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The Mechanisms of the Rearrangements of Peroxides

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The results of studies on the mechanisms of the rearrangements of organic and organoelemental peroxides are surveyed and the similarity of the mechanisms regardless of the structure of the peroxides is emphasised. The rearrangements of peroxides are regarded as intramolecular processes involving a concerted redistribution of bonds in a polar or radical-ion activated complex.
The bibliography includes 151 references.

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I. INTRODUCTION

The rearrangements of organic and organoelemental peroxides involve a change in the structure of the initial molecule to that of an isomeric compound without the peroxy-group. The peroxides undergoing the rearrangement do not induce the polymerisation of unsaturated compounds and are unaffected by inhibitors and initiators of radical reactions, but are extremely sensitive to the action of protic and Lewis acids. The rearrangement of organic peroxides was observed by Wieland and Maier[1] as early as the 1930's. The oxidation of aldehydes and ketones by hydrogen peroxide or peracids (the Baeyer–Villiger reaction) is also classified as a process involving an intramolecular rearrangement of intermediate peroxyesters[2]. In essence, it was not until the beginning of the 1950's that attention was drawn to reactions of this type; at that time the first factory in the work manufacturing phenol by the cumene method, based on the acid-catalysed rearrangement of peroxides, was set up in the USSR.[3,4] The possibility, in principle, of the catalytic rearrangement of cumenyl hydroperoxide was also demonstrated by Hock and Lang[5].

Since the determination of the principal products of the thermal decomposition of diacyl peroxides by Wieland and Razuvaev[6] and the introduction of Waters' concept of the homolysis of the peroxy-bond[7], a considerable time elapsed before practical applications of the reactions of peroxides were discovered. The urgent need for polymeric materials brought peroxides to the forefront as effective initiators of radical polymerisation and vulcanisation processes[8,9]. As knowledge of the reactions of peroxides deepened, investigators observed with increasing frequency simultaneous non-radical reactions.

The rearrangements of peroxides are encountered much more frequently than might have been supposed at the time when the chemistry of peroxides was established. They have been observed for all classes of peroxy-compounds (hydroperoxides, diacyl peroxides, peroxyesters, and organoelemental peroxides), in certain cases as the only possible reaction pathway.

There is not yet a unanimous view concerning the mechanism of the rearrangement. In some cases the rearrangement is regarded as a heterocytic process and in others as a homolytic process. The asymmetry of peroxyester and hydroperoxide molecules suggests the polarisation of the O–O bond already in the initial state. Even when the initial state is only weakly polar, for example, in symmetrical diacyl and silyl peroxides, the polarisation of the activated state has been postulated. The significant influence of the polar effects of substituents and the medium on the rate of reaction as well as the non-radical nature of the reaction products were regarded as the principal features of a heterolytic process[10]. However, an increasing amount of experimental data indicating that the above features are characteristic also of radical reactions has appeared. The radical formation reactions undergone by certain t-butylperoxesters constitute a homolytic fragmentation of a polar activated state[11].

The study of homolytic and heterolytic reactions led to the observation of an increasing number of facts which make it possible to treat these processes as inter-related. It is not fortuitous that evidence has been adduced in a number of studies for a radical-ion mechanism of the rearrangement of peroxides[12].

The aim of the present review was to analyse the mechanisms of the rearrangements of peroxides known at the present time and to determine how far they are consistent with the modern ideas of theoretical and experimental chemistry.

II. ACID-CATALYSED REARRANGEMENT OF HYDROPEROXIDES

The rearrangements of hydroperoxides of different structures involve their sensitivity to the action of electrophiles, which is common to all of them. Here the hydroperoxide behaves as a base in relation to protic or aprotic acids. The most effective electrophiles exhibiting catalytic activity are protic acids[13–15]. Acid anhydrides and chlorides as well as Lewis acids cannot be regarded as true catalysts of the rearrangement, because in the course of the reaction they interact irreversibly with the hydroperoxide[14].

The acid-catalysed rearrangement of the hydroperoxide takes place readily in polar and non-polar solvents. Depending on the direction of attack by the electrophile (HA), there is a possibility of either a rearrangement, if the oxygen atom O_β is attacked,

$$(R_f)_3 - C - O_\alpha - O_\beta - H,$$

or of a transformation of the hydroperoxide molecule into a carbinol and hydrogen peroxide if the oxygen atom O_α is attacked. The latter reaction occurs with triphenylmethyl hydroperoxide and its derivatives in water-containing media[16,17]: it is not characteristic of cumenyl hydroperoxide[16,17].

