for the most effective per-acids in particular reactions and for the most convenient paths for effecting epoxidations with a per-acid is still continuing[10-12]: for example, there is the use of *o*-sulphoperbenzoic acid as an epoxidating agent allows *trans*-1,2-cyclohexane-1,2-diol to be obtained at 25°C in yields of up to 88% from cyclohexene[12] via the oxide.

The per-acids exist in solutions in various forms depending upon the nature of the solvent[13-15]. When the solvent does not form hydrogen bonds the per-acid is a monomer with an intramolecular hydrogen bond[14]. The stretching frequency of the hydroxyl of the per-acid (3600–3750 cm^{-1}) is depressed to 3000–3500 cm^{-1} under the influence of a hydrogen bond. Below we show peracetic acid in various states with the corresponding vibration frequencies of the hydroxyl of the acid[15]:

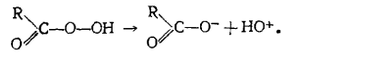


The reactivity of the per-acids is quite different in solvents which form a hydrogen bond—nitromethane, acetone, etc. Thus it is well known that perbenzoic acid which is formed in the oxidation of benzaldehyde can be isolated solely in acetone, since in solvents which do not form hydrogen bonds the per-acid reacts rapidly with benzaldehyde by the Bayer–Villiger reaction[16].

The per-acids are weaker acids than their analogues which do not contain a peroxide group[17]:

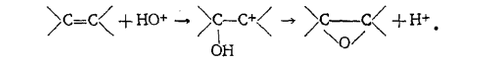
Acid	p*K*
HCOOH	3.7
HCO_3H	7.1
CH_3COOH	4.8
CH_3CO_3H	8.2

Organic per-acids are readily polarised and they have a tendency to heterolytic breaking of a weak O–O bond:



However, the hydroxy-cation HO^+ cannot exist in the free form, since it would be a species with a very high energy.

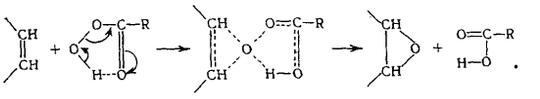
Even in the first kinetic investigations the Prilezhaev reaction[18,19] was found to be first order with respect to both components and it was shown that this reaction is bimolecular like other heterocyclic reactions of per-acids with amines, sulphides, phosphines, phosphites, azo-compounds, and aryl iodides[20]. In early studies it was suggested that the epoxidating species is the free hydroxy-cation HO^+, which attacks the alkene[21,22]:



But as stated above the cation HO^+ cannot be formed.

A study of the relative reaction rates of per-acids with various alkenes showed that per-acids are typical electrophilic agents[23]. The per-acids can be arranged in a series in order of decreasing electrophilic character in full agreement with the values of the Taft σ constant for the R groups: CF_3CO_3H (+2.6), $C_6H_5CO_3H$ (+0.6), HCO_3H (+0.49), CH_3CO_3H (0).

A systematic study of the rates of epoxidation of substituted alkenes by substituted perbenzoic acids[24] provided a basis for a molecular mechanism of the reaction of a per-acid with an alkene[25-28]:



This reaction mechanism, in which the π-bond of the alkene is attacked, is supported by experimental facts found in the epoxidation of *trans*-stilbene and its derivatives (4-OCH_3, 4-CH_3, 4-Cl, 4-NO_2, 3-Cl, 3-NO_2) with per-benzoic acid and its derivatives (4-NO_2, 4-Cl, 3-NO_2, 3-Cl, 4-CH_3, 4-OCH_3).[24]

1. As a result of a study of these reactions at 20–40°C in benzene the activation parameters ΔG^*, ΔH^*, and ΔS^* were determined and it was found that despite the small range, the variation in ΔH^* (14.0–16.0 kcal $mole^{-1}$) and ΔG^* (20.0–23.0 kcal $mole^{-1}$) by the effect of substituents on the electron density of the reaction centre.

Electron-donating substituents in *trans*-stilbene decrease ΔG^* and ΔH^*, but electron-withdrawing substituents increase ΔG^* and ΔH^*. On the other hand, electron-withdrawing substituents in perbenzoic acids decrease ΔG^* and ΔH^*, but electron-donating substituents in perbenzoic acid increase ΔG^* and ΔH^*. Hence the alkene behaves as a nucleophilic agent in the reaction, and the per-acid as an electrophilic one.

2. The addition of the salt $Mg(ClO_4)_2$ to the reaction has no effect whatsoever on the rate of the process, that is, it does not possess ionic limiting stages.

3. The reactivity of substituted ethylenes falls with decrease in the order of the double bond: styrene > *trans*-stilbene > triphenylethylene > tetraphenylethylene (Table 1).

4. The effect of solvent on the rate of epoxidation of the alkenes is completely connected with the formation of hydrogen bonds between the per-acids and molecules of the solvent (Table 2).

Hence all the above results show that the reaction of an alkene with a per-acid is bimolecular. The rate constant for the reaction of *trans*-stilbene with perbenzoic acid is, in the usual form[24]: $1.78 \times 10^8 \exp(-15\,850/RT)$ litre $mole^{-1}$ s^{-1}.

The intermediate formation of a π-complex has recently been demonstrated kinetically in the reaction of propene

with peracetic acid[29]. The reaction is effected in benzene solution at 20–60°C. The absence of radical stages in the reaction was shown by the introduction into the system of an inhibitor of radical processes—2,6-di-t-butyl-4-methylphenol; the inhibitor introduced had no effect on the reaction rate. A detailed kinetic investigation of the reaction of peracetic acid with propene allowed the following scheme to be suggested for the process:

$$CH_3CO_3H + n\,C_3H_6 \underset{k_2}{\overset{k_1}{\rightleftarrows}} [CH_3CO_3H \cdot n\,C_3H_6] \xrightarrow{k_3} C_3H_6O + CH_3COOH.$$

Table 1. Kinetic characteristics of the epoxidation of alkenes by perbenzoic acid in benzene at 20–40°C.[24]

Alkene	$10^4k^{20°}$, litre mole^{-1} s^{-1}	$\Delta H^{\neq}$, kcal mole^{-1}	$\Delta G^{\neq}$, kcal mole^{-1}	$-\Delta S^{\neq}$, cal mole^{-1} deg^{-1}
Styrene	6.12	14.2	21.7	24.8
cis-Stilbene	5.70	14.1	21.7	25.2
Triphenylethylene	—	15.7	22.6	22.7
Tetraphenylethylene	—	17.2	24.1	22.6
Cyclohexene	127	12.7	19.9	24.0
Cyclohexene*	3.72	15.3	22.0	22.0

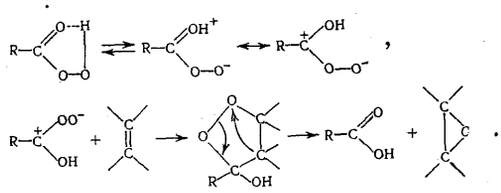
* Reaction in diethyl ether.

It was shown that one molecule of per-acid reacts with two molecules of propene ($n = 2$) and the equilibrium constant was determined: $K = k_1/k_2 = 3 \times 10^3 \exp(-5500/RT)$ litre^2 mole^{-2}. The rate constant of the decomposition of the π-complex is $k_3 = 6.7 \exp(-11\,600/RT)$ s^{-1}.

Table 2. Effect of the solvent on the epoxidation rate constant at 30°C.

trans-Stilbene + CF_3CO_3H (Ref.11)		Ethyl crotonate + *m*-chloroperbenzoate (Ref.24)	
solvent	10^4k, litre mole^{-1} s^{-1}	solvent	10^4k, litre mole^{-1} s^{-1}
CCl_4	14.6	CCl_4	0.115
$CHCl_3$	36.0	C_6H_6	0.173
CH_2Cl_2	36.1	$CH_3COOH+(CH_3CO)_2O$	0.0075
$ClCH_2CH_2Cl$	32.7		
$(CH_3)_3COH$	0.42	CH_3COOH (90%)+H_2O (10%)	0.053
C_6H_6	18.9		

A few papers have also suggested that per-acids react with alkenes by a bipolar 1,3-addition mechanism[30], which is well known[31] and is realised in the ozonation of alkenes[32–34]:



In support of the mechanism of bipolar 1,3-addition there is the low value of ρ in the Hammett equation (−0.8) for the reaction of per-acids with alkenes and the same effect of the solvent on this reaction as in the oxonation of alkenes[35]. However, there is no clear proof of the bipolar 1,3-addition mechanism in the reaction of alkenes and per-acids, whereas the reaction of an alkene and per-acid with the formation of a π-complex has been proved convincingly[24,29]. In the reaction of propene with peracetic acid the limiting stage is the decomposition of the π-complex[29]; in all the other instances studied the reaction is limited by the bimolecular reaction of the alkene with the per-acid. It is possible that the kinetic investigations of the reactions of alkenes and per-acids over wide ranges of concentration of the two components will give new examples of such reactions where the decomposition of an intermediately-formed complex of the per-acid with the alkene is limiting.

