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THE MECHANISMS OF SOME PEROXIDE REACTIONS

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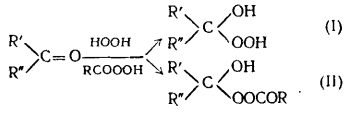
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The reactions of peroxides in organic chemistry are usually interpreted as free radical or ionic processes, but this is not always so. In addition to the large number of reactions in which free radicals are formed, there are a few in which molecules react, with the simultaneous cleavage of some bonds and formation of others; this is also true for peroxides, in which the O–O bond is known to be very reactive. Because of the low energy of the O–O bond, molecular reactions of peroxides can take place with an activation energy which is considerably less than the effective activation energy of a radical reaction. The polarity of the bonds in the peroxide group (OR, OH, and in some cases O–O) is also a factor which favours a molecular reaction. The present article is an attempt at a critical review of a large number of reactions, with the aim of finding those mechanisms which agree with the experimental facts or at least do not contradict them. In particular, we have attempted to explain the role of activated cyclic complexes in the reactions of peroxidic compounds.

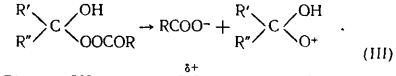
1. THE OXIDATION OF KETONES AND ALDEHYDES WITH PER-ACIDS AND HYDROGEN PEROXIDE

The oxidation of carbonyl compounds with hydrogen peroxide in the presence of acids and with mineral or organic per-acids (the Bayer–Villiger reaction[1]) is used in preparative organic chemistry to obtain acids, esters, anhydrides, and lactones[2]. The kinetics of this reaction, exemplified by the oxidation with organic per-acids of acetylcycloalkanes[3], cycloalkanones[4,5], *m*- and *p*-substituted acetophenones[6], certain other ketones[7,8], and acetaldehyde[9], shows that in almost every case the reaction obeys a kinetic equation of second order and is catalysed by acids; this agrees with a mechanism in which the first stage of the reaction is the formation of a hydroxy-peroxide of type (I) or (II) by the reaction of the carbonyl compound with hydrogen peroxide or the per-acid:

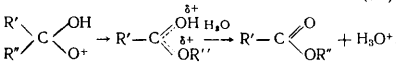


(1)

It has been suggested[10] that the second stage is the unimolecular decomposition of the hydroxy-peroxide with the formation of a stable anion and a cation with positively charged oxygen (III)*. The oxidation products of the carbonyl compound are formed as a result of the rearrangement of the cation (III):



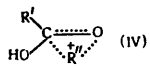
(2)



(3)

* This view point is sometimes erroneously ascribed to Criegee[11], whose views will be given when considering the rearrangement of 9-decalylaroyl peroxides.

According to another variant of this mechanism[4,12], the hydroxy-peroxide ionises to form a "non-classical" ion (IV), which rearranges to the corresponding ester with simultaneous liberation of a proton:

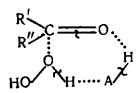

(IV)

In discussing the oxidation of ketones, it has been suggested[4,6] that stage (1) is slow and requires an acid catalyst, while the unimolecular decomposition into ions (2) and the subsequent rearrangement (3) are rapid.

The intermediate formation of compounds of types (I) and (II) in the oxidation of carbonyl compounds seems to us to be highly probable. Lyubarskii and Kagan[9] have shown experimentally that an intermediate of type (II) (R' = R = CH_3, R'' = H) is formed in the oxidation of acetaldehyde with peracetic acid; they found that there is equilibrium between the hydroxy-peroxide and the starting materials. The formation of the hydroxy-peroxide takes place in toluene with an activation energy of 7 kcal/mole and pre-exponential factor 5.2×10^5 $mole^{-1}\,cm^3\,sec^{-1}$. The decomposition of the hydroxy-peroxide, which controls the reaction, requires an activation energy of about 16 kcal/mole, which is almost identical with the activation energy for the overall oxidation process found experimentally.

In a number of cases type (I) compounds have been separated as the reaction products of ketones or aldehydes with hydrogen peroxide[13]. In addition to rearranging to the corresponding esters and lactones, compounds of this type show a tendency to form cyclic and linear polymeric peroxides. Depending on the conditions of the reaction between the peroxide and the carbonyl compound, and on the relative rates of rearrangement and polymer formation of the reaction products, either compounds which do not contain active oxygen or various types of peroxidic compounds may be obtained.

The formation of hydroxy-peroxides from aldehydes is catalysed by acids and by pyridine, but is unaffected by daylight[14]. Probably this reaction, like others in which addition to carbonyl compounds takes place, passes through an activated cyclic complex of the type

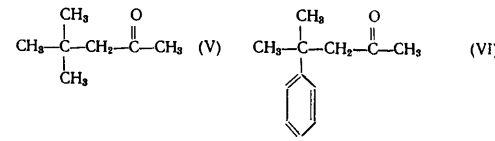


This is an example[15] of an acidic catalyst (HA = H_2O, H_3O^+, RCOOH, etc.) reacting and being regenerated in a single process.

The decomposition of the neutral hydroxy-peroxide molecule into ions [reaction (2)] requires a considerable energy uptake, even in aqueous solutions. In this respect it is extremely improbable that the activation energy of about 10–15 kcal/mole, which is normally found for the Bayer–Villiger reaction, relates to the decomposition of the hydroxy-peroxide into ions.

In chloroform, in which most kinetic studies are made, the formation of ions is energetically unfavourable, even in the case of such strong carboxylic acids as trichloracetic and trifluoracetic. When these acids react with a base such as pyridine in chloroform solution, only ion pairs of various structure are formed[16]. In the case of weaker acids such as acetic and β-chloropropionic, the reaction with pyridine leads only to the formation of complexes containing an ordinary hydrogen bond.

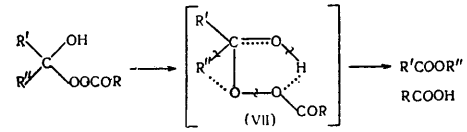
The suggestion that a cation (IV), in which the migrating group carries a partial positive charge, is formed as an intermediate, is not in accord with experimental results on the oxidation of neopentyl methyl ketone (V) and β-phenylisobutyl methyl ketone (VI) with trifluoroperacetic acid[17].


(V) (VI)

It is known that when the secondary carbon atom of the neopentyl group carries an effective positive charge (for example, in the reaction of the corresponding alkyl halide with a Friedel–Crafts catalyst), the alkyl group isomerises, with a transfer of the positive charge to the tertiary carbon atom; however, when the ketones (V) and (VI) were oxidised, only the corresponding acetates were obtained[17]. The retention of the neopentyl and β-phenylisobutyl structures during the oxidation shows that when the corresponding peroxides isomerise, the partial charge on these groups is very small or even zero.

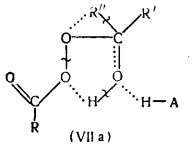
Hawthorne, Emmons, and McCallum[18] have recently shown that the ability of the alkyl groups to migrate when the phenyl alkyl ketones are oxidised with trifluoroperacetic acid changes to a considerably lesser extent than would be expected if the migrating group has carbonium-ion character. Thus, for example, the ratio of the migrating ability of the t-butyl and ethyl groups is ~ 555, while the ratio of the rates of solvolysis of the corresponding alkyl halides varies from 10^6 to 10^8.[19] This can be taken as proof that the partial positive charge on the migrating group in the oxidation of ketones is smaller than the charge on the alkyl group when the corresponding alkyl halide undergoes solvolysis. Hawthorne and coworkers consider[18] that in addition to its ability to form a carbonium ion, the volume of the migrating group has a substantial influence; with increase of the volume, the ability to migrate also increases. This is confirmed by the fact that the rate of migration of the benzyl group is commensurable with that of secondary alkyl groups, and that the neopentyl group migrates at the same rate as the ethyl group, although the carbonium ion must be more stable in the latter case. The oxidation with peracetic acid is more selective than the oxidation with trifluoroperacetic acid, which can only be explained if the migration of the alkyl group takes place simultaneously with the splitting out of the acid residue from the intermediately formed peroxide.

It seems to us more probable that the isomerisation of the hydroxy-peroxide proceeds by way of the activated six-membered cyclic complex (VII):


(4)

The existing experimental data are not sufficient for the part played by the acid in this stage of the oxidation to be definitely established. When ketones and aldehydes are oxidised with hydrogen peroxide in the absence of acids, only the corresponding ketone and aldehyde peroxides are usually formed[2,13].

The results obtained in the study of the kinetics of the oxidation of cycloalkanones, aryl alkyl ketones, and dialkyl ketones (including acetone) with trifluoroperacetic acid[20] favour the hypothesis that the decomposition of the hydroxy--peroxide is catalysed by acid and is the rate determining stage of the Bayer–Villiger reaction. It is therefore possible that the decomposition of the peroxide is more complex than Eqn. (4) would indicate. In particular, the formation of an intermediate of type (VIIa) is not excluded:



(VII a)

The acid is joined to the hydroxy group of the hydroxy--peroxide by an ordinary hydrogen bond and in some cases may transfer its proton to the peroxide molecule with the formation of an ion pair. This would facilitate the transfer of the hydrogen atom of the hydroxy group and the rearrangement as a whole.

In the transition state of the isomerisation (VII) there may be partial heterolysis of the O–O bond, but the reaction of the electron-deficient oxygen atom with the migrating alkyl group and the transfer of the hydrogen atom proceed simultaneously with the separation of charges in the O–O bond.

These views agree with the increased effectiveness of trifluoroperacetic acid as compared with perbenzoic acid. Thus, for example, methyl cyclopropyl ketone does not react with perbenzoic acid[21], but with trifluoroperacetic acid it forms cyclopropyl acetate in good yield[22].

By means of the isotope O^{18}, it has been established that in the oxidation with peracetic acid of benzophenone, 4-methoxybenzophenone[23], and fluorenone[24] in acetic acid in the presence of H_2SO_4, and in the oxidation of benzophenone with perbenzoic acid in benzene[25], the oxygen of the carbonyl group of the ketone becomes the carbonyl oxygen of the ester.

In the oxidation of optically active 3-phenylbutan-2-one with perbenzoic acid to form α-phenylethyl acetate, the configuration of the asymmetric group $C_6H_5CHCH_3$ is retained[26]. The configuration is also retained when certain ketones of the cyclohexane and cyclopentane series are oxidised[27]. All these results are in agreement with the cyclic mechanism reviewed above, and cannot be satisfactorily explained by means of processes involving the intermediate formation of kinetically free carbonium ions.

The oxidation of alkyl methyl ketones[17,22,25], acetylcycloalkanes[3], and substituted acetophenones[6] yields only the corresponding acetates. The absence of methyl esters in the reaction products of trifluoroperacetic acid with alkyl methyl ketones (alkyl = C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11}, cyclo-C_3H_5) is considered[18] as confirming the mechanism according to which the migrating group is a cation stablished by hyperconjugation. However, the absence of methyl esters in the products of the oxidation, under the same conditions, of neopentyl and β-phenylisobutyl methyl ketones[22] indicates that the possible stabilisation of the hypothetical alkyl cation by hyperconjugation does not explain the ability of the alkyl group to migrate. Apparently, all other alkyl groups migrate more easily than methyl. In the oxidation of *para*-substituted benzophenones[12], the ability of the group to migrate increases with its electron-donating properties; however, cyclohexyl benzoate predominates in the oxidation products of cyclohexyl phenyl ketone[7,12]. This may probably be explained by the additional gain of energy, when the reaction goes in this direction, of the transition state (VII), because of conjugation of the phenyl ring with the system of breaking and forming bonds in the transition state. The oxidation of *ortho*--substituted benzophenones shows[28] that under otherwise equal conditions, the presence of an *ortho*-substituent may hinder the migration of the group, by preventing the conformation in which the π-electrons of the ring overlap with the partially free p-orbital of the oxygen atom to which the migrating group is joined[29].

Cyclohexyl methyl ketone reacts ten times as rapidly as acetophenone[7], probably because of the increase in the activation energy in the latter case caused by the destruction, in the transition state (IV), of the conjugation between the carbonyl and phenyl groups; this loss of conjugation is only partly compensated by the conjugation of the phenyl ring in the transition complex. In the case of the *meta*- and *para*-substituted benzophenones, the rate of reaction decreases in the series[6]:

$$p\text{-}CH_3O > p\text{-}CH_3 > m\text{-}CH_3O > H > p\text{-}Cl > p\text{-}OCOCH_3 > p\text{-}Br,$$

generally in accordance with the decrease in the electron--donor properties of the substituent groups. From the results given in Table 1 for substituted acetophenones, however, the substituent group affects the entropy of activation as well as the activation energy.

It is interesting that on passing from one group of compounds to another (Table 1), the energy, entropy, and free energy of activation change only slightly. The introduction of electron-accepting substituents (Cl, Br, $OCOCH_3$, NO_2) in the *meta*- and *para*-positions of acetophenone causes a change in the order of the reaction (first order with respect to per-acid, zero order with respect to ketone), the value of $\Delta F^{\neq}$ increasing slightly.