On the basis of general considerations concerning acid–base reactions, in early studies of catalytic reactions of hydroperoxides it was assumed[18,19] that the interaction of alkyl hydroperoxide with a strong acid leads to the formation of a peroxyester in which the O–O bond is ionic. The process was represented by two consecutive elementary reactions:

$$PhMe_2COOH + H_2SO_4 \rightarrow PhMe_2\overset{+}{C}O\overline{O}SO_2H + H_2O\ , \quad (1)$$

$$PhOH + Me_2CO + H_2SO_4 \xleftarrow{H_2O} (PhO)\,Me_2COSO_2H\ . \quad (2)$$

However, the attempts to demonstrate the existence of the cation $\geq C-O^{(+)}$ were unsuccessful. Even under the influence of superacids of the type FSO_3H/SbF_5, only the formation of alkoxycarbonium ions was detected (by NMR).[20]

The following objections were raised against the above mechanism[21]. First, it was shown that the peroxyesters of strong acids decompose via the reactions

$$PhMe_2COOSO_2R \rightarrow (PhO)\,Me_2COSO_2R\ , \quad (3)$$

$$(PhO)\,Me_2COSO_2R \rightarrow PhOC(Me)=CH_2 + RSO_3H \quad (4)$$

and cannot be intermediates in reactions (1) and (2). Secondly, when reactions (1) and (2) take place, the phenol and the ketone should contain the ^{18}O isotope on decomposition of the hydroperoxide in the presence of $H_2S^{18}O_4$ and $H_2{}^{18}O$.[22] Isotopic studies showed that the phenol did not contain an excess of ^{18}O compared with its natural abundance. In the ketone ^{18}O was detected in amounts corresponding to direct isotope exchange between $H_2{}^{18}O$ and the ketone[22]. The following mechanism is most plausible[21]:

$$(R_i)_3COOH + HA \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (R_i)_3COOH_2A\ ; \quad (5)$$

$$(R_i)_3COOH_2A \xrightarrow{k_2} \left[\begin{array}{c} R_i \quad R_i \\ \diagdown\ \ \diagup \\ C \\ R_i\ \delta+ \quad \delta-\ OH_2A \\ \diagdown\ \ \diagup \\ O \end{array}\right]^{\#} \rightarrow R_iO(R_i)_2COH + HA\ ; \quad (6)$$

(I)

$$R_iO(R_i)_2COH \xrightarrow{k_3} R_iOH + (R_i)_2C{=}O\ . \quad (7)$$

The protonation of the hydroperoxide is a rapid reversible reaction [reaction (5)]. In the rate-limiting stage [reaction (6)] the electron density is redistributed and the internal nucleophile migrates to one of the peroxide oxygens.

The linear dependence of the logarithm of the rate constant for the rearrangement of the hydroperoxide on the acidity function[23,24] as well as the positive kinetic isotope effect[25] support a rapid reversible interaction of hydroperoxides with the acid, leading to the formation of a hydroperoxide–acid complex. Simple calculations[26] lead to an expression for the experimental rate constant k for the rearrangement:

$$k = \frac{k_1}{k_{-1}} k_2 [HA]_0, \quad (8)$$

where $[HA]_0$ is the initial concentration of the acid.

Kinetic measurements[27–30] have shown that there is a linear relation between the apparent rate constant and the initial acid concentration. The order of the reaction with respect to the acid can be greater than unity if the acid is associated[31]. The experimental rate constants are effective quantities [see Eqn.(8)]. It is therefore difficult to expect the activation parameters to reflect fully the nature of the rate-determining stage of the process. Nevertheless one should turn attention to the fact that the pre-exponential factors correspond to a negative entropy of activation[26,32]. This agrees to some extent with the claim[26] that the rate-determining stage in the rearrangement of hydroperoxides involves a rigid cyclic complex.

Kinetic measurements have made it possible to elucidate a number of significant factors: firstly, the sequence in which the capacity for migration of the groups R_i varies has been established and, secondly, the nature of the interaction of the migrating group with the peroxide oxygen has been determined.

The aryl group in arylalkyl hydroperoxides is known to migrate in preference to the methyl group[23]. In substituted cumenyl hydroperoxides $Y_iC_6H_4C(Me)_2OOH$ the capacity of aryl groups for migration increases with enhancement of the electron-donating properties of the substituent Y.[23,26] The observed dependence of the logarithm of the reaction rate constant on the substituent constant σ^+ confirms the occurrence of a steric interaction between the migrating aryl group and the α-peroxide oxygen. The heterolysis of the peroxide linkage is accompanied by the simultaneous weakening of the Ar–C bond. This results in a transition from the sp^3-hybridisation of the tertiary carbon atom to the sp^2-hybridisation, which leads to an alteration of the valence angles in the activated state. The presence in the hydroperoxide molecule of a group acting as an internal nucleophile whose capacity for migration is comparable to that of the phenyl group, is the main condition for a high rate of the rearrangement.