Table 3. Rate constants for the epoxidation of substituted cyclohexenes by perbenzoic acid at 5°C in benzene[38].

Compound	10^4k, litre mole^{-1} s^{-1}	Relative rate
Cyclohexene	63.3	1.0
3-Hydroxycyclohexene	34.5	0.55
3-Methoxycyclohexene	4.25	0.067
3-Ethoxycyclohexene	4.72	0.075
3-Acetoxycyclohexene	2.90	0.046
4-Hydroxycyclohexene	2.67	0.042

The reaction of per-acids with cycloalkenes is stereospecific[36–40]: when a cyclic alkene reacts, the oxygen atom of the epoxide that is formed occupies an axial position and the π-bond of sterically hindered molecules is attacked from the less hindered side. The formation of epoxides from cyclic allyl alcohols takes place in the *cis*-position to the OH group[38], which shows the strong accelerating action on epoxidation:

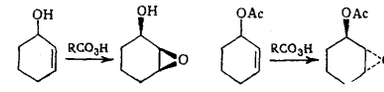


Table 4. Rate constants for the epoxidation of substituted cyclohexenes by *m*-chloroperbenzoic acid in ether at 25°C.[40]

Compound	10^3k, litre mole^{-1} s^{-1}	Relative rate
Cyclohexene	1.88	1.0
4-t-Butylcyclohexene	1.76	0.94
3-Methylcyclohexene	1.77	0.94
4-Methylcyclohexene	1.52	0.81
trans-4,5-Dimethylcyclohexene	1.49	0.79
cis-4,5-Dimethylcyclohexene	0.87	0.46
3,3-Dimethylcyclohexene	0.83	0.44
cis-4,5-(CH_2OCH_2)-Cyclohexene	0.94	0.50
trans-4,5-(CH_2OCH_2)-Cyclohexene	0.55	0.29

The epoxidation of 3-acetoxycyclohex-1-ene takes place much more slowly than reaction with cyclohexen-3-ol and is accompanied by the preferential formation of the *trans*-epoxide. Stereospecificity strongly affects the rates of epoxidation of cycloalkenes by per-acids (Table 3).

The introduction of alkyl groups into cyclohexene retards epoxidation, the action being purely steric, and not inductive, in nature[40] (Table 4).

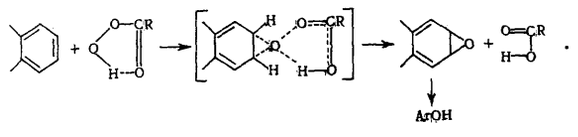
Stereoselectivity is pronounced in the epoxidation of substituted cyclohexenes:

Substituent in cyclohexene	% of *trans*-epoxide in reaction with *m*-chloroperbenzoic acid at 25°C
4-t-Butyl	39.5
4-Methyl	53.6
cis-4,5-Dimethyl	87.0

The electrophilic properties of per-acids were convincingly confirmed and used in the hydroxylation of aromatic compounds[41-50]. Use of such a strongly electrophilic agent as CF_3CO_3H with additions of BF_3 for the hydroxylation of mesitylene allowed mesitol to be obtained in 88% yield[48]. Hydroxylation of phenol with the system (H_2O_2 + HF) gives 54% hydroquinone and 42% pyrocatechol[49], and the use of performic and peracetic acids with additions of polyphosphoric acid and P_2O_5 gives 52.5% pyrocatechol and 16.6% hydroquinone[50]. There has been hardly any investigation of the kinetics and mechanism of hydroxylation of aromatic compounds by per-acids, although it has been clearly established that there are no radical steps in this reaction[46,47]. It has also been shown that the distribution of the isomers of substituted benzenes during hydroxylation with CF_3CO_3H is typical of electrophilic substitutions in the benzene nucleus[47]:

Compound	Phenols			Reactivity in relation to benzene
	ortho	*meta*	*para*	
Anisole	73.7	0	26.3	530
Toluene	78.2	2.3	19.7	11.7
Fluorobenzene	17.2	0	82.8	0.27

It was shown very recently that, in the combined oxidation of aromatic compound plus benzaldehyde, phenols are formed and the rate at which they accumulate does not alter when inhibitors of radical reactions are introduced into the system[51,52]. The formation of the phenols proceeds by the reaction of benzenes with perbenzoic acid formed in the oxidation of the benzaldehyde. The behaviour of an inhibitor confirms that the hydroxylation of aromatic compounds by perbenzoic acid does not proceed by a radical mechanism. We assume that the mechanism of the hydroxylation of aromatic compounds by per-acids is molecular by analogy with the epoxidation of alkenes:



The formation of epoxides of aromatic compounds, which rapidly isomerise into phenols is now not in doubt[53].

3. EPOXIDATION OF ALKENES WITH HYDROPEROXIDES AND WITH HYDROGEN PEROXIDE WITH PARTICIPATION OF CATALYSTS

Organic hydroperoxides possess the capability of heterolytic breaking of the O–O bonds to a lesser extent than per-acids. However, such breaking can be facilitated with the aid of catalysts—metals of variable valency, which can be divided into two groups according to their type of reaction with organic hydroperoxides. To the first group belong metals such as Fe, Co, and Cu, for which the lower and higher valence states differ by unity. These metals usually facilitate homolysis of the O–O bond in hydroperoxides and generate radicals in the reactions with them. The second group includes such metals as V, Mo, W, and Cr, which in their highest oxidation states can cause heterolysis of the O–O bond in organic hydroperoxides.

Investigation of epoxidation by t-butyl hydroperoxide (TBHP) with participation of the acetylacetonates of various metals showed that the epoxidation of 2,4,4-trimethylpent-1-ene, oct-1-ene, and 4-vinylcyclohexene is accelerated especially effectively by the acetylacetonates of Cr, V, VO, and MoO_2, whereas those of Co, Cu, and Fe are not effective[54]. Epoxidation of propene with ethylbenzene hydroperoxide lies at the basis of a method for obtaining propene oxide developed by the firm Halcon[55]. Salts and compounds (naphthenates, acetylacetonates, oxalates, nitrates, etc.) of molybdenum, tungsten, titanium, vanadium, niobium, tantalum, and rhenium that are readily soluble in the reaction medium are used as catalysts. Recently, not only various compounds of metals having variable valency but also various organic hydroperoxides have been widely used in the epoxidation of alkenes. TBHP and vanadium and vanadyl acetylacetonates are used for the epoxidation of cyclohexene[56], cumene hydroperoxide (CHP) and molybdenum naphthenate and also $MoCl_5$ are used for the epoxidation of cyclohexene[57] and of cyclohexen-3-ol[58]. The epoxidation of propene with molybdenum resinate and various hydroperoxides—TBHP, CHP, and ethylbenzene hydroperoxide (EBHP)—has been studied in special detail[59,60]. The epoxidation of 2-methylpent-2-ene[61] and various butenes[62] has been studied. The kinetics and mechanism of these reactions have been investigated[56,59,60,62,63].

Table 5. Epoxidation of oct-1-ene with t-butyl hydroperoxide in the presence of $Mo(CO)_6$.

Solvent	Conversion, %	Yield of epoxide, %
Benzene	75.0	92.0
Methylcyclohexane	72.0	84.0
Ethanol	40.0	37.0
t-Butyl alcohol	16.0	58.0
Acetone	39.0	5.0

The effect of the alkene structure, the hydroperoxide structure, the temperature, and the solvent on the epoxidation of alkenes and the kinetics of epoxidation of oct-1-ene and oct-2-ene with participation of TBHP and molybdenum hexacarbonyl $Mo(CO)_6$ have been investigated in detail[63]. It was found that out of a great number of various salts and coordination compounds of metals of various valency the greatest catalytic activity in epoxidations is exhibited by coordination compounds of molybdenum. The conversion of the alkene and the yields of the oxide are greater in non-polar solvents (benzene or cyclohexane) than in polar (Table 5).

We think that Sheng and Zajacek[63] were wrong in attributing the effect of the above solvents solely to their polarity, since the solvents, which in this instance are polar, can affect the reaction in various other ways; acetone and alcohols form hydrogen bonds with TBHP and reduce its activity, alcohols can enter the coordination

sphere of the catalyst and lower its effectiveness, as several investigations have confirmed [56,59].

