Russian Chemical Reviews **63** (9) 751 – 766 (1994)
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UDC 541.422:542.943:678.019.3

Degradation of the carbon chain in the liquid-phase oxidation of saturated compounds

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Abstract. The reaction pathways leading to the degradation of the carbon chain in the liquid-phase oxidation reactions of saturated hydrocarbons and their oxygen-containing derivatives are examined. The relative importance of the pathways and their dependence on the structure of the substrate and of the oxidation conditions are discussed. The bibliography includes 151 references.

I. Introduction

Reactions involving the extensive oxidation of saturated hydrocarbons by molecular oxygen in the liquid phase lead to a wide variety of oxygen-containing compounds. The formation under these conditions of compounds with a lower molecular mass than that of the initial hydrocarbon is associated with the degradation of the carbon chain, which occurs to some extent in virtually all the stages of these complex radical-chain processes.

In conformity with the ideas which arose in the 1950s – 1960s and which have been quite fully surveyed in monographs [1,2] and reviews, [3,4] it was assumed that the carbon chain is ruptured mainly in the stages following the formation of ketones, for example in the stage involving the decomposition of α-ketohydroperoxides. However, later experimental data were obtained indicating that, in the oxidation of alicyclic, [5] aliphatic, [6] and to a lesser extent aromatic [7–9] ketones, the decomposition of α-hydroperoxyketones leads preferentially to α-ketoalcohols and α-diketones and that the reactions of these substances actually provide the main routes to the degradation of the carbon chain, including those associated with the formation of carboxylic acid anhydrides. [10–20]

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Received 5 April 1993
Uspekhi Khimii **63** (9) 793 – 809 (1994); translated by A K Grzybowski

The possibilities for the occurrence of reactions leading to the dissociation of the C – C bond in liquid-phase oxidation processes are discussed in the present review. An attempt is made to trace the influence of the structure of the substrate, temperature, and the medium on the probability of the occurrence of such reactions. The principal pathways leading to the formation of esters in autoxidation reactions are examined.

II. Dissociation of C – C bonds in the stages involving the formation and decomposition of hydrocarbon hydroperoxides

The oxidation reactions of hydrocarbons and their oxygen-containing derivatives in the absence of initiating additives are known to include [1,2,21,22] the chain initiation (1), propagation (2, 3), and termination (4) stages:

$$RH + O_2 \longrightarrow R^{\cdot} + HO_2^{\cdot}, \quad (1)$$

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}, \quad (2)$$

$$RO_2^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}, \quad (3)$$

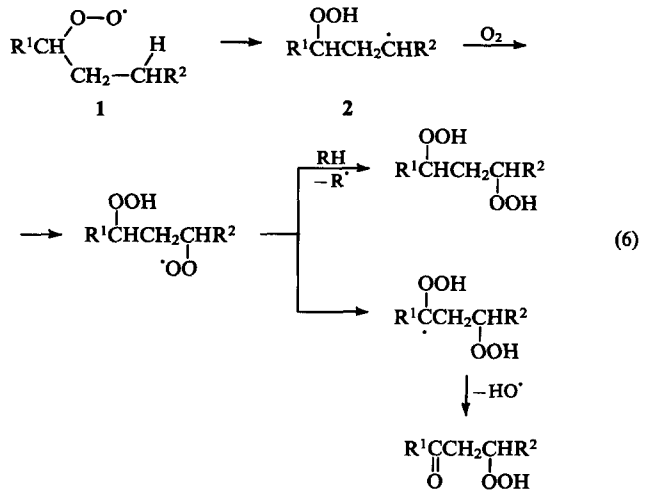
$$2\,RO_2^{\cdot} \longrightarrow \text{molecular products}. \quad (4)$$

They also involve the degenerate branching stage — unimolecular decomposition of hydroperoxides, i.e.

$$ROOH \longrightarrow RO^{\cdot} + HO^{\cdot}, \quad (5)$$

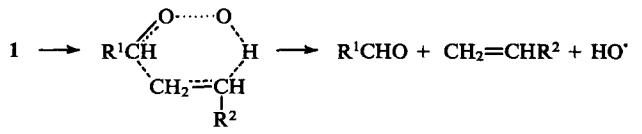
or decomposition with participation of the substrate and the oxidation products, which leads, incidentally, also to the radicals $RO^{\cdot}$. [21,22]

The peroxyl radicals $RO_2^{\cdot}$, formed by reaction (2), are capable of abstracting hydrogen from the substrate molecules [1,2,21–25] [reaction (3)] and of isomerising to type **2** radicals, which are subsequently converted into β- or γ-dihydroperoxides or hydroperoxyketones. [25]



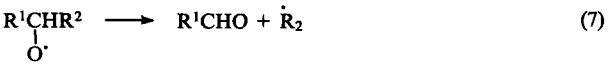
(6)

There are data indicating that the secondary peroxyl radicals can decompose with degradation of the carbon chain.[26]



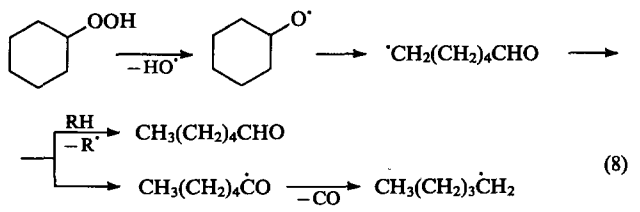
Incidentally, the probability of the degradation via this route is apparently low; it has been shown[26] that, in the sensitised oxidation of pentadecane at 130 °C, the rate of accumulation of unsaturated compounds is only 0.04% of the rate of the radical-chain oxidation.

Secondary monohydroperoxides decompose predominantly without the cleavage of the carbon skeleton, affording approximately equal amounts of alcohols and ketones. The reaction products were then found to include also those whose origin can be explained by the degradative decomposition of oxyl radicals.[27,28]



(7)

Thus the cyclohexyl hydroperoxide decomposition pathway leads to caproic aldehyde[27-29] and carbon monoxide.[29]



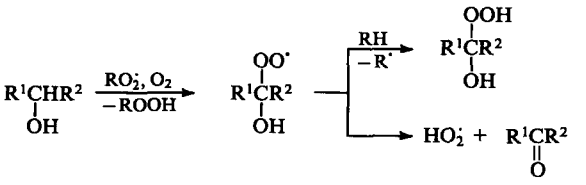
(8)

It has been shown[29] that 56% of the cyclohexyloxyl radicals generated from *tert*-butyl cyclohexyl peroxide (TBCHP) in cyclohexane are converted into cyclohexanol and only 8% decompose with decarbonylation. This factor as well as data[21] indicating a low contribution of the homolytic pathway to the overall decomposition of hydroperoxides indicate a low contribution of type (7) reactions to the formation of the hydrocarbon chain degradation products in the extensive oxidation process. Incidentally, their role may increase when the radical decomposition of hydroperoxides is stimulated, for example in the presence of cobalt salts,[21] and also with increase in temperature and in an inert solvent.[29]

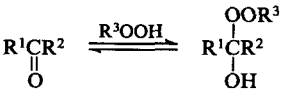
Reliable data concerning the mechanism of the reaction of the dihydroperoxides formed via reactions (6) have apparently not been obtained hitherto. It is postulated that they are less stable than the secondary monohydroperoxides.[30]

III. Degradation of the carbon chain in the oxidation of secondary alcohols and in the interaction of ketones with peroxide compounds

The secondary alcohols formed on decomposition of monohydroperoxides readily undergo the radical-chain oxidation at the α-C–H bonds, the reactivity of which is significantly higher than in hydrocarbons.[1,2,29] The reaction proceeds via the intermediate formation of the α-hydroxyperoxyl radical, which either abstracts hydrogen from a substrate molecule and is converted into a α-hydroxyhydroperoxide or decomposes into a ketone and a hydroperoxyl radical.[2,31]



Secondary α-hydroxyhydroperoxides can also be formed as a result of the acid-catalysed reversible nucleophilic addition of H_2O_2 to ketones; in the analogous addition of hydroperoxides or peracids, α-hydroxyperoxides or α-hydroxyperesters are formed respectively.[2]

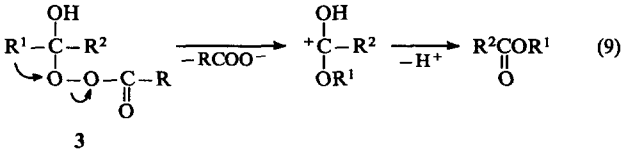


R^3 = H, Alk, Ac.

The mechanism of the subsequent reactions of the α-hydroxyperesters differs significantly from the mechanisms of the decomposition of α-hydroxyhydroperoxides and α-hydroxyperoxides.

The principal aspects of the oxidation of ketones by peracids (the Baeyer–Villiger reaction), leading to the rupture of the carbon chain, have been considered in reviews.[32-34] The reaction takes place under the conditions of general acid catalysis.[35-37] The peroxide 3 (the Criegee intermediate) formed in the first stage [reaction (9)] undergoes a rapid 1,2-rearrangement. In hydrocarbon solvents, the first stage of the process is rate-limiting.[35] In the oxidation of cyclic ketones by perbenzoic acid, the rate of reaction decreases in the sequence cyclohexanone > cyclopentanone > cycloheptanone, which is consistent with the decrease in the reactivity of the carbonyl groups of the above ketones in the same sequence.[36]

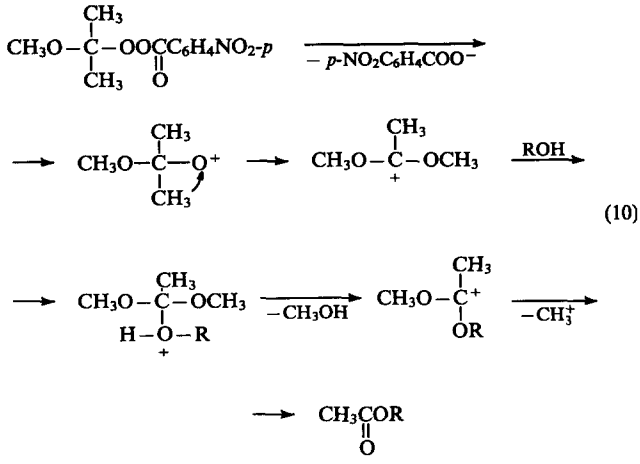
The rearrangement of the Criegee intermediate proceeds via an ionic mechanism[32,37,38] [reaction (9)], which is consistent with data indicating the transfer of the carbonyl oxygen of the ketone to the carbonyl group of the ester.[37]



(9)

3

The ionic nature of reaction (9) has been quite convincingly demonstrated by studying the decomposition of 2-methoxy- and 2-ethoxy-2-propyl *p*-nitroperbenzoates in methanol or ethanol.[38] Methyl acetate is formed in a ~100% yield in the decomposition of 2-methoxy-2-propyl *p*-nitroperbenzoate in methanol, whereas in the case where the reaction is carried out in ethanol up to 93% of ethyl acetate is obtained. Similarly, methyl acetate is formed preferentially from 2-ethoxy-2-propyl *p*-nitroperbenzoate in methanol. It has been suggested[38] that the carbonium ion formed in the stage involving the rearrangement of 2-alkoxy-2-propyl *p*-nitroperbenzoates interacts with the solvent and is converted into an orthoester and then into an ester.



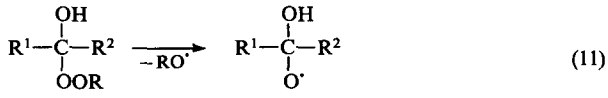
(10)

Robertson and Swelin [39] concluded that the homolytic decomposition of the Criegee intermediate can take place in parallel with the ionic decomposition, but this hypothesis apparently requires an additional experimental test.