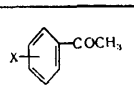
It has been suggested[6] that in the case of acetophenones containing electron-accepting substituents in the ring, the rate determining stage of the reaction is the decomposition of the per-acid into ions:

$$RCOOOH \rightarrow RCOO^- + HO^+. \qquad (5)$$

The resulting cation HO^+ is supposed to react rapidly with the ketone to form a complex, which then decomposes to the oxidation products.

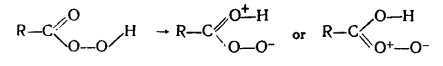
This explanation cannot be considered satisfactory. It was mentioned above that decomposition into ions, as in reaction (5), is a strongly exothermic process, and probably requires a considerably greater expenditure of energy than the observed activation energy (14–15 kcal/mole). The absence of exchange between C^{14}-benzoic acid and perbenzoic acid in chloroform at 25° [30] excludes both the possible formation of ions under these conditions and the formation of ion pairs of the type $RCOO^-HO^+$. Using C^{14} and S^{35} it has been shown[31] that there is no transfer of the hypothetical cation HO^+ even in aqueous solutions of peracetic, perbenzoic, and persulphuric acids and their anions.

Apparently, in the case of acetophenones with electron--accepting substituents, the reaction between the ketone and the per-acid is preceded by the isomerisation of the latter into some active form, as a result of which the oxidation proceeds by some mechanism other than that discussed above. To explain the considerable decrease in entropy in the transition state of the unimolecular process, it is

Ketone	$\Delta H^{\neq}$, kcal/mole	$\Delta F^{\neq}$ kcal/mole	$\Delta S^{\neq}$ e.u.	Reference
$\left[\begin{matrix}CH_3\\(CH_2)_n\end{matrix}\right]CH-CO-CH_3$				3
$n=2$	10.1	22.3	−43	
$n=3$	11.5	22.7	−40	
$n=4$	11.0	22.7	−41	
$n=5$	10.5	22.8	−43	
$(CH_2)_n\begin{matrix}CH_3\\CH_3\end{matrix}C=O$				5
$n=1$	9.1	24.0	−54	
$n=2$	15.4	22.1	−24	
$n=3$	11.6	20.7	−33	
$n=4$	13.3	24.0	−38	
$n=5$	14.7	24.3	−34	
				
$X=p$-OCH_3	11.4	23.7	−42	6
p-CH_3	11.4	24.2	−44	
m-OCH_3	14.9	24.3	−33	
p-Cl*	15.0	25.6	−37	
p-$OCOCH_3$*	14.0	25.5	−40	
m-Br*	13.9	25.6	−40	

* With these ketones the rate of reaction is independent of the ketone concentration and proportional to the per-acid concentration. In all other cases the rate of reaction is proportional both to the ketone concentration and to the per-acid concentration.

natural to suggest that the isomerisation is accompanied by a separation of charges in the per-acid molecule. A possible process is

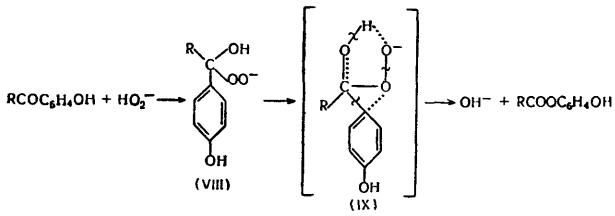


(6)

The presence of intramolecular hydrogen bonding in the ground state of the per-acid molecule facilitates the transfer of the proton.

The reason for the change in the mechanism of the oxidation of acetophenones is probably the appearance, under the influence of the electronegative substituent, of a partial positive charge on the carbon atom next to the acetyl group. In this connection it is pointed out that the oxidation of aromatic carbonyl compounds to form an ester group in alkaline medium also takes place only with compounds of a similar structure. The preparation of pyrocatechol, hydroquinone, and their derivatives by the oxidation of *o*- and *p*-hydroxybenzaldehydes and acetophenones with hydrogen peroxide in alkaline medium is known as the Dakin reaction[32].

Attempts to utilise benzoyl peroxide, lead and manganese peroxides, and silver oxide to effect reactions of this type were unsuccessful. Light, which accelerates the oxidation of benzaldehyde, does not initiate a corresponding reaction, either in the presence or in the absence of benzaldehyde. Neither sodium peroxide nor sodium perbenzoate react with *o*-hydroxybenzaldehyde in dry ether. Clearly, all these facts cannot be explained by a radical mechanism, but indicate the ionic nature of the reaction. Probably the first stage of the Dakin reaction is the addition of the ion HO_2^- to the carbonyl double bond to form the ion (VIII), which rearranges by way of the transition state (IX) to form the ester:



The dihydroxybenzene is formed on hydrolysis of the ester.

It is seen from this mechanism that an increase or decrease of the electron density at the ring atom joined to the carbonyl carbon atom will have a substantial influence on the rearrangement. An electron-donating substituent such as the hydroxy group in the *ortho*- or *para*-position will favour the reaction by increasing the electron density at the reacting atom of the aromatic nucleus; however, an electron-donating group in the position *ortho* or *para* to the carbonyl group must react with it, reducing the partial positive charge on the carbonyl carbon atom and at the same time reducing the rate of formation of the ion (VIII). Thus the factors which facilitate the second stage of the reaction inhibit the first, apparently rate-determining stage. This explains the lack of reaction in the case of certain amino and methoxy derivatives of benzaldehyde and acetophenone[32]. The introduction of the electron-accepting nitro group in position 3 of 4-hydroxybenzaldehyde causes the NO_2 and OH groups, in the *ortho*-position relative to one another, to interact so as to reduce the effect of the OH group on the carbon atom in the 1-position, so that no reaction is observed with 3-nitro-4-hydroxybenzaldehyde. For the same reason, 3-nitro-4-hydroxy-5-methoxybenzaldehyde does not react, while 2-nitro-4-hydroxybenzaldehyde and 2-nitro-3-methoxy-4-hydroxybenzaldehyde give the corresponding quinols[32]. The effects on the 1-carbon atom of the 2-nitro and 4-hydroxy groups are opposite, and it may be expected that the effect of the nitro group will prevail, reducing the electron density at the 1-carbon atom.

The decomposition of α-diketones and α-ketocarboxylic acids by hydrogen peroxide is probably analogous:

$$RCOCOR + H_2O_2 = 2RCOOH,$$

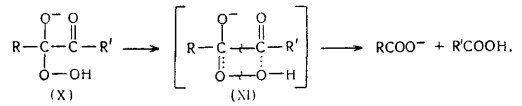
$$RCOCOOH + H_2O_2 = RCOOH + CO_2 + H_2O.$$

A study of the kinetics of this reaction[33] using diacetyl, dibenzoyl, and the sodium salts of pyruvic and benzoylformic acids has shown that the reaction is catalysed by bases. In the case of dibenzoyl and benzoylformic acid enolisation cannot take place, which shows that enolisation is not an essential step in the oxidation. The presence of acidified ferrous or ferric salts, which favours the formation of free radicals in such systems, does not cause decarboxylation of benzoylformic acid.

Pyruvic acid is also not decomposed in solutions containing hydrogen peroxide and ferrous sulphate, and it may even be prepared by oxidising lactic acid with Fenton's reagent[34]. These facts show that free radicals do not take part in this decomposition of ketoacids.

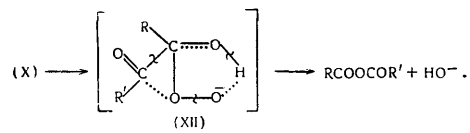
Bunton[33] suggests that the intermediate ion (X), formed by the reaction of the diketone (or ketoacid) with the ion

HO_2^-, decomposes by way of the four-membered activated complex (XI):



(X) (XI)

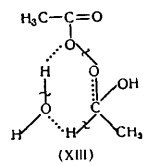
We think it probable that just as in the Dakin reaction, the ion (X) may undergo conversion by way of the six-membered transition state (XII):



(XII)

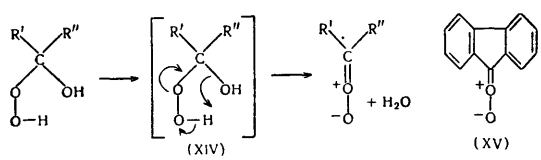
Hydrolysis of the resulting anhydride yields the acids as final reaction products.

The mechanisms reviewed above for the oxidation of carbonyl compounds are not the only possible ones. Probably, in some cases the reaction proceeds by way of an acyclic linear transition state; other types of activated cyclic complexes are also possible. Thus to explain the accelerating action of water on the decomposition of the hydroxy-peroxide formed by the peracetic-acid oxidation of acetaldehyde, Lyubarskii and Kagan[9] put forward a suggestion which is essentially that the peroxide decomposes by way of the activated cyclic complex (XIII):



(XIII)

Under appropriate conditions, other than those of the Bayer–Villiger reaction, ketone hydroxy-peroxides are converted to oxo-oxides, which probably play a significant part in the formation of cyclic and linear peroxides:



(XIV) (XV)

In the transition state (XIV), six electrons (four from the C–O and OH bonds and the unshared pair from the oxygen) move in the field of five nuclei. This is an example of a five-membered cyclic complex[35].

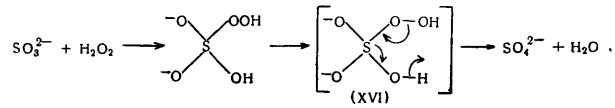
In the case of fluorenone the oxo-oxide (XV) was obtained by reacting fluorenone with hydrogen peroxide in absolute ether in the presence of dehydrating agents[36]. Fluorenone oxo-oxide is a yellow substance, m.p. 108°, soluble with difficulty in benzene and easily in methanol, while fluorenone dissolves easily in benzene and with difficulty in methanol. On cooling a solution of (XV) in acetic acid and acetic anhydride in the presence of H_2SO_4, it is partly converted to the isomeric lactone of 2-hydroxydiphenyl-2'-carboxylic acid, and partly decomposes with the evolution of oxygen and the regeneration of the starting fluorenone. The explosions which sometimes occur when attempting to prepare polymers of ketone peroxides may be due to the decomposition of the intermediate oxo-oxides of type (XV).

A general feature of the above mechanisms is the formation of intermediate products by the addition of hydrogen peroxide to the carbonyl bond. There are grounds for assuming that certain oxidation reactions of inorganic compounds also pass through the intermediate formation of corresponding addition products. It is known that the oxidation of sulphite with hydrogen peroxide in alkaline solutions follows an equation of the first order with respect to the sulphite concentration and the hydrogen peroxide concentration[37]. The activation energy at pH 10 is 15.2 kcal/mole and the pre-exponential factor 3×10^{10} litres $mole^{-1}$ sec. In addition to this reaction an acid-catalysed oxidation also takes place. It has been established by using O^{18} that in the oxidation of sulphite in acid[38] and weakly alkaline[39] solutions, oxygen is transferred to the sulphite directly from the hydrogen peroxide.

In the reduction with an aqueous sodium sulphite solution of the optically active (+)2-phenylbutane 2-hydroperoxide in the corresponding alcohol

$$ROOH + SO_3^{2-} \rightarrow ROH + SO_4^{2-},$$

the configuration of the 1-methyl-1-phenylpropyl group is retained[40]. These facts all agree with the following mechanism for the oxidation:

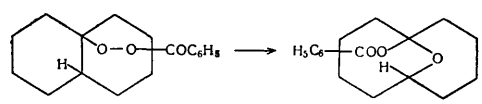


(XVI)

In the transition state (XVI) six electrons (including two from the sulphur atom) are delocalised in the field of five nuclei.

2. THE REARRANGEMENT OF 9-DECALYL PERBENZOATE

9-Decalyl perbenzoate (XVII) is converted to the benzoic-acid ester of 1-hydroxy-1,6-epoxycyclodecane (XVIII) by heating in benzene solution[41].



(XVII) (XVIII)

The rate of reaction increases on passing from benzene solution to acetone, pyridine, chloroform, acetonitrile, and nitromethane solutions[11]. 9-Decalyl perbenzoate and peracetate react considerably more slowly than the *p*-nitroperbenzoate and trichloroperacetate. t-Butyl perbenzoate and *p*-nitroperbenzoate are more stable to rearrangement than the corresponding 9-decalyl esters.

A comparison of these data led Criegee[11] to conclude that "the cause of the rearrangement is the polarisation of the O–O bond of the per-ester, which in the (unattainable) limit would lead to the formation of the benzoate anion and a cation whose positive charge would lie on the oxygen atom".

In Criegee's opinion[11], analogous heterolysis of the O–O bond takes place in the rearrangement of the hydroxy-peroxide in the Bayer–Villiger reaction, the oxidation of

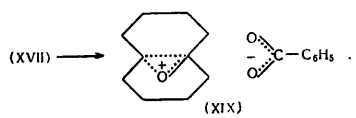
olefines and amines, the conversions of ozonides, and other reactions. In none of these cases, he considers, is there formation of free cations with positively charged oxygen.

In the rearrangement of 9-decalyl perbenzoate in methanol solutions in the presence of sodium *p*-bromobenzoate[42] and lithium *p*-nitrobenzoate[43], the resulting ester does not contain *p*-bromo or *p*-nitro-substituted aryl groups; even in the rearrangement of 9-decalyl *p*-nitroperbenzoate in the presence of lithium benzoate[43], there is no exchange of *p*-nitrobenzoyl and benzoyl groups. These results prove the intramolecular nature of the rearrangement and are in complete agreement with Criegee's views as given above.