For the epoxidation of oct-1-ene hydroperoxides (HP) can be arranged in the following sequence of decreasing activity: *p*-nitrocumene HP > cumene HP > t-butyl HP. [63]

Carrying out the reactions in an atmosphere of CO retards the epoxidation catalysed by $Mo(CO)_6$. The epoxidation of *cis*- and *trans*-but-2-enes shows the stereospecificity of the process, since the *cis*-epoxide is obtained exclusively from the *cis*-butene whereas *trans*-butene yields exclusively the *trans*-epoxide. In an investigation of the kinetics of the epoxidation of oct-1-ene with TBHP and $Mo(CO)_6$ it has been shown that the reaction is first order with respect to all three components. Oxygen does not affect the rate of epoxidation but influences the life of the catalyst.

The combination of such facts as the absence of an effect of O_2 on the epoxidation rate, the passivity of Co, Mn, and Fe complexes which react with the hydroperoxides with the formation of radicals, and the stereospecificity of epoxidation show that there are no radical steps in the epoxidation. The proposed mechanism of epoxidation is [63]:

$$ROOH + Mo^{n+} \rightarrow Mo^{n+}_{cat} , \quad (1)$$

$$ROOH + Mo^{n+}_{cat} \rightleftarrows \left[\begin{matrix} ROOH \\ \vdots \\ Mo^{n+}_{cat} \end{matrix}\right] \quad (2)$$

$$\left[\begin{matrix} ROOH \\ \vdots \\ Mo^{n+}_{cat} \end{matrix}\right] + >C=C< \rightarrow >C-C< + ROH + Mo^{n+}_{cat} .$$
$$\qquad\qquad\qquad\qquad\qquad\quad O$$

In the first reaction the catalyst is activated, in the second a complex of the catalyst and ROOH is formed, the reaction of which with the alkenes limits the rate of the whole process. The drawback of this scheme is the absence of specific indications of the activation and regeneration of the catalyst. In addition, according to the above scheme at high ROOH concentrations the rate of epoxidation should be independent of [ROOH], as has been noted in several instances [63], but this fact is interpreted as the consequence only of the decomposition of ROOH by a side-reaction. It was subsequently shown [56,59,60,64] that the kinetics of epoxidation are more complex and ways of regenerating the catalyst were also demonstrated.

As an example we will consider the mechanism of the epoxidation of cyclohexene with participation of TBHP and V and VO acetylacetonates [56].

t-Butyl hydroperoxide oxidises (activates) the catalyst:

$$VO(acac)_2 \xrightarrow{TBHP} -\overset{|}{\underset{|}{V^{V}}}- .$$

The activation is rapid and irreversible. The active form of the catalyst rapidly forms a complex with TBHP by the reverse reaction:

$$-\overset{|}{\underset{|}{V^{V}}}- + BuO_2H \overset{K_{equil}}{\rightleftarrows} -\overset{|}{\underset{|}{V^{V}}}-O-\overset{Bu}{\underset{OH}{|}} .$$

The equilibrium constant is $K_{equil} = 10.3$ litre mole^{-1} at 50.6°C.

The complex reacts with cyclohexene; this determines the rate of the entire process:

$$-\overset{|}{\underset{|}{V^{V}}}-O-\overset{Bu}{\underset{OH}{|}} + \bigcirc \xrightarrow{k} HO-\bigcirc + -\overset{|}{\underset{|}{V^{V}}}-O-\overset{Bu}{\underset{|}{|}} .$$

The following two reactions then occur rapidly:

$$HO-\bigcirc + -\overset{|}{\underset{|}{V^{V}}}-OBu \rightarrow O=\bigcirc + -\overset{|}{\underset{H}{V^{V}}}-OBu ,$$

$$-\overset{|}{\underset{|}{V^{V}}}-O-\overset{Bu}{\underset{H}{|}} + BuO_2H \rightleftarrows -\overset{|}{\underset{|}{V^{V}}}-O-\overset{Bu}{\underset{OH}{|}} + BuOH .$$

The last reaction is confirmed by the retarding action of alcohols on the epoxidation of cyclohexene [56]. The above scheme agrees with all the experimental results; an equation typical for such schemes is obtained for the initial rate of accumulation of epoxide:

$$W_0 = \frac{k \cdot K_{equil}[TBHP][V_0][ol]}{1 + K_{equil}[TBHP]}$$

where $[V_0]$, and [ol] are the concentrations of VO acetylacetonate and cyclohexene respectively, and k is the velocity constant of the rate-limiting step. The activation parameters of the rate-limiting process of the reaction are:

$$\Delta H^{\neq} = 12.7 \text{ kcal mole}^{-1}, \Delta S^{\neq} = -19.8 \text{ e.u.}$$

An analogous mechanism is proposed for the epoxidation of propene by various hydroperoxides with participation of a molybdenum-containing catalyst [59,60]. In the epoxidation of propene, alcohols can be arranged in the following order according to their inhibiting action [59]: MeOH > EtOH > Pr^nOH > n-octanol > 1-phenylethanol. The reactivity of hydroperoxides is determined by a combination of electronic and steric factors: in the epoxidation of propene the hydroperoxides can be arranged in the series: EBHP (2,4), TBHP (1,3), and CHP (1). CHP is the least effective in the reaction with propene. For the rate-limiting reaction between the complex of the hydroperoxide with the molybdenum catalyst and propene the rate constants in the temperature range 50–80°C and the activation energy of this reaction were determined:

Hydroperoxide	Activation energy, kcal mole^{-1}
EBHP	15.2
TBHP	15.0
CHP	15.6

In the technological realisation of the epoxidation of propene by ethylbenzene hydroperoxide with the participation of a molybdenum-containing catalyst it was shown that above 90°C the selectivity of the process is reduced significantly, since the hydroperoxide is destroyed by undesirable side-reactions [64]. A study of the reaction at 76–120°C aimed at obtaining equations for the optimisation of the process yielded the multistage mechanism:

$$R_1(R_2)(R_3)COOH + Mo \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [R_1(R_2)(R_3)COOH \cdot Mo] , \quad (I)$$

$$X + C_3H_6 \xrightarrow{k_2} C_3H_6O + [R_1(R_2)(R_3)COH \cdot Mo] , \quad (II)$$

$$[R_1(R_2)(R_3)COH \cdot Mo] + R_1(R_2)(R_3)COOH \xrightarrow{k_3} R_1(R_2)(R_3)COH + X , \quad (III)$$

$$X + R_1(R_2)(R_3)COOH \xrightarrow{k_4} 2R_1(R_2)C{=}O + 2R_3OH + Mo , \quad (IV)$$

$$X + R_1(R_2)(R_3)COOH \xrightarrow{k_5} [R_1(R_2)(R_3)COH \cdot Mo] + R_1(R_2)(R_3)COH + O_2 . \quad (V)$$

The distinguishing features of this mechanism are the irreversibility of stage (III) and the side-reactions (IV) and (V) for decomposition of the hydroperoxide. On the basis of this scheme differential equations describing the consumption of the hydroperoxide and accumulation of propene oxide (PO) were written. Having used the experimental results on the rates of consumption of hydroperoxide w_{HP} and the rates of accumulation of the epoxide w_{PO} and having solved the equations by the Runge–Kutta method the investigators obtained a set of constants, the values of which were approximated to the Arrhenius equation. The coefficients of the Arrhenius equation were found by the least squares method.

The resulting equations for the rate of consumption of hydroperoxide and accumulation of the epoxide had the following form:

$$w_{HP} = K_I[Mo][HP](2K_{II}[HP] + k_2[propene])/(1 + K_{III}[HP]),$$

$$w_{PO} = K_1 \cdot k_2 \cdot [HP][Mo] \cdot [propene]/(1 + K_{III} \cdot [HP]),$$

where $K_I = \kappa_1/k_{-1}$, $K_{II} = k_4 + k_5$, $K_{III} = k_4/k_{-1}$.

The following values of the constants were obtained for the temperature range 76–120°C:

$$K_I = 49.6 \exp(-3480/RT) \text{ litre mole}^{-1};$$

$$K_{II} = 2.19 \cdot 10^5 \exp(-5960/RT) \text{ litre mole}^{-1} \text{ min}^{-1};$$

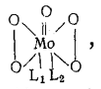
$$K_{III} = 113 \exp(-15800/RT) \text{ litre mole}^{-1};$$

$$k_2 = 5.7 \cdot 10^7 \exp(-10500/RT) \text{ litre mole}^{-1} \text{ min}^{-1}.$$

The results obtained can serve as the basis for the optimisation of the epoxidation of propene by ethylbenzene hydroperoxide in various types of reactor [64]. It is noteworthy that stage II, the rate-limiting step for the entire process has an activation energy of 10.5 kcal mole^{-1}, which differs significantly from the activation energy for this stage obtained in the epoxidation of propene by the same hydroperoxide with a molybdenum-containing catalyst at 50–80°C, 15.2 kcal mole^{-1}. [59,60] The various butenes can be arranged in the following series according to reactivity in their epoxidation by hydroperoxides in the presence of a molybdenum catalyst [62]: *cis*-but-2-ene : *trans*-but-2-ene : but-1-ene = 36.6 : 14.2 : 1.0. This ratio shows the effect of steric factors on the reaction rate in the epoxidation by hydroperoxides with participation of catalysts.