The ability of the radicals to migrate in the Baeyer–Villiger reaction depends on their structure [40–43] and decreases in the sequence *tert*-butyl > cyclohexyl > isopropyl > benzyl > cyclopentyl > neopentyl > ethyl > methyl. [40]

In contrast to α-hydroxyperesters, α-hydroxyperoxides are in all probability incapable of undergoing heterolytic decomposition under the conditions of liquid-phase oxidation in nonpolar media because its products should be, as in reaction (9), esters or lactones which are not formed in appreciable amounts in this instance. [44,45] This factor is evidently associated with the fact that the HO and RO groups are poorer leaving groups compared with RCOO. [46] The heterolysis of the O–O bond in the α-hydroxyhydroperoxide or α-hydroxyperoxide is therefore possible only after the modification of the leaving groups, for example by protonation. Aliphatic carboxylic acids are probably incapable of participating in such a modification. However, it is known that esters or lactones are formed in the oxidation of ketones by hydrogen peroxide in the presence of inorganic acids [32] and also in the oxidation by a hydroperoxide + Lewis acid mixture. [47]

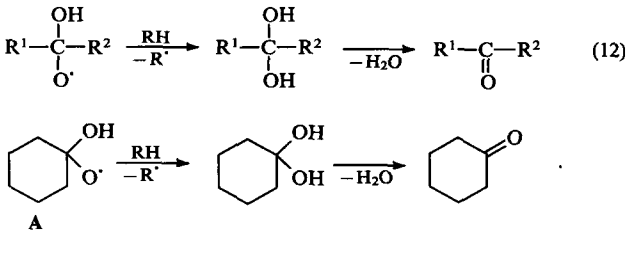
The principal pathway to the formation of products of the degradation of α-hydroxyhydroperoxides and α-hydroxyperoxides involves homolytic decomposition and leads initially to α-hydroxyoxyl radicals.



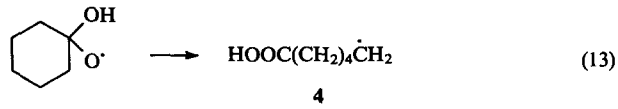
(11)

The rate constant for reaction (11) is known to be approximately an order of magnitude greater than the rate constant for the homolytic decomposition of hydrogen peroxide or hydroperoxides. [2,48–52]

The subsequent reactions of the α-hydroxyoxyl radicals depend on the reaction conditions. [29,53] It has been shown for the 1-hydroxycyclohexyloxyl radical **A** [29] that, in a reactive solvent at a temperature below 80 °C, it is converted preferentially into a ketone via the reaction

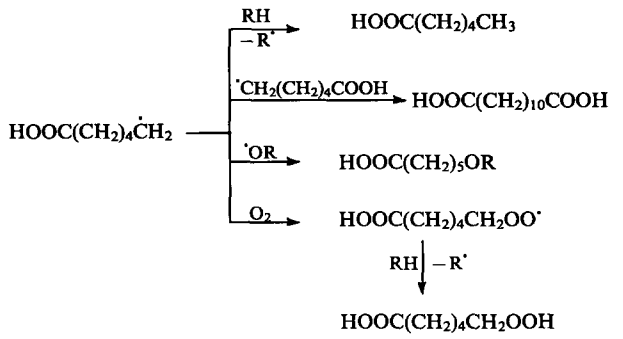


With increase in temperature [29] and in an inert solvent (for example, in benzene), [53] the isomerisation of the radical **A** to the ω-carboxyalkyl radical **4**, occurring with dissociation of the C–C bond, is more probable.



(13)

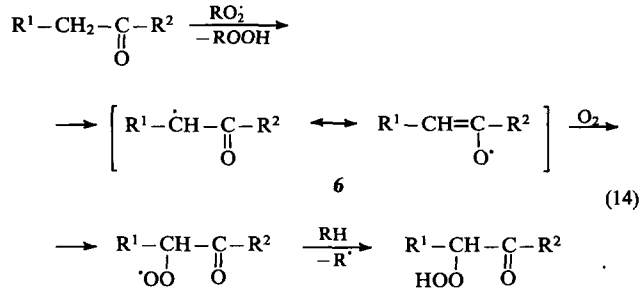
The radical **4** can combine with oxygen, being converted subsequently into the ω-carboxyhydroperoxide **5**, can dehydrogenate the substrate with formation of caproic acid, [54,55] can dimerise to decanedicarboxylic acid [54–56] (which, incidentally, is unlikely under oxidation conditions), and can recombine in a solvent cage with the oxyl radical [52,57] formed simultaneously with the radical **4** via a type (11) reaction.



The role of type (11) reactions should increase on stimulation of the radical decomposition of α-hydroxyperoxides, for example in the presence of variable-valence metal salts. It is significant that this route to oxidative degradation can lead to carboxylic acids, bypassing the ketone formation stage. [53]

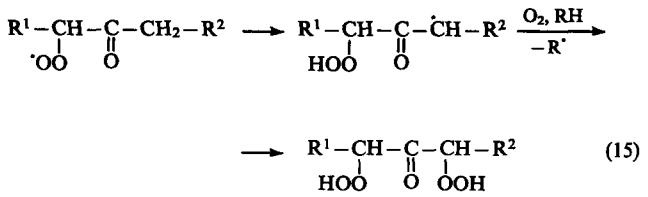
IV. Reactions of α-ketohydroperoxides in the radical-chain oxidation of ketones

Apart from the nonchain interactions with peroxide compounds, ketones are capable of undergoing oxidation via a free-radical mechanism preferentially at the α-C–H bonds. [1,2] The reactivity of the α-C–H bonds of ketones is 12–16 times higher than in hydrocarbons, [1,29,58–60] which is due to the resonance stabilisation of the intermediate radical **6** (stabilisation energy ~17 kJ mol^{-1}) [61]



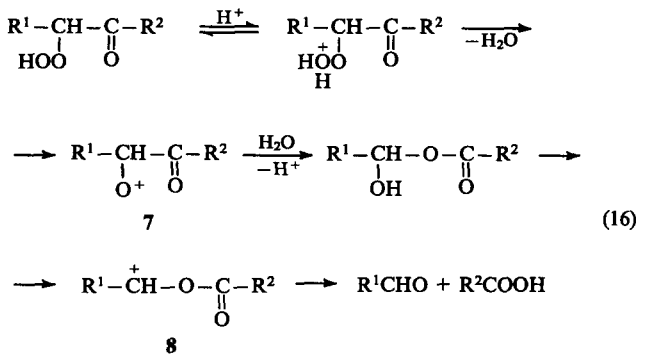
(14)

In the oxidation of long-chain aliphatic ketones, [62–65] significant deviations of the composition of the products from that postulated on the basis of the α-mechanism are observed, which is a consequence of the involvement in the oxidation process of C–H bonds remote from the carbon atom of the carbonyl group, and of the isomerisation of α-ketoperoxyl radicals [a type (6) reaction], [1,24] which can also proceed via the intermediate formation of a six-membered reaction ring incorporating the carbonyl group. [24,66–67]



(15)

It was assumed that the α-ketohydroxyperoxides formed via reaction (14) decompose preferentially with degradation of the carbon chain, which leads, in conformity with the familiar acid-catalytic Langenbeck–Pritzkov mechanism, to compounds with functional carbonyl and carboxy-groups.[2,68–76]



(16)

Results casting doubt on the universality of the Langenbeck–Pritzkov mechanism as the principal route to the degradation of the carbon chain in liquid-phase oxidation processes have been obtained comparatively recently. Pritzkov's data[69,70] indicating the preferential formation of 6-oxo-1-hexanoic acid in the decomposition of 2-hydroperoxycyclohexanone were not confirmed in the studies of Perkel' and Freidin[5] and Korsak et al.;[77] the yield of the acid in this reaction did not exceed 15%. The yield of 6-oxo-1-hexanoic acid did not increase also when the reaction was carried out in the presence of cobalt salts[5,77] and acetic acid.[77] These factors are associated with the fact that 2-hydroperoxycyclohexanone is largely converted into 2-hydroxycyclohexanone.[5]

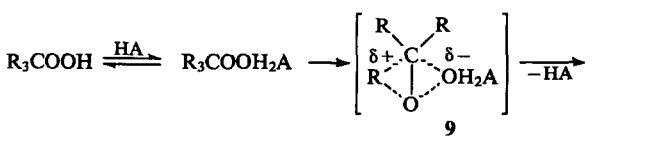
The yield of the ketoalcohol in the thermal decomposition (at 120 °C) of hydroperoxycyclohexanone, obtained by the oxidation of cyclohexanone, depends on the conversion of the ketone and averages 60%.[5] Together with 2-hydroxycyclohexanone (74%), another compound, also formed from the hydroperoxide without the degradation of the carbon chain, namely cyclohexane-1,2-dione (12%), was found among the products of the cobalt naphthenate-catalysed decomposition of 2-hydroperoxycyclohexanone at 80 °C.[5] The conversion of 2-hydroperoxycyclohexanone into 2-hydroxycyclohexanone not only on decomposition of the hydroperoxide under an inert atmosphere but also under oxidation conditions is indicated by the formation, in the initial stages of the noncatalysed and chromium and cobalt salt-catalysed oxidation of cyclohexanone, of a ketoalcohol as the main product.[11,78]

Decomposition without the destruction of C–C bonds is not characteristic solely of 2-hydroperoxycyclohexanone.[6–9] Thus the main products of the thermal reaction of 3-hydroperoxybutanone in oxidised butanone were found to be diacetyl and acetoin.[6] Although the yield of the products (benzoin and benzil) formed without the rupture of the carbon chain in the thermal decomposition of 2-hydroperoxy-1,2-diphenylethanone in oxidised 1,2-diphenylethanone was in fact lower than in the decomposition of 2-hydroperoxycyclohexanone or 3-hydroperoxybutanone, nevertheless it reached 38%–40% in this case also relative to the hydroperoxide which has reacted.[7–9]

It follows from the data presented above that the yield of the products associated with the dissociation of C–C bonds is significantly lower in the decomposition of aliphatic and alicyclic α-ketohydroperoxides than had been supposed earlier. On the other hand, in the decomposition of the hydroperoxides of aromatic ketones the degradation of the carbon chain may predominate.[45,67,79–82]

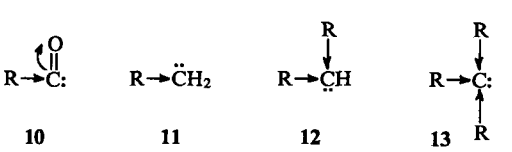
The mechanism of the degradation of the hydrocarbon chain in the decomposition of α-ketohydroperoxides is apparently obscure. Apart from the acid-catalytic mechanism mentioned above [Eqn (16)] postulated by Langenbeck and Pritzkov, homolytic[3,29,67,79–82] and dioxetane[83–85] mechanisms have been described.

The main evidence in support of the acid-catalytic mechanism is the similarity of the yields of compounds with carbonyl and carboxy-groups observed in the oxidation of a series of ketones and the acceleration of the decomposition of α-ketohydroperoxides in the presence of acids. However, the formation of the oxonium cation **7** has not yet been confirmed experimentally. Yablokov[86,87] demonstrated quite convincingly in relation to cumenyl hydroperoxide that hydrocarbon peroxides do not decompose via the acid-catalytic mechanism [Eqn (16)], since even in a strongly acid medium (HA) the rearrangement of cumenyl hydroperoxide proceeds most probably via the cyclic activated state **9** and not via the type **7** oxonium cation.[86,87]

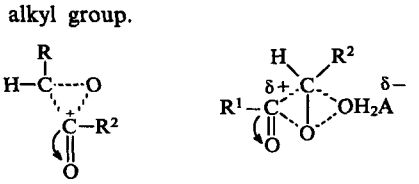


(17)

The mechanism (16) presupposes the preferential migration of the acyl carbanion. This hypothesis is controversial for the following reasons. In the mechanisms (16) and (17), the most nucleophilic group, which stabilises most effectively the transition state and the carbonium ion **8** formed after the migration, should migrate to the electron-deficient oxygen atom.[89] However, the acyl carbanion **10** is a weaker nucleophile than the primary, secondary, and especially tertiary hydrocarbon carbanions **11**–**13** respectively, and the probability of its migration should therefore be minimal from the standpoint of nucleophilicity.



