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The Present State of the Theory of the Oxidation of Cyclo-olefins

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The review deals with various methods for the oxidation of cyclo-olefins by molecular oxygen, nitric acid, aqueous solutions of palladium and gold chlorides, and also ozonolysis. The effect of the structure of the olefin, the solvent, and reaction conditions on the mechanism of action of the oxidant have been analysed. The aim of the review is to formulate, by examining the reaction mechanisms, the principal trends in the applied studies on the synthesis of aliphatic oxygen-containing compounds (acids, aldehydes, and alcohols) from cyclo-olefins. It has been shown that the use of ozone fulfills most closely the desired aim.
The bibliography contains 182 references

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Introduction

The view that processes involving oxidation by molecular oxygen of straight-chain alkanes, alkylbenzenes, and cycloalkanes constitute the most rapid and cheapest methods for the synthesis of acids, alcohols, and compounds with mixed functional groups has now become firmly established. Indeed, considerable advances have been made in studies on the oxidation of these compounds and many processes have been applied in industry. At the same time, the use of cyclo-olefins for this purpose is of no less interest but studies in this field have not yet gone beyond the initial research stage.

Cyclo-olefins are cyclic compounds with a double bond in the ring. According to modern quantum-mechanical views [1] on the nature of the double bond, one of the bonds between the carbon atoms is formed by hydrid sp^2 orbitals. A vacant $2p$ orbital remains at each carbon atom and these two form a π bond by partial overlapping of the electron clouds. The plane of the $2p$ orbitals is perpendicular to that of the sp^2 orbitals. The mutual overlapping of the electronic orbitals is greater in σ bonds than in π bonds and the former are more stable.

There exists also another description of the double bond, proposed by Pauling [2,3]: two tetrahedrally disposed orbitals at each carbon atom overlap one another forming "banana" bonds.

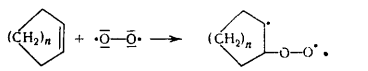
Since the π bond is highly polarisable, multiple C–C bonds readily react with electrophilic agents, i.e. have nucleophilic properties, and are also capable of combining with radicals if the latter are sufficiently reactive.

To facilitate the addition of radicals, it is evidently necessary either to weaken the π bond or to activate the radical. Powerful electrophilic agents such as chlorine, bromine, nitric acid, lead tetra-acetate, potassium permanganate, ozone, and others react as oxidants. In the oxidation the two electrons forming the covalent bond may be transferred either in two stages, one electron at a time (giving a radical process) or by an ionic mechanism, both electrons being involved at once. Substituents at the double bond with a negative inductive effect ($-I$ effect) (carbonyl, nitryl, and nitro-groups and others) diminish its nucleophilic properties. The electron density of the π bond and hence also the rate of electrophilic addition are then reduced [4].

I. OXIDATION OF CYCLO-OLEFINS BY MOLECULAR OXYGEN

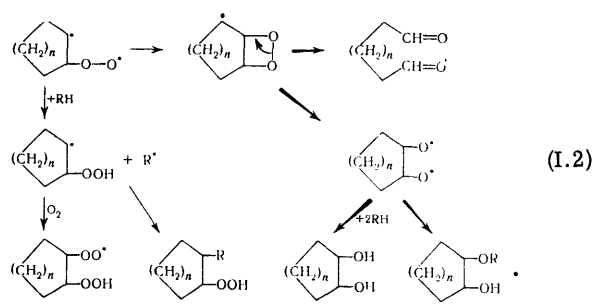
1. The Addition of Oxygen to the Double Bond

The discovery of processes underlying the mechanism of the oxidation is inconceivable without the knowledge of the structure of the oxygen molecule. Mulliken [5] was the first to devote much attention to this problem. According to physical data, the oxygen molecule should have the properties of biradicals (the presence of two unpaired electrons, triplet state, paramagnetism). Therefore oxygen should add directly to the double bond in cyclo-olefin oxidation reactions:



(I.1)

The most probable pathway of further reaction is the formation of a cyclic peroxide, the subsequent rearrangement or radical decomposition of which may lead to the formation of both aliphatic dialdehydes and cycloalkanediols:



(I.2)

However, it is known also that the double bond in the oxygen molecule is fairly stable, the O–O distance (1.2074 Å) being close to the length of the C=O double bond [6] (1.21 Å).

All these data suggest that the electronic structure of the oxygen molecule is more complex than would appear on the basis of the biradical hypothesis. The outer electronic shell of the oxygen atom is known to contain six

electrons (two electrons in the 2*s* orbitals and four electrons in the 2*p* orbitals). It is suggested that a three-electron bond is formed when the atoms are combined to form a molecule [7]. Then each oxygen atom uses one of its four valence orbitals for an unshared pair, one for the formation of a single bond, and two for the formation of three-electron bonds:

$$:O\dot{\div}\dot{\div}O: \qquad (I.3)$$

The saturated O=O structure is also possible but it is less favourable energetically and is encountered in one of the excited states (singlet). The reactions with participation of singlet oxygen (for example the oxidation of cyclo-olefins) constitute a new developing branch of chemistry and are outside the scope of the present review†.

The problem of the electronic state of the oxygen molecule has been discussed on the basis of the molecular orbital method in books by Slater, Spice, and Coulson [25-27]. The molecular orbital method explained for the first time why the oxygen molecule is paramagnetic.

In order to convert O_2 into a biradical, it is necessary to raise the energy by 60–70 kcal mole^{-1}: [28]

$$:O\dot{\div}\dot{\div}O: \rightarrow \cdot\underline{O}-\underline{O}\cdot \qquad (I.4)$$

Such rearrangement of the electron clouds can be induced either thermally or photochemically and at temperatures $\leqslant 200°C$ it probably takes place to an insignificant extent (about 10^{-5}%). Consequently, under ordinary conditions the oxidation of hydrocarbons could take place if the activation energy for the removal of hydrogen by the oxygen molecule (or for the addition of the latter to the double bond) were sufficiently low. However, experimental activation energies for the initial steps in the oxidation [29] of various hydrocarbons,

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot}, \qquad (I.5)$$

$$\rangle C{=}C\langle + O_2 \rightarrow \rangle C(O{-}O^{\cdot})-C\langle, \qquad (I.6)$$

amount to 15–30 kcal mole^{-1}.