A characteristic feature of catalysed epoxidations with hydroperoxides is that the catalyst oxidised at the start of the process is not reduced at the end but is regenerated in an active form by exchanging an alcoholic ligand for hydroperoxide [56,59]. There remains a series of unexplained details in the mechanism of these reactions: the activation step of the catalyst, the chemistry of the limiting reaction, etc. Evidently these problems cannot be solved with the aid of kinetic investigations alone. An important part in the explaining of the details of the mechanism of these reactions should be played by the use of physicochemical methods of investigation of intermediate complexes formed during the course of the process and also a study of the reactions of the complexes themselves with alkenes. Such a type of investigation of the covalent peroxo-complexes of Mo^{VI} has been made [65].

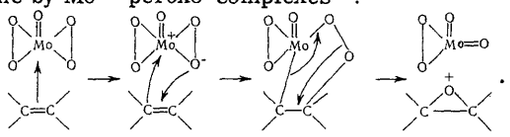
The epoxidation of alkenes by peroxo-complexes of Mo^{VI} of the following structure:



where L_1 and L_2 are aromatic amines, amides, phosphoramides, or phosphines, has been studied in various solvents at various temperatures.

The selectivity of the epoxidation with participation of such complexes reaches 50–95%, depending upon the conditions. The epoxidation of cyclohexene in dichloroethane at 10–30°C by the complex $[Mo(O_2)O]$–HMPTA (where HMPTA is hexamethylphosphorictriamide) proceeds through the intermediate formation of an associate of this complex with cyclohexene, the decomposition of which limits the rate of the process. The reaction was followed by the decrease in active oxygen (1 mole of the complex gives 2 atoms of active oxygen) and the process characterised by the effective first-order rate constant; the effective activation energy is 15.9 kcal mole^{-1}, very close to the values of E_{act} obtained for the epoxidation of propene by hydroperoxides in the presence of molybdenum-containing catalysts [60].

Solvents with various dielectric constants do not markedly affect the rate of epoxidation of a peroxo-complex although some of them can act on the reaction, by entering into the coordination shell of the complex. The coordination ability of some of the solvents used decrease in the order: HMPTA > DMF > tetramethylurea. The accumulated experimental results allowed a bipolar 1,3-addition mechanism to be proposed for the epoxidation of an alkene by Mo^{VI} peroxo-complexes [65]:



In addition to organic peroxides, hydrogen peroxide can be used in the epoxidation of alkenes [66–72]. The reaction of hydrogen peroxide with alkenes is catalytically accelerated by the addition of tungstic acid and tungstates [66–70], molybdenyl acetylacetonate [71], and isocyanate [72]. The mechanism of the catalytic action of tungstic acid and tungstates has now been well studied [68,70]. The epoxidation of allyl alcohol in an aqueous medium by hydrogen peroxide with addition of H_2WO_4 or Na_2WO_4 is characteristically zero order with respect to peroxide, and first order with respect to allyl alcohol and tungstate. The effective activation energy of this reaction is 14.6 kcal mole^{-1}. The following results have been obtained on the reactivity of alkenes in epoxidation by hydrogen peroxide (40°C) in the presence of tungstate:

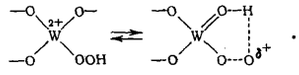
Hydrocarbon	$10^6 k$, s^{-1}
Cyclohexene	4.0
Allyltrimethylsilane	2.7
Allylmethylether	1.6
Allyl bromide	1.0
Allyl chloride	0.9

The logarithm of the constant is related linearly with the Taft σ constant, the coefficient ρ in the Taft equation being −0.44.

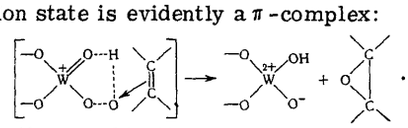
On the addition of tungstic acid or a tungstate to the peroxide the anion of pertungstic acid is formed rapidly:

$$HWO_4^- + H_2O_2 \rightleftarrows HWO_5^- + H_2O.$$

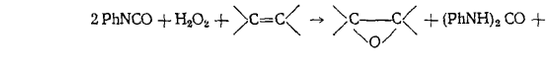
The actual anion HWO_5^- is the active species in the epoxidation of alkenes [70]; it exists in cyclic form owing to the formation of an intramolecular hydrogen bond and has an oxygen atom capable of electrophilic attack at the double bond:



The transition state is evidently a π-complex:



An interesting combination of epoxidation by hydrogen peroxide with the use of isocyanate has been described [72]. At 20°C cyclohexene, styrene, and hex-2-ene are epoxidised with 33–69% yield in reaction with hydrogen peroxide and phenyl isocyanate. The stoichiometry of the reaction is:



Two molecules of phenyl isocyanate and hydrogen peroxide form a complex (maximum absorption corresponds to a wavelength of 314 nm), which is also an epoxidising agent. It was found that under these conditions peroxocarbamic acid does not epoxidise alkenes.

Hence whereas in several instances the reaction mechanism is clear, for example, in the epoxidation of alkenes by hydrogen peroxide and tungstates, many problems of the reaction mechanism in the catalytic epoxidation by hydroperoxides have still not been settled. It is not clear whether the metal in the complex with hydroperoxide undergoes valency changes during the reaction or regeneration of the catalyst is effected solely by exchange of ligands[56,59]. The oxidation of a catalyst by hydroperoxides with the formation of active species has not yet been investigated, and the reaction between the complex of a metal with hydroperoxide and an alkene has not been studied at the level of the physical chemistry of the elementary act. Complexes of hydroperoxides with metals are not always capable of epoxidating an alkene, and in several instances such complexes generate radicals from the hydroperoxides and accelerate the autoxidation of the alkene, for example, in the autoxidation of oct-1-ene with participation of t-butyl hydroperoxide and Cr^{III} acetylacetonate[73]. In isolated instances an important part is played by the catalytic decomposition of the peroxides with participation of the metals, which becomes an undesirable side-process in epoxidation[60].

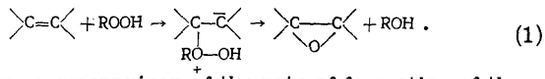
Despite a series of unsolved problems in the catalytic epoxidation of alkenes with hydroperoxides, requirements which are presented to the catalysts by this reaction can be formulated: (1) the central atom should be present in a high oxidation state; (2) the metal atom should have vacant *d*-orbitals capable of adding a pair of electrons; (3) one-electron redox reactions should be absent; (4) the metal should be employed in the form of a complex with labile ligands.

Clearly, all these requirements are not unique, are general in nature, and are typical for many catalytic reactions of coordination compounds.

4. NON-CATALYSED OXIDATION OF ALKENES WITH OXYGEN

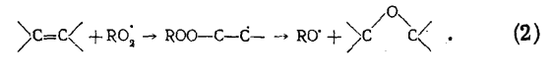
The mechanism of non-catalysed oxidation of unsaturated hydrocarbons has been studied in detail and described in several monographs and papers[74-76]. There can now be no doubt as to the radical-chain nature of the oxidation of unsaturated hydrocarbons by oxygen. This is confirmed by the photochemical sequence in the oxidation of alkenes[77], by the initiating action of peroxides[78], by the accumulation during the reaction of hydroperoxides, aldehydes, ketones, and acids. However, in addition to the above products in the oxidation of alkenes by oxygen, epoxides are formed. The aim of the present section will be to consider the mechanisms by which the alkene oxides are formed. Comparison of the oxygen absorbed with the amount formed in the oxidation of alkenes by peroxides showed that the alkenes absorb oxygen more than is observed with peroxides[79]. It appeared that in addition to hydroperoxides alkene oxides are formed; they were observed in the oxidation by oxygen of di-isobutene[80], styrene[81], methylstyrene[82], methyl elaidate[83], 2,4,4-trimethylpentene[84], cyclohexene[84], but-1-ene and but-2-ene[85], propene[86-90], and 2-methylpent-2-ene[91]. In isolated instances[87-91] alkene oxides can be obtained with yields which are of practical value (40–50% on the alkene which has been oxidised).