The rate of the rearrangement in methanol solution follows an equation of the first order. The rate of reaction is increased by adding LiCl to the solution, and slightly more increased by adding HCl[42]. Even in 0.2*N* HCl the "non-catalysed" fraction of the reaction exceeds the increase in the rate caused by the presence of the HCl. The effect caused by the HCl is little different from that of the LiCl, and may be explained as a specific salt effect of the HCl. The rate of reaction increases on passing from absolute methanol to aqueous methanol[43]. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in absolute methanol are 23.1 kcal and -0.9 e.u. respectively.

Electron-withdrawing substituents in the benzene ring of the ester (XVII) (NO_2, *p*-Br) accelerate, and electron-donating substituents (*p*-CH_3, *p*-OCH_3) retard the rate of reaction[42]. The velocity constants for the substituted esters obey the Hammett equation with $\rho = 1.34$.

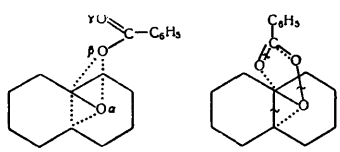
To explain the Criegee rearrangement, which has features of both an intramolecular and an "ionic" reaction[42], it has been suggested that the limiting stage is the formation of an ion pair:



(XVII) (XIX)

Denney[44,45] showed that the oxygen atoms in the COO^- group of the anion of the ion pair are not equivalent. 98% of the excess O^{18} in the carbonyl group of the original ester was found in the carbonyl group of the final rearrangement product when the reaction was carried out in methanol and in acetic acid, proving that the ion pair is not formed in this case, or that the ion pair formed during this rearrangement is unsymmetrical, one of the oxygen atoms of the anion being closer to the positively charged oxygen atom of the cation than the other.

Denney[44] suggested that the reaction passes through a transition state or intermediate compound containing a four-membered ring (XX):



(XX) (XXI)

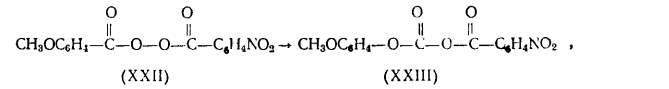
In the opinion of Denney and Denney[45], the cation in the ion pair (XIX) must be unstable, since the positive charge is on the bridgehead atom of the [4,4,1]-bicyclic system. They consider that the explanation of the reaction passing through the four-membered ring (XX) and not through the six-membered activated complex (XXI), as suggested earlier[43], is that in most of the conformations of the per-ester molecule in the normal state, the β-oxygen atom is closer to the 9-carbon atom than is the γ-atom.

Another reason why the four-membered ring is more favourable than the six-membered in the present case is the relationship between the energy of deformation of the molecule in the transition state and the change in the conjugation energy in the transition state as compared with the normal state, on the one hand, and the gain of energy because of delocalisation of the electrons of the breaking and forming bonds, on the other. In the transition state (XX) the conjugation between the carbonyl group and the phenyl ring is retained, and there is also conjugation between the carbonyl group and the transition state system. In the six-membered cyclic complex (XXI) the conjugation between the benzene ring and the carbonyl group is destroyed, but there is a gain in energy because of the formation of the benzenoid system of the transition state and its conjugation with the phenyl ring. The energy of the electrons in the ring (XXI) depends essentially on the distance between the 9-carbon atom and the oxygen of the carbonyl group, a reduction in this distance requiring energy for the deformation of the molecule. In each individual case the relationship between these factors determines which mechanism is favoured.

The recently studied[46] rearrangement of t-butyl arylpersulphonates is probably analogous to the rearrangement of 9-decalyl hydroperoxide, but with a greater separation of charges in the O–O bond.

In the rearrangement of unsymmetrically substituted aroyl peroxides, there is a competition of the mechanisms involving the four-membered and six-membered activated complexes.

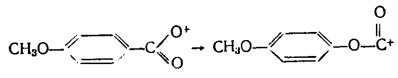
The conversion of *p*-methoxy-*p*'-nitrobenzoyl peroxide[47] (XXII) to methoxyphenyl *p*-nitrobenzoyl carbonate (XXIII) and the analogous reaction of 4-methoxy-3',5'-dinitrobenzoyl peroxide[48] (XXIV):



(XXII) (XXIII)

have features indicative of ionic reactions, among which are: (1) an increase in the rate of conversion on passing from the non-polar solvent benzene to nitrobenzene and thionyl chloride; (2) the complete absence of the ability, in the case of (XXIV), and the reduced ability, in the case of (XXII), to initiate the polymerisation of acrylonitrile and styrene under the conditions of the rearrangement; and (3) the strong catalysis by protonic acids, the action of which follows Brönsted's equation, and the catalysis by such electron acceptors as picric acid and trinitrobenzene[48]. It is interesting that in the decomposition of benzoyl peroxide, where the reaction probably takes place predominantly by way of radicals, the rate of reaction is unchanged on replacing benzene by nitrobenzene[49]. Heating (XXII) in styrene solutions causes only slight polymer formation, while with benzoyl peroxide polymerisation takes place explosively[47]. However, even in the case of benzoyl peroxide, a non-radical reaction takes place in addition to the decomposition through the intermediate formation of free radicals, as is shown by the small accelerating effect of protonic acids in acetic-acid solutions and the catalysis by acids of the $AlCl_3$ type in benzene and chloroform[50,51].

It has been suggested[47,52] that the rearrangement takes place by the heterolysis of the O–O bond with the formation of the cation (XXV) and the *p*-nitrobenzoate anion. The rearrangement of the cation XXV,

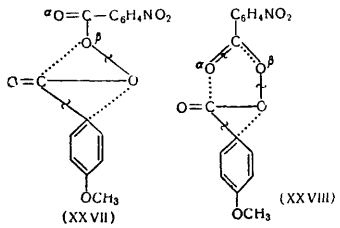


(XXV) (XXVI)

and the subsequent recombination of the cation (XXVI) with the anion would then give the reaction products.

However, experiments with *p*-methoxy-*p'*-nitrobenzoyl peroxide labelled with O^{18} in the anisoyl carbonyl group[53] have shown that the *p*-methoxyphenol formed by the hydrolysis of the rearrangement product does not contain the excess O^{18}. Thus in this case also there is no formation of a cation with a positively charged monovalent oxygen atom. Since such a cation is not formed even with such favourable structural factors, and in a solvent such as thionyl chloride, it is doubtful whether hypothetical ions of this type take part in other reactions and with other less favourable conditions.

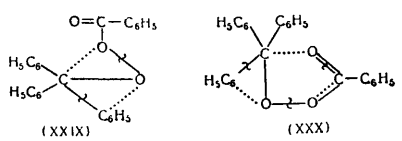
The above experimental results can be satisfactorily explained if the reaction is considered to pass through an activated four-membered (XXVII) or six-membered (XXVIII) complex:



(XXVII) (XXVIII)

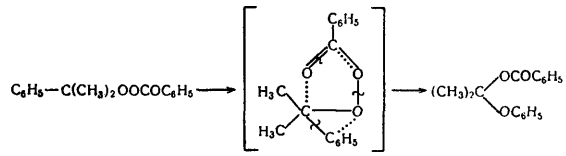
Analysis of the rearrangement products of *p*-methoxy-*p'*-nitrobenzoyl peroxide labelled with O^{18} in the *p*-nitrobenzoyl carbonyl group[45] has shown that only 66% of the carbonyl oxygen is retained during the rearrangement. Clearly in this case the reaction does not pass solely through the four-membered transition state (XXVII), in which the carbonyl oxygen remains in the carbonyl group of the rearrangement product, but also passes through the six-membered complex (XXVIII).

Denney and Denney[45] have noted that in the case of *p*-methoxy-*p'*-nitrobenzoyl peroxide, steric effects are less apparent than for *trans*-9-decalyl perbenzoate, but here also, in the majority of conformations, the β-oxygen atom is nearer the anisoyl carbonyl carbon atom than is the α-oxygen. When the distortion of the valency angles requires less energy, the six-membered cyclic complexes may apparently be expected to play a greater part in the reaction. In this connection, the conversion of triphenylmethyl perbenzoate to phenoxydiphenylmethyl benzoate is of interest, since a four-membered (XXIX) and a six-membered (XXX) activated complex are both theoretically possible.

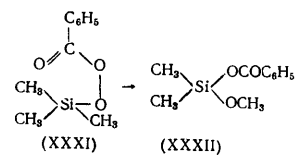


(XXIX) (XXX)

For both mechanisms there is a substantial conjugation between the cyclic transition-state system and the neighbouring groups. Thus, for example, the rearrangement of triphenylmethyl perbenzoate is so rapid, that on causing benzoyl chloride to react with triphenylmethyl hydroperoxide, only its rearrangement product, phenoxydiphenylmethyl benzoate, is obtained[54]. On the other hand, dimethylphenylmethyl perbenzoate[55] is relatively stable, melting at 45°, and slowly decomposing on keeping according to the reaction



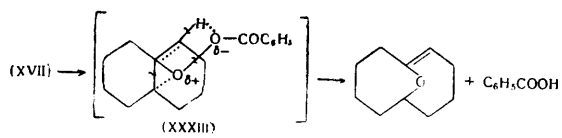
The rearrangement of trimethylsilyl perbenzoate (XXXI) to dimethylmethoxysilyl benzoate[56] (XXXII) probably belongs to this type of reaction:



(XXXI) (XXXII)

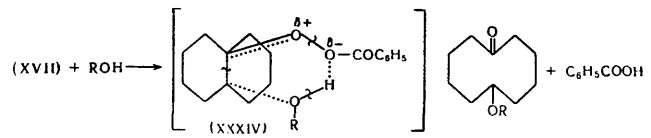
It is interesting that in the rearrangement of silyl per-esters, as with alkyl per-esters, the phenyl group migrates more easily than the methyl group.

The elimination of benzoic acid (7) which accompanies the rearrangement of *trans*-9-decalyl perbenzoate[42] probably takes place by way of the activated six-membered cyclic complex (XXXIII), the formation of which does not meet with the steric hindrance mentioned above:



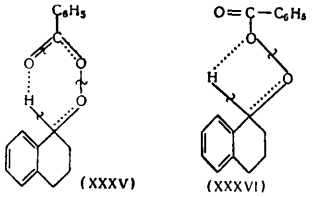
(7)

Goering and Olson[43] have obtained evidence that in the solvolysis of the per-ester (XVII), which takes place in addition to the rearrangement in aqueous methanol, the per-ester molecule undergoes the same changes as in the rearrangement. It is possible that in this case the separation of charges in the O–O bond is accompanied by the close approach of a solvent molecule to the per-ester molecule, so that the reaction passes through the activated six-membered cyclic complex (XXXIV):



The decomposition of 1-tetralyl perbenzoate to benzoic acid and α-tetralone is another example of the rearrangement of a hydroperoxide ester in which polarisation of the O–O bond plays a substantial part. In this case also, the

reaction can pass through the activated cyclic complexes (XXXV) and (XXXVI):



(XXXV) (XXXVI)

The decomposition of the terephthalic esters of isopropyl and n-propyl hydroperoxides with the formation of acetone and propionaldehyde respectively[57] belongs to this type of reaction. The formation of alcohols and carbonyl compounds by the decomposition of secondary and tertiary hydroperoxides is catalysed by acids[58-63]. The decomposition of cumene hydroperoxide, which is the basis of the industrial production of phenol and acetone[59,64,65], has been studied in greatest detail.

Isopropylbenzene hydroperoxide remains unchanged over a prolonged period of time in glacial acetic acid at room temperature. In the presence of strong acids ($HClO_4$, etc.), it decomposes quantitatively into phenol and acetone[60]. The reaction takes place at an observable rate even at -80°. Under these conditions, hydrogen chloride is a less effective catalyst, although even traces of HCl in pure cumene hydroperoxide cause explosive decomposition, probably because the process is strongly exothermic[66]. In alcoholic solution ferric chloride does not catalyst the reaction, but in benzene $FeCl_3$ is a strong Lewis acid and accelerates the decomposition of cumene hydroperoxide into phenol and acetone. Boron trifluoride, aluminium chloride, and sulphuric acid in benzene and dioxane, act analogously[60].

The rate of the reaction is proportional to the hydroperoxide concentration[67-70]. In 50% acetic acid in the presence of small amounts (up to 0.2 M) of *p*-toluenesulphonic acid and with the ionic strength of the solution maintained constant with lithium chloride, the rate of reaction is proportional to the acid concentration[67]. The reaction is not catalysed by molecular acetic acid. In 50% aqueous alcoholic solutions containing HCl, $HClO_4$, or $CH_3C_6H_4SO_3H$, the rate of reaction increases on adding the corresponding lithium salts in proportion to the increase in acidity of the solutions[70]. The acid concentration in these experiments did not exceed 0.5 M, and the total electrolyte concentration was not more than 2.5 M. In the equation relating the velocity constant to the acidity function of the solution,

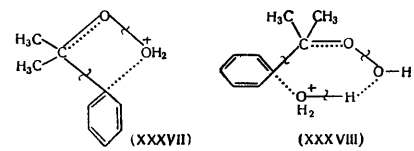
$$\log k = a - \rho H_0,$$

the values of the coefficient ρ for the various solutions were: $HClO_4 - LiClO_4$ 1.45; $HCl - LiCl$ 1.01; and $CH_3C_6H_4SO_3H - CH_3C_6H_4SO_3Li$ 0.76.