The rearrangement of electron clouds in the oxygen molecule takes place very readily only on interaction with a radical already present in the system, which gives rise to the possibility of the development of a radical reaction chain. The theory of slow radical branched-chain reactions, based largely on the work of Semenov [30] and his school, has been developed in studies on the liquid-phase oxidation of hydrocarbons, in particular cyclo-olefins, which have been activated in some way.

We shall consider in greater detail the existing hypotheses on the oxidation of unsubstituted and substituted cyclo-olefins by molecular oxygen and by other oxidants.

2. Oxidation of Unsubstituted Cyclo-Olefins

The oxidation of cyclohexene and cyclopentene (60° and 80°C) is known to involve the formation [31-42] of a fairly stable hydroperoxide with an HOO group in the α-position relative to the double bond. The process kinetics and the mechanism of the formation of the α-hydroperoxide from cyclohexene were investigated by Hendry and Russell [43], Erofeev and coworkers [44-49], Mayo and coworkers [50], and others [51].

†For the chemistry of singlet oxygen, see Refs. 8–24.

Numerous studies have been made on the composition and structure of the oligomeric peroxide products formed in the oxidation of cyclohexene [52-57].

In 1956 Reppe and coworkers [58,59] reported the synthesis of epoxycyclo-octane by the oxidation of cyclo-octene by molecular oxygen at 60°C in the presence of a cobalt catalyst. This advance led to new investigations of the effect of ring size on the oxidation mechanism. According to the cummunication by Mayo and coworkers [50], in the oxidation of a series of cyclo-olefins ranging from C_5 to C_8 at 50–80°C there is a gradual change in reaction mechanism. Thus in the oxidation of cyclopentene 86% of the initial olefin reacts by a mechanism involving the abstraction of the allyl hydrogen atom with ultimate formation of cyclopentenyl hydroperoxide:

$$RO_2^{\cdot} + \rangle C(H)-C{=}C\langle \rightarrow RO_2H + \rangle C^{\cdot}-C{=}C\langle, \qquad (I.7)$$

while in the reaction of cyclo-octene the addition mechanism predominates (70%):

$$RO_2^{\cdot} + \rangle C{=}C\langle \rightarrow RO_2\rangle C-\dot{C}\langle, \qquad (I.8)$$

with formation of the epoxide, suberic aldehyde, and polymers [58].

These data are consistent with the observation of de Rosh and Balaceanu [28], who suggested the following reaction mechanism:

$$\text{initiator} \longrightarrow 2X^{\cdot}, \qquad (I.9)$$

$$X^{\cdot} + (CH_2)_n \longrightarrow XH + (CH_2)_n^{\cdot}. \qquad (I.10)$$

In order to assess the possibility that oxygen adds to the double bond of the cyclo-olefin, we shall consider elementary chain initiation steps in the absence of initiating additives:

$$(CH_2)_n + O_2 \longrightarrow (CH_2)_n^{\cdot} + HO_2^{\cdot}. \qquad (I.11)$$

Reaction (I.11) is endothermic, since its heat is

$$q_{(I.11)} = q_{\text{allyl C-H}} - 47 \text{ kcal mole}^{-1} \text{ (the O-H bond dissociation energy in the } HO_2^{\cdot}\text{radical)},$$

$$84 \text{ kcal mole}^{-1} \geqslant q_{\text{allyl C-H}} \text{ (Ref.60)} \geqslant 77 \text{ kcal mole}^{-1}.$$

The experimental activation energies [29] $E_{(I.11)}$ for reaction (I.11) amount to 15–30 kcal mole^{-1} for different compounds:

$$-CH{=}CH- + O_2 \rightarrow -CH(O{-}O^{\cdot})-CH^{\cdot}-. \qquad (I.12)$$

The activation energy for reaction (I.12) is probably fairly high. In the case of styrene [61] it is 30 ± 2 kcal mole^{-1}. To calculate the heat of reaction (I.12) for cyclohexene, we have

$$C_6H_{12} \rightarrow C_6H_{11}^{\cdot} + {}^{\cdot}H - 88^{62} \text{ (Ref.62) kcal mole}^{-1}, \qquad (a)$$

$$C_6H_{11}^{\cdot} + O_2 \rightarrow C_6H_{11}OO^{\cdot} + 20 \text{ (Refs 28 and 61) kcal mole}^{-1}, \qquad (b)$$

$$\text{cyclohexene-}(O{-}O^{\cdot}) \rightarrow \text{cyclohexene-}(OO^{\cdot}) \cdot H^{\cdot} - (\Delta H_b) + 88 \text{ kcal mole}^{-1}, \qquad (c)$$

since the effect of the peroxy-group O–O· on the elimination of a hydrogen atom from the α-position is probably

insignificant. Next we used the tabulated heats of formation of the substances from the elements [63]:

$$\text{cyclohexene } \Delta H_{form} = -6.4 \text{ kcal mole}^{-1},$$

$$\text{cyclohexene } \Delta H_{form} = -29.5 \text{ kcal mole}^{-1},$$

$$2H \rightarrow H_2 + 104 \text{ kcal mole}^{-1}.$$

Hence, according to Hess's law the heat of reaction is

$$\Delta H_b = 88 - \Delta H_H + [-20 + 83 + \Delta H_{C_6H_{12}} - \Delta H_H],$$

$$q_{(I.12)} = \Delta H_b - \Delta H_{C_6H_{10}} = 28.9 \text{ kcal mole}^{-1}.$$

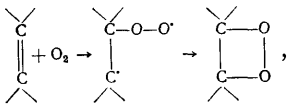
Since we do not know the heat of formation of cyclo-octene, it will be calculated from the known heats of hydrogenation of *cis*-cyclo-octene (−23.53 kcal mole^{-1}) and the heat of formation of cyclo-octane (−29.81 kcal mole^{-1}):[63,64]

$$\Delta H_{form} = -6.28 \text{ kcal mole}^{-1}.$$

Then, assuming that the energy of the dissociation of a hydrogen atom from the methylene group of cyclo-octane [65] is 94 kcal mole^{-1}, we determine the heat of addition of oxygen to the double bond of cyclo-octene, as in the procedure described above: 40.47 kcal mole^{-1}.