The second cause is that the transition states formed on migration of the acyl group are less stable than those formed on migration of the hydrocarbon carbanion, because the sp^2-hybridised carbon atom of the acyl group, the valence bonds of which are disposed at an angle of 120°, produces a greater strain in the reaction ring than the sp^3-hybridised carbon atom in the alkyl group.



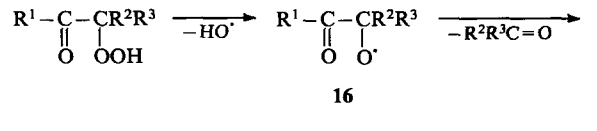
Furthermore, the transition state in the rearrangement of α-ketohydroperoxides is less stable than that obtained in the reaction of alkyl hydroperoxides because the oxygen atom increases the partial positive charge on the acyl carbon atom.

There are three possible types of the 1,2-rearrangement of the oxyl cation **7** which lead to the carbonium ions **8**, **14**, and **15** (Scheme 1).

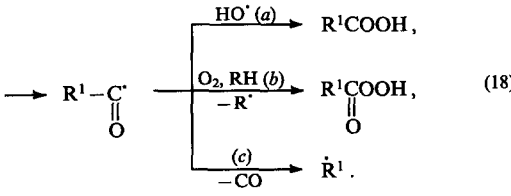
Examination of the resonant structures **8a, b, 14a–c**, and **15a–c** shows that they can be arranged in the following sequences in order of decreasing stability: **8a** > **14a** ~ **15a**, **14b** ~ **15b** > **8b**, and **14c** > **15c**. At first sight, it appears that the structure **8a** should be more stable than the structures **14a** and **15a**, but the cation **8** is apparently less stable than the cations **14** and **15** because it can have only two limiting structures and there is no structure which would make it possible to stabilise it in the way typical of the allyl carbonium ion, as happens in the cations **14** and **15**.

Thus the existing theoretical ideas [the mechanisms (16) and (17)] concerning the mode of the oxidative degradation reaction of hydrocarbons are in poor agreement with the preferred conversion of the α-ketohydroperoxide into a carboxylic acid and a carbonyl compound. Consequently they are inconsistent with the Langenbeck–Pritzkov mechanism.

The homolytic mechanism of the degradative reaction of α-ketohydroperoxides has been justified in a number of studies.[29,45,67,79–82] Thus the composition of the products of the oxidation of isopropyl methyl ketone indicates, according to Itoh et al.,[82] the decomposition of the primary reaction product (3-hydroperoxy-3-methylbutan-2-one) via the mechanism



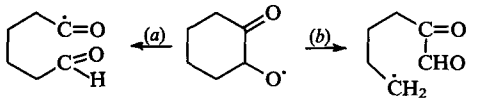
16



(18)

The reactions of tertiary α-ketohydroperoxides, studied by Ogata and Savaki,[79–81] proceed via a similar mechanism. α-Diketones are then formed in a small amount, probably via the elimination of hydrocarbon groups from the radical **16**. It has been shown that the photolysis of α-ketohydroperoxides in the presence of oxygen leads to a peracid (pathway *b*).[81] The rate of decomposition of α-acyloxyl radicals with destruction of a C–C bond is approximately two orders of magnitude higher than the rate of abstraction of a hydrogen atom from the solvent by this radical with formation of a α-ketoalcohol. This factor is apparently associated with the increased stability of the benzoyl radicals obtained on fragmentation. They are stabilised by the $+E$ effect of the aromatic ring.

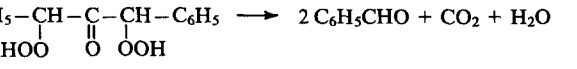
The study of the composition of the products of the oxidation of cyclohexanone led Pritzkov and Hahn[29] to the conclusion that two pathways are possible in the reaction of the 2-oxocyclohexyloxyl radical with degradation of the carbon chain.



(19)

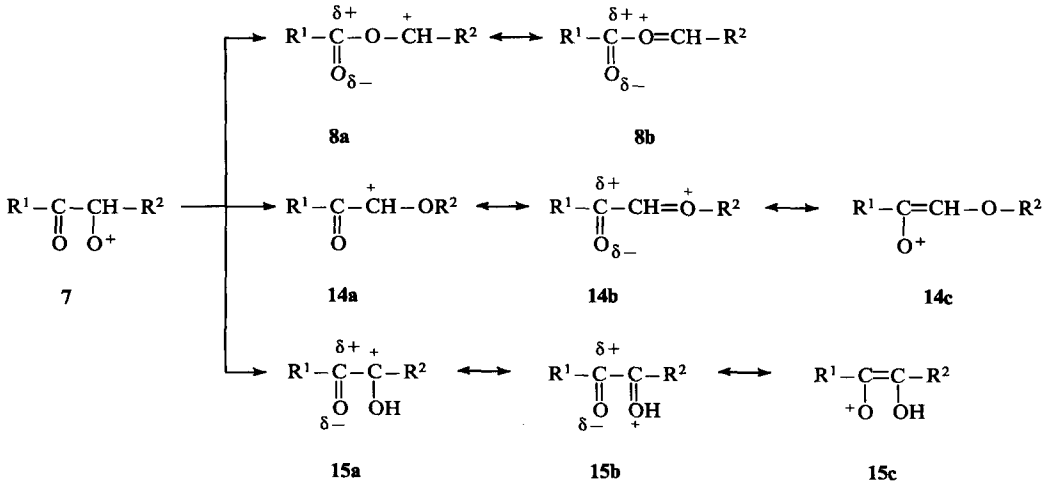
Pathway *a* explains the formation in the oxidation reaction of 6-oxo-1-hexanoic, monoperadipic, and adipic acids,[29] whilst pathway *b* accounts for the formation of glutaric acid, δ-valerolactone, and valeric acid.[29,90]

The homolytic decomposition of the secondary α-ketohydroperoxide (the β′-mechanism) has been observed in the oxidation of dibenzyl ketone.[45,67,91] This is indicated by the deviation of the composition of the product from that expected on the basis of the Langenbeck–Pritzkov mechanism (the α-mechanism). The phenylacetyl radical formed via reaction (18) is almost completely decarbonylated to the benzyl radical (pathway *c*); pathways *a* and *b* do not occur. Therefore, on the basis of the ratio of the initial rates of accumulation of phenylacetic acid and of benzyl hydroperoxide together with benzyl alcohol (the benzyl radical reaction products), it is possible to estimate the contribution of the homolytic mechanism to the overall decomposition of the α-ketohydroperoxide. In the noncatalysed oxidation of dibenzyl ketone at 100 °C, the contribution of the homolytic decomposition is not less than 50% according to Perkel' et al.[45] The composition of the products of the decomposition of dibenzyl ketone α-dihydroperoxide, formed in the oxidation of dibenzyl ketone [a type (15) reaction, β″-mechanism],[20,67] also deviates from that expected on the basis of the α-mechanism.

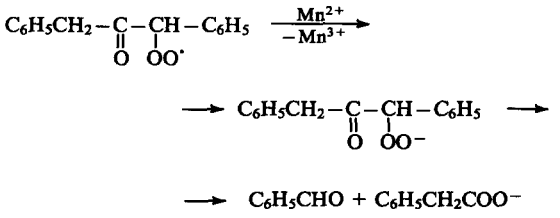


The relative contributions of the different routes to the oxidative degradation of ketones can be altered by introducing catalytic amounts of variable-valence metals.[20,67] According to the data of Perkel' and co-workers,[20,67] the relative contributions of the α-, β′-, and β″-mechanisms (expressed as percentages) in the oxidative degradation of dibenzyl ketone at 100 °C in chlorobenzene are 9 : 49 : 42 in the presence of cobalt(II) naphthenate as the catalyst, 26 : 27 : 47 in the presence of chromium(III) naphthenate, and 40 : 50 : 10 in the presence of manganese(II) naphthenate. Since the contribution of the α-mechanism in the noncatalysed oxidation

Scheme 1



under the same conditions is only 18%, the above data demonstrate that chromium and manganese naphthenates increase the selectivity of the dibenzyl ketone oxidation reaction as regards the formation of phenylacetic acid compared with the noncatalysed process.[20,67] In the case of chromium naphthenate, the increase in the contribution of the α-mechanism to the overall process is associated with the decrease in the proportion of the homolytic decomposition of the α-ketohydroperoxide, whilst in the case of manganese naphthenate it is associated with the suppression of reaction (15).[20,67]

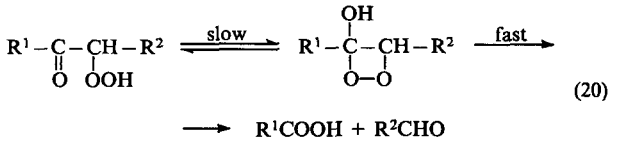


The yield of the products of the degradation of α-ketohydroperoxides in conformity with the Langenbeck–Pritzkov mechanism can also be explained satisfactorily by resorting to the dioxetane mechanism. The formation of 1-hydroxy-1,2-dioxetanes (Kohler peroxides[48]) was already postulated in early investigations of the oxidation of the enolic forms of ketones. However, after evidence had been obtained in support of the existence of ketone α-hydroperoxides predominantly in the acyclic keto-form, these ideas were abandoned for a long time.

The interest in the dioxetane mechanism was manifested anew in the 1970s–1980s when chemiluminescence characteristic of 1,2-dioxetanes (this class of organic compounds had been well investigated by that time) was observed[83–85] in the base-catalysed oxidation of ketones and in the decomposition of α-ketohydroperoxides in an alkaline medium.[92] These ideas have not gained wide currency as the explanation of the oxidation reaction in a neutral medium.

The dioxetane mechanism of the reaction of α-ketohydroperoxides does not conflict with the available experimental data on the decomposition of these hydroperoxides and it accounts for some of them more satisfactorily than the acid-catalytic and homolytic mechanisms.