The occurrence of a linear relationship between the logarithm of the observed velocity constant and the acidity function is usually considered an indication that the mechanism is one in which the rate determining stage is the unimolecular decomposition of a protonated substrate molecule[71,72]. Without entering the discussion[73,74] as to the validity of this criterion, we note that the existing experimental data are insufficient for selecting any one particular detailed mechanism for the decomposition of the hydroperoxide. If the hydroperoxide is protonated in these solutions, the activation energy for the reaction, 21 kcal/mole, includes the energy required for the protonation of the hydroperoxide (8-9 kcal/mole [75,76]) and the activation energy for the rate-determining step.

Apparently the existence of cations with positively charged oxygen[60,62] or carbon[67] atoms in weakly acid solutions is as improbable as in the other rearrangements of peroxides and oxidation reactions whose mechanisms were discussed above. The absence of the formation of a stable cation with positively charged oxygen in the decomposition of 1-phenylethyl hydroperoxide in acid solution is proved[77] by the absence of exchange between the unreacted hydroperoxide and H_2O^{18}.

The conversion of cumene hydroperoxide probably takes place through the activated cyclic complexes (XXXVII) or (XXXVIII):



(XXXVII) (XXXVIII)

It is possible that in non-aqueous solutions in the presence of Lewis acids the reaction passes through a transition state of structure analogous to (XXXVII).

The activation energy for the decomposition of *p*-nitrocumene hydroperoxide is 6.6 kcal greater than for cumene hydroperoxide; this agrees with the structures (XXXVII) and (XXXVIII), since for *p*-nitrocumene hydroperoxide the formation of the transition state will require additional energy to decrease the positive charge in the position *para* to the nitro group. The energy of conjugation of the nitro group with the phenyl ring in nitrobenzene is probably[78] not more than the above difference in the activation energies for cumene hydroperoxide and its *p*-nitro derivative.

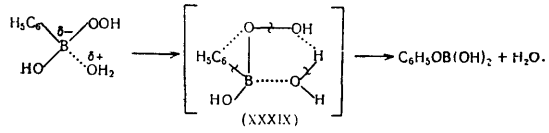
Activated cyclic complexes probably also take part in the oxidation of phenylboric acid by hydrogen peroxide and peroxidic compounds:

$$C_6H_5-B(OH)_2 + H_2O_2 = C_6H_5OH + B(OH)_3.$$

When phenylboric acid labelled with O^{18} is oxidised in water enriched in H_2O^{18} with ordinary hydrogen peroxide, the phenol formed has the normal content of oxygen isotopes[79]. A similar result was obtained in the oxidation of [O^{18}]phenylboric acid with 1,2,3,4-tetralyl hydroperoxide in O^{18}-aqueous dioxane. When phenylboric acid is oxidised with optically active 1-phenylethyl hydroperoxide, the configuration of the 1-phenylethyl radical is retained[79]. The rate of the reaction is first order with respect to the hydrogen peroxide concentration. At pH values of 2-6, in addition to a first-order reaction with respect to phenylboric acid, another reaction occurs, the rate of which is proportional to the square of the acid concentration. At pH 1.5-3 the rate of reaction is independent of pH. On increasing the hydrogen-ion concentration, an acid-catalysed reaction appears, whose rate is determined by the acidity function of the solution[81]. The reaction presumably passes through the intermediate formation of phenylboric acid hydroperoxide, $C_6H_5B(OH)OOH$, which rearranges to give the oxidation products[80,81]. The conversion of this hydroperoxide probably takes place, as in the case of tertiary alkyl hydroperoxides, by way of transition states of type (XXIX) to the easily hydrolysed phenylborate $C_6H_5OB(OH)_2$, or by way of an activated cyclic complex, similar to (XXXVII), to phenol and metaboric acid, which is then hydrated.

However, it may also be considered that in aqueous solutions the phenylboric acid reacts in the hydrated form, because of the vacant atomic orbital of the boron. The above experimental data agree with the mechanism by which the

reaction passes through the activated cyclic six-membered complex (XXXIX):

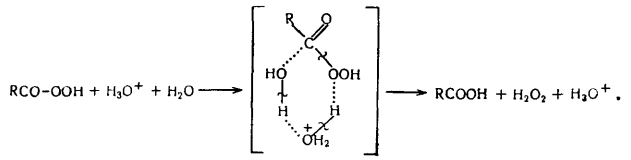


(XXXIX)

The reaction of the boron atom with the water molecule, because of its vacant orbital, increases its acidic properties, and facilitates the transfer of the hydrogen atom in the active cyclic complex (XXXIX). In solutions of acids the complex of the phenylboric acid hydroperoxide with water becomes protonated and the protonated complex reacts. The increase in the rate of reaction is proportional to the pH in the pH range 3–6, probably because of the splitting out of a hydrogen ion from the peroxide group.

3. THE HYDROLYSIS OF PER-ACIDS AND THE REACTION OF HYDROGEN PEROXIDE WITH ALCOHOLS

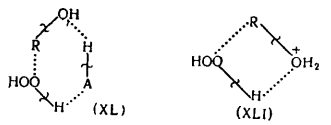
The hydrolysis of per-acids yields the corresponding acid and hydrogen peroxide. Using O^{18} and organic per-acids, it has been established[24] that the reaction proceeds with cleavage of the acyl–oxygen bond. Kinetic measurements in solutions of perchloric acid, which accelerates the reaction, have shown that the rate of reaction is proportional to the hydrogen-ion concentration and not the acidity of the solution. The absence of a salt effect, which is specific for reactions whose rate is proportional to the acidity of the solution[70,82], makes it unnecessary to consider a mechanism involving protonation of the per-acid molecule and unimolecular decomposition of the protonated molecule. The experimental facts can be satisfactorily explained on the basis of the mechanism which has already been put forward for certain hydrolysis reactions of organic esters[83]:



The reaction of tertiary and certain secondary alcohols with 30% hydrogen peroxide in excess 70% sulphuric acid[84-87] or their reaction with concentrated (85–90%) hydrogen peroxide in the presence of small quantities of concentrated mineral acids[88-92] leads to the formation of the corresponding hydroperoxides. Using alcohols containing O^{18} in the hydroxyl group, it has been established that the reaction proceeds with cleavage of the alkyl–oxygen bond[77]. Analysis of the experimental data[89,90] shows that the polarity of this bond has a substantial influence on the reaction.

When optically active 1,2,3,4-tetrahydronaphthol is reacted with 85–90% H_2O_2 in the presence of H_2SO_4, the inactive hydroperoxide is formed[89]; this can be considered proof that in this case there is intermediate formation of carbonium ions.

The formation of carbonium ions is the limiting stage in the heterolysis of the C–O bond, and is apparently by no means always realised; thus, for example, the reaction of *trans*-decalol with concentrated H_2O_2 in the presence of H_2SO_4 yields the *trans*-hydroperoxide[89]; optically active 2-phenylbutan-2-ol and its acid phthalate give 1-methyl-1-phenylpropyl hydroperoxide in which the configuration of the carbon skeleton is to a large part retained, both in acid and neutral conditions[41]. An analogous result was obtained in the reaction of 1-phenylbutanol and 2'-(1-naphthyl)ethanol with H_2O_2 in the presence of H_2SO_4.[91] Apparently, the hydrogen peroxide molecule acts as an acid in the neutral conditions. This reaction, like certain esterification reactions of alcohols in which the alkyl–oxygen bond is broken, probably passes through activated cyclic complexes[83] of type (XL) and (XLI):

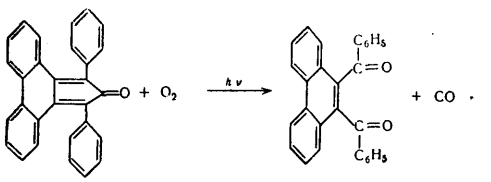


(XL) (XLI)

The reactions in which inversion of the configuration predominates, as is observed in the case of 1-phenylethanol[92], or 1-phenylpropanol and 1-phenylethyl ether[91], probably combine the cyclic mechanisms with mechanisms in which carbonium ions are formed as part of ion pairs.

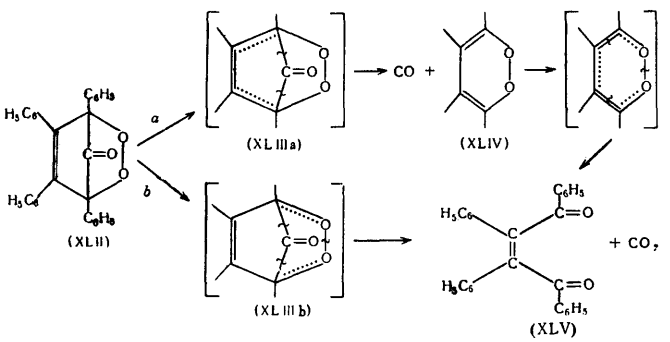
4. THE THERMAL DECOMPOSITION OF PEROXIDES

In the photochemical oxidation of arylcyclopentadienes, carbon monoxide is split off, and there is no formation of transannular peroxides as in the case of other dienoid hydrocarbons[93]; thus, for example, phencyclone, on standing in toluene solutions in the light, is oxidised by the oxygen of the air to form dibenzoylphenanthrene[94]:



Under analogous conditions acecyclone is converted to dibenzoylacenaphthylene.

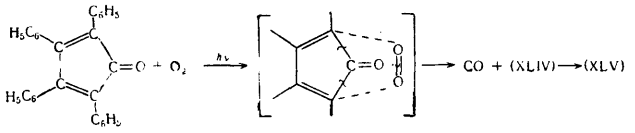
The sensitised photo-oxidation of tetraphenylcyclopentadienone proceeds very smoothly, with splitting out of CO and formation of *cis*-dibenzoylstilbene[95]. It can be assumed that the transannular peroxide (XLII) is first formed,



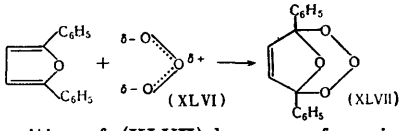
(XLII) (XLIIIa) (XLIV) (XLIIIb) (XLV)

and then decomposes with a transition state (XLIIIb) to the final reaction product (XLV), or gives the intermediate peroxide (XLIV) which then isomerises to (XLV). We have already suggested an analogous mechanism for the splitting

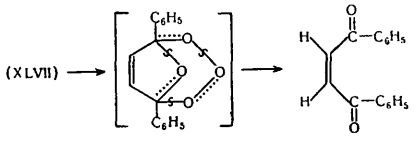
out of CO from the adducts of cyclopentadienones with dienophilic reagents[96]. As in this case, the reaction passes through a transition state (XLIIIa) or (XLIIIb), in which six electrons move in the field of five nuclei. This is an example of a five-membered cyclic complex. In addition to the conjugation between the phenyl rings and the "aromatic" system of the transition state, the fact that two electrons of the transition complex are transferred to the bonding orbital of the CO molecule also plays a substantial part in the reaction. The question of which of the two routes (*a* or *b*) is taken by the reaction has not been satisfactorily settled. This depends not only on the energy of the breaking bonds, but also on the energy of conjugation in the active complex. A third route is also theoretically possible, in which the cyclopentadienone reacts with the oxygen molecule to split out CO and form the peroxide (XLIV), which rapidly isomerises to *cis*-dibenzoylstilbene:



It is probable that in certain ozonolysis reactions the decomposition of the peroxides passes through activated cyclic complexes. For example, in the ozonation of 2,5-diphenylfuran (XLVI) in acetone or methanol at -40°, after the absorption of one mole of ozone per mole of (XLVI), *cis*-1,2-dibenzoylethylene can be separated, instead of the expected product in which the double bonds of the original furan have been split[97]. The first stage of the reaction may be the addition of the ozone molecule to the 1,4-position of the diene system of the 2,5-diphenylfuran to form the peroxide (XLVII):



The decomposition of (XLVII) by way of a six-membered cyclic complex yields the *cis*-1,2-dibenzoylethylene:



The *cis*-configuration of the benzoyl groups is in agreement with the suggested opening of the furan ring after the formation of a double bond between these atoms.