For endothermic reactions, $E > q$ and therefore, by comparing the heats and activation energies for reactions (I.11) and (I.12), it is not difficult to show that reaction (I.11) is more likely in the cyclo-olefin series.

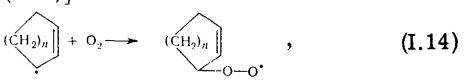
The hypothesis of the possible formation of a cyclic peroxide [33,57,66]:



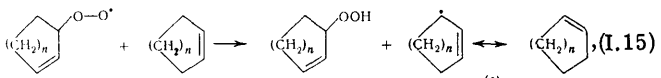
(I.13)

have not so far found experimental confirmation but it still has some supporters [67,68].

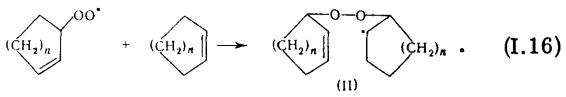
Usually the removal of a hydrogen atom from the allyl system by a peroxy-radical [stage (I.15)] requires a smaller activation energy than its radical addition to a double bond [stage (I.16)]:[69]



(I.14)

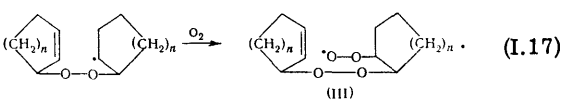


(I.15)



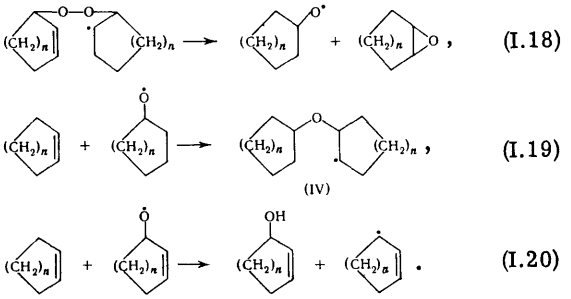
(I.16)

The formation of the allyl radical (I) was established in early studies described in the review of Criegee [70] and Rosenwald [71]. According to Waters [69], the competing radical addition reaction becomes appreciable as the reaction temperature increases. However, Mayo [50] did not find a difference in the reaction mechanism when cycloheptene was oxidised at 60° and 80°C. Probably, the 20 deg difference is insufficient:



(I.17)

The peroxy-radical (III) formed in the reaction of (II) with oxygen by mechanism (I.17) may undergo further reactions similar to (I.15) or (I.16). The decomposition of the radical (II) [reaction (I.18)] competes with reaction (I.17). It probably predominates in the oxidation of cyclo-octene:



(I.18)

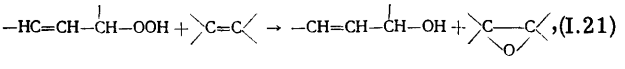
(I.19)

(I.20)

According to Mayo [72], owing to the competition between the elementary stages (I.17) and (I.18), the pathway taken by the oxidation reaction should depend on the partial pressure of oxygen‡.

The yield of epoxides cannot exceed 50% if they are formed only as a result of reaction (I.18). The Prilezhaev reaction occurring simultaneously makes a definite contribution to the accumulation of peroxides in amounts exceeding 50%. [28,50,74-78]

The possibility that epoxides are formed by the mechanism proposed by Hock [37] cannot be excluded [79]:



(I.21)

but special experiments [80] confirmed that the ability of α-peroxides derived from cyclo-olefins to give rise to epoxides in the presence of catalysts at the concentrations usually employed in oxidation reactions is insignificant.

Some investigators [81] believe that the principal epoxide-forming agents in the oxidation of acyclic (C_3) and cyclic (C_6) olefins are acylperoxy radicals, since alkenylperoxy-(alkylperoxy-)radicals are insufficiently reactive in reactions of this kind. Alcohol was not found in the early stages of oxidation in these experiments [79]. It is believed [81] that this supports the above hypothesis.

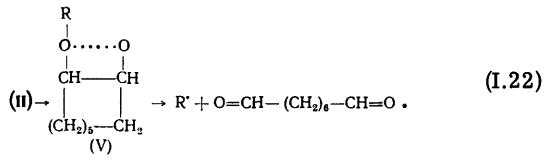
An epoxyalkane was not found in the simultaneous oxidation of isopropylbenzene and propene at 80–90°C in the presence of azobis(isobutyronitrile) as an initiator [81], although a high concentration of $RO_2^{\cdot}$ radicals was detected by the ESR method [82]. Possibly, under the conditions chosen by these investigators [81], the reaction $RO_2^{\cdot} + \diagup C{=}C \diagdown$ does not occur because of steric hindrance or insufficient reactivity of the peroxy-radical.

The behaviour of radicals in reactions involving addition to a double bond or the abstraction of an allylic hydrogen atom has for a long time attracted the attention of chemists, since it provides information about the energy of a particular radical [83,84]. Kinetic [85-87] and thermochemical [60] data are now available which confirm the hypothesis [88,89] of the interaction of $RO_2^{\cdot}$ with the olefin double bond.