The formation of 1-hydroxy-1,2-dioxetanes from α-ketohydroperoxides is energetically unfavourable owing to the ring strain arising under these conditions.[92] The equilibrium in the reversible first stage of the reaction should therefore be displaced towards the keto-form, which is additionally stabilised by an intramolecular hydrogen bond.[93] The sequence of the slow reversible and rapid irreversible reactions should be manifested kinetically as an irreversible first-order reaction,[94] which is in fact usually observed in the decomposition of α-ketohydroperoxides of different structure.[1,2]



(20)

Although the base catalysis in reactions involving nucleophilic addition to the carbonyl group is usually preferred,[46,89] the interaction of carbonyl compounds with hydroperoxides takes place readily also without a catalyst[95] and under the conditions of general acid catalysis by weak acids such as carboxylic acids.[20] Furthermore, the carbonyl group of α-ketohydroperoxides should be significantly activated by the $-I$ effect of the hydroperoxide group and by the intramolecular bond, as happens in the case of α-ketoalcohols.[13]

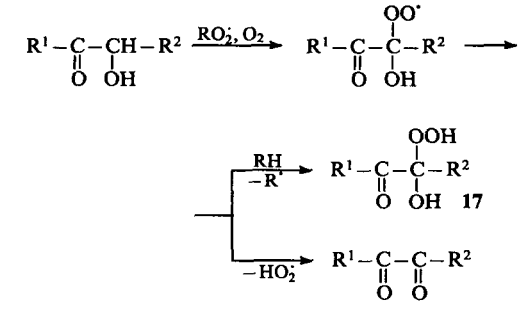
Evidently, when the dioxetane mechanism operates, a correlation should be observed between the reactivity of the carbonyl groups of the α-ketohydroperoxides and the stability of the latter. Indeed, tertiary α-ketohydroperoxides the carbonyl group of which is linked to an aromatic ring are the most stable (and therefore have been most thoroughly investigated).[3] Aromatic groups are known to reduce the reactivity of the carbonyl group in nucleophilic addition reactions because, when the ketone is converted into the adduct, the stabilisation via delocalisation is disturbed.[46] The presence of substituents at the α-carbon atom also lowers significantly the reactivity of the carbonyl groups owing to steric effects.[46] Evidently this is the reason why 2-hydroperoxy-2,4-dimethylpentanone is much more stable than the α-ketohydroperoxides of normal aliphatic ketones.[2]

In the decomposition of tertiary aromatic α-ketohydroperoxides in the presence of alkoxide ions[96] taken in large amounts, or in the presence of trifluoroacetic acid,[97] 1,2-dioxetanes are not formed. This finding may be associated with the low reactivity of such hydroperoxides in intramolecular nucleophilic addition reactions accompanied by the competing reaction of the carbonyl group with a stronger nucleophile—the alkoxide ion, and also with the suppression of reaction (20) as a consequence of the associative interactions of trifluoroacetic acid with the hydroperoxy- and carbonyl groups of the hydroperoxide. The possibilities of the dioxetane mechanism for the explanation of the characteristic features of the decomposition of α-ketohydroperoxides in autoxidation reactions are apparently still not exhausted.

V. Oxidative degradation of α-ketoalcohols

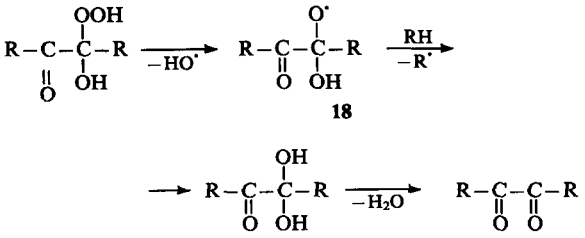
It was noted above that α-ketoalcohols are the principal products of the decomposition of α-ketohydroperoxides not involving the degradation of the carbon chain. The reactions of α-ketoalcohols in hydrocarbons undergoing oxidation involve both a radical-chain process[10,11,13–17,20,98–101] and their interactions with peroxide compounds.[13,17,20]

The mechanism of the radical-chain oxidation of α-ketoalcohols has been investigated in relation to 2-hydroxycyclohexanone,[10,11,13–17,20,98] 11-hydroxy-10-eicosanone,[20] and benzoin.[99–101] As secondary alcohols, α-ketoalcohols are oxidised via the reactive α-C–H bond, which is additionally activated by the carbonyl group. The intermediate α-hydroxy-α-oxoperoxyl radicals in the oxidation of ketoalcohols either abstract hydrogen from the substrate with formation of α-hydroperoxy-α-hydroxyketones **17** or decompose to the radical $HO_2^{\cdot}$ and a diketone.[13,16,20,99–101]



α-Hydroperoxy-α-hydroxyketones dissociate reversibly in their turn into hydrogen peroxide and an α-diketone[15,20,98–101] or undergo degradation via homolytic and nonhomolytic mechanisms[14,17,20,99] with formation of α-diketones, carboxylic acid anhydrides, or free carboxylic acids.

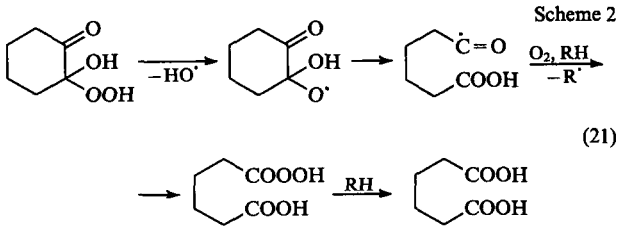
The homolytic decomposition of α-hydroperoxy-α-hydroxyketones proceeds via 1-hydroxy-2-oxoalkoxyl radicals **18**,[14,17,19] the principal pathway in the reaction of which does not involve the formation of a new carbonyl group, as in the case of α-hydroxyalkoxyl radicals (see Section III), but takes place with dissociation of the carbon chain.[14,17,20,99]



18

It has been shown in relation to 2-hydroperoxy-2-hydroxycyclohexanone that such degradation in the presence of oxygen leads to adipic acid via a monoperacid (Scheme 2).[14,17,20]

Scheme 2

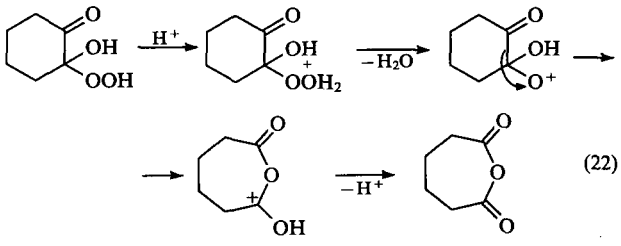


(21)

By comparing the potential yield of the peracid with the yield of adipic acid formed in the oxidation of 2-hydroxycyclohexanone at 50 °C, it was found that about 50% of the adipic acid is obtained via reaction (21).[17,20]

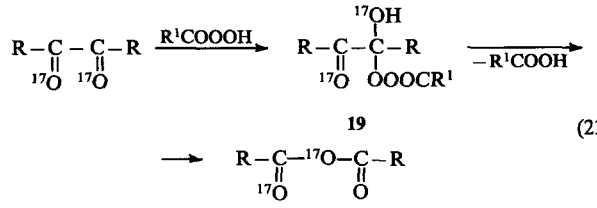
Mechanisms involving both the heterolytic[14,16] and pericyclic[17,20] rearrangements have been put forward to account for the formation of adipic anhydride from 2-hydroperoxy-2-hydroxycyclohexanone.

A heterolytic rearrangement of the Baeyer–Villiger type,



(22)

which presupposes the migration of the acyl carbon atom, is unlikely for the same reason as in the acid-catalytic decomposition of α-ketohydroperoxides (see Section IV). Furthermore, there are data[102] showing that, in the oxidation of ^{17}O- or ^{18}O-labelled benzil by *m*-chloroperbenzoic acid, which proceeds via the α-acylperoxy-α-hydroxyketone **19**, one of the carbonyl atoms of the α-diketone becomes the bridging atom of the anhydride, i.e.



19

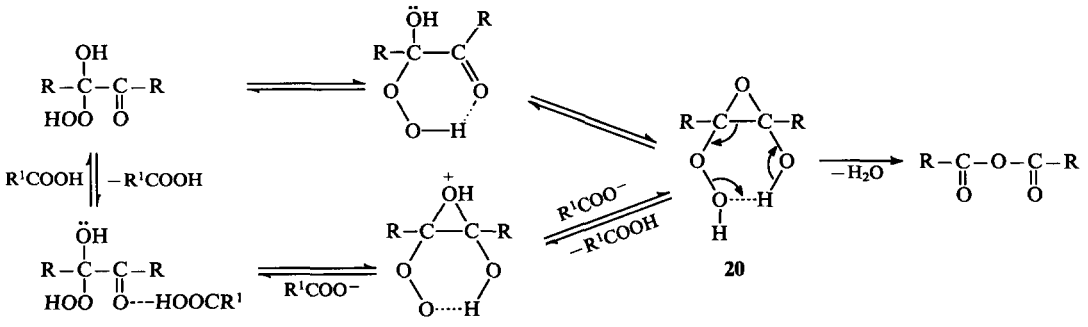
(23)

which cannot be explained by a Baeyer–Villiger rearrangement [reactions (10) and (22)].

The data on the distribution of the labelled oxygen agree well with the hypothesis that the peroxides **17** and **19** are converted into the anhydride via the slow reversible intramolecular nucleophilic addition of the hydroxy-group to the carbonyl group with subsequent rapid pericyclic rearrangement of the oxirane intermediate **20** (Scheme 3).[17,20]

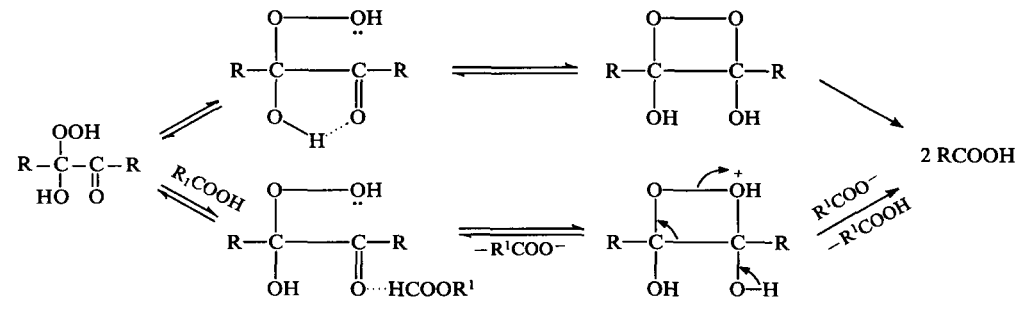
Reaction (24) takes place under the conditions of general acid catalysis; the effective rate constant for the first-order reaction involving the decomposition of 2-hydroperoxy-2-hydroxycyclohexanone to adipic anhydride in 2-hydroxycyclohexanone undergoing oxidation varies linearly with the concentration of carboxy-groups.[17,20] The mechanism (24) explains fairly satisfactorily the influence of the solvent and of the structure of the α-hydroperoxy-α-hydroxyketone on the yield of anhydrides. It has been established that adipic anhydride is hardly formed in the oxidation of 2-hydroxycyclohexanone in a solvent such as dimethylformamide,[17,20] which suppresses the nucleophilic addition of the hydroxy- and hydroperoxy-groups[17] to the carbonyl group, preventing thereby the formation of the intermediate **20**. One of the causes of the low yield of benzoic anhydride in the oxidation of benzoin may be the reduced reactivity of the carbonyl group of the α-hydroperoxy-α-hydroxyketone linked to the aromatic ring.[46]

Scheme 3



(24)

Scheme 4



(25)

It has been concluded [17,20] that the adipic acid formed in the oxidation of 2-hydroxycyclohexanone is produced mainly not via reaction (21) but as a result of the rearrangement of 2-hydroperoxy-2-hydroxycyclohexanone [reaction (25)] similar to that examined above the α-hydroperoxides [reaction (20)], i.e. the dioxetane mechanism operates (Scheme 4).