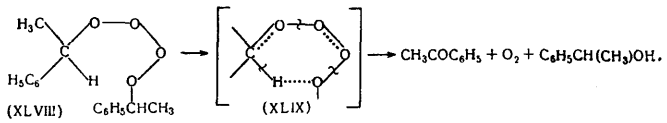
The idea of an activated cyclic complex was recently put forward in discussing the mechanism of the oxidation of alkylbenzenes with oxygen[98]. The rate of oxidation of cumene, ethylbenzene, and some of their deuterated derivatives in the presence of azodiisobutyronitrile is independent of the oxygen pressure in the range 200–760 mm Hg. This is considered proof that only peroxide radicals take part in the breaking of the chain reaction. In the oxidation of cumene and α-*D*-cumene the yield of hydroperoxide is 96–98% and is independent of the chain length (the ratio of the number of oxidised molecules to the number of initiating particles). This confirms the suggestion[99] that the peroxide radicals react as follows:

$$2C_6H_5C(CH_3)_2OO\cdot \rightarrow C_6H_5C(CH_3)_2OOH + C_6H_5CCH_3{=}CH_2 + O_2.$$

In the case of ethylbenzene the yield of hydroperoxide varies from 64 to 85% and increases with increase of the chain length, indicating the formation in the chain-breaking reaction of oxygen-containing compounds which are not peroxides. The amount of acetophenone formed in this reaction agrees with the suggested chain-breaking step:

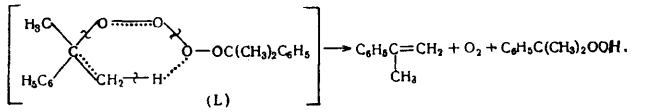
$$2C_6H_5CHCH_3OO\cdot \rightarrow C_6H_5COCH_3 + C_6H_5CHOHCH_3 + O_2.$$

The presence of an isotope effect in the chain-breaking reaction ($k_H/k_D = 1.9$) shows that the C–H bond is broken in the rate-determining stage of this reaction. It is supposed that in the case of ethylbenzene the peroxide radicals recombine to form the peroxide (XLVIII):



The peroxide (XLVIII), which is in equilibrium with the original peroxide radicals, decomposes by way of the six-membered activated complex (XLIX) to form acetophenone, oxygen, and α-phenetole.

It may be supposed that in the case of cumene an analogous dimeric peroxide is formed, decomposing through the transition state (L):

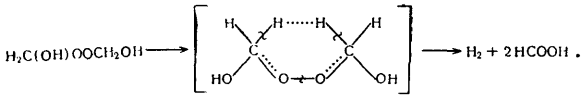


The cleavage in (L) of a C–H bond more stable than in (XLIX) and the cleavage of an O–O bond in (XLIX) instead of a C–O bond in (L) explain, in our view, the longer chain length in the oxidation of cumene as compared with the oxidation of ethylbenzene (10–25 as against 2–4). Russel[98] suggests that an analogous chain-breaking mechanism takes place in the photosensitised oxidation of ethanol[100].

The reaction of hydrogen peroxide with formaldehyde in alkaline solutions[101] (used for the quantitative determination of formaldehyde) takes place according to the equation

$$2CH_2O + H_2O_2 + 2NaOH \rightarrow H_2 + NaOOCH + 2H_2O.$$

Wieland and Wingler[102] studied this reaction and concluded that the hydrogen is evolved in the molecular and not the atomic form, since under the reaction conditions methylene blue is not decolourised. This is confirmed by the absence of HD or D_2 when the reaction is carried out in D_2O solution[103]. Wieland and Wingler considered that the reaction proceeds through the intermediate formation of di(hydroxymethyl) peroxide, which decomposes as follows:



The decomposition of primary hydroperoxides to form hydrogen and the corresponding acid[104–106] apparently also takes place through the intermediate formation of alkyl hydroxyalkyl peroxides. The thermal decomposition of n-butyl hydroperoxide has been studied in detail[106–108]. At 80°–100° the main reaction products are hydrogen and butyric acid in equimolecular quantities[107], others being propane, carbon monoxide, carbon dioxide, water, butyl butyrate, butyraldehyde, butanol, butyl formate, and propionic acid. The amount of gas given off in the decomposition of n-butyl hydroperoxide in a quartz flask in ultraviolet light at 25° is not more than a third of the amount

obtained by thermal decomposition at 86°, the yield of hydrogen, acid, and butyl butyrate being less and the yield of methane, propane, butanol, and butyl formate being more, which indicates that the latter are formed by free-radical reactions, while the former are products of non-radical reactions.

The hydrogen given off in the decomposition of n-butyl deuteroperoxide does not contain D_2 or HD:[107]

$$C_3H_7CH_2OOD \rightarrow C_3H_7C(=O)-OD + H_2.$$

Experiments in which the hydroperoxide was decomposed in the presence of D_2 showed that the hydrogen formed does not exchange with deuterium, no HD being formed. Under the same conditions, the decomposition of t-butyl hydroperoxide and the reaction of cobaltous cyanide with water[108] are accompanied by exchange. These experiments, like those with methylene blue[108], show that when n-butyl hydroperoxide decomposes, hydrogen is given off in the molecular and not in the atomic form.

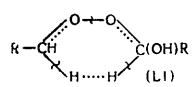
In the absence of aldehydes there is an induction period; in the presence of a small quantity of butyraldehyde there is no induction period and decomposition takes place more rapidly. This confirms the suggestion[108] that the hydrogen is split off from the aldehyde-peroxide compound, and not from the peroxide itself. The induction period is therefore that time in which the aldehyde concentration, and so the intermediate aldehyde-peroxide compound concentration, becomes sufficiently great for the reaction to be observable. The aldehyde is probably formed in accordance with the equation

$$RCH_2OOH \rightarrow RCHO + H_2O.$$

At room temperature, n-butyl 1-hydroxyalkyl peroxides, the suggested intermediates in this reaction, are formed rapidly.

Experiments on the decomposition of n-butyl 1-hydroxyalkyl peroxides, where alkyl = methyl, ethyl, and butyl, have shown that the main products, as in the case of n-butyl hydroperoxide, are hydrogen, the corresponding acid, and butyraldehyde. When n-butyl hydroperoxide is decomposed, hydrogen, butyric acid, and butyraldehyde are formed in equimolecular amounts. When n-butyl 1-hydroxybutyl peroxide decomposes in the presence of toluenesulphonic acid, the amount of hydrogen given off is only one-fifth of the amount obtained in the thermal decomposition. In the presence of alkali, n-butyl 1-hydroxyethyl and n-butyl 1-hydroxybutyl peroxides decompose rapidly, but unlike the decomposition of n-butyl 1-hydroxymethyl peroxide, no hydrogen is formed. Thus the thermal decomposition of these compounds is not catalysed by acids or bases.

From a comparison of the results obtained in this study, the authors concluded that during the reaction there is reversible formation of the butyl 1-hydroxyalkyl peroxides, which decompose with loss of hydrogen by way of the transition state (LI):



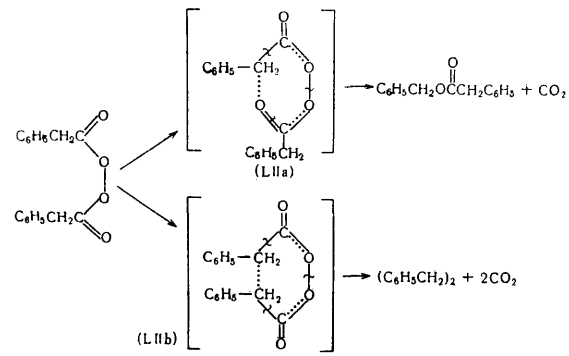
(LI)

The decomposition of per-acids, per-esters, and acyl peroxides with the evolution of CO_2 sometimes takes place completely or partially by a molecular mechanism without the participation of free radicals. It must be said here that in many cases it is difficult or even impossible to distinguish a molecular reaction from a radical reaction in a "cage" of solvent[109] (the "cage" effect). The cage effect is considered below.

Phenylacetyl peroxide[110] decomposes at 0° somewhat more rapidly than does benzoyl peroxide at 70°. When the reaction is carried out in *o*-chlorotoluene, no chlorine-containing products are obtained; however, in addition to the molecular reaction, a radical mechanism is operative to a certain extent, because when the reaction is carried out in the presence of oxygen or iodine, some benzaldehyde or benzyl iodide is formed, and because the velocity constant of the reaction depends on the initial peroxide concentration. The reaction is strongly catalysed by acids, the velocity constant increasing with the dissociation constant of the acid in water in accordance with Brönsted's equation. These authors consider that the results cannot be completely explained by an ionic or radical mechanism, which affect only the O—O bond, and in addition to mechanisms of the type

$$C_6H_5CH_2-CO(=O)-CO(=O)-CH_2C_6H_5 \rightarrow C_6H_5CH_2^{\cdot} + CO_2 + C_6H_5CH_2-COO^{\cdot},$$
$$C_6H_5CH_2-CO(=O)-CO(=O)-CH_2C_6H_5 \rightarrow C_6H_5CH_2^{+} + CO_2 + C_6H_5CH_2-COO^{-},$$

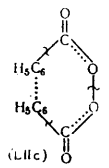
they consider it necessary to introduce mechanisms involving cyclic complexes of the type (LIIa) or (LIIb) to explain the increased rate:



Because there is no conjugation between the phenyl ring and the carbonyl group, in phenylacetyl peroxide the cleavage of the O—O bond to form free carboxyl radicals is less probable than in the case of benzoyl peroxide, and decomposition by way of the cyclic active complexes of type (LIIa) and (LIIb) becomes more probable, since the conjugation between the phenyl rings and the activated-cyclic-complex system is a source of further reduction in the activation energy. These are apparently the two basic reasons why phenylacetyl peroxide, as opposed to benzoyl peroxide, decomposes by a non-radical route. The same arguments against the presence of ions in such media as toluene and carbon tetrachloride may be adduced as in the discussion of the mechanism of the oxidation of ketones by per-acids and the rearrangements of aroyl peroxides.

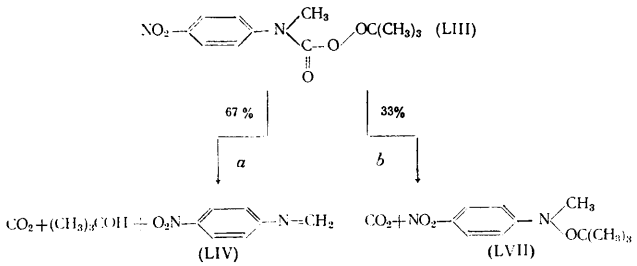
Razuvaev[111] recently showed that the diphenyl formed in the photochemical decomposition of benzoyl peroxide in [C^{14}]benzene does not contain labelled phenyl groups, in agreement with the mechanism in which the photo-activated benzoyl peroxide molecule decomposes by way of a cyclic

transition state of type (LIIc):

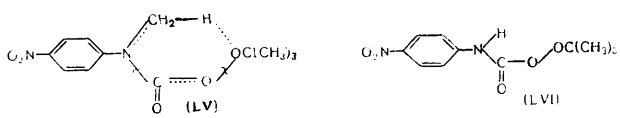


(LIIc)

Pedersen[112] has recently studied an interesting case of photochemical decomposition in a crystal. He found that t-butyl *N*-methyl-*N*-(*p*-nitrophenyl)percarbamate (LIII) decomposes at 30° with a half-decomposition period of 2 days by two routes:



In the presence of moisture *N*-methylene-*p*-nitraniline [(LIV), identified by its infra-red spectrum] is rapidly hydrolysed to form formaldehyde and *N*,*N*'-methylene-bis-*p*-nitraniline; in the absence of moisture no formaldehyde is formed. In Pedersen's opinion, the decomposition of (LIII) to form (LIV) is an intramolecular reaction passing through the cyclic transition state (LV):

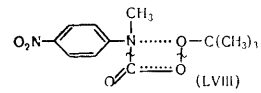


(LV) (LVI)

As proof of this, he showed that t-butyl *N*-(*p*-nitrophenyl)-percarbamate (LVI), for which a similar mechanism is impossible, is much more stable than (LIII), the half-decomposition period being 600 days at room temperature. Similarly liquid $(CH_3)_2NCOOOC(CH_3)_3$ decomposes more rapidly (half-period 65 days) than crystalline $C_2H_5NHCOOOC(CH_3)_3$ (half-period 800 days).

Pedersen considers that the increased rate of decomposition of (LIII) as compared with (LVI) is due to the possibility of the reaction passing through the six-membered cyclic complex, whose formation is facilitated by the ready decomposition of the molecule in the crystal. In cumene solution at 50°–80°, (LIII) and (LVI) decompose into free radicals (the polymerisation of styrene is initiated) with subsequent formation of CO_2 and *N*-methyl-*p*-nitraniline and *p*-nitraniline respectively.

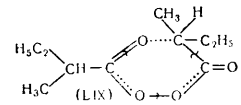
The decomposition of (LIII) to (LIV) is strongly exothermic. According to Pedersen[112], the energy of this process enables neighbouring molecules of (LIII) to decompose with the liberation of CO_2 and the formation of free radicals, which then recombine to give (LVII). The absence of acetone among the reaction products is explained by the cage effect, which favours the recombination of the free radicals, and by the low energy of the radicals formed. However, it cannot be said that the formation of (LVII) (reaction *b*) does not take place by an intramolecular reaction passing through the four-membered ring (LVIII) and so requiring a higher activation energy than reaction *a*:



(LVIII)

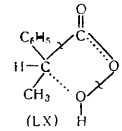
Another possible intramolecular mechanism involves the conversion of the peroxide to a carbonate as an intermediate stage[112].