The absence of an alcohol in the initial reaction period can be readily explained if it is assumed that reaction (I.19)

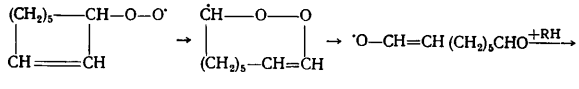
‡For a more detailed description of this problem, see Mayo [73].

predominates over reaction (I.20). The aliphatic aldehydes are probably formed as a result of the decomposition of radical (V):



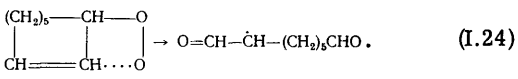
(I.22)

However, together with the mechanism quoted above, one cannot exclude other pathways involving the isomerisation and breakdown of the peroxy-radical [reactions (I.23) and (I.24)]:



(I.23)

The incorporation of the peroxy-group O–O in the cyclo-octene chain reduces the strain in the ring [4]:

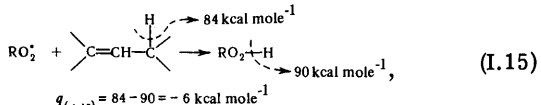


(I.24)

In the oxidation of n-butane and propene [81,90–93] it was shown that such reactions may occur in the liquid phase. Under oxidation conditions, aldehydes are converted into peracids and the latter undergo the Prilezhaev reaction and participate in the formation of epoxycycloalkanes. However, aldehydes and the corresponding acids were found in insignificant amounts in the oxidation of cyclo-octene.

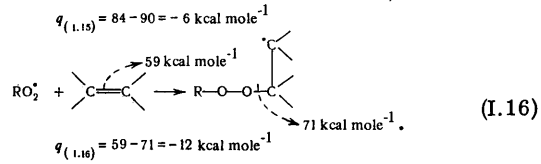
Probably the different compositions of the final products found in the oxidation of cyclohexene and cyclo-octene must be explained on the basis of the differences between the structures of the two cyclo-olefins. It is therefore necessary to assume that in the oxidation of cyclo-octenes the activation energy $E_{(I.15)} > E_{(I.16)}$, while in the oxidation of cyclohexene the opposite relation holds: $E_{(I.15)} < E_{(I.16)}$.

If account is taken of Benson's data [60] on bond dissociation energies, it becomes clear that reaction (I.16) is more exothermic than reaction (I.15):



(I.15)

$q_{(I.15)} = 84 - 90 = -6$ kcal mole^{-1}



(I.16)

$q_{(I.16)} = 59 - 71 = -12$ kcal mole^{-1}

In accordance with the concepts developed by Vitvitskii [94], we suggest that the activation energy $E_{(I.16)}$ for reaction (I.16) does not vary in the series of cyclo-olefins, while $E_{(I.15)}$ must depend greatly on the structural characteristics of the given cyclo-olefin. In fact, the number of hydrogen atoms which may participate in the radical substitution reaction (I.15) decreases from 4 in cyclopentene to 2 in cyclo-octene [50].

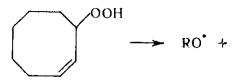
Since among $\geq C_5$ cyclo-olefins the cyclopentene ring is the most planar [95], the removal of an α-hydrogen atom from cyclopentene by a peroxy-radical according to mechanism (I.15) leads to the formation of an allyl radical, which may be regarded as a hybrid of two resonance forms and which does not require the expenditure of additional energy on the rearrangement of the ring. An analogous conclusion, which explains the formation of cyclohexenyl α-hydroperoxide, can be readily reached by examining the stereochemistry of cyclohexene.

Cyclohexene is known to have the "half chair" conformation in which four carbon atoms are located in one plane. Two of the remaining atoms are below and above this plane [96]. The "half boat" form is then less stable than the "half chair" form by only 2.7 kcal mole^{-1}. [97]

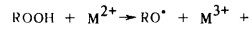
For the principle of maximum overlap of the orbitals to operate in the allyl radical derived from cyclohexene [50], it is necessary that one of the two non-coplanar carbon atoms should move to the plane of the four carbon atoms. According to the data of Anet and Haq [98], this can be achieved by overcoming a potential barrier of only 5.2 kcal mole^{-1}. For comparison, we may note that a similar inversion of the cyclohexane ring can occur only by overcoming a potential barrier of 14 kcal mole^{-1}. [99] Even under ordinary conditions the fraction of molecules having the "half boat" conformation may be appreciable and in substituted cyclohexenes can actually predominate [100,101].

The low yield of cyclo-octenyl α-hydroperoxide in the oxidation of *cis*-cyclo-octene is probably due to hindrance by energy factors, since in reaction (I.15) it would be necessary to overcome a fairly high energy barrier, which consists of the normal heat of reaction, the energy which must be expended to rearrange the ring in the formation of the allyl radical, and the energy necessary for the rearrangement of the valence shell of the carbon atom attacked.

The homolytic decomposition of cyclo-octenyl α-hydroperoxide with subsequent isomerisation is probably not the only pathway, since epoxides are already detected in the early stages of the oxidation reaction:

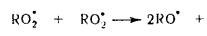


(I.25)

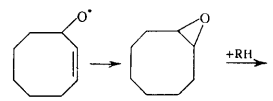


(I.26)

or



(I.27)



(I.28)

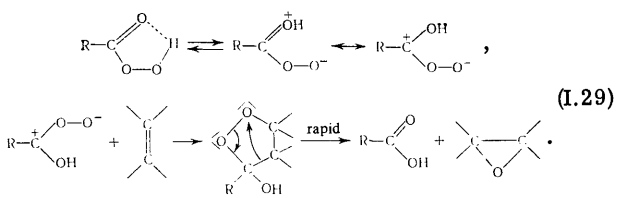
The probability of reaction (I.28) should be greater for cyclo-octene than for cyclohexene, bearing in mind the internal steric saturation of the first compound.

The presence of trigonal carbon atoms reduces the ring strain and it would appear that the C_8 ring, in which the angle between the C–C bonds is 135°, should enter into reactions involving addition to the double bond with considerable difficulty, much less readily at any rate than cyclohexene. The cyclohexane molecule is known to be very stable when all the carbon atoms are in the tetragonal form [4]. Nevertheless attempts at a direct conversion of cyclohexene into an epoxy-derivative by oxygen have so far been unsuccessful. This contradiction is difficult to explain at present.