In the acid-catalysed rearrangement of 2,2,4-trimethyl-2-pentyl hydroperoxide the neopentyl group migrates[33]:

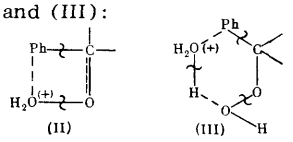
$$Me_3C{-}CH_2{-}CMe_2OOH \xrightarrow{HA} Me_3C{-}CH_2OH + Me_2CO\ . \quad (9)$$

9-Decalinyl hydroperoxide[34,35] rearranges with insertion of one of the peroxide oxygen atoms in the ring. A rearrangement with cleavage or expansion of the ring is characteristic of hydroperoxides derived from polynuclear hydrocarbons which have been partly or completely hydrogenated, as well 9-decalinyl hydroperoxide[36].

Competing reactions involving the migration of phenyl and cycloalkyl groups have been noted[37]. According to the proposed mechanism [reactions (5)–(7)], the rearrangement can be accounted for by the reaction of the hydroperoxide in a polar activated complex. Acid-catalysed rearrangements of tertiary hydroperoxides containing two or three hydroperoxy-groups are also known[38].

In tertiary arylalkyl hydroperoxides the methyl group cannot compete with the aryl group in the rearrangement. The consecutive replacement of the methyl group in cumenyl hydroperoxide by the ethyl, isopropyl, or t-butyl groups showed that the ethyl group, like the methyl group, does not migrate. The isopropyl group competes with the phenyl group as regards migration, while the t-butyl group has a much higher capacity for migration than the phenyl group[30].

In discussing the structure of the activated complex [structure (I), reaction (6)], mention should be made of a study[39] in which the mechanisms of molecular and acid-base catalytic reactions were considered. The authors[39] suggested that the rearrangement of the hydroperoxide can take place in complexes (II) and (III):

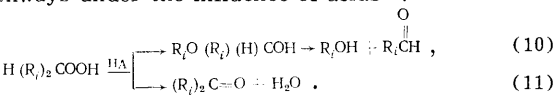


(II) (III)

The formation of the above complexes is inconsistent with experimental data. According to reactions (5)–(7), the hydroperoxide rearranges in the rate-limiting stage to a hemiketal [reaction (6)]. Such hemiketals are not always stable, but in some cases it has been possible to isolate them[40]. Complex (II) is a closed structure in which the protonated hydroperoxide molecule is converted into a phenol and a ketone, by-passing the stage involving the formation of a hemiketal.

There is a well-founded objection also against the transformation of the hydroperoxide in complex (III). The structure of the complex presupposes the involvement of the H_3O^+ ion in the reaction. According to the ring structure, the reaction in $H_2{}^{18}O$ could lead to the formation of [^{18}O] phenol, while studies have shown[21,22] that the phenol does not contain an excess of ^{18}O.

Primary and secondary hydroperoxides decompose via two parallel pathways under the influence of acids[29]:

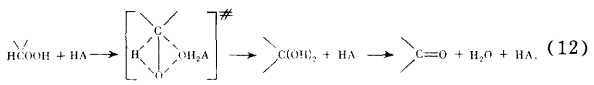


$$H(R_i)_2COOH \xrightarrow{HA} R_iO(R_i)(H)CO + R_iOH \rightarrow R_iCH \quad (10)$$

$$(R_i)_2C{=}O + H_2O \quad (11)$$

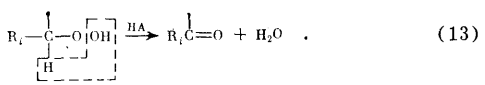
With enhancement of the electron-donating properties of the substituent R_i, the fraction of the products of the rearrangement involving the migration of the group R_i increases.