Certain results obtained with the peroxides of optically active acyl groups indicate the existence of molecular as well as radical processes in the decomposition of acyl peroxides. In the decomposition of (+)α-methylbutyryl peroxide in α-trichlorotoluene[113], s-butyl α-methylbutyrate is formed in 30–40% yield, and on hydrolysis gives optically active s-butanol of the same configuration with respect to the asymmetric carbon atom as the original peroxide. The optically active ester may be formed by way of the cyclic activated complex (LIX):



(LIX)

In the reaction of sodium peroxide with α-phenylpropionyl chloride[114] in a mixture of ether with a little water or in aqueous solution at -15°, instead of the corresponding per-acid or peroxide, α-phenylethyl α-phenylpropionate, 2,3-diphenylbutane, α-phenylethanol, acetophenone, and styrene are obtained. The alcoholic portion of the α-phenethyl α-phenylpropionate and the α-phenylethanol are optically active and retain the configuration of the original α-phenylethyl group, but with 25–50% racemisation. It may be considered that in this case the ester is formed by a combination of a radical and an intramolecular reaction. Control experiments have shown that α-phenylethanol is not a hydrolysis product of the ester under the reaction conditions and is not formed by other reactions during its separation from the reaction mixture. Greene[114] considers that the formation of the alcohol retaining the configuration of the α-phenylethyl group is the result of the decomposition of the per-acid formed, by way of the cyclic four-membered activated complex (LX):

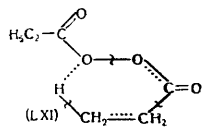


(LX)

In the decomposition of optically active β-phenylisobutyryl peroxide, the alcoholic portion of the ester formed retains the configuration of the original 1-phenyl-2-propyl group to the extent of 90%,[115] which may be considered to be in agreement with the hypothesis that the peroxide decomposes by way of a cyclic activated complex of type (LIX). De Tar and Weiss[115] have remarked that since there is no reason for thinking that more than one intramolecular mechanism for the rearrangement exists, to explain the partial racemisation it is necessary to assume that some of the ester is formed in a free-radical reaction. The varying amounts of racemic ester formed in each individual decomposition of a peroxide are caused not only by the differences in the activation energy for the inversion of the free alkyl radical, but also by the varying parts played by free-radical reactions in each individual case.

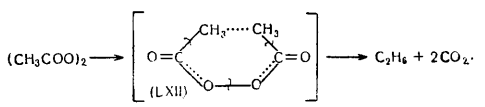
In other cases of the decomposition of acyl peroxides, the results enable ideas on the competition of radical and intramolecular processes to be more soundly based.

In the decomposition of propionyl peroxide[116] in solution in isooctane at 65° in the presence of inhibitors (*p*-benzoquinone, iodine), a certain quantity of the ethylene and ethane formed is independent of the concentration and nature of the inhibitor and remains constant when they are changed; this may be explained either by assuming that the decomposition takes place by way of a cyclic activated complex, or by assuming that the ethyl radicals formed by the decomposition of $C_2H_5COO\cdot$ disproportionate in a "cage" of solvent. In the latter case, the ratio $C_2H_6 : C_2H_4$ should be one, but it has been established mass-spectrometrically and by hydrogenation that this ratio is close to 0.35; the quantity of ethylene formed is therefore almost three times the quantity expected if it is formed only by disproportionation of ethyl radicals. The authors therefore conclude that in addition to the disproportionation of radicals in the solvent cage, in the present case an intramolecular reaction also takes place, probably by way of the cyclic active complex (LXI):



(LXI)

The decomposition products of acetyl peroxide in dilute solutions of isooctane are methane, ethane, carbon dioxide, and the disproportionation products of isooctyl radicals[117]. The yield of ethane is decreased as the temperature increases; this disproves the suggestion that the source of the ethane is the bimolecular recombination of free methyl or acetate radicals, since the concentration of these radicals increases with temperature. If the reaction is carried out in the presence of iodine at 85°, the rate of reaction is unchanged, the yield of methane is greatly reduced, and the yield of ethane remains unchanged. These results can be explained either by the assumption that the ethane is formed as a result of the recombination of radicals in a solvent "cage", or by the hypothesis that the source of the ethane is an intramolecular reaction passing through the cyclic activated complex (LXII):



(LXII)

This reaction should apparently proceed at the same rate in the liquid and gaseous phases. Indeed, ethane is the main product in the decomposition of acetyl peroxide vapour[118]. However, when the reaction is carried out in the gaseous phase (initial partial pressure of acetyl peroxide 0.1 mm and of toluene 15 mm Hg) at 188° in the presence of iodine[119] the yield of ethane falls almost to zero, even with an iodine vapour pressure of only 0.23 mm Hg. The rate of reaction is independent of the iodine concentration, showing that the peroxide does not react with the iodine. On the basis of these results, it was concluded[118] that ethane appears in the reaction products exclusively as a result of the recombination of methyl radicals. Apparently, the first stage of the reaction is the decomposition of the molecule into acyloxy radicals, as was found in the case of the thermal uninitiated decomposition of benzoyl peroxide[49,120-122]. The methyl radicals are formed, according to this mechanism, as the result of decarboxylation of the acyloxy radicals*. The recombination of radicals immediately after their formation has been called "primary recombination"[109].

5. THE CAGE EFFECT

Let us suppose that in a gas two radicals are formed at a certain moment of time as a result of a reaction; they fly apart in opposite directions and each particle before its next collision traverses a distance equal to its free path. What is the probability that the same two particles will again come together and collide? An approximate answer may be obtained as follows. Around the position of each particle we describe a spherical surface of radius half the distance between the particles, i.e. equal to a length of the order of the free path. Then the probability of a second meeting is the probability that they will both be at the point of contact of two spherical surfaces on a sector of the order of πd^2. The probability of one particle arriving there (if all directions of motion are equally probable) is $\pi d^2/4\pi\lambda^2$, and the same applies to the second particle. Thus the resultant probability is $(d^2/4\lambda^2)^2$. If the distance between the particles is less than twice the free path, the probability of meeting will be more than this value. The probability of a second meeting is thus very small, less than 10^{-10}. This is not surprising. If it is considered that the total number of collisions per second in 1 cm^3 of gas is $\sim \pi d^2 u n^2$ (where d is the diameter of the molecule, u is the average velocity, and n the number of molecules in unit volume), and the number of binary combinations of n particles is $n(n-1)/2 \cong n^2/2$, the probability of a collision per second of any one definite pair is $2\pi d^2 u$, i.e, $\sim 10^{-10}$. Thus in a gas the probability of a second meeting of two radicals which have just been formed is negligibly small.

The position is quite different in solutions. The kinetics of reactions in solutions have been reviewed by one of us[125]; part of this work is given below.

In gases the molecules collide once in one combination and then fly apart to collide with others in other pairs. In a solution with a coefficient of diffusion $D \cong 10^{-5}$, the length of elementary displacement of a molecule is $\sim 10^{-11}$ cm, i.e. considerably less than the molecular diameter. Two colliding molecules are surrounded by a tight ring of solvent, so that the collision is repeated many times with the same pair, until finally one of the particles manages to break through the surrounding solvent to a distance of the order of 3×10^{-8} cm, i.e. much greater than the length of a single elementary displacement. A molecule of solvent will then wedge between the two molecules and they will have become separated. This picture of repeated collisions is specific for solutions.

The total number of binary collisions of molecules of one sort in the solution is given by the formula

$$S = \frac{c^2 n^2}{6ND},$$

* A recent paper[123] has presented data favouring a mechanism in which in the decomposition of t-butyl per-esters there is simultaneous cleavage of C — C and O — O bonds with the formation of a molecule of CO_2 and t-butoxy and alkyl radicals in a single act. An analogous mechanism is probably also possible in the case of δ-phenylvaleryl peroxide[124].

where n is the number of dissolved molecules of the given sort in unit volume, N is the total number of molecules in unit volume, D the coefficient of diffusion, and c the velocity of the molecules.

This number of collisions includes all repeated collisions, each of which is treated by this formula as a new act. It is important for us to know the number of collisions of the "second type", i.e. the number of collisions of two particles from the time of their approach until they are separated by the solvent. For this we must know the number of collisions which one molecule experiences in unit time, and the period of time for which two molecules of one sort are together.

From the fundamental equation for unidimensional diffusion,

$$\frac{du}{dt} = D\frac{d^2u}{dx^2},$$

it follows that the probability of finding a particle at time t in the interval from x to $x + dx$, if at zero time it is at the origin, is

$$\omega(x)dx = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right)dx.$$

Hence the probability of radical displacement is

$$\omega(r)dr = \frac{4\pi}{(4\pi Dt)^{3/2}}\exp\left(-\frac{r^2}{4Dt}\right)r^2dr.$$

The average radical displacement in time t is

$$\bar{r} = \int \frac{4\pi}{(4\pi Dt)^{3/2}}\exp\left(-\frac{r^2}{4Dt}\right)r^3dr.$$

The most probable displacement in time t is

$$r = \sqrt{4Dt}\,.$$

It may be assumed that the repeated collisions of one pair will continue until the displacement has reached a certain value of r, i.e. until a solvent molecule comes between the colliding pair. This time will be

$$t = \frac{r^2}{4D}.$$

The solution may be considered as an aggregate of fairly densely packed molecules. If an instantaneous picture is taken of the solution, there would be a certain number of binaries. The probability that a molecule of solute taken at random will be a member of a pair is $n - 1/N - 1$. Hence the total number of pairs is

$$\frac{(n-1)n}{2(N-1)} \cong \frac{n^2}{2N}.$$

Each of the $n^2/2N$ binaries exists for time t as regards repeated collisions, i.e. until the pair separates. We may assume that in each $r^2/4D$ sec, $n^2/2N$ new binaries will be formed. Thus we obtain for the number of primary collisions, without considering repeated collisions,

$$S' = \frac{2n^2D}{Nr^2}.$$

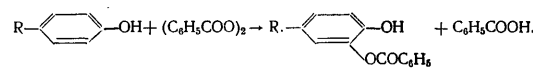
Calculation shows that a meeting with a new molecule takes place on an average approximately within 10^{-8} sec. Moreover, from the formula for S each collision is repeated within $\sim 3 \times 10^{-11}$ sec. This means that once having collided, the molecule in a given pair will continue to collide repeatedly several hundred times, until a solvent molecule comes between them and breaks up the pair. In our calculations we have assumed normal conditions and have shown only the orders of the values.

The above considerations apply in full measure not only to colliding molecules, but also to radicals and atoms formed in the thermal or photochemical decomposition of molecules. If the particles formed in these processes do not possess sufficient excess energy to allow them to break through the "wall" of solvent, they continue to collide repeatedly with each other and with the surrounding solvent molecules. This may lead to the formation of new bonds between them, to disproportionation, etc., before one of the particles is able to react with any other dissolved molecule. This explains, in particular, why some ethane was formed in the experiments of Szwarc and coworkers in isooctane solution, even in the presence of iodine and p-benzoquinone, which react rapidly with free radicals.

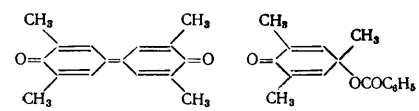
This effect of the possible reaction of two radicals or molecular fragments during the time when they are held in a "cage", i.e. surrounded by solvent without being able to separate, is the "cage" effect, which is of importance in the mechanisms of certain reactions in solutions.

6. THE OXIDATION OF PHENOLS WITH ACYL PEROXIDES

When benzoyl peroxide reacts with phenols unsubstituted in the *ortho*-position, the reaction products are mainly the monobenzoates of the corresponding pyrocatechols[126]:



Under these conditions 2,6-dimethylphenol is converted to 3,3',5,5'-tetramethyl diphenoquinone (LXIII); 2,4,6-trimethylphenol gives mainly 2,4,6-trimethyl-4-benzoyloxycyclohexa-2,5-dienone (LXIV):



(LXIII) (LXIV)

Similar results were obtained in the oxidation of cresols with acetyl peroxide in acetic acid[127].

The rate of the reaction between various phenols and benzoyl peroxide follows an equation of the second order (first order with respect to phenol concentration and first order with respect to benzoyl peroxide)[128]. The reaction of *ortho*-substituted phenols is somewhat slower than in the case of *para*-substituted phenols. In a solution of 2,6-di-t-butylphenol at 30° no reaction at all is observed. Electron donating substituents (OCH_3, CH_3) in the *para*-position accelerate the reaction. Phenols containing electron withdrawing substituents (p-Cl, p-Br) react somewhat more rapidly than unsubstituted phenol, but more slowly than p-cresol and p-anisole.

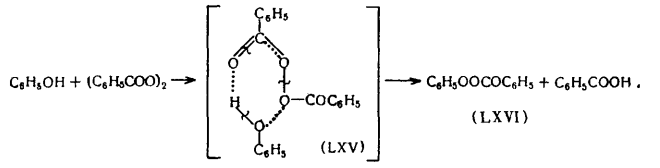
The reaction is not catalysed by acids or bases. The rate of reaction depends in a complex manner on the nature of the solvent. Increase in the polarity of the solvent causes an increased rate of reaction. Apparently a substantial part is also played by the presence of hydrogen bonding between the solvent and the phenol, such bonding probably causing a reduction in the rate.