Thus, according to the concepts developed, cyclic α-hydroperoxides, allyl alcohols, and ketones are obtained by a radical substitution mechanism [reaction (I.15)] and the epoxides and products formed on ring opening at the site of the double bond (i.e. aliphatic aldehydes and acids) are formed by a radical addition mechanism.

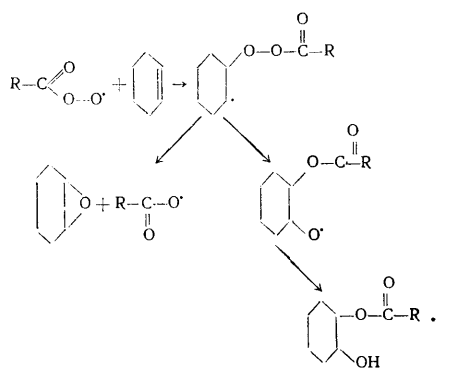
(a) The coupled oxidation reactions of olefins with aldehydes, which are used to synthesize epoxides[102-106] in yields greater than 50% or ethers[107,108], have been known for a long time. The study of the oxidation of cyclohexene in cumene[109], ethylbenzene, and other compounds which readily give rise to hydroperoxides, and also (its oxidation) in the presence of various aldehydes showed that coupled processes of this kind involve a radical-chain mechanism.

At the same time, systematic studies on the kinetics and mechanism of the interaction of peracids with various olefins (the Prilezhaev reaction) were begun in order to discover the component most active in the formation of chains in joint oxidation reactions. For a long time it was believed that the first stage of this reaction is the heterolytic breakdown of the peracid. However, Kwart and Hoffman[110] suggest a 1,3-dipolar addition mechanism to account for the experimental results:

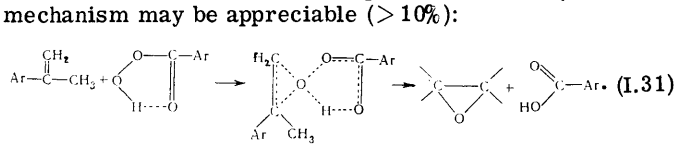

(I.29)

It is now believed, on the basis of kinetic investigations, that the conversion of olefins into epoxy-derivatives by reaction with peracids involves the intermediate formation of an olefin–peracid π complex[111,112,113].

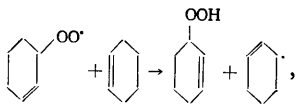
In his study of coupled oxidation, Wittig[114] noted that olefins retard the oxidation of aldehydes. Walling[115] and Ikawa[80] found an explanation for this phenomenon: when aldehydes are oxidised in the presence of olefins, the concentration of acylperoxy-radicals falls, since the latter participate in the following reaction:


(I.30)

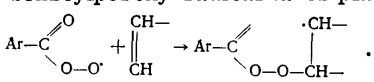
This mechanism has been generally accepted[28,80,116-118], but, as shown, for example, by studies on the oxidation of methylstyrene in the presence of benzaldehyde[119], in some reactions the fraction of epoxides formed by a radical mechanism may be appreciable (>10%):


(I.31)

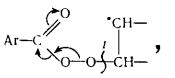
Using the data on the oxidation of cyclohexene in the presence of a small amount of benzaldehyde, Ikawa[80] concluded that, together with benzoylperoxy-radicals, cyclohexenylperoxy-radicals also participate in the epoxide-formation reaction. Indeed, the formation of the α-hydroperoxide predominates in the oxidation of cyclohexene on its own:


(I.32)

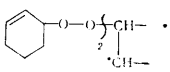
while in the joint oxidation of benzaldehyde and cyclohexene under comparable conditions, the reaction involving the addition of the benzoylperoxy-radical takes place:


(I.33)

As a result of the inductive effect (shown by arrows)


(I.34)

the dissociation energy of bond 1 should be less than that of bond 2:

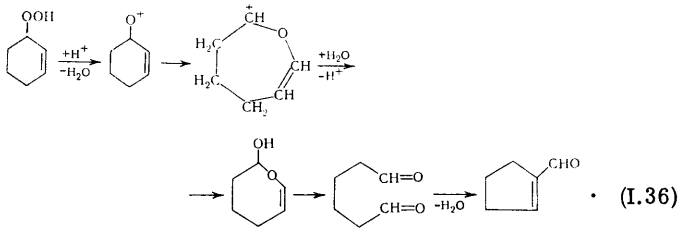

(I.35)

Therefore the addition of the cyclohexenylperoxy-radical to the cyclohexene double bond may be easier, since the following relation has been observed in many radical addition reactions: the greater is the heat of reaction of the radical with the molecule the lower is the activation energy[30].

Thus, according to the current views on the oxidation mechanism, in order to obtain aliphatic oxygen-containing compounds (aldehydes and acids) from cyclo-olefins, either the addition of the peroxy-radical at the site of the double bond or its isomerisation is necessary.

The question arises what conditions would favour the isomerisation of peroxy-radicals or their addition at the site of the double bond. Apparently this requires the choice of appropriate solvents, catalysts, and material for the walls of the reactor in which the oxidation is carried out[120,121] (i.e. the study of the mechanism of homogeneous-heterogeneous catalysis) or deliberate preparation of the required site for attack by oxygen (activation of the double bond, the use of more reactive peroxy-radicals, etc.).

(b) Effect of the solvent. Shine and Snyder[122] investigated the oxidation of cyclohexene by oxygen at 60–80°C in the presence of acetic anhydride and showed that under these conditions cyclohexenyl α-hydroperoxide decomposes heterolytically:


(I.36)

It is known that strongly associated solvents frequently alter the mode of the chain oxidation process[123]. However, so far there is very little information about the effect of such solvents on the mechanism of cyclo-olefin oxidation[124,125].