By which reactions are the epoxides formed in the oxidation of the alkenes by oxygen? One of the first reactions was proposed by Farmer and coworkers[92]:



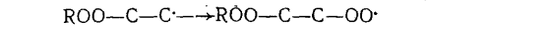
(1)

However, a comparison of the rate of formation of the epoxide in the alkene being oxidised with the rate of conversion of the hydroperoxide showed that in the initial period of reaction the epoxide is formed in parallel with the hydroperoxide and is one of the primary products of the oxidation of the alkene[81]. A mechanism by which the epoxide is accumulated in parallel with the hydroperoxide has therefore been proposed[93]:



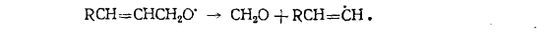
(2)

This reaction has been studied by the example of styrene[81] and methylstyrene[82]. In addition to reaction (2) in the oxidation of styrene the intermediate radical is converted into a peroxide radical:



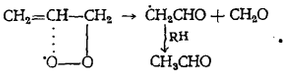
and a polymeric peroxide is formed[81]; in the oxidation of di-isobutene a polymeric peroxide is not formed: only the oxide and hydroperoxide accumulate. This allowed Mayo[80] to suggest that reaction (2) proceeds in a single step. Others have expressed similar opinions[94,95]. However, as further investigations showed, this reaction does not agree with several experimental facts[86].

The common oxidation of isopropylbenzene or ethylbenzene with propene at 80–90°C in the presence of an initiator is not accompanied by the formation of propene oxide, although a sufficiently high concentration of peroxide radicals was observed in the oxidation of cumene and ethylbenzene by EPR[96]. The formation of epoxide by reaction (2) should be accompanied by the accumulation of an equivalent amount of alcohol, but in the oxidation of cyclohexene, for example, alcohol is not observed in the early stages of reaction[94]. A second difficulty can be avoided by assuming that the RO· radical decomposes before the formation of alcohol, according to the scheme adopted for the oxidation of di-isobutene[80]:

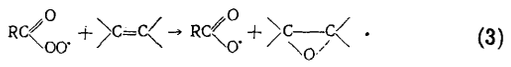


The assumption that the alkene oxide is formed at later stages than by reaction (1) as well as by reaction (2) does not agree with the experimental facts: the rate of formation of the alkene oxides by reaction (1) in an atmosphere of nitrogen is many times less than under oxidation conditions[94].

These difficulties can be avoided by postulating that in the oxidation of an alkene the epoxidising species is not the radical $RO_2^{\cdot}$ but the acyl peroxide radical RCOOO·, which is formed in the oxidation of aldehydes[86]. Actually, at 120–145°C during the oxidation of propene the accumulation of propene oxide precedes the formation of acetaldehyde[86]. The relation of the rates of accumulation of acetaldehyde and hydroperoxide tend towards a constant value at $t \to 0$ that is, the aldehyde accumulates in parallel with the hydroperoxide. Therefore the reaction proposed for the formation of the aldehyde is the unimolecular decomposition of the peroxide radical by analogy with the gas-phase oxidation of aldehydes[97]:



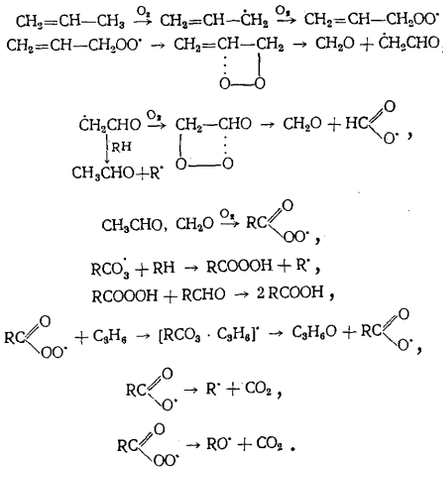
The oxidation of the aldehydes which are formed leads to acylperoxy-radicals, which are more reactive towards a double bond than the alkenylperoxy-radicals, and form oxides by the reaction:



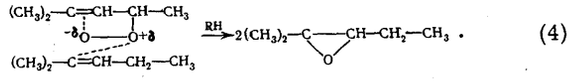
(3)

Reaction (3) can be one of the main paths for the formation of an alkene oxide, since aldehydes almost always accumulate in the oxidation of an alkene[85,86,90]. A detailed study of the liquid-phase oxidation of propene in non-metallic reactors (Teflon) showed that the intermediate products of the oxidation are formaldehyde and acetaldehyde, by way of which ~ 90 mole % of the propene reacts[87-90].

A scheme for the oxidation of propene in non-metallic reactors has been proposed[90]:



In the oxidation of 2-methylpent-2-ene at 120°C in a stainless steel reactor it was shown quite recently[91] that the rate of formation of the epoxide is much greater than the rate of accumulation of the conversion products of the acyl and alkenyl peroxide radicals, that is, reactions (2) and (3) cannot be explained by the accumulation of 2-methylpent-2-ene oxide in the quantities which are obtained experimentally (42% oxide in the conversion of methylpentene). A new reaction scheme for the epoxidation of alkenes was therefore proposed:



(4)

During the interaction of the unpaired electron of the radical with the π-bond the O–O bond in the radical is polarised, which facilitates the transfer of oxygen to the double bond and the detachment of a second oxygen atom by the neighbouring alkene molecule.

On making an overall examination of the epoxidations of alkenes during their oxidation it can be stated that hydroperoxides hardly participate at all in the epoxidation processes; during the epoxidation of the lower alkenes an important part is played by reaction with acylperoxy-radicals (3), but reaction of the double bond with alkenylperoxy-radicals (2) cannot be excluded completely. However, evidently there are also other paths of epoxidation, for example, reaction (4): the structure of the alkene plays a large part in the epoxidation.

5. MECHANISM OF COMBINED OXIDATION OF ALKENES AND ORGANIC COMPOUNDS OF OTHER CLASSES

It is well known that the combined oxidation of alkenes with aldehydes gives the possibility of increasing the yield of epoxide compounds to 50% or over[98-104]. This fact was used to create a new method of preparing alkene oxides[101,104]. Blyumberg and coworkers proposed to use the active oxygen of peroxide radicals formed during the oxidation of organic compounds for the epoxidation of alkenes. In one stage of the combined oxidation alcohols, ketones, acids, etc. are formed simultaneously with the alkene oxides. Substances which are carriers of active oxygen can be ketones or aliphatic and aromatic hydrocarbons in addition to aldehydes[105]. The best results are achieved by use of acetaldehyde and ethyl methyl ketone. The process is carried out in an inert solvent and air serves as oxidant. In the oxidation of propene plus acetaldehyde the optimal temperature is 55–60°C, the pressure 50 atm, the ratio acetaldehyde:propene = 1–2 : 8–9. 0.05 wt.% cobalt acetate is introduced as a catalyst. An excess of propene, benzene, ethyl acetate, acetone, dichloroethane, or acetic acid is used as solvent. Table 6 gives the results for the combined oxidation of alkenes with other organic compounds[105]. An analogous process was proposed by the Institut français de Pétrole[104]: the epoxidation of propene, but-1-ene, hex-1-ene, or 2-ethylhex-1-ene is effected at a partial pressure for the alkene of 22–30 atm in the presence of acetaldehyde, propionaldehyde, or butyraldehyde. Benzene, chlorobenzene, dichlorobenzene, toluene, or xylene is used as solvent. The temperature for the process is determined by the nature of the alkene being oxidised. Azo-compounds, organic peroxides, or salts of metals of variable valency are used as initiators of the epoxidation.

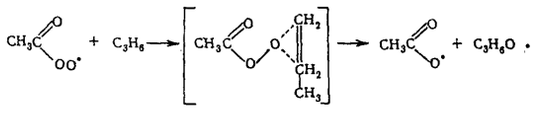
Table 6. Characteristics of the combined oxidation of alkenes and other compounds[105].

Conjugated pair	Temp., °C	Concn., wt.%	Yield of oxide, kg per 100 kg first component
Acetaldehyde + propene	55—80	34.0	70.0
Propionaldehyde + propene	70	12.0	50.0
Ethyl methyl ketone + propene	145	10.0	96.0
Butane + propene	145	3.0	11.0
Isopropylbenzene + propene	130	3.0	13.4
Ethylbenzene + propene	120—140	3.0	15.0
Acetaldehyde + 2-methylpropene	80	12.0	82.0
Acetaldehyde + ethylene	80	8.5	13.0

The problems of the combined oxidation of alkenes and aldehydes were investigated using the pair propene plus acetaldehyde[106-108]. A study of the kinetics and mechanism of oxidation of this pair of substances at 70–80°C and 50 atm in an inert solvent (benzene) showed that the main epoxidating species is the acylperoxy-radical formed in the oxidation of acetaldehyde by oxygen[106]. At the moment of reaching the maximum rate of accumulation of propene oxide in the reaction mixture an inhibitor of radical reactions was introduced—2,6-di-t-butyl-4-methylphenol. After the introduction of the inhibitor the propene oxide concentration rose very slightly, that is, the bulk of the oxide is accumulated from the reaction of propene with free radicals, and a smaller part by reaction with the per-acid.