O-Deuterated phenols react with benzoyl peroxide at a rate which is 1.32 times slower than the non-deuterated. The magnitude of the isotope effect is independent of the structure of the phenol and remains unchanged on passing from benzoyl to acetyl peroxide; CO_2 is not given off in either case[128,130,131]. Oxygen, which is a strong inhibitor of the decomposition of benzoyl peroxide in alcohols and ethers, has almost no influence on the rate of decomposition of benzoyl peroxide in solutions of phenols[132]. The rate of reaction of *p*-methoxyphenol with various peroxide compounds in benzene is greatly dependent on the structure of the peroxide[128], the changes of rate not following the order in which the rate of thermal decomposition of the peroxides changes. In this connection it is interesting that the activation energy for the oxidation of *m*-cresol and *p*-methoxyphenol in benzene with benzoyl peroxide (17.4 and 15.3 kcal/mole respectively) is approximately half the activation energy for the thermal unimolecular decomposition of benzoyl peroxide in the same solvent[49].

Iodine and methyl methacrylate do not affect the rate of oxidation of phenols. In phenolic solutions of benzoyl peroxide styrene undergoes only thermal polymerisation[129]. The radical-initiated polymerisation of styrene in solutions of acetyl peroxide at 60°, like the evolution of CO_2 from these solutions, is greatly inhibited by the addition of 0.1 mole of *m*-cresol per litre; moreover, the rate of polymerisation of styrene initiated by azodiisobutyronitrile is slightly reduced in the presence of *m*-cresol[128].

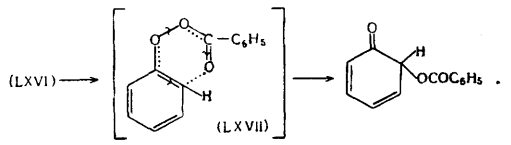
It is difficult to explain all the above facts if it is assumed[126,130,131] that free radicals take part in the oxidation of phenols. We consider it also unlikely that the radicals formed in the decomposition of the peroxide will rapidly form a complex with the phenol[133-135]. Apparently, such a reaction mechanism can be reconciled neither with the kinetic first-order reaction with respect to the phenol (since the dissociation of the peroxide into radicals would probably in this case limit the process), nor with the hydroxyl isotope effect in the phenol, or other data.

To explain the observed features of this reaction, a mechanism has been proposed[128] according to which the benzoyl peroxide and phenol react in the first and slowest stage of the reaction to form the transition state (LXV):



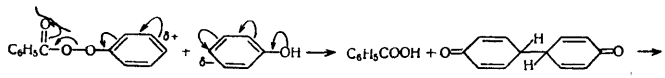
The negative entropy of activation (-26.7 e.u. for *m*-cresol, -22.3 e.u. for *p*-methoxyphenol) is in agreement with this mechanism.

The phenyl perbenzoate (LXVI) formed in the first stage rapidly isomerises by way of the cyclic activated complex (LXVII), similar to that formed in the Claisen *ortho*-rearrangement:



The resulting 2-benzoyloxycyclohexa-3,5-dienone then either undergoes prototropic rearrangement to form pyrocatechol monobenzoate, or is converted by anionotropic rearrangement to the benzoyloxydienone, as in the case of 2,4,6-trisubstituted phenols. Both these rearrangements probably also involve cyclic activated complexes.

The presence of the partial positive charge in the *para*-position of the phenyl group of phenyl perbenzoate enables compounds of type (LXIII) to be formed:



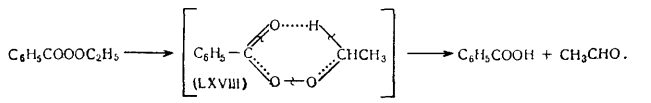
→ (LXIII).

It may be thought that the formation of esters of per-acids by way of (LXV) takes place by the reaction of acyl peroxides with alcohols[132,136-139], as well as by other reactions. The high yield of the acid corresponding to the acyl group obtained in these experiments (usually more than 1 mole of acid per mole of peroxide) supports this suggestion. In the thermal decomposition of acyl peroxides the yield of acid is usually low; thus, for example, acetyl peroxide in isooctane or cyclohexane gives mainly methane, ethane, and CO_2.

The reaction of acetyl benzoyl peroxide with alcohols[140,141] is of great interest in this respect. Because of the asymmetrical structure of the peroxide, the O—O bond is probably polar, the oxygen attached to the benzoyl group carrying a partial negative charge. This is apparently the reason why, in its reaction with methyl, ethyl, isopropyl and n-butyl alcohols, the yield of benzoic acid is ~1 mole per mole of initial peroxide.

Depending on its structure, the resulting per-ester can react by an intramolecular or a radical mechanism.

The main decomposition products of benzoyl peroxide in ethyl alcohol are acetaldehyde and benzoic acid[137]. This can be explained by the decomposition of the intermediate ethyl perbenzoate as follows:



The radical-chain decomposition of peroxidic compounds in such systems is inhibited by the addition of α,α-diphenyl-β-picrylhydrazyl[142]; for example, in the presence of α,α-diphenyl-β-picrylhydrazyl, the active-oxygen concentration in a solution of acetyl benzoyl peroxide in isopropyl alcohol at 45° is constant over a period of 120 min, i.e. a time sufficient for 80% reaction in the absence of the inhibitor[141]. Thus for isopropyl alcohol the radical-chain mechanism predominates over the intramolecular reaction. However, in solutions of methyl alcohol in the presence of α,α-diphenyl-β-picrylhydrazyl, only processes connected with gas-formation are inhibited; benzoic and acetic acids have been separated from the reaction products. Probably in the case of methyl alcohol the intramolecular reaction with a transition state of type (LXVIII) is more rapid than in the case of isopropyl alcohol.

It is interesting that the decomposition of acetyl peroxide in primary and secondary alcohols apparently takes place mainly by a radical mechanism[143]. This difference between acetyl peroxide and benzoyl peroxide[137] can be explained by the probably greater ease of formation of the perbenzoate, and also by the reduction of the energy of the transition

state (LXVIII) because of conjugation of the phenyl group with the activated complex. Consequently, the intramolecular reaction with acetyl peroxide requires a greater activation energy than for benzoyl peroxide.

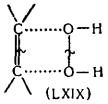
t-Butyl per-esters decompose mainly with the formation of free radicals[123]. This is probably because the formation of the cyclic activated complex of type (LXVIII) is here hindered.

In addition to radical and intramolecular reactions of the per-ester in the system acyl peroxide–alcohol, decomposition of the acyl peroxide itself is thus also possible. The relative parts played by intramolecular and radical processes are altered as the temperature is changed, which probably explains the increased yield of CO_2 at increased temperatures in the decomposition of benzoyl peroxide[138] and acetyl benzoyl peroxide[140,141] in alcohols.

7. THE OXIDATION OF OLEFINES

Depending on the conditions, the reaction of hydrogen peroxide with olefines can give various products. There is usually no reaction if olefines are brought into contact with dilute hydrogen peroxide for several days in the dark in the absence of catalysts, but irradiation with a mercury lamp of solutions of allyl alcohol, crotonic or maleic acid, or diethyl maleate in 5–10% hydrogen peroxide for 20–30 h causes addition of H_2O_2 across the double bond[144].

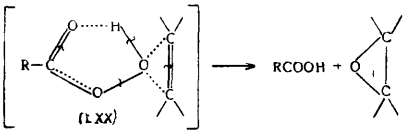
Apart from addition reactions, the hydrogen peroxide decomposes into water and oxygen, and side oxidation reactions take place when the olefinic molecule contains carboxyl or other functional groups. In spite of the extremely favourable conditions for the development of radical mechanisms for the addition to the double bond, such reactions apparently did not occur under the conditions studied[144]. Thus when maleic acid and diethyl maleate are oxidised, the products are mesotartaric acid and its diethyl ester, corresponding to *cis*-addition of H_2O_2 to the olefine. For a radical mechanism, the formation of mixed products or even predominantly the product of *trans*-addition would be expected. For an explanation of the mechanism of this reaction, it is natural to consider the formation of the four-membered cyclic transition complex (LXIX), which is made up of a photo-activated hydrogen peroxide molecule and an olefine molecule:


(LXIX)

The OH· radicals also formed under the reaction conditions cause the decomposition of the hydrogen peroxide into water and oxygen. The radicals also participate in various side oxidations, but probably do not take part in addition reactions*.

In sulphuric-acid solutions, certain olefines add on hydrogen peroxide to form the corresponding hydroperoxides[89,90,146]. The reaction is probably analogous to the acid-catalysed hydration of olefines.

When olefines react with per-acids, epoxides are formed (the Prilezhaev reaction[147]). Numerous investigations[148] have shown that reaction occurs easily in non-polar media. The reaction is of second order[149,150] (first order in respect of olefine and of per-acid). The velocity constant remains unchanged if the initial per-acid concentration is altered and if small amounts of benzoic acid and mineral salts are added[150]. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the reaction of substituted stilbenes with perbenzoic acids are 13–17 kcal/mole and from -21 to -23 e.u. On passing from benzene to a more polar solvent, such as diethyl ether, the values of the enthalpy of activation ($\Delta H^{\neq}$) are slightly increased. This, and the absence of any influence by acid or mineral salts on the velocity constant, are not in agreement with the view that the reaction mechanism is ionic[10,151]. The small increase in the values of $\Delta H^{\neq}$ as the double-bond character of the $>C=C<$ bond decreases in a series of substituted styrenes favours the view that the per-acid reacts with the carbon double bond, and not with one of the carbon atoms of the ethylenic bond. The introduction of electron-accepting groups into the perbenzoic acid also slightly reduces the enthalpy of activation. The experimental data are satisfactorily explained by a mechanism involving the transition state (LXX):[152]



(LXX)

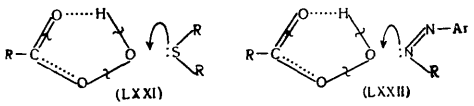
A mechanism involving such a transition state* is in agreement with the existing data on the stereospecificity of the Prilezhaev reaction[153].

It may be assumed that the oxidation with per-acids of the phenylhydrazones of substituted benzaldehydes[154], of 4,4'-dichlorodibenzylsulphide[155], and of diphenylsulphoxide[156] also takes place by an intramolecular mechanism through a transition state analogous to (LXX). All these reactions are characterised by low energies of activation (5–16 kcal/mole) and highly negative entropies of activation (from -20 to -40 e.u.). The rate of reaction and the activation parameters for the oxidation of the disulphide, olefines, and benzaldehyde phenylhydrazones are little altered on passing from benzene to diethyl ether and are independent of the presence in the solution of benzoic acid or inorganic salts. The oxidation of 4,4'-dichlorobenzylsulphide takes place 25 times as rapidly in toluene as in isopropyl alcohol, which may be explained, in accordance with mechanism (LXXI), by the destruction in this solvent of intramolecular hydrogen bonding in the per-acid. Electron-accepting substituents in the reacting molecule increase the activation energy, and in the per-acid decrease it.

* A short communication on the influence of allyl alcohol on the photochemical decomposition of hydrogen peroxide has recently appeared[145]. The authors found that the main reaction products of allyl alcohol with the peroxide under these conditions are the isomeric tetrahydroxyhexanes. These results cannot be compared with those of Milas[144], who obtained glycerol by the photochemical oxidation of allyl alcohol with hydrogen peroxide, until a more detailed account is published.

* The method of molecular orbitals gives for the system  three strongly bonding levels - 2.46 β, - 1.48 β, and - 0.618 β, one zero level, and three anti-bonding levels. This gives an energy of - 9.12 β for six and for eight electrons.

These results can be satisfactorily explained by the mechanism[155] in which the oxidation of 4,4'-dichlorobenzylsulphide passes through the transition state (LXXI):



(LXXI) (LXXII)

In the case of the disulphide, the sulphur atom, possessing an unshared pair of electrons, is the donor.

In the case of the phenylhydrazones of substituted benzaldehydes, it has been suggested[154] that there is an equilibrium,

$$C_6H_5CH=N-NH-Ar \rightleftharpoons C_6H_5CH_2-N=N-Ar,$$

further reaction,

$$C_6H_5CH_2-N=N-Ar + C_6H_5COOH \rightarrow$$

$$\rightarrow C_6H_5CH_2-\overset{+}{N}=N-Ar + C_6H_5COOH,$$

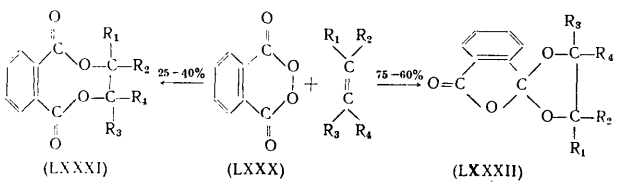
$$\quad\quad\quad

the reaction of atomic oxygen with the solvents, which makes it doubtful whether this scheme can explain the observed reaction. Moreover, the existence of acid catalysis and certain other features in this reaction indicate that it proceeds by another more complex route, with the formation of molecular and not atomic oxygen. Further study of this reaction is necessary before the mechanism can be considered in more detail.

Processes involving the above decomposition of (LXXIX) probably occur in certain oxidations, particularly of aldehydes (see, for example, Knorre and Emanuel'[168]).