It has now been established that the formation of intermolecular hydrogen bonds in the oxidation of hydrocarbons has a significant effect on the kinetics, for example in the radical decomposition of hydroperoxides[29]. Together with alcohols and ketones, the latter participate in the reaction

with the peroxy-radical and the new radicals thereby formed lead to chain branching. The rate of the elementary steps and hence the rate of the overall oxidation process depends significantly on the properties of the solvent [126,127]. This is because the elementary chain propagation ($RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot}$) and chain termination ($RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_6}$ molecular product) reactions, which determine the overall rate of the process, involve the interaction of two dipoles, the magnitude of which depends on the dielectric constant of the medium. The effect of the solvent is particularly pronounced in the oxidation of polar organic compounds (ethyl methyl ketone, ethanol, etc.). The composition of the reaction product is determined by the competition between two pathways in the chain propagation reaction [128]: the interaction of $RO_2^{\cdot}$ with the initial molecule:

$$RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot} \qquad (I.37)$$

and the breakdown of $RO_2^{\cdot}$ into products with lower molecular weights:

$$RO_2^{\cdot} \xrightarrow{k_1} R'O^{\cdot} + R''CHO. \qquad (I.38)$$

Dilution of ethyl methyl ketone or ethanol with a non-polar solvent (benzene) increases the amount of $RO_2^{\cdot}$ radical decomposition products, since benzene reduces the dielectric constant of the medium. As a result, the rate of reaction W_2 falls. At the same time, the rate of the mutual recombination reaction

$$[2RO_2^{\cdot} \xrightarrow{k_6} \text{molecular products}] \qquad (I.39)$$

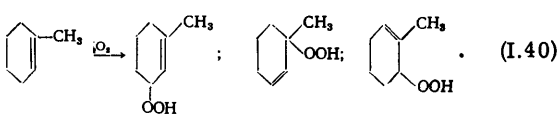
decreases even faster than the rate of reaction (I.37). [129]

However, the amount of theoretical and experimental information about the effect of the solvent on the elementary stages in radical reactions (for example, in the oxidation of non-polar substances) is still inadequate. This makes deliberate control of liquid-phase oxidation reactions significantly more difficult.

3. Oxidation of Substituted Cyclo-olefins

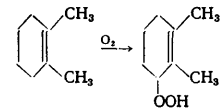
The role of substituents in the oxidation of cyclo-olefins can be followed on the basis of studies already carried out. It is known that the site chosen for attack by oxygen depends in many ways on the nature of the substituent and also on the relative positions of the double bond and the substituent.

(a) Oxidation by molecular oxygen of compounds in which the substituents have a positive inductive effect. Only methylolefins have been investigated on these lines [51,130,131]. Bolland [131], who oxidised methylcyclohex-1-ene, isolated only three of the theoretically expected six α-hydroperoxide isomers:


(I.40)

The determination of the position of the hydroperoxy-group is fairly difficult and therefore the experimental results are contradictory.

In the oxidation of a cyclo-olefin with methyl substituents at the double bond, which should increase its nucleophilic properties and should apparently facilitate the addition of the peroxy-radical at the site of the double bond, Criegee [70] obtained the hydroperoxide

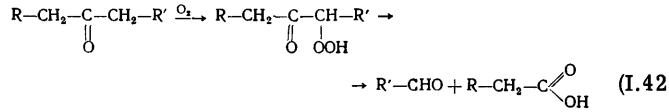

(I.41)

In contrast, Dupont [132] showed that the oxidation of 1,2-dimethylcyclohex-1-ene yields 1,2-dimethylcyclohexane-1,2-diol and 1,2-dimethylcyclohex-1-ene-3-one and a very small amount of $\alpha\omega$-diacetylbutane.

It should be noted that, apart from the inductive effect exerted via 2–3 carbon atoms, the number of methylene groups in the chain is of considerable importance.

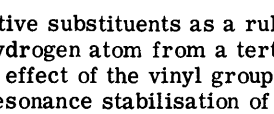
The South African investigators Arndt et al. [133] reported that in the oxidation of 5-methylnonane the substitution of the hydrogen atom at the tertiary carbon atom is 19 times faster than at a secondary carbon atom. However, under these conditions oxygen does not attack solely the tertiary carbon atom.

A departure from the α-mechanism

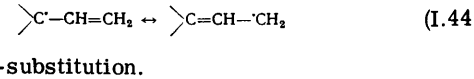

(I.42)

suggested by Langenbeck and Pritzkow [134] (cyclohexanone, tetralone) was observed by Obukhova et al. [135] in the oxidation of 6-undecanone.

(b) Effect of substituents with a negative inductive effect. According to the data of Brill [136] and Tepenitsyna [137], the main reaction product in the oxidation of 4-vinylcyclohexene is a tertiary hydroperoxide:

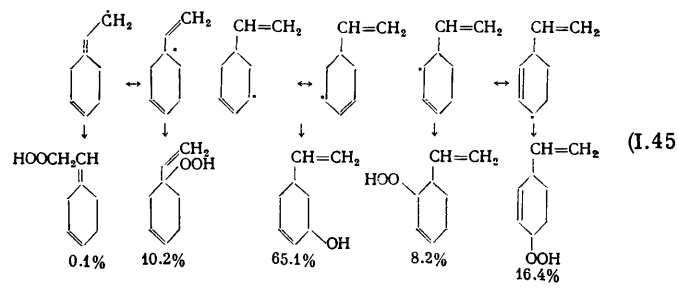

(I.43)

Electronegative substituents as a rule facilitate the removal of a hydrogen atom from a tertiary carbon atom. Since the polar effect of the vinyl group is not very pronounced, the resonance stabilisation of the radical


(I.44)

should favour α-substitution.

Nevertheless, Farrissey [138] observed the formation of a complex mixture of hydroperoxides in the oxidation of 1-vinylcyclohex-4-ene:


(I.45)

A similar deviation from the normal relative activity is shown by those cyclic olefins in which either the tertiary allyl carbon atom or the double bond in which it is involved are outside the ring [138]. According to the transition state

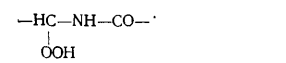
theory, the formation of an allyl radical requires the maximum overlapping of the p and π orbitals, for which it is necessary that the C–H bond dissociated should be axial relative to the plane of the double bond. If the double bond or its allyl carbon atom are outside the ring, this requirement involves a loss of a degree of freedom of rotation [139]. Moreover, the H–H interaction between the allyl and the vinyl hydrogen in such a conformation is a maximum [140].