The carbonyl group of α-hydroperoxy-α-hydroxyketones is additionally activated (compared with α-ketohydroperoxides) by the $-I$ effect of the hydroxy-group. [17,20] As in reaction (24), carboxylic acids accelerate the conversion of the peroxide. [17,20]

Thus the possibility of the selective preparation of anhydrides from α-hydroperoxy-α-hydroxyketones is determined by the contribution of reactions (24) and (25) to the overall oxidation process. On the grounds that these reactions have stages with similar mechanisms and virtually identical activation energies, [16,17,20] it was concluded that the process selectivity is low. Data on the oxidation of 2-hydroxy-cyclohexanone in chlorobenzene at 95 °C [16] showed that the ratio of the yields of adipic anhydride and adipic acid reaches 2.2 under these condtions, i.e. reaction (24) predominates. An increase in the selectivity of the conversion of α-hydroperoxy-α-hydroxyketones into carboxylic acids can be achieved by stimulating their homolytic decomposition and(or) by suppressing reaction (24). Thus, in the oxidation of 2-hydroxycyclohexanone the significance of reaction (21) increases with increase in the initial concentration of the ketoalcohol, when the reaction is carried out in a reactive solvent, and when variable-valence metal salts are used as catalytic additives. [14-17,20]

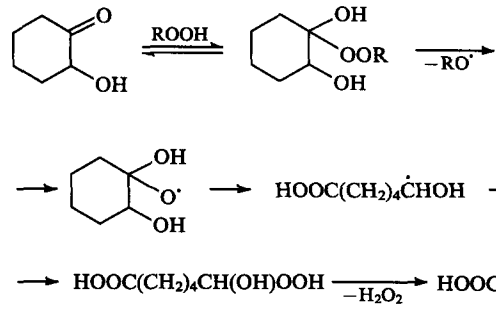
When the concentration of 2-hydroxycyclohexanone is varied in the range from 0.24 to 1.47 M (95 °C, chlorobenzene), the ratio of the initial rates of accumulation of adipic acid and its anhydride increases from 0.5 to 1.05. [16,20] In the oxidation of 2-hydroxycyclohexanone in ethylbenzene (95 °C, 1.2 M), this ratio reaches 1.8. [16] The increase in the yield of adipic acid in the cases indicated above is associated with the increase in the contribution of the homolytic decomposition of the α-hydroperoxy-α-hydroxyketone, with participation of compounds R^1H containing reactive C–H bonds, as a result of the occurrence of reaction (26). [16,20,56]

$$ROOH + R^1H \longrightarrow RO^{\cdot} + H_2O + \dot{R}^1 \qquad (26)$$

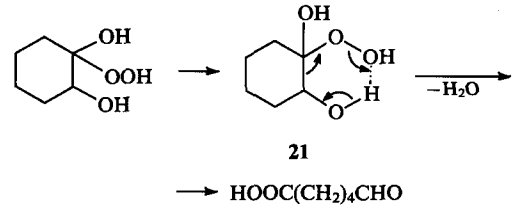
In the study of the influence of cobalt(II), nickel(II), chromium(III), and iron(III) naphthenates on the oxidation of 2-hydroxycyclohexanone, it was established that the yield of adipic acid in the presence of all the catalysts is higher than in the noncatalysed reaction, while the yield of adipic anhydride is correspondingly lower, especially in the presence of the cobalt salt. [11,20] The results of the decomposition of the peroxide compounds formed in the oxidation of 2-hydroxycyclohexanone under a nitrogen atmosphere showed that the mode of the decomposition and oxidation reactions is as a rule the same. [20] The decrease in the yield of the anhydride with simultaneous formation of the acid in the presence of variable-valence metals has been explained by the increasing role of a type (21) reaction. [20]

An increase in the relative yield of adipic acid has been observed also in the oxidation of 2-hydroxycyclohexanone in dimethylformamide, although the rate of its formation was lower than in the oxidation in chlorobenzene. [17,20] It has been suggested [17,20] that this phenomenon is associated with the suppression of reactions (24) and (25) in dimethylformamide as a consequence of the suppression of the intramolecular nucleophilic addition to the carbonyl group in this solvent. [17,20]

α-Ketoalcohols can not only participate in the radical-chain oxidation but can also interact with peroxide compounds. (The rate of decomposition of peroxide compounds in the presence of ketoalcohols is much higher than in the presence of monofunctional alcohols and ketones. [13,20]) Apart from reactions (26), such interaction can include the addition of the peroxide compounds to the carbonyl group of the α-ketoalcohol, [13,20] which has been observed, for example, in the cooxidation of 2-hydroxycyclohexanone together with ethyl methyl ketone [13] and cyclohexanol [17] and also in the oxidation of benzoin. [99] Thus, when 2-hydroxycyclohexanone is introduced into ethyl methyl ketone undergoing oxidation, ε-caprolactone, ε-hydroxycaproic acid, and 6-oxo-1-hexanoic acid are formed in a yield of about 40% relative to the ketoalcohol which has reacted. The reaction probably proceeds via the following mechanism: [13]



It has been suggested [17] that, in the cooxidation of 2-hydroxycyclohexanone together with cyclohexanol, 6-oxo-1-hexanoic acid is obtained both as a result of reaction (27) and as a result of the pericyclic rearrangement of 1-hydroperoxy-1,2-dihydroxycyclohexane **21**.



21

$\longrightarrow HOOC(CH_2)_4CHO$

The formation of benzaldehyde in the liquid-phase oxidation of benzoin is associated with the reaction of the latter with peroxide compounds. [99] This possibility is supported also by data for the oxidation of benzoin by *m*-chloroperbenzoic acid. [103]

VI. Oxidation of α-diketones by peroxide compounds

α-Diketones, which together with α-ketoalcohols are the main products of the reaction of α-ketohydroperoxides without the degradation of the carbon chain (see Section IV), are also capable of interacting with peroxide compounds in hydrocarbons undergoing oxidation.

There are few data on the radical-chain oxidation of α-diketones. The oxidation of diacetyl by oxygen at 80 °C has been investigated. [104] It is suggested that the reaction proceeds via the intermediate formation of acetic anhydride, which, however, was not identified. [104] The main product of the reaction is acetic acid.

In the oxidation of cyclohexane-1,2-dione by oxygen in solution in chlorobenzene, only tarry products were detected. [105] This finding is probably associated with the fact that cyclohexane-1,2-dione exists predominantly as the monoenol (2-hydroxycyclohex-2-en-1-one), [12] which can be readily oxidised at the carbon atom in the α-position relative to the double bond and evidently polymerises under the influence of free radicals. Since there are no data on the enolic form of cyclohexane-1,2-dione in the cyclohexane oxidation reaction, the selection of the latter as a model reaction appears controversial. There is no doubt that

problems concerning the radical-chain oxidation of α-diketones still await solution.

Problems associated with the reactions of α-diketones with peroxide compounds (H_2O_2, hydroperoxides, peracids), used for preparative purposes, have been investigated to a greater extent. A study has been made of the influence of equimolar amounts of added oxygen-containing compounds of different classes on the rate of the thermal decomposition of *tert*-butyl hydroperoxide (TBHP) in benzene at 160 °C under a N_2 atmosphere. The effective rate constants for the decomposition of THBP in the presence of various additives have the following values:[13,20]

Additive	$10^4 k_{eff}/s^{-1}$
Eicosane-10,11-dione	25.0
Cycloheptane-1,2-dione	11.0
2-Hydroxycyclohexanone	10.0
11-Hydroxyeicosan-10-one	5.0
2-Hydroxycyclohex-2-en-1-one	1.27
Cyclohexanone	0.20
Cyclohexanol	0.17
Nonan-5-ol	0.14
Nonadecan-10-one	0.13
Without additive	0.025

It is seen from the data presented that, in terms of their capacity to decompose hydroperoxides, α-diketones are more effective than not only monofunctional alcohols and ketones but also α-keto-alcohols.

The interaction of α-diketones with peroxide compounds in autoxidation reactions is not only an important route to the conversion of the latter but also serves as a pathway to the formation of degradation products, in particular carboxylic acid anhydrides. It was found that these reactions proceed at fairly high rates even in nonpolar solvents close to room temperature. The first stage of the interaction of hydroperoxides and peracids with α-diketones involves their reversible nucleophilic addition to one of the carbonyl groups of the α-diketone with formation of α-hydroperoxy-α-hydroxy-, α-alkylperoxy-α-hydroxy-, and α-acylperoxy-α-hydroxy-ketones.[12,18,19,32,102,106–110] The rate-limiting stage is the subsequent degradative composition of α-hydroperoxy-α-hydroxy- and α-alkylperoxy-α-hydroxy-ketones.[20,111]

The main products of the oxidation of hexadecane-8,9-dione by hydrogen peroxide are caprylic anhydride and caprylic acid.[18,20] Caprylic anhydride is formed via reaction (24), whilst the acid is formed via reactions (21) and (25).[20] In the interaction of hexadecane-8,9-dione with TBHP, *tert*-butyl caprylate was obtained in addition to caprylic anhydride and caprylic acid.[18,20] The yield of caprylic anhydride is in this case significantly higher than in the reaction with hydrogen peroxide, whilst caprylic acid is formed either in the homolytic decomposition of the peroxide [reaction (21)] or from caprylic anhydride simultaneously with *tert*-butyl percaprylate, and not via reaction (25).[18,20] The effective decomposition rate constants increase linearly under these conditions as the degradation products accumulate,[18] which is apparently associated with the catalytic effect of caprylic acid.

The high equilibrium constants in the interaction of hexadecane-8,9-dione with hydrogen peroxide and TBHP at 23 °C (41.5 and 49.0 litre mol^{-1}) are due to the stabilisation of the adducts by the formation of an intramolecular hydrogen bond.[20,112]

Di-*tert*-butyl peradipate was detected together with mono-*tert*-butyl peradipate among the products of the oxidation of cyclohexane-1,2-dione by TBHP.[12] The formation of the former has been explained by the interaction of the hydroperoxide with a polymeric form of adipic anhydride.[12]

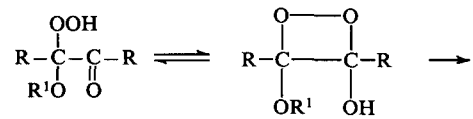
Acetic anhydride is formed selectively in the oxidation of diacetyl by TBHP in solution in acetic acid, while in the case where the reaction is carried out in *tert*-butyl alcohol the acid is formed predominantly.[112] Evidently acetic acid accelerates the conversion of the corresponding α-alkylperoxy-α-hydroxyketone via reaction (24), while *tert*-butyl alcohol has the opposite effect, suppressing this degradation pathway (as a result of the competing interactions of the OH group of the alcohol with the carbonyl group of the α-alkylperoxy-α-hydroxyketone); acetic acid is then formed homolytically via reaction (21).

In the interaction of diacetyl with 2-hydroperoxy-2-methyltetrahydrofuran or 2-hydroperoxytetrahydropyran in chlorobenzene, the homolytic decomposition of α-alkylperoxy-α-hydroxyketones predominates.[106] The reaction products are formed as a result of the recombination of the acyl radical of the α-diketone and oxyl or carbon-centred radicals of the hydroperoxide within a cage.[106] Thus the relative contributions of the different routes to the degradation of α-alkylperoxy-α-hydroxyketones are affected not only by the medium but also by the structure of the α-diketones and hydroperoxides.

In the oxidation of α-diketones by peracids, the rate-limiting stage is the acid-catalysed nucleophilic addition of the peracid to the carbonyl group of the α-diketone. The effective rate constants for the second-order reaction (given in brackets in litre $mol^{-1} s^{-1}$) involving the oxidation of α-diketones by perlauric acid at 23 °C diminish on passing from hexadecane-8,9-dione (0.37) to 1-phenylpropane-1,2-dione (0.036) and then to benzil (0.0071) as a consequence of the decrease in the reactivity of the carbonyl groups of the α-diketones under the influence of aromatic substituents.[20,111] Lauric acid increases the effective rate constant for the reaction of hexadecane-8,9-dione with perlauric acid almost by a factor of 100.[19,20,111] Consequently the importance of such reactions increases at advanced stages in the autoxidation reactions of hydrocarbons.

It was first established in Karrer's studies[32,113–117] that the main products of the oxidation of α-diketones by peracids are carboxylic acid anhydrides. It was postulated that such reactions proceed via a heterolytic rearrangement of α-acylperoxy-α-hydroxyketones [reaction (22)][32] or via oxirane intermediates.[20,102,111]

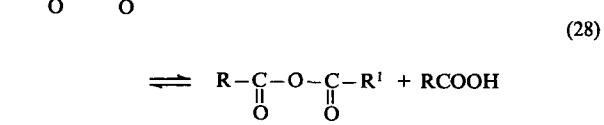
The data[102] indicating the preferential conversion of the α-acylperoxy-α-hydroxyketones into an anhydride [see reaction (23)] cannot be accounted for by resorting to heterolytic rearrangement, but the formation of the anhydride is described satisfactorily by Eqn (24), which involves the oxirane intermediates **20**. The important role of the OH group in the formation of the anhydride is indicated also by the fact that esters and not anhydrides are formed in the decomposition of α-alkoxy-α-hydroperoxyketones **22**.[118] The mechanism (24) does not operate in this case and the ester is formed via a reaction analogous to reaction (25).