A study of the epoxidation of propene with peracetic acid under the same conditions made it possible to estimate the contribution of this reaction to the total accumulation of

propene oxide[29]. It was found that at 70–80°C only ~ 15% of the propene oxide is formed by reaction with peracetic acid and the rest comes from the reaction with acylperoxy-radicals[106]:



In addition to the epoxide, methanol, methyl acetate, biacetyl, and methyl formate are formed in the combined oxidation of acetaldehyde and propene[106]. The composition of the oxidation products is greatly dependent upon the oxygen partial pressure[107].

The principal reactions which occur during the combined oxidation of acetaldehyde and propene are[107]:

$$CH_3CHO + O_2 \xrightarrow{k_1} CH_3\dot{C}O + HO_2^{\cdot},$$

$$CH_3\dot{C}O + O_2 \xrightarrow{k_2} CH_3COOO^{\cdot},$$

$$CH_3COOO^{\cdot} + CH_3CHO \xrightarrow{k_3} CH_3COOOH + CH_3\dot{C}O,$$

$$CH_3CHO + CH_3COOOH \xrightarrow{k_4} 2\,CH_3COOH,$$

$$\left.\begin{array}{l} 2\,CH_3CO^{\cdot} \xrightarrow{k_5} (CH_3CO)_2 \\ CH_3CO^{\cdot} + CH_3COOO^{\cdot} \xrightarrow{k_6} \\ 2\,CH_3COOO^{\cdot} \xrightarrow{k_6} \end{array}\right\} \text{chain breaking,}$$

$$CH_3COO\dot{O} + C_3H_6 \xrightarrow{k_7} CH_3COO^{\cdot} + C_3H_6O,$$

$$CH_3COO^{\cdot} + CH_3CHO \xrightarrow{k_{2'}} CH_3COOH + CH_3\dot{C}O\ .$$

The rate of oxidation of CH_3CHO (RH) in the absence of propene is described by the formula:

$$w_0 = \frac{k_2[RH]\sqrt{w_i}}{\sqrt{k_6}}\left\{1 + \frac{k_5 k_2[RH]}{k_6 \cdot k_1[O_2]} + \frac{k_4}{k_6}\left(\frac{k_2[RH]}{k_1[O_2]}\right)^2\right\}^{-1/2}.$$

When the rate of oxidation is independent of $[O_2]$:

$$w_\infty = \frac{k_2[RH]\sqrt{w_i}}{\sqrt{k_6}}.$$

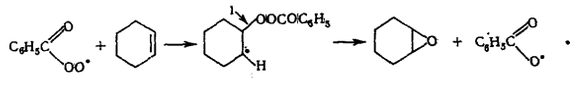
The validity of the above formulae is confirmed by the linear relation between $[(w_\infty/w_0)^2 - 1][O_2]$ and $[O_2]^{-1}$ obtained from experimental results[107].

From the above scheme, clearly a change in O_2 concentration will affect the composition of the radicals participating in recombination and also affect the composition of the reaction products. Actually when the O_2 concentration is reduced there is an increase in, for example, the quantity of biacetyl formed.

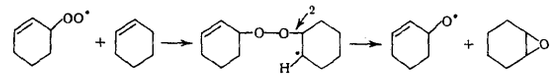
In an investigation of the common oxidation of propene and acetaldehyde in dimethyl phthalate solution (70–90°C, 55 atm air) the effective rate constants for the consumption of acetaldehyde and the effective activation energy (9.6 kcal mole^{-1}) were determined[109,110].

In some studies the combined oxidation of benzaldehyde and unsaturated compounds was investigated[111,112].

In studying the oxidation of cyclohexene and benzaldehyde with participation of cobalt acetate, which reacts rapidly with per-acids, it was noted that only ~ 3% of perbenzoic acid reacts with cyclohexene with the formation of epoxide; all the remaining epoxide is formed by the reaction of cyclohexene with peroxide radicals[111]:

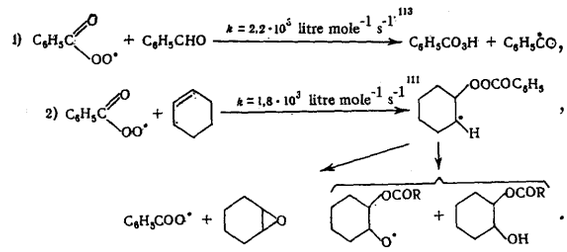


It is suggested[111] that cyclohexenylperoxy-radicals also participate in the epoxidation:



This reaction is quite possible, since the energy of bond 2 is greater than the energy of bond 1.

It is known[102,103] that alkenes retard the oxidation of aldehydes. This is easy to understand on considering that the rate constant for chain propagation in the oxidation of benzaldehyde at room temperature is close to the rate constant for the reaction of acylperoxy-radicals with a double bond:



Clearly, either stable products or radicals with little activity in chain propagation are obtained in the second reaction.

The kinetic results examined above obtained in the combined oxidation of propene with plus aldehydes[105–107] and of cyclohexene plus benzaldehyde[111] show that the principal reaction in epoxidation is the interaction of radicals with the double bond and the per-acids—oxidation products of the aldehydes—make a relatively small contribution to epoxidation. Only in isolated instances, for example, in the oxidation of α-methylstyrene and benzaldehyde does non-radical epoxidation of the double bond by reaction with a per-acid amount to more than 10–15%.[112]

6. CATALYSED OXIDATION OF ALKENES BY THE OXYGEN IN AN OXIDE

The use of catalysts in processes of liquid-phase oxidation of alkenes allows the temperature of the reaction to be significantly reduced and the selectivity of the processes to be increased. In the oxidation of propene suspensions in dibutyl phthalate of finely ground copper, silver, or their oxides are used as catalysts. The yield of propene oxide on these catalysts reaches 87%. It has also been proposed to use Co, Cu, Mn, V, or Cr promoted with Ba or Pb salts for these purposes[114,115]. Various catalysts based on Cu and Ag are used in the oxidation of butenes. A special copper catalyst containing alkali metal halides has been developed[116]. In addition, it is thought that in the oxidation of butenes to the epoxide it is not necessary to employ catalysts but it is quite sufficient to use initiators to shorten the induction period[117].

The catalysts used until now for the liquid-phase oxidation of alkenes to epoxide are usually heterogeneous and selected by analogy with the catalysts for the gas-phase oxidation of alkenes. The mechanism of action of the heterogeneous catalysts in the epoxidation will not be examined in the present review. We will concentrate attention on the use of homogeneous catalysts in the oxidation of alkenes to epoxides, since there have been many recent studies in this direction and in several instances

alkene oxides have been obtained in high yields under comparatively mild conditions. An investigation of the liquid-phase oxidation of propene with oxygen with participation of chelates of MoO_2^{2+}, WO_2^{2+}, Co^{2+}, Cr^{3+}, and Cu^{2+} (various azo-compounds obtained by diazotisation of substituted phenols and naphthols were used as chelating ligands) showed that the complexes of MoO_2^{2+} and WO_2^{2+} are the most selective in the oxidation of propene to its oxide, and allow the oxide to be obtained in up to 70% yield in the conversion of ~ 7% of the propene (temperature: 150°C; solvent: benzene; total pressure: 45 atm).[118,119] The remaining cations with the same ligands are less selective in this reaction and give a lower yield. A detailed investigation of the catalysis of the oxidation of propene with participation of chelates obtained from MoO_2^{2+}, $MoCl^{4+}$, and $OMo(OH)_2^{2+}$ and the study of the magnetic properties of these chelates suggested that the catalyst in this reaction takes up a molecule of oxygen and activates it[120-126].