Consequently when an H atom is dissociated from a tertiary carbon atom, both of the above factors can markedly increase the energy of the transition state.

The polar effect of the carboxy-group should hinder the dissociation of a hydrogen atom from H–C(–)–COOH more than from H–C(–)–CH_2–COOH because the electric field due to the dipole of the HOOC group decreases in proportion to the cube of the distance [69].

The oxidation of compounds with an unprotected carboxy-group is frequently accompanied by decarboxylation. This side reaction may become the main one under certain conditions. For example, in the oxidation of cyclohexanecarboxylic acid in acetic acid the main product is cyclohexanone [141] and in the oxidation of methyl cyclohexanecarboxylate [142] the main products are the monomethyl esters of butanetricarboxylic and α-oxopimelic acids. Evidently in this case it is important to know the location in space of both the C(=O) group and the hydrogen atom at the tertiary carbon atom.

Azanovskaya and Ablova [143,144] investigated the effect of substituents on the oxidisability of cyclo-olefins without determining the position of the hydroperoxy-group formed in this process. They investigated ethers and esters (acetate and benzoate) and halogeno- and amino-derivatives of cyclohex-1-en-3-ol. It was found that ethers are oxidised most readily. Cyclohexenol is oxidised with greater difficulty than with cyclohexene [145]. Esters react only in the presence of initiators. The amino-derivatives were not oxidised at all (even in the presence of an initiator). However, the inhibiting effect of the amino-group is not always shown. For example, in the oxidation of ϵ-caprolactam a hydroperoxide is formed:



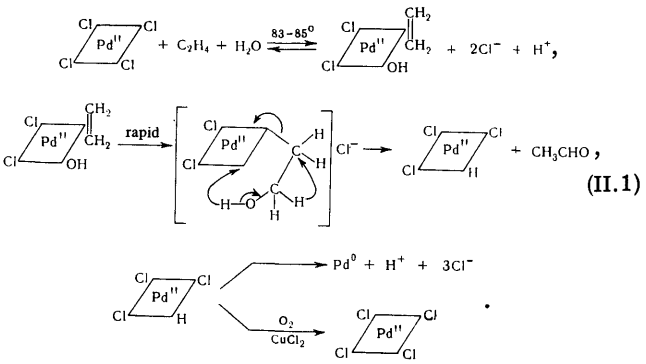
(I.46)

together with its decomposition products [147]. Here the basicity of the imino-group is low due to the conjugation of the carbonyl π bond and the unshared electron pair of the nitrogen atom.

Thus the data discussed in the present review lead to the conclusion that the total experimental and theoretical facts available at present on the oxidation of cyclo-olefins by molecular oxygen are insufficient to allow a reliable prediction of the conditions for the selective ring opening at the site of the double bond and the formation of aliphatic dicarboxylic acids.

II. OXIDATION OF CYCLO-OLEFINS TO CARBONYL COMPOUNDS. CATALYSIS BY PALLADIUM, GOLD, MERCURY, AND THALLIUM SALTS

The oxidation of cyclo-olefins in the presence of aqueous solutions of palladium and gold salts has not been adequately investigated, since the main effort of investigators has been concentrated on the elucidation of the mechanism of the oxidation of aliphatic olefins [148]. It is now known that saturated cyclic ketones can be obtained in this way from cyclic olefins [149,150], while aliphatic olefins yield acyclic aldehydes and ketones [151]. For example, when ethylene is introduced into an aqueous solution of palladium chloride, reaction probably takes place by the following mechanism [152]:



(II.1)

The studies on the oxidation of olefins in the presence of mercury and palladium salts have been reviewed by Halpern [152].

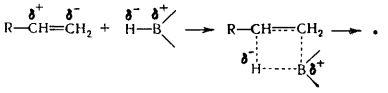
III. OXIDATION OF CYCLO-OLEFINS BY ELECTROPHILIC AGENTS

In order to obtain aliphatic oxygen-containing compounds from cyclo-olefins, it is probably more convenient (compared with molecular oxygen) to employ typical electrophilic agents such as lead and thallium acetates, nitric acid, ozone, etc. [153]

The mechanism of the oxidising action of lead tetra-acetate has been elucidated to a considerable degree by the fundamental work of Criegee [153]. However, because of their high cost, lead tetra-acetate and especially thallium tri-acetate [154,155] cannot compete with molecular oxygen or nitric acid.

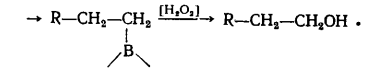
1. Hydroboration–Oxidation

The addition of boranes to unsaturated compounds involves a four-centre transition state [156]:



(III.1)

However it is still not clear which factor is more important in this step: electrophilic attack by boron or nucleophilic attack by hydrogen:

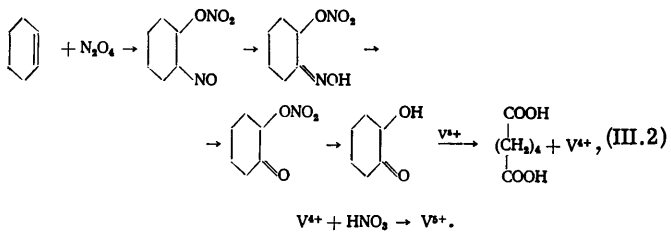


Hydroboration may be a convenient method for the preparation of alcohols when a cheap source of diborane is available [157,158]. These problems are dealt with in greater detail in Brown's monograph [156].