It has been suggested[171] that the oxidation of olefines in the presence of inorganic per-acids (pertungstic, pervanadic, etc.) proceeds analogously to the Prilezhaev reaction. From the literature on the formation of glycols in the presence of osmium tetroxide and pertungstic, permolybdic, and other inorganic per-acids, it appears that the reaction proceeds by a non-radical mechanism. In the case of OsO_4 *cis*-products are predominantly formed[172-176]; in the presence of pertungstic and permolybdic acids and selenium dioxide, *trans*-addition takes place[172], as in the bromination of olefines. These differences in the action of inorganic per-acids makes it doubtful whether a single mechanism exists for the oxidation of olefines by their action. A detailed discussion of this question is outside the scope of this article.

The recently studied reaction of phthaloyl peroxide (LXXX) with olefines is of interest[177,178]; cyclic phthalates (LXXXI) and lactones (LXXXII) are formed. Study of the reaction products of *cis*- and *trans*-stilbenes has shown that the addition is very stereospecific:



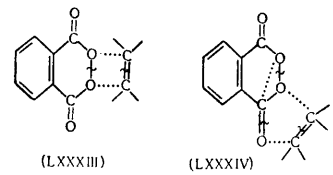
(LXXXI) (LXXX) (LXXXII)

At 20°–80° in CCl_4 the reaction is of second order in the conversion range 0–90% for all the olefines studied[177,178]. As in the oxidation of olefines with per-acids, the presence of electron-donating substituents in the olefine increases the rate of reaction. For 1,1-diphenylprop-1-ene, *trans*-*p*-methoxystilbene and tetraphenylethylene the enthalpy of activation is from 11.6 to 14.5 kcal/mole, and the entropy of activation about -27 e.u.

The second order reaction, the low activation energy, and the stereospecificity of the reaction are difficult to explain on the assumption that addition of phthaloyl peroxide to the olefine is preceded by the isomerisation of the peroxide to a biradical. Considering the second order reaction over a wide range, such an assumption[177,178] would require the sum of the heat change of the isomerisation step and the activation energy for the addition of the biradical to the olefine to be 11.6–14.5 kcal/mole (the observed activation energy), which is not very probable. Green and Rees[178] also concluded that the reaction proceeds without the participation of free radicals, after comparing the relative rates of reaction of various olefines with phthaloyl peroxide, perbenzoic acid, bromine, and the trichloromethyl radical.

It is not very probable, but not impossible, that ion pairs take part in this reaction[178]. Comparison of the activation parameters for this reaction in CCl_4 with the values of $\Delta H^{\neq}$ and ΔS for the reactions of per-acids with azo compounds[154], olefines[155], and sulphoxides[156] considered above shows that all these reactions have a low activation energy and a low entropy of activation (from -20 to -40 e.u.). The presence of ions or ion pairs, as indicated above, does not agree with the experimental data on the kinetics of the reaction of per-acids with unsaturated compounds and compounds possessing unshared pairs of electrons. The same is apparently true for the reaction of phthaloyl peroxide with olefines.

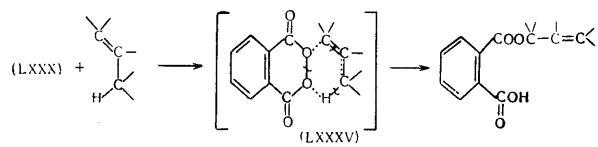
Cyclic phthalates may be formed by way of the transition state (LXXXIII), and lactones by way of the six-membered activated complex (LXXXIV):



(LXXXIII) (LXXXIV)

The distortion of the angles in the original peroxide facilitates the formation of the six-membered ring in (LXXXIV).

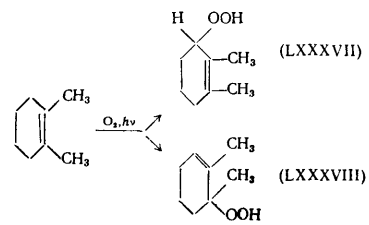
When the olefine contains an α-hydrogen atom, the reaction is more complex, because of the formation of an acid phthalate in addition to the cyclic phthalate and the lactone[178]. This reaction probably proceeds as follows:



(LXXXV)

For example, cyclohexene produces 2-cyclohexenyl acid phthalate. Separate experiments showed that the cyclohexene cyclic phthalate and lactone are completely stable under the reaction conditions, and are not intermediates in the formation of the acid phthalate.

The formation of acid phthalates by the reaction of phthaloyl peroxide with certain olefines is similar to the auto-oxidation of olefines[179,180], which is also accompanied by the migration of the double bond. Apparently, in many cases this reaction proceeds by splitting off the α-hydrogen atom to form a free radical of the allyl type: $-C_1-\dot{C}_2-\dot{C}_3-$. Recombination of this radical with the peroxide radical yields a hydroperoxide in which the peroxide group is attached to one of the carbon atoms formerly forming part of the double bond, or to the α-carbon atom. For example, the oxidation of 1,2-dimethylcyclohexene (LXXXVI) gives the isomeric peroxides (LXXXVII) and (LXXXVIII):[180]



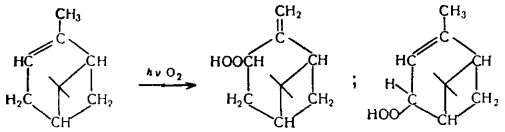
(LXXXVII) (LXXXVIII)

(LXXXVI)

The relative yields of the oxidation products clearly depend on the electron-density distribution in the free radical.

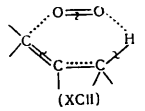
However, the photo-sensitised oxidation almost exclusively produces hydroperoxides in which the double bond has migrated, as many experiments by Schenk and coworkers have shown[181]. Such an exceptionally smooth reaction (yields

80–90% of theory) is difficult to explain merely by electronic effects in the free radical. For example, α-pinene (LXXXIX) would be expected to form a free radical by splitting off the hydrogen atom attached to a secondary carbon atom; in fact the auto-oxidation of α-pinene proceeds through the formation of the hydroperoxide (XC), while in the photo-sensitised oxidation the hydroperoxide (XCI) is formed in 80% yield:



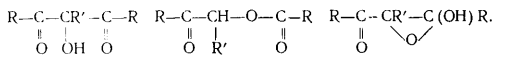
(LXXXIX) (XCI) (XC)

The reaction probably proceeds by way of the photo-activated cyclic transition complex (XCII), analogous to that suggested for the phthaloyl peroxide reaction:



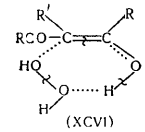
(XCII)

Enolisable β-diketones are easily split by per-acids[182–187], the main reaction products when the reactants are taken in equivalent quantities being an α-hydroxy-β-diketone (XCIII) and an ester of a ketoalcohol and an acid (XCIV). The ester (XCIV) is apparently formed by the thermal or base-catalysed rearrangement of the α-hydroxy-β-diketone[183,187] or of the isomeric epoxide (XCV):[186]



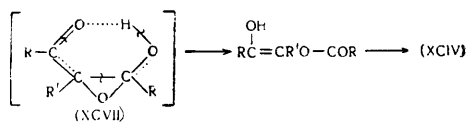
(XCIII) (XCIV) (XCV)

The first step is probably the reaction of the enolised β-diketone with the per-acid. House and Gannon[186] consider that this reaction can form either the epoxide (XCV) or the hydroxydiketone (XCIII) by way of (XCVI):



(XCVI)

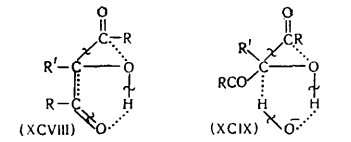
They suggest that the ester (XCIV) forms as a result of the thermal rearrangement of the epoxide (XCV) by way of the transition state (XCVII):



(XCVII)

or by the action of a base through an intermediate carbanion.

The formation of an epoxide by the reaction of an enolised diketone with a per-acid under the mild conditions in which the reaction is carried out appears improbable. For example, α,β-unsaturated acids are oxidised with difficulty by per-acids, but at increased temperatures give mainly hydroxy compounds[149]. With per-acids, α,β-unsaturated ketones usually undergo the Bayer–Villiger reaction[182,188–190]. It is possible that the only product of the reaction of the enolised diketone with the per-acid is a hydroxydiketone. The ester may be formed by the thermal rearrangement of the hydroxydiketone by way of (XCVIII):

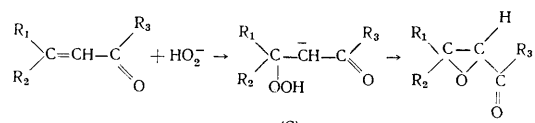


(XCVIII) (XCIX)

or by the action of bases by way of the transition state (XCIX). The question of the competition of mechanisms in which the epoxide and hydroxydiketone take part requires further studies, first and foremost of the tautomeric equilibrium between these compounds.

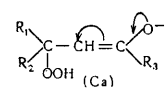
In aqueous or alcoholic alkaline solutions, where radical reactions do not usually occur, hydrogen peroxide does not react with hydrocarbons containing an isolated double bond or a double bond in conjugation with a group other than a carbonyl or nitrile group. α,β-Unsaturated nitriles and carbonyl compounds, including certain quinones[191,192], form the corresponding epoxides. Weitz and Scheffer[193] were the first to study this reaction, using α,β-unsaturated ketones. It has recently been shown[194] that α,β-unsaturated ketones can be converted to epoxides in benzene solutions by means of t-butyl peroxide in the presence of small quantities of benzyltrimethylammonium hydroxide. The catalyst is added to the benzene solution as a 36% solution in methanol.

The kinetic study of the hydrogen peroxide oxidation of mesityl oxide and ethylideneacetone in alkaline solution has shown that the rate of reaction is proportional to the concentrations of the HO_2^- ion and olefine[195]. Bunton and Minkoff consider the reaction to pass through the intermediate formation of the carbanion (C), the rate of its formation determining the overall rate:



(C)

Apparently, the formation of an addition product of the HO_2^- ion and the double bond of the α,β-unsaturated carbonyl compound is not in general excluded, but bearing in mind existing data on the electron affinities of the carbon and oxygen atoms[196], the negative charge residing mainly on the carbonyl oxygen, we consider that the structure of the anion is more correctly given by (Ca):

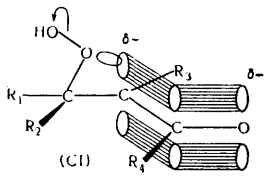


(Ca)

The formation of epoxides by the alkaline hydrogen peroxide oxidation of *cis*- and *trans*-benzalacetones[197,198], β-methyl-*trans*-benzalacetophenone and other derivatives[199,200] shows that the reaction is not stereospecific. For example, both benzalacetophenone isomers yield only the *trans*-oxide, while β-methyl-*trans*-benzalacetophenone gives a mixture of the *cis*- and *trans*-epoxides. The oxidation of *cis*- and *trans*-3-methylpent-3-en-2-one produces only 3-methyl-*trans*-3,4-epoxypentan-2-one[201].

From an analysis of the large mass of experimental material on the stereochemistry of the conversion of α,β-unsaturated ketones into epoxides and the oxidation of

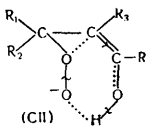
α,β-unsaturated nitriles, it has been concluded[202] that the stereochemistry of the formation of the epoxide is determined by the minimum steric hindrance to coplanarity in the group $-\overset{|\curvearrowleft}{C}=\overset{|\curvearrowleft}{C}-O-$ in the transition state of the following structure (CI):



(CI)

It is suggested that the repulsion of the group COR_4 by the groups R_3 and R_2 is the main hindrance to coplanarity. Coplanarity strengthens conjugation and reduces the activation energy, but slight distortions of the valency angles (within 20%) cannot substantially affect the energy of delocalisation of the electrons in the transition state.

The existing data on this reaction do not contradict the suggestion that the reaction passes through the cyclic activated complex (CII). The repulsion caused by the spatial distribution of the groups R_3 and R_2 must affect the activation energy.



(CII)

In the present article we have restricted ourselves to a review of a few reactions, and, of course, we have not exhausted all the various processes in which peroxides take part. Intramolecular mechanisms are found in many reactions outside those reviewed here, such as the decomposition of tertiary hydroperoxides in alkaline solutions into alcohols and oxygen, the decomposition of dialkyl peroxides containing a secondary carbon atom at the peroxide bond into acetone and alcohol under the action of amines or alkali-metal alcoholates, the oxidation of organoboron compounds, etc., many of which pass through cyclic activated complexes.

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STRAIN AND REACTIVITY IN MONOCYCLIC SYSTEMS

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INTRODUCTION

The idea of strain in cyclic molecules, as a measure of their stability and, in certain respect, their reactivity, was introduced into organic chemistry by A. Baeyer in 1885. Subsequently, Baeyer's original conceptions underwent considerable modification as a result, primarily of the new theoretical ideas, developed by Sachse and Mohr and appearing in the twenties and thirties in the work of Ružicka, Hückel, etc.

The last 10–15 years have witnessed a new stage in the development of the strain theory. A vast quantity of experimental material has accumulated by the widespread use of modern methods in organic chemistry, which provide thermochemical values to a hitherto unattainable degree of accuracy, and reliable spectral and kinetic data. These data are now of paramount importance in interpreting the physical properties and chemical behaviour of cyclic molecules. Strain cannot now be regarded as a function only of the deformation of the valence angle; other types of strain can be distinguished, which are sometimes of greater importance in determining the properties of cyclic compounds. A characteristic feature of many recent chemical investigations of ring strain is that they reflect the influence of strain on chemical properties not related to the rupture or