In a study of the mechanism of activation of oxygen in the oxidation of propene to its oxide with participation of molybdenum chelates, the effect of a large number of chelating azo-compounds on the state of the central ion, on the magnetic properties of the chelate which adds to oxygen, and on the activity of the chelate in the epoxidation was investigated[120-126]. For each of the inorganic cations MoO_2^{2+}, $MoCl^{4+}$, and $OMo(OH)_2^{2+}$, chelates were obtained with compounds of the azonaphthoquinone type containing various substituents; for all the chelates their magnetic susceptibility was measured and their magnetic moments calculated[121]. For each of the three inorganic cations a linear relation was found between the magnetic moment and the Hammett σ constant for the ligand:

$$\mu-\mu_0=R-S\sigma_{lig},$$

furthermore,

$$R=U+T\sigma_{cation},$$

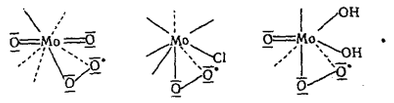
where σ_{cation} is the characteristic of the donor–acceptor capability of the cation with inorganic ligands. Hence:

$$\mu=\mu_0+U+T\sigma_{cation}-S\sigma_{lig},$$
$$U=1.83,\quad T=1.15\ \mu_B.$$

The values of the other constants in these equations are:

Constants	MoO_2^{2+}	$MoCl^{4+}$	$OMo(OH)_2^{2+}$
σ_{cation}	1.00	0.23	−0.24
R, μ_B	3.00	1.47	2.20
S, μ_B	0.57	0.57	0.40

Hence the effect of the ligands and the state of the central atom were connected and characterised quantitatively. All three series of molybdenum chelates were used as catalysts for the epoxidation of propene and it was found that the selectivity of this reaction is linked with the state of the complex. For all three series of complexes the most selective were the chelates in which 0.7 of an unpaired electron is localised on the molybdenum. A departure from this optimal figure to one side or the other decreases the selectivity of the chelate in the epoxidation of propene. An investigation of the magnetic properties of the complexes and the parameters for the activation of oxygen by the complexes in relation to their selectivity in epoxidation suggested[122-126] that the epoxidating species are paramagnetic associates of the chelates with oxygen having the following structure:



In all three species the molybdenum is sexivalent.

In the homogeneous-catalytic reactions complexes of other metals which add an oxygen molecule in the coordination sphere were also employed: thus the complexes $IrX(CO)(PPh_3)_2$ and $RhX(CO)(PPh_3)_2$ (where X = Cl, Br, or I), first prepared by Vaska[127,128] were used in the oxidation of styrene[129,130], cyclohexene[131], and ethylbenzene[132]. Before turning to an examination of the mechanism of epoxidation of alkenes with participation of metal complexes which activate oxygen, we will consider the characteristic properties of these complexes. Complexes have recently been obtained that are capable of adding a molecule of oxygen and have as central atom iron, cobalt[133,134], iridium[127,128], rhodium[127,128], or ruthenium[135].

An oxygenated complex of a metal necessarily has a central atom which exhibits redox activity:

$$Co^{II}\rightarrow Co^{III};\quad Ir^{I}\rightarrow Ir^{III};\quad Fe^{II}\rightarrow Fe^{III},$$

and oxygen, which also exhibits redox activity as a ligand. Here the concept of valency loses significance and one can speak only of partial charges on the partners in the bond, when the total molecular orbital is predominantly localised at the metal or the ligand. The internuclear distance in the O–O group is a reliable measure of these partial charges. In the complex $[(Cl)Ir(CO)(PPh_3)_2]$ (I), which adds oxygen reversibly, both oxygen atoms are equivalent and at equal distances from the iridium. The distance between the oxygen atoms is 1.30 Å, which is greater than in molecular oxygen (1.21 Å) but significantly less than in O_2^{2-} (1.49 Å), and corresponds to the distance in $O_2^{\cdot-}$ (1.28 Å). Despite this it cannot be assumed that the oxygen in the iridium complex is the radical-anion $O_2^{\cdot-}$ since this complex is diamagnetic.

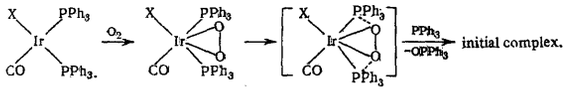
A characteristic feature of complex (I), extremely significant from the standpoint of the catalysis of the epoxidation of alkenes, is the capability of this complex to add ethylene reversibly[136]; an analogous complex is formed with tetrafluoroethylene[137]. A comparison of the bonding of oxygen with the bonding of the alkenes in these complexes is quite permissible, since the electronic structure of the oxygen molecule in the ligand field corresponds to the electronic structure of ethylene[138].

We will consider yet another property of the complexes which bond oxygen—the strength of the bonding of the oxygen with the central atom. If the Cl in complex (I) is replaced by iodine, the strength of the bonding of O_2 with the metal increases and the complex $[(O_2)Ir(CO)(I)(PPh_3)_2]$ (II) bonds oxygen irreversibly. An X-ray diffraction analysis of complex (II) gave an interesting result: the change from reversible (I) to irreversible (II) oxygen-containing complex is associated with an increase in the length of the O–O bond from 1.30 Å to 1.47 Å, but the equidistance of the oxygen atoms is retained. This distance corresponds to the anion O_2^{2-} (1.49 Å), hence the transfer of electrons from the metal to the O_2 ligand increases when chlorine is replaced by iodine[139]. Replacement of chlorine by phosphine also leads to the stabilisation of the compound of oxygen with $Ir[(PPh_2-[CH_2]_2-PPh_2)_2]^+$.[128,140] The addition of O_2 to the phosphine complexes of nickel, palladium, and platinum is irreversible[141]. In these complexes an intramolecular

redox reaction rapidly takes place, leading to the oxidation of the phosphine. In peroxo-complexes, such as the derivatives of Cr^{V}, Cr^{VI}, CrO_5, or $[CrO_8]^{3-}$, there should be preferential transfer of charge from O_2^{2-} to the central atom (a strong acceptor) and as a consequence of this the O–O bond length is 1.40 Å.[142]

Hence there is a continuous increase in the bond strength and the O–O internuclear distance in the series: labile compounds of oxygen → compounds with reversible addition of oxygen → peroxo-complexes.

Vaska complexes have been used as catalysts for the epoxidation of styrene with oxygen[129–130]:



The addition of $SnCl_3^-$ to the complexes allows the yield of epoxide to be increased 477% relative to the catalyst used. Iridium and palladium chlorides ($IrCl_3$ and $PdCl_2$) are also used as catalysts of the epoxidation of styrene. At 110°C they give 51 and 184% styrene oxide respectively[129]. The use of $RhCl_3$ as catalyst enables 1232% styrene oxide to be obtained after reaction for 8 h at 110°C.[130] It is noteworthy that Takao and coworkers[129,130] did not suggest any reaction mechanism for the epoxidation and oxidation of styrene. A great drawback of these Japanese studies is that the reaction was investigated in the most inappropriate solvent (toluene). Under the conditions employed (110°C, 1 atm oxygen, presence of the catalysts $IrCl_3$, $PdCl_2$, etc., there must be oxidation of the toluene with formation of benzaldehyde and other reaction products. Actually, the main product of the oxidation of styrene in toluene is almost always benzaldehyde[129]. The benzaldehyde which is formed, on being oxidised in combination with styrene can give styrene oxide, as was shown by the example of the oxidation of α-methylstyrene plus benzaldehyde[112]. Undoubtedly, toluene should be oxidised under the experimental conditions of the Japanese investigators, as was confirmed by the success in using Vaska complexes for the oxidation of ethylbenzene at 130°C and *p*-xylene at 120°C with the formation of acetophenone (90%) and *p*-tolylaldehyde respectively[132]. The unfortunate choice of solvent hinders the interpretation of the results of the Japanese investigators: possibly the catalytic epoxidation of styrene actually takes place but undoubtedly benzaldehyde—the oxidation product of toluene when any catalyst is used—plays an important part in the epoxidation.

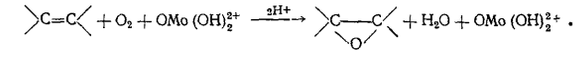
Only kinetic investigations of the epoxidation of alkenes with participation of Vaska complexes in an inert solvent will make it possible to judge their true catalytic activity in this reaction and its mechanism. An investigation of the catalytic influence of Vaska complexes on the oxidation of cyclohexene in benzene and CH_2Cl_2 at 25–60°C showed that the main oxidation product is cyclohexen-3-one[131]. Hence the catalytic activity of Vaska complexes—transporters of the oxygen atom—is certain[131,132] but it is difficult to judge to what extent these complexes are selective in epoxidations on the basis of the results that have been published.

We will now return to the problems of the activation of oxygen in the epoxidation of propene with participation of molybdenum chelates. As already noted, the epoxidating species is a paramagnetic associate of the chelate with an oxygen molecule[122]. In this associate the molybdenum is in the highest oxidation state. After the act of epoxidation has occurred or during the course of this act the molybdenum should be reduced to the quinquevalent state.