22

$$\longrightarrow RCOOR^1 + RCOOH$$

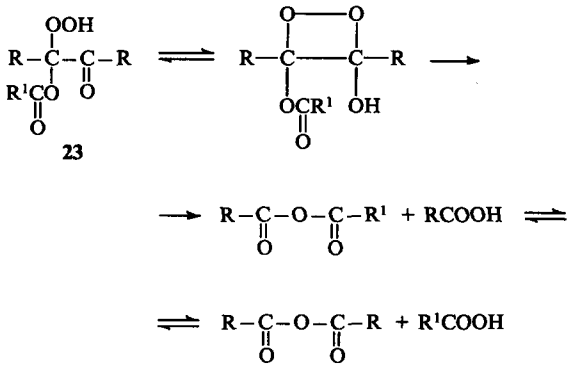
Together with the expected symmetric anhydride [reaction (24)], mixed anhydrides, including acylperacids, were also found in the reactions of hexadecane-8,9-dione and benzil with perlauric acid.[19,20,111] Their formation is associated with the transacylation of the symmetrical anhydride by reaction with lauric acid obtained by the reduction of the peracid.[19]



(28)

The occurrence of reaction (28) leads to a decrease in the selectivity of the overall reaction with respect to the target anhydride. This is probably why the yield of the expected anhydrides did not as a rule exceed 50% in the early studies.[32,113-117]

The formation of symmetrical anhydrides in the decomposition of α-acyloxy-α-hydroperoxyketones **23** is probably associated with transacylation.[119]



23

Thus not only the composition of the products of the reactions of α-hydroperoxy-α-hydroxy-,α-alkylperoxy-α-hydroxy-, and α-acylperoxy-α-hydroxy-ketones, formed in the radical-chain oxidation of α-ketoalcohols and in the oxidation of α-diketones by peroxide compounds, but also the composition of the related peroxides **22** and **23** can be explained on the basis of the mechanisms (21), (24), and (25).

The importance of different mechanisms of the oxidative degradation of the hydrocarbon chain, examined in Sections V and VI, for the hydrocarbon oxidation reactions is still to be assessed. However, there is no doubt that the reactions leading to carboxylic acid anhydrides occupy a special place among them. The formation of the anhydrides was detected not only in the oxidation of the α-ketoalcohols and α-diketones but also in the oxidation reactions of cyclohexane,[10] cyclohexanone,[11,78] ethyl methyl ketone,[120,121] dibenzyl ketone,[45,91] and benzyl phenyl ketone.[7-9,45] Being highly reactive in nucleophilic addition reactions, carboxylic acid anhydrides interact during the autoxidation processes with the water produced in the reaction, alcohols, hydroperoxides, and carboxylic acids[20] and this is why it is usually difficult to establish the amount in which they are actually formed in the reaction. According to the data of Bogomol'nyi and Freidin,[121] not less than 20% of acetic acid is obtained during the oxidation of ethyl methyl ketone as a result of the hydrolysis of acetic anhydride. The problems associated with the participation of the anhydrides in the formation of esters and other oxidation products will be examined in Sections VII and VIII.

VII. The formation of esters in autoxidation processes

Esters are side products of the reactions involving the autoxidation of hydrocarbons and their oxygen-containing derivatives to carboxylic acids.[1,2] To facilitate the consideration of the mechanisms of the formation of esters, the latter will be divided into three groups.

The first group includes the esters of primary (more rarely secondary) alcohols containing the same total number of carbon atoms as the compound oxidised (for example, ethyl acetate and ε-caprolactone obtained in the oxidation of butane and cyclohexane respectively, or isopropyl acetate, which is a side product in the oxidation of isopropyl methyl ketone,[82] etc.).

The esters of secondary alcohols (with the same number of carbon atoms as in the initial compound) and acids containing as a rule fewer carbon atoms than the alcohols (for example, *sec*-butyl acetate—the product of the oxidation of butane or *sec*-butyl alcohol,[1] the cyclohexyl esters of mono- and di-carboxylic acids—the products of the oxidation of cyclohexane, cyclohexanol,[19] etc.) should be included in the second group.

Finally, the third group incorporates γ- and δ-lactones containing the same or a smaller number of carbon atoms than the initial compound (for example, γ-methyl- and γ-ethyl-butyrolactones obtained by the oxidation of undecan-6-one[24,62] and γ-octyl-butyrolactone and δ-heptylvalerolactone formed in the oxidation of lauric acid[2]).

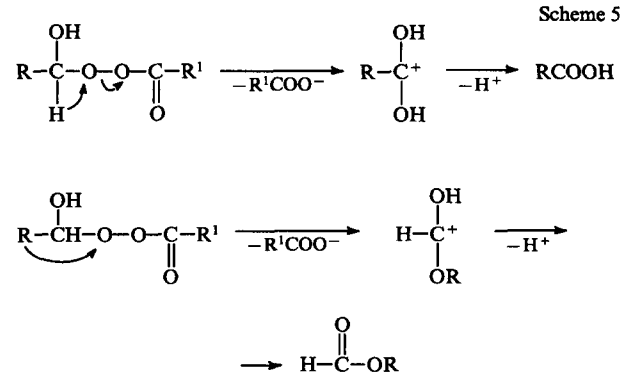
Since the esters of the first group can be formally obtained by inserting an oxygen atom into the C–C bond closest to the carbonyl group, it was postulated that they are formed in the oxidation of the corresponding ketones by peracids,[44,45,68,82,122] The peroxyl radical,[2] and hydroperoxides[123] and also as a result of the homolytic rearrangement of α-ketohydroperoxides.[1]

The fairly high rate of oxidation of ketones by peracids in nonpolar solvents and at moderate temperatures (see Section III) as well as the existence of theoretical preconditions for the formation of peracids in liquid-phase oxidation processes makes it possible to give preference to the Baeyer–Villiger reaction. An experimental test of the importance of this reaction was achieved comparatively recently for the oxidation reactions of cyclohexanone[44] and aromatic ketones.[45]

In a study of the influence of added diphenyl sulfide and diphenyl sulfone (reagents which reduce peracids) on the composition of the cyclohexanone oxidation products, it was established that the main side product of this reaction—ε-caprolactone—is formed predominantly by the interaction of the ketone with the peracid.[44] It was shown that the alternative mechanisms of the formation of ε-caprolactone, presupposing the oxidation of the ketone by peroxyl radicals or hydroperoxides, as well as the reactions of α-ketohydroperoxides unrelated to the appearance of peracids do not occur on an appreciable scale under the conditions of the process.[20,44] It was found that benzyl benzoate and benzyl phenylacetate are also formed as a result of the oxidation of benzyl phenyl ketone and dibenzyl ketone respectively by the peracid.[20,45]

The formation of formic acid esters in the oxidation of aldehydes is apparently also associated with the Baeyer–Villiger reaction. In this case, the 1,2-rearrangement of the α-hydroxyperester may entail the migration of both a hydride ion and of a hydrocarbon group, which lead respectively to an acid and an ester (Scheme 5).[2]

Scheme 5



The mechanism of the formation of the esters of secondary alcohols, which we assigned to the second group, remained obscure for a long time. The esterification of alcohols by carboxylic acids, postulated in a number of studies (see, for example, Emanuel' et al.[1]) as the main reaction, makes only a 10%–25% contribution to the observed rate of accumulation of esters even according to the most optimistic estimates.[126-129] This is evidence in support of the existence of a nonacid (unrelated to carboxylic acids) route to the formation of esters.

Such a route is apparently provided by the esterification of alcohols by anhydrides. This hypothesis has been tested[10] in relation to the oxidation of cyclohexane. A satisfactory agreement

was found between the rate of accumulation of monocyclohexyl adipate observed in the oxidation of cyclohexane at 150 °C, and the rate of formation of this ester calculated from kinetic data for the reaction of adipic anhydride with cyclohexanol.

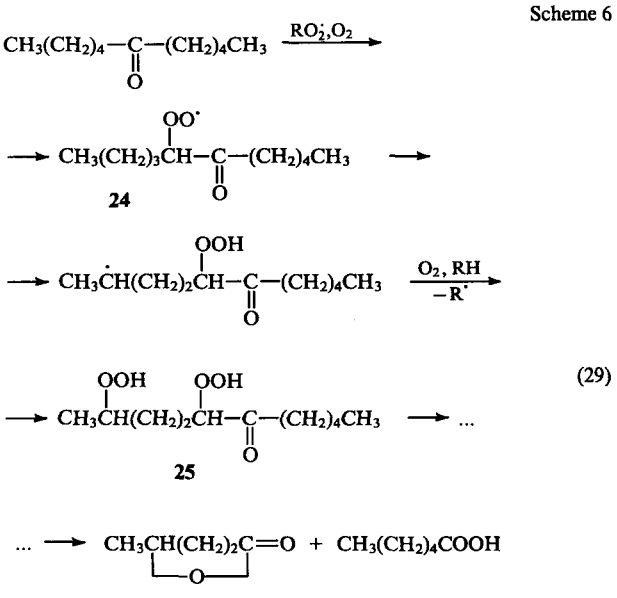
The transacylation of the anhydrides with the free acids results in the formation of mixed anhydrides [reaction (28)]. Their interaction with alcohols leads to esters incorporating the acyl residues from the carboxylic acid participating in the transacylation. It has been demonstrated for the oxidation reactions of cyclohexane, cyclohexanol, and cyclohexanone that cyclohexyl or 2-oxocyclohexyl esters of mono- and di-carboxylic acids are formed with participation of adipic anhydride.[19,20]

The pathways leading to the formation of γ- and δ-lactones in the oxidation of long-chain hydrocarbons are still insufficiently clear and are apparently associated with the multistage nature of such reactions and with the difficulty of identifying and determining the intermediates. According to the most widely held view, the lactones are formed from the corresponding hydroxyacids.[1,2]

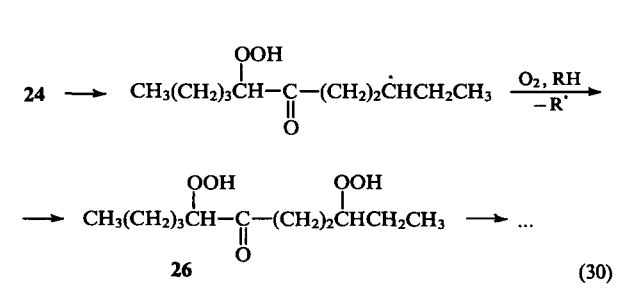
It has been suggested[24,62] that the γ-lactones arise in the stages which follow the formation of the ketones. The products of the oxidation of undecan-6-one were found to contain γ-methyl- and γ-ethyl-butyrolactones, the origin of which has been attributed[24,62] to the intramolecular isomerisation of the ketoperoxyl radical **24** and the subsequent reaction of the dihydroperoxides **25** and **26** (Scheme 6).