2. Oxidation of Cyclo-olefins by Nitric Acid

The interest in the use of nitric acid for the selective cleavage of the ring at the double bond increased greatly after the discovery of the catalytic effect of ammonium

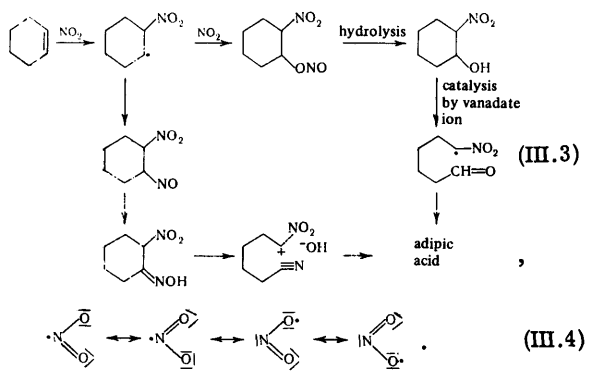
metavanadate mixed with copper powder[159]. However, this process has many disadvantages, most of which are associated with the high corrosivity of nitric acid. The mechanism of the oxidation of cyclo-olefins by nitric acid in the presence of a catalyst is still obscure in many ways[160,161]. Franz[162] suggests that in this reaction nitrogen tetroxide is the most active reagent. The tetroxide is formed on decomposition of intermediate compounds produced as a result of the oxidative dissociation of nitric acid:



(III.2)

$$V^{4+} + HNO_3 \rightarrow V^{5+}.$$

Gut and Lindenmann[163] put forward a mechanism according to which the oxidation begins with a free radical addition of NO_2 to the cyclo-olefin double bond:

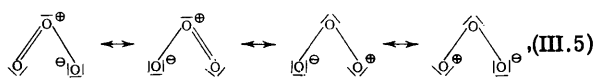


(III.3)

(III.4)

3. Ozonolysis

It has been firmly established that ozone[6],



(III.5)

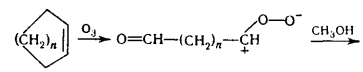
adds quantitatively at the site of the double bond. An extensive literature shows a pronounced interest in the problem of the utilisation of ozone as an oxidant[164,165]. There is no doubt that, after improvement in the design of ozonisers, ozone will find very wide application.

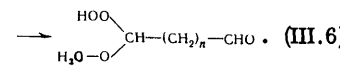
Data are already available on the technical application of ozone for the conversion of aliphatic olefins into alcohols and aldehydes and also for the conversion of oleic acid into azelaic and pelargonic acids in high yields[167,168]. There has been a recent report on the construction of a factory for the ozonolysis of soya bean oil with a projected output of 4500 tons per year[169].

The addition of ozone to the double bond of an olefin is very rapid and therefore the rate of reaction is limited mainly by the rate of migration of ozone to the olefin.

The application of modern physical experimental methods made it possible to begin an investigation of the kinetics of the interaction between ozone and olefins. According to the data of Williamson and Cvetanovic[170,171], the rate constant for the second-order reaction between ozone and cyclopentene in carbon tetrachloride at 25 °C is 2×10^5 litre $mole^{-1}$ s^{-1}.

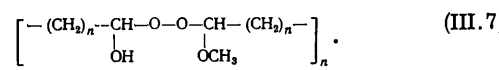
Without considering the problem of the mechanism of the primary attack on the double bond by ozone, we may note that the composition and origin of the ozonolysis products of cyclo-olefins in proton-donating solvents (for example in methanol at ±50 °C) can be accounted for by Criegee's mechanism:





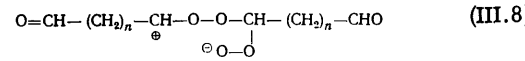
(III.6)

The formation of methoxyhydroperoxides constitutes the main reaction pathway. One cannot exclude the possibility that aldehyde and hydroperoxy-groups react with one another during ozonolysis[172,173] with formation of an oligomer:



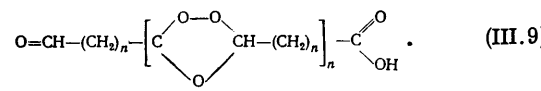
(III.7)

Moreover there is a possibility of the dimerisation of dipolar ions by the following mechanism:



(III.8)

or their polymerisation:



(III.9)

Pathways (III.8) and (III.9) are not unique and their contribution to the overall reaction mechanism is small.

Methoxyhydroperoxides (together with polyperoxides) can be subsequently oxidised by a suitable oxidant[174,175] to acids or reduced catalytically to aldehydes or alcohols[176,177].

The attempts to combine in one stage processes involving the ozonolysis of cyclo-olefins and the oxidation *in statu nascendi* of the peroxy-products are extremely interesting. For this purpose, cyclo-olefins have been subjected to ozonolysis in acetic acid[178] (at 40–80 °C) and also in aqueous emulsion or an alkaline solution of hydrogen peroxide[179] (at 20–25 °C). The yield of dicarboxylic acids was ≥ 80%.

Oxidation by lower peracids (C_1–C_3) of alkoxyhydroperoxides obtained by the ozonolysis of substituted cyclo-olefins in alcohols permits the synthesis of various derivatives of aliphatic polycarboxylic acids (for example, butane-1,2,4-tricarboxylic acids from 4-vinylcyclohex-1-ene or cyclohex-1-ene-4-carboxylic acid[180,181]).

The ozonolysis proper takes place fairly readily without the need for special apparatus and the solvents employed are as a rule available commercially. A certain risk of detonation of peroxides and ozonides can be eliminated by selecting appropriate process conditions.

It is noteworthy that many aspects of the detailed mechanism of the ozonolysis of cyclo-olefins have not yet been elucidated[182] and the composition of the products depends to a considerable extent on the solvent and the ozonolysis conditions.

Nevertheless, regardless of the composition of the peroxy-products, their subsequent processing by oxidation or reduction gives a fairly high final yield of acids, aldehydes, or alcohols (≥ 80%). Therefore, bearing in

mind the likely availability of oxidants (O_2, H_2O_2, and $CH_3-C(=O)-OOH$) and reductants [H_2, (iso-$C_3H_7O)_3Al$, $LiAlH_4$, CH_3-S-CH_3, etc.), we are inclined to believe that ozonolysis may be the most suitable method for the conversion of cyclo-olefins into aliphatic oxygen- containing compounds.

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