Various investigations[118–126] did not show any specific reduction paths for the molybdenum, that is, the regeneration of the catalyst during the course of the reaction. We can presume that in the reduction of molybdenum reaction products participate, for instance acetaldehyde formed in parallel with propene oxide by the non-catalysed oxidation of the latter:

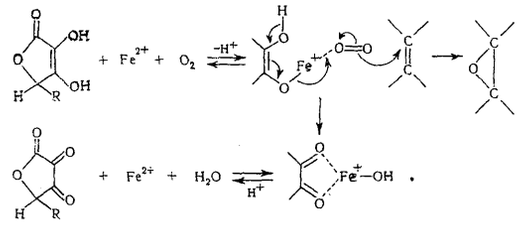
$$CH_3CHO + Mo^{VI} \rightarrow CH_3\dot{C}O + Mo^{V} + H^+ .$$

We represent the epoxidation itself as follows:



Such a type of transfer of an oxygen atom from an O_2 molecule to a substrate is known to be effected by oxidases with mixed functions[143,144], which epoxidise alkenes, oxidise aliphatic compounds to alcohols, and hydroxylate aromatic compounds to phenols.

Several systems which can be regarded as models of oxidases with mixed functions have been studied recently[53,145]. The study of such models helps to answer the problem of how many electrons are transported on the O_2 molecule and how this transport is linked with the epoxidation of the substrate. A scheme of epoxidation of an alkene with participation of one of the oxidase models with mixed functions—the Fe^{2+} + O_2 + ascorbic acid system—is given below[53]:



As this scheme shows, the epoxidising agent is a complex, the function of the ferrous ion in which is to unite with the reducing agent and oxygen and to convey to the latter electrons to form the transition state. The iron ion allows a singlet oxygen atom to be transferred from the combined O_2 molecule to the substrate in such a manner that the intermediate biradical compound is unnecessary. If a triplet oxygen atom were transferred the process would be less favourable energetically owing to the formation of a triplet reaction product, which is less stable than the singlet. The transfer of a proton of ascorbic acid into the complex with O_2 is evidently simultaneous with the transfer of electrons through the ferrous ion leading to the reduction and stabilisation of the oxygen atom which is not passed on to the substrate. The other oxygen atom, which has 6 electrons (hence the analogy with carbenes and nitrenes, which also have 6 electrons around the carbon or nitrogen and are extremely reactive) is introduced into the substrate. In this way four-electron exchange is effected with minimal motion of the nuclei.

If it is assumed that the reduction of the molybdenum is brought about by the ligand (which is not excluded) then the scheme for the epoxidation of propene with participation of molybdenum chelates does not differ from that discussed above. If the reduction of molybdenum is effected in interactions with the oxidation products of propene—acetaldehyde, etc.—then we have a new example of models of oxidases with mixed functions, distinguished by the fact that the reducing agent does not enter the coordination sphere of the complex, but reacts with the oxidised complex after the act of epoxidation has been completed. Unfortunately,

the most interesting studies of epoxidation with participation of molybdenum chelates[118-126] do not provide results on the regeneration of the catalyst, and we cannot now choose between these two possibilities. It is very significant that it could be shown which of the forms of active oxygen:

$$[Mo^{5+} \ldots O_2] \leftrightarrow [Mo^{6+} \ldots \dot{O}_2^-] \leftrightarrow Mo^{6+} + \dot{O}_2^-$$
(I) (II) (III)

is the main one in the epoxidation of propene.

It is form (II). However, this does not signify that in all other instances this form of the reacting species will be predominant. As Hamilton thinks[53], the nature of the attack of the substrate in different model systems can vary from radical to electrophilic and even nucleophilic. It all depends upon which state of the attacking species predominates. And this state is in turn determined by the type of metal and especially the ligands which are around it. In general there can be several forms of attacking species and the determination of the valence state of the metal or oxygen in it has no significance in itself. It is necessary to know which of the resonance forms is the most important because this will determine the nature of the attack of the substrate. The difficulty in determining the nature of the bonding in oxygen complexes was descriptively characterised by Alfred Werner, founder of the chemistry of complexes, 70 years ago, but his words are still true today: "The labile bonding of oxygen .... is so peculiar, that it is very difficult to give a satisfactory answer to the question of whether there is a valence bond or simply addition of the oxygen as a molecule, if this question has meaning at all".[146]

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Not all the epoxidations that we have considered can at present be characterised by rate constants of the limiting stages. However, for several epoxidising agents the energetic characteristics of the limiting reactions have been determined—the enthalpies of activation or the energies of activation. Table 7 gives the values of these energetic characteristics.

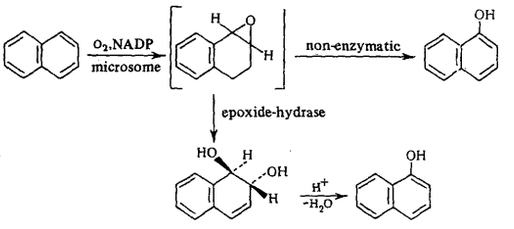
Table 7. Energetic characteristics of limiting reactions in the epoxidation of alkenes.

Epoxidising agent	Alkene	$\Delta H^{\times}$ or E_{act}, kcal mole^{-1}	Reference
Perbenzoic acid and its substituted derivatives	*trans*-stilbene and its substituted derivatives	$\Delta H^{\times}=14.0+16.0$	24
Perbenzoic acid	cyclohexene	$\Delta H^{\times}=12.7$	24
Peracetic acid	propene	$E=11.6$	29
HWO_5^-	allyl alcohol	$E=14.6$	70
TBHP + Mo-cat.	propene	$E=15.0$	60
CHP + Mo-cat.	propene	$E=15.6$	60
EBHP + Mo-cat.	propene	$E=15.2$	60
EBHP +Mo-cat.	propene	$E=10.5$	64
TBHP + $VO(acac)_2$	cyclohexene	$\Delta H^{\times}=12.7$	56
$[Mo(O_2)_2O]L_1L_2$	cyclohexene	$E=15.9$	65

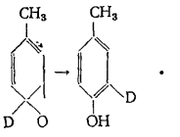
From Table 7, the activation energies or activation enthalpies for various epoxidising species are rather similar. This fact is not unexpected, since in almost all the reactions considered the epoxidating agent is an electrophilic species which attacks the π-bond of the alkene.

The nature of the alkene naturally affects the activation energy of the epoxidation: thus $\Delta H^{\times}$ in epoxidation with perbenzoic acid varies from 12.7 kcal mole^{-1} for cyclohexene to 17.2 kcal mole^{-1} for tetraphenylethylene (see Table 1). The epoxidation of a single alkene, for example, cyclohexene or propene by different agents leads to a change in the energetics within the limits of 2–4 kcal mole^{-1} (see Table 7), from which it seems that epoxidating agents are close to one another in their electrophilic properties. Unfortunately, there are no results on the energetics of the reactions in the epoxidation of alkenes by acylperoxy-radicals and molybdenum complexes which activate oxygen. In these two instances the epoxidating agents evidently exhibit a smaller electrophilic capacity than per-acids or complexes of hydroperoxides with ions of metals of variable valency.

A study of the mechanisms of epoxidation of alkenes helps a deeper understanding of the processes in the hydroxylation of aromatic compounds, since in several instances it has been reliably shown that arene oxides are intermediate products in the formation of phenols[53,147,148]. In the oxonation of benzene, for example, benzene epoxide is isolated but rapidly isomerises at room temperature into phenol[53]. Microsomal oxidation of aromatic compounds showed that arene oxides can play a part in the metabolism of aromatic substrates[147,148]:



3,4-Epoxy[4-^{2}H]toluene has been synthesised[148] and is converted into 4-hydroxy[3-^{2}H]toluene, with displacement of the deuterium:



Without the intermediate formation of the epoxide this fact cannot be explained. The unity of the mechanisms of epoxidation of alkenes and hydroxylation of aromatic compounds is confirmed by the fact that most of the epoxidating agents are simultaneously hydroxylating agents for aromatic substrates. Per-acids effectively epoxidate alkenes and hydroxylate aromatic compounds to phenols[41-50], oxidases with mixed functions and their models are also active in these two reactions[53,145]. It is quite possible that acylperoxy-radicals are not only epoxidating agents but can also hydroxylate aromatic compounds[51,52].

The practical significance of epoxidation is particularly great: new technological processes have now been developed on the basis of epoxidations with hydroperoxides with participation of catalysts[149,150]. An investigation of catalysts which activate oxygen and the study of their mechanism of action will undoubtedly open new prospects of direct epoxidation of alkenes with molecular oxygen under mild conditions. This direction of investigation of epoxidation seems to us to be the most important now.

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Institute of Chemical Physics,
Academy of Sciences of the USSR,
Moscow