The intramolecular isomerisation of the radical **24** in conformity with reaction (29) is entirely realistic, while the isomerisation of this radical via reaction (30) is improbable.[1] If it is supposed that such isomerisation is possible, then it should lead to δ-lactones in the oxidation of long-chain ketones, for example tridecan-7-one (Scheme 7). However, only γ-lactones were found among the tridecan-7-one oxidation products.[24]

Scheme 6

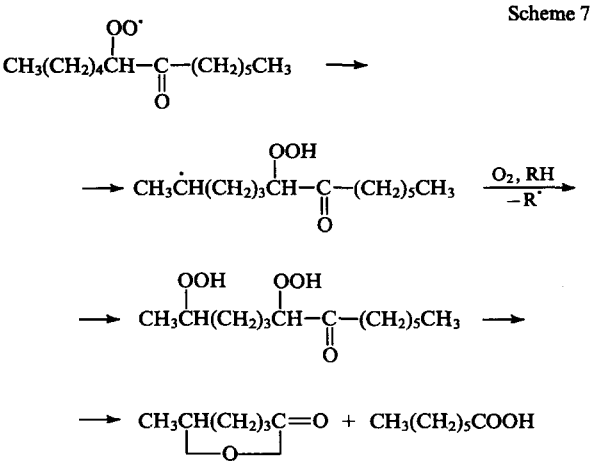


(29)



(30)

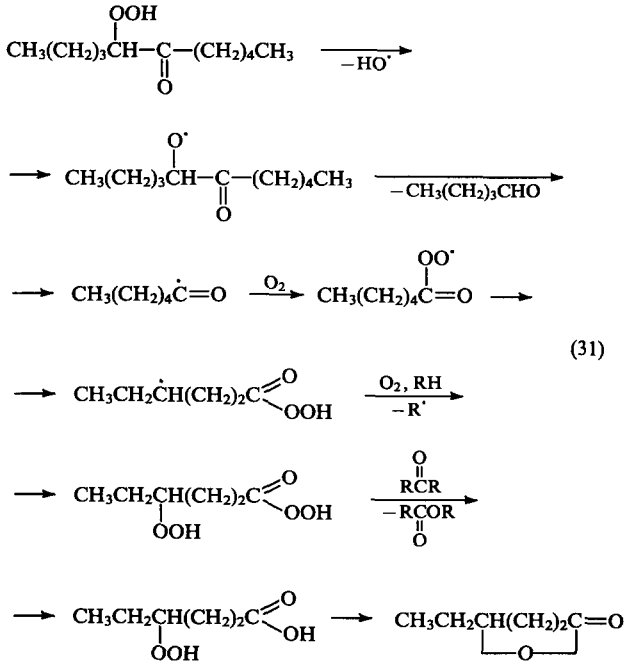
Scheme 7



The hypothesis has been put forward that the formation of γ-lactones is associated not only with the intramolecular isomerisation of the α-ketoperoxyl radical[24] but also with the oxidation of ketones at the γ- and δ-C–H bonds.[1,2] The possibility of these reaction pathways is not open to doubt, but, in order to achieve the formation of γ- and δ-lactones, it is essentially to subject γ- and δ-ketohydroperoxides to a secondary oxidation at the α- C–H bonds, which is unlikely to occur in the initial stage of the process. Incidentally, the intramolecular isomerisation of the δ-ketoperoxyl radical can also lead to a hydroperoxide of type **25**. The probability of the latter reaction should be fairly high in view of the enhanced reactivity of the α-C–H bonds of ketones.

The oxidation of carboxylic acids at the γ- and δ-C–H bonds can also lead to the formation of γ- and δ-lactones. The reactivities of these bonds are approximately the same[130] and hardly differ from the reactivities of the methylene C–H bonds of hydrocarbons. Indeed, the products of the oxidation of lauric acid were found to contain γ-octylbutyrolactone and δ-heptylvalerolactone.[2] However, the parallel formation of acids and γ-lactones in the oxidation of undecan-6-one and tridecan-7- one[24] as well as the absence of δ-lactones among the tridecan-7-one oxidation products mentioned above cannot be explained by the occurrence of this reaction.

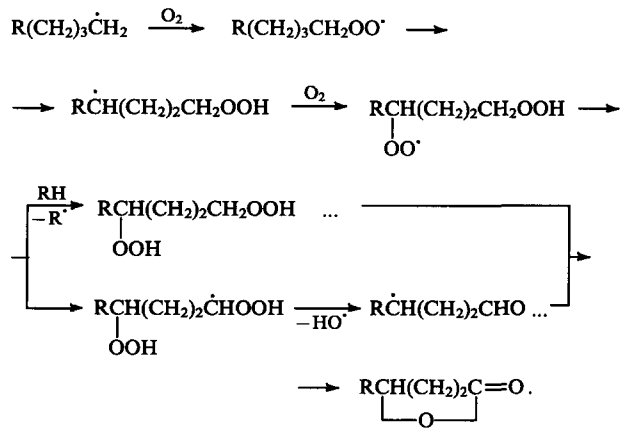
It appears that the formation of γ-ethylbutyrolactone in the oxidation of undecan-6-one can be associated with the



(31)

homolytic decomposition of α-ketohydroperoxide in the presence of oxygen and with subsequent intramolecular isomerisation of the hexanoylperoxyl radical. The fact that the possibility of the occurrence of such a reaction in the oxidation of aldehydes is usually disregarded[1,2] is apparently associated with its suppression in the presence of readily oxidisable substances such as aldehydes. Since acyl radicals may be formed in the oxidation of aldehydes, α-ketoalcohols, and α-diketones (see Sections V and VI), it follows that reaction (31) is an important source of the accumulation of γ-lactones in autoxidation processes.

One cannot rule out the possibility that γ-lactones may be obtained also from primary alkyl radicals via the mechanism



The homolytic decomposition of secondary hydroperoxides and α-hydroxyhydroperoxides [reactions (7) and (13)] as well as decarbonylation and decarboxylation reactions, which will be examined below, lead to primary alkyl radicals.

The experimental data presented show that the structure of the esters formed in the oxidation reactions depends on the method of their synthesis. The esters of primary alcohols (as well as lactones) with the same number of carbon atoms as in the initial hydrocarbon are obtained mainly in the oxidation of ketones by peracids, whereas the esters of secondary alcohols are produced as a result of the esterification of the alcohols by carboxylic acid anhydrides. The formation of γ-lactones is apparently associated with intramolecular isomerisation reactions of the peroxyl radicals.

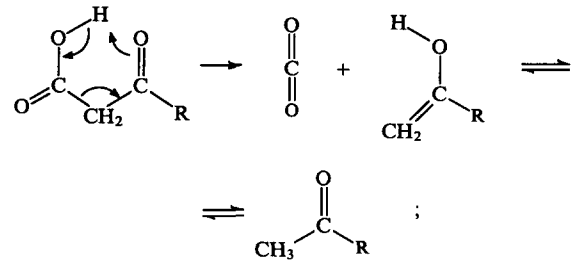
VIII. Certain aspects of the decarbonylation and decarboxylation reactions in the oxidation reactions of hydrocarbons and their oxygen-containing derivatives

The decarbonylation and decarboxylation reactions occur in virtually all the stages of the oxidative degradation of the carbon chain[1,2] and lower the selectivity of the autoxidation processes.

The available literature data permit the conclusion that the decarbonylation process is associated predominantly with the homolytic reactions of the oxidation products.

Under the autoxidation conditions, the acyl radicals formed in reactions (8) (18), and (21) either combine with oxygen [reaction (18, b)] or are decarbonylated [reaction (18, c)] when aldehydes are treated with peroxyl radicals. The relative contributions of these pathways depend both on temperature and on the structure of the hydrocarbon radical.[131,132] Since the activation energy for reaction (2) is close to zero[1] and that for reaction (18, c) involving aliphatic acyl radicals with a normal structure is of the order of 40–91 kJ mol^{-1},[131] one may conclude that the relative importance of the decarbonylation reactions should increase with increasing temperature. The rate constant for reaction (18, c) depends significantly on the stability of the hydrocarbon radicals formed on decarbonylation and increases in the sequence $C_6H_5^{\cdot} \ll CH_3^{\cdot} < CH_3CH_2CH_2^{\cdot} \ll C_6H_5CH_2^{\cdot}$ at 25 °C.[131] The decarbonylation reaction is favoured by the branching of the chain at the α-carbon atom.[132]

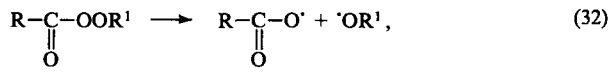
With the exception of the cleavage of β-oxoacids and β-dicarboxylic acids, which proceeds readily via a cyclic transition state,[46,89] i.e.



R = Alk, OH;

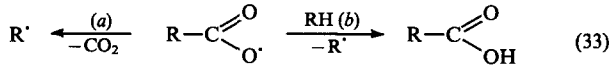
the decarboxylation reactions in autoxidation processes are mainly associated with the homolytic reactions of the oxidation products.[1,2] Certain features of the decarboxylation resulting from the reactions of peracids, peresters, and carboxylic acids are examined below.

The homolytic decomposition of peracids and peresters leads to acyloxyl radicals,[54] i.e.



(32)

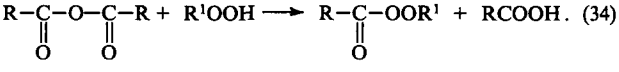
the subsequent reactions of which proceed via two competing pathways—decarboxylation (pathway *a*) and abstraction of hydrogen atoms from the substrate (pathway *b*).[2]



(33)

The relative contributions of these pathways depend on the structure of the radical R$^{\cdot}$, temperature, concentration and the reactivity of the C–H bond of the substrate. Reaction (33, a) is promoted by the stability of the hydrocarbon radical formed on decarboxylation,[21] by unreactive or weakly reactive solvents, and also by a high temperature.[133] Reactive substrates, for example, aldehydes, suppress the decarboxylation reaction.[133]

Since peracids are able to oxidise readily carbonyl compounds, being themselves converted into the acids, the role of reactions (32) and (33, a) in decarboxylation processes is probably small. The influence of the perester formation and decomposition reactions on the autoxidation processes is still being elucidated at the present time. Thus the presence in the reaction medium of carboxylic acid anhydrides makes the following reaction probable:



(34)

The study of the kinetics of the accumulation of products in the cyclohexane oxidation reactions and in the interaction of adipic anhydride with cyclohexanol and *tert*-butyl hydroperoxide led to the conclusion that the reaction with the hydroperoxide is an important route to the consumption of the anhydride in the oxidation of cyclohexane. The decomposition of the peresters formed in this process should lead to products with less than 6 carbon atoms.[20] On the hypothesis that peresters are formed in the autoxidation processes, it is possible to account also for the characteristic features of the decarboxylation reactions of carboxylic acids.

Numerous studies, examined in detail in a monograph,[2] have been devoted to the problem of the decarboxylation of carboxylic acids coupled with the oxidation reaction. It was postulated that, in the case of mono- and di-carboxylic acids with a normal structure, the acyloxyl radical, formed on treatment with peroxyl radicals, is decarboxylated.[2]

$$RCOOH + R^1OO^{\cdot} \xrightarrow[-R^1OOH]{} RCOO^{\cdot} \longrightarrow R^{\cdot} + CO_2 \qquad (35)$$

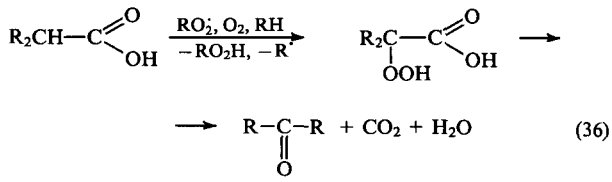
On the basis of the comparatively low values of the kinetic isotope effect (KIE) in the replacement of the carboxyl hydrogen by deuterium and the acceleration observed on the kinetic curves for the evolution of CO_2 in the cooxidation of carboxylic acids together with cumene or other reactive substrates, it was later concluded that the decarboxylation proceeds not only via reaction (35) but also via the intermediate formation of molecular products of the type of hydroperoxyacids and α- or β-oxoacids.[2]

Such a molecular product may be evidently also a perester. The perester can be obtained via reactions (28) and (34). The anhydrides required for these reactions are apparently formed as a result of the oxidative degradation of both the hydrocarbon group of the acid and of the substances employed as the cooxidants.

The hypothesis of the involvement of peresters in the decarboxylation of acids explains satisfactorily a series of experimentally observed facts. The low relative yields of $^{14}CO_2$ in the decarboxylation of acids labelled in the carboxy-group[1,2] may be associated with the possibility of attack by the hydroperoxide on both the initially formed anhydride and on the anhydride incorporating the acyl group of the labelled acid; in the latter case, a perester not containing ^{14}C may also be formed. As nonradioactive acids accumulate in the reaction medium, the probability of the formation of labelled peresters and hence of $^{14}CO_2$ should diminish, as in fact has been observed.[1,2] As was to be expected, the rate of formation of the nonradioactive CO_2 increased under these conditions.[2] The carbon-centred radical obtained by reaction (35) should be readily converted into a carboxylic acid under the oxidation conditions. The similarity of the rates of formation of valeric acid and CO_2 in the oxidation of caproic acid therefore becomes understandable.[2]

In the transacylation of anhydrides by carboxylic acids, the stage involving the attack on the carbon atom of the anhydride group by the oxygen atom of the acid hydroxyl should be rate-limiting.[44,89] The O–H bond is then ruptured in a nonrate-limiting stage and the replacement of the carboxyl hydrogen by deuterium should not therefore lead to an appreciable kinetic isotope effect, which in fact has been established in the case of acids with a normal structure.[2]

In order to explain the characteristic features of the decarboxylation of acids containing a tertiary hydrogen atom in the α-position, a mechanism involving the oxidation of the acids at the α-C–H bonds and unimolecular decomposition of α-hydroperoxyacids was proposed.[2]

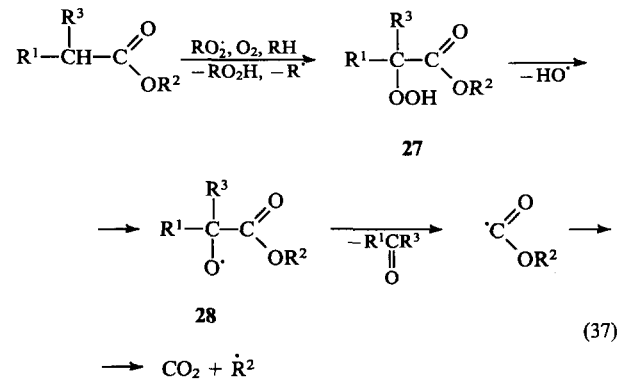


(36)

The proposed mechanism agrees well with the decrease in the rate of decarboxylation of isobutyric acid on replacement of a tertiary hydrogen atom by deuterium (KIE = 6.6).[2] Data indicating a low kinetic isotope effect (1.1) in the replacement of the carboxyl hydrogen by deuterium indicate in their turn an insignificant contribution of the mechanism (35) to the decarboxylation of this acid.[2]

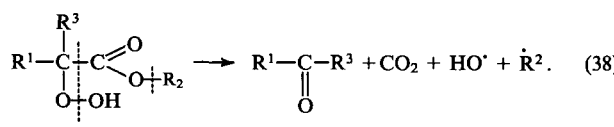
The decarboxylation of isobutyric and trimethylacetic acids apparently proceeds without the participation of peresters, since there are certain difficulties in the formation of anhydrides on oxidation of branched short-chain acids and in addition the probability of the attack on the acyl residues of such acids in the molecules of mixed anhydrides by hydroperoxides diminishes as a consequence of the steric factors mentioned above. The preferential formation of one of the two possible esters in the alcoholysis of mixed anhydrides has been noted.[45,134]

The formation of CO_2 is observed in the oxidative degradation of the ester group.[2,135–139] Carbon dioxide is obtained as a result of the homolytic decomposition of the primary molecular product of the oxidation of the ester at the acyl α-C–H bonds — the α-alkoxycarbonylhydroperoxide **27** [Eqn (37)].



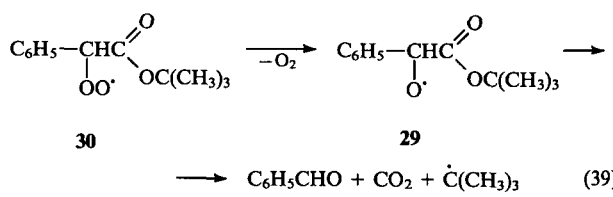
(37)

According to Denisov,[21] such a reaction may occur as a result of the concerted dissociation of several bonds in the hydroperoxide molecule [Eqn (38)]



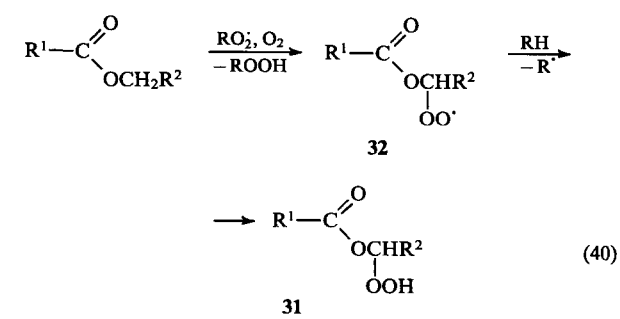
(38)

The high relative yield of benzaldehyde in the autoxidation of *tert*-butyl phenylacetate at 140 °C indicates the importance of the homolytic route to the decomposition of the intermediate *tert*-butyl α-hydroperoxyphenylacetate with the degradation of the carbon chain via reactions (37) and (38).[140] The formation of α-*tert*-butoxycarbonylbenzyloxyl radicals **29** and their degradation, leading to benzaldehyde, take place on recombination of the α-*tert*-butoxycarbonylbenzylperoxyl radicals **30** without chain termination.[140]



(39)

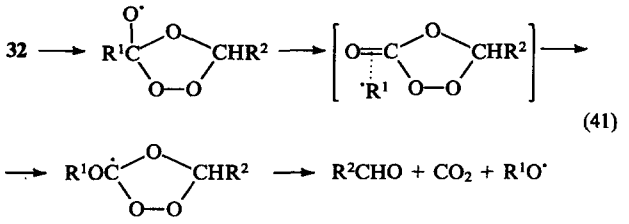
The α-acyloxyhydroperoxides **31**, obtained on oxidation of esters,[2,138,141–145] decompose preferentially via a nonhomolytic pathway.



(40)

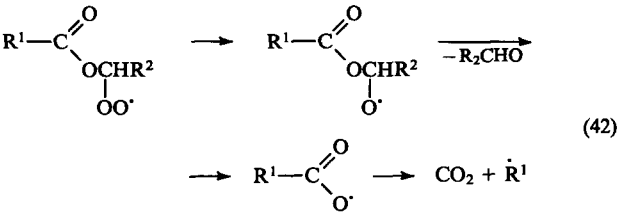
This was demonstrated in relation to the oxidation of the esters of polyhydric alcohols by Martem'yanov[138,142-145] and was later confirmed in the oxidation of benzyl benzoate[146] and benzyl phenylacetate.[147] The formation of CO_2 from compound **31** in these cases is unlikely.

It has been suggested[138] on the basis of kinetic data and the detection among the ester oxidation products of alcohols of the type R^1OH that CO_2 may be formed in these reactions as a result of the transformations of the α-acyloxyperoxyl radicals **32** [Eqn (41)].



(41)

The formation of CO_2 from compound **31** is also possible as a result of the recombination of the latter without chain termination[146] and the decomposition of the oxyl radicals **33** obtained under these conditions.



(42)

The importance of reactions (37)-(42) for hydrocarbon oxidation processes is still insufficiently clear. There is no doubt that it cannot be considerable because the data on the reactivity of the α-C-H bonds of aromatic esters in relation to the *tert*-butylperoxyl radical[148,149] and of pentaerythritol esters in the reaction with cumenylperoxyl radicals[138,150] indicate the deactivation of the C-H bonds in both α-positions of the ester molecule compared with the hydrocarbon molecule. The oxidation of esters at the C-H bonds remote from the functional group is therefore more probable.[151] In such cases, the degradation of the carbon chain evidently occurs in conformity with the rules examined above for hydrocarbons.

IX. Conclusion

The experimental data obtained during the last 15-20 years permit a fresh look at the importance of the known reaction pathways leading to the rupture of the carbon chain and make it possible to justify new routes to oxidative degradation in autoxidation processes.

When the homolytic decomposition of hydroperoxides is stimulated, for example on catalysis, the degradation of the carbon chain to an appreciable extent can apparently occur already in the stages involving the reaction of the α-hydroxyhydroperoxides formed on oxidation of alcoholic functional groups.

On the other hand, the principal pathways in the oxidative degradation reaction include a stage in which ketones react. The ketones are oxidised by peroxide compounds and are involved in the radical-chain process. The oxidation of ketones by hydroperoxides proceeds via a stage involving the formation of α-hydroxyperoxides, which decompose like α-hydroxy- α-hydroperoxides. When ketones are acted upon by peracids, the carbon chain is degraded with formation of esters. In the radical-chain oxidation of ketones at the most reactive α-C-H bonds, the products are α-ketohydroperoxides, which decompose both with and without the degradation of the carbon chain. The available data show that aliphatic and alicyclic α-ketohydroperoxides react preferentially without the rupture of the carbon chain, affording α-ketoalcohols and α-diketones. The fraction of α-ketohydroperoxides decomposing with destruction of the C-C bonds depends on the reaction conditions and the structure of the α-ketohydroperoxides.

α-Ketohydroperoxides decompose via homolytic and nonhomolytic mechanisms with formation of compounds having functional carbonyl and carboxy-groups. It is not clear what is the principal route to the nonhomolytic degradation of α-ketohydroperoxides. Some preference is given to the dioxetane mechanism, which explains more effectively than the familiar acid-catalytic Langenbeck-Pritzkov mechanism the available experimental data on the characteristic features of the reactions of α-ketohydroperoxides. In the oxidation of ketones at other C-H bonds and also in the intramolecular chain transfer and in the decarbonylation of acyl radicals during the homolytic reactions of α-ketohydroperoxides, the latter do not decompose via the α-mechanism.

In their turn, α-ketoalcohols and α-diketones interact with peroxide compounds in hydrocarbons undergoing oxidation and are themselves subjected to radical-chain oxidation. The influence of these bifunctional compounds on the rate of decomposition of hydroperoxides is much greater than that of monohydric alcohols and monoketones.

The radical-chain oxidation of α-ketoalcohols leads to α-hydroperoxy-α-hydroxyketones, which are also formed on reversible nucleophilic addition of hydrogen peroxide to α-diketones. The interaction of the latter with hydroperoxides and peracids affords α-alkylperoxy-α-hydroxy- and α-acylperoxy-α-hydroxy-ketones, which, like α-hydroperoxy-α-hydroxy-ketones, also decompose with degradation of the carbon chain even at room temperature. The principal products of the degradation of these compounds are carboxylic acid anhydrides and the free acids. The anhydrides are evidently formed as a result of the pericyclic rearrangement of the oxirane intermediate, while the acids are formed via the dioxetane mechanism or on homolytic decomposition of the above peroxides. The relative importance of each of these three main mechanisms for the reactions of α-hydroperoxy-α-hydroxyketones is determined by the relative yields of the corresponding anhydrides and acids and depends on the structure of the peroxide, the medium, and the additives stimulating the homolytic decomposition of the peroxide.

Being extremely reactive, carboxylic acid anhydrides interact during the autoxidation processes with the water produced by the reaction, alcohols, acids, hydroperoxides, and other nucleophiles, participating thereby in the formation of numerous degradation products. In particular, not less than 20% of acetic acid is obtained in the oxidation of ethyl methyl ketone via acetic anhydride, while the cyclohexyl esters of mono- and di-carboxylic acids are formed in the oxidation of cyclohexane predominantly with participation of adipic anhydride. The influence of the homolytic decomposition reactions of the peresters, formed on esterification of hydroperoxides by acid anhydrides, on the rate of initiation and decarboxylation in the autoxidation processes is still to be estimated. However, it is believed that it may be extremely significant.

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