It is not at present clear which mechanism operates in the formation of water and carbonyl compounds from primary and secondary hydroperoxides. It may be that the acid-catalysed decomposition proceeds either via the reaction



$$HCOOH + HA \rightarrow [\ldots]^{\#} \rightarrow C(OH)_2 + HA \rightarrow C{=}O + H_2O + HA, \quad (12)$$

or constitutes a dehydration reaction:



$$R_i{-}C(H){-}O{-}OH \xrightarrow{HA} R_iC{=}O + H_2O \quad (13)$$

III. THERMAL REARRANGEMENT OF PEROXYESTERS

Peroxyesters (PE) are the most convenient objects for the investigation of the mechanism of the rearrangement. These compounds can rearrange both in media with a high dielectric constant and in non-polar solvents. The reaction products have almost no influence on the rate of rearrangement. The experimental rate constant for the rearrangement of the peroxyester (k_{exp}) is formally a complex quantity. However, it can be regarded as equal to the rate constant for the elementary reaction of the rearrangement (k_2), provided that the equilibrium in the reaction between the peroxyester and an electrophile, which can be a solvent molecule (SH), is strongly displaced to the right [reaction (14)]:



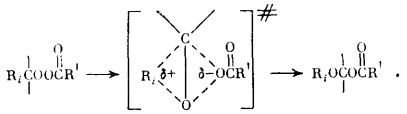
$$PE + SH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PE.SH(fast), \quad (14)$$



$$[PE.SH] \xrightarrow{k_2} P + SH(slow) \quad (15)$$

(P is the product of the rearrangement).

The activated state in reaction (15) is a highly structured polar complex. It was shown, first, that there is no transesterification during the rearrangement, because the peroxyester anion is not exchange for a salt anion[41,42] and, secondly, that the ^{18}O oxygen of the carbonyl group is fully retained in the isomeric product of the rearrangement[43,44]:



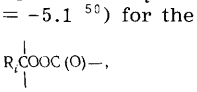
$$R_iCOOCR' \rightarrow [\ldots]^{\#} \rightarrow R_iOCOCR' \quad (16)$$

(IV)

Peroxyesters containing the R_i aryl group rearrange on heating in polar and non-polar solvents regardless of the strength of the acid whose anion enters the peroxyester. The aryl group has a high capacity for migration, behaving as an internal nucleophile [activated complex (IV), reaction (16)]. An alkyl group R_i participates in the rearrangement only under severe conditions, where the medium consists of a superacid[45] or when the anion entering the peroxyester is a powerful electron acceptor[46].

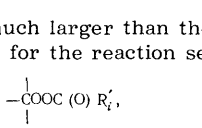
The claim that the highly structured activated state is polar and exhibits the features of a heterolytic process is based on kinetic measurements published by different workers. The rate of rearrangement increases with enhancement of the electron-donating properties of the groups R_i [47,48] and of the electron-accepting properties of R_i'.[42,49]

The reaction constant ($\rho = -5.1$ [50]) for the reaction series



$$R_iCOOC(O)-,$$

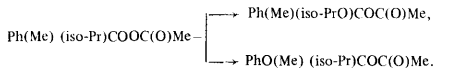
in which R_i is varied, is much larger than the reaction constants ($\rho = 1.1$,[49] 1.21 [51]) for the reaction series



$$-COOC(O)R_i',$$

involving variable R_i'. The high sensitivity of the reaction to the electronic effects of R_i is probably caused by the involvement of the nucleophilic migrating group in direct interaction with the peroxide oxygen. Only this can explain the appreciable deviation of the reaction series of *para*-substituted cumenyl peroxybenzoates from the linear relation between $\lg k$ and σ.[52]

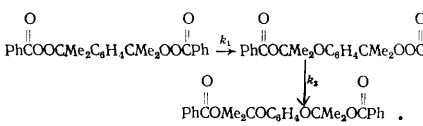
The role of the direct polar conjugation of the substituents with the reaction centre has been observed in the analysis of kinetic data[21] for the rearrangement of 2-propyl *p*-nitroperoxybenzoates in methanol, published by Hedaya and Winstein[47]. An increase in the size of the groups located in the alkyl fragment of the peroxyester should give rise to steric hindrance in the ground state and should remove it from the activated state. For peroxyesters containing alkyl or cycloalkyl groups R_i, such effects have an insignificant influence on the rate of rearrangement[47]. However, it was shown in a later study[51] that the rate of migration of the phenyl group increases with increase of the size of the adjacent alkyl group in the sequence methyl < ethyl < isopropyl. In the latter case the rate of rearrangement is so high that the peroxyester rearranges in the course of synthesis in toluene solution at room temperature:



$$Ph(Me)(iso\text{-}Pr)COOC(O)Me \rightarrow Ph(Me)(iso\text{-}PrO)COC(O)Me, \quad (17)$$

$$\rightarrow PhO(Me)(iso\text{-}Pr)COC(O)Me. \quad (18)$$

The successive transformation of the peroxy-groups in polyperoxyesters has been postulated[51]:

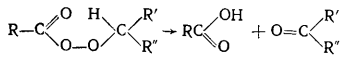


$$PhCOOCMe_2C_6H_4CMe_2OOCPh \xrightarrow{k_1} PhCOCMe_2OC_6H_4CMe_2OOCPh, \quad (19)$$

$$\downarrow k_2$$

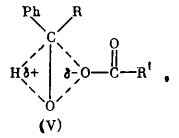
$$PhCOMe_2COC_6H_4OCMe_2OCPh. \quad (20)$$

Derivatives of secondary and primary alcohols occupy a special place among peroxyesters. These peroxyesters are extremely unstable and decompose to acids and carbonyl compounds[9]:



(21)

The simultaneous presence of a hydrogen atom and a phenyl group in the alkyl component of the peroxyester does not alter the nature of the decomposition. The thermal decomposition of peroxyesters having the structure PhRCHOOC(O)Me (R = Me or Ph) involves the quantitative formation of acetic acid and acetophenone or benzophenone; not even traces of phenol have been detected. Either the phenyl group is unable to compete with the proton in the rearrangement occurring in the cyclic complex[51]



(V)

or the rearrangement proceeds via a many-centre mechanism [reaction (21)].

The study of the influence of solvent polarity on the rate of rearrangement of peroxyesters[44,52-57] showed that, with increase of solvent polarity, the rate of rearrangement also increases. For example, in nitromethane ($\varepsilon = 38.6$) the rate constant for the rearrangement of cumenyl peroxybenzoate is 20 times greater and in aqueous ethanol ($\varepsilon = 31.8$, mole fraction of water 0.35) 100 times greater than in benzene ($\varepsilon = 2.28$).

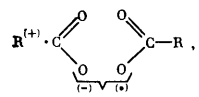
The choice of the Kirkwood parameter $(\varepsilon - 1)/(2\varepsilon + 1)$ as a measure of solvent polarity made it possible to observe a linear relation between $\lg k$ and $(\varepsilon - 1)/(2\varepsilon + 1)$ for the rearrangement of cumenyl peroxybenzoate. For each pair of the binary mixtures nitrobenzene–octane, methanol–water, and ethanol–water, the Kirkwood equation holds, but a general correlation could not be obtained for all the binary solvents[53].

The reason for the deviation from linearity and for the appearance of independent linear relations is the occurrence of specific interactions of the solvents with the peroxyester involving the formation of a hydrogen bond or coordination. Calculations have shown[53] that an increase of solvent polarity and specific solvation of the peroxyester favour the rearrangement of cumenyl peroxybenzoate involving the transition of the initial molecule to a more polar activated state. When the solvent polarity becomes sufficiently high, peroxyesters, which decompose via a radical mechanism in media with a low dielectric constant, undergo a rearrangement[58].

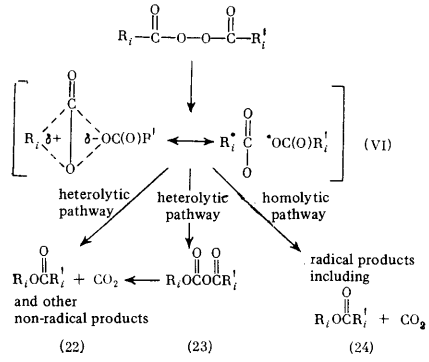
IV. THERMAL AND CATALYTIC REARRANGEMENTS OF DIACYL PEROXIDES

One of the possible pathways leading to the rearrangement of diacyl peroxides is carboxy-inversion, similar in type to the rearrangement of hydroxyperoxides and peroxyesters.

Several years ago studies were published[59-61] in which the thermal decomposition of diacyl peroxides, leading to the formation of radical and polar products, was regarded as a single process. Walling[59] believes that in the activated state a diacyl peroxide exists simultaneously as an ion pair and a biradical. Leffler and Moore[61] adhere to the same concept: they proposed the resonance hybrid intermediate

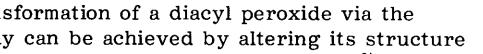


which is converted either into an ion pair or a radical pair, ensuring the development of a homolytic or a heterolytic reaction pathway. The most probable mechanism, which agrees with the available experimental literature data, can be represented by reactions (22)–(24):[62]



(VI)

The formation of a radical pair in the thermolysis of diacyl peroxides and the subsequent reactions of the radicals in the solvent cage or outside it are well known[62,63]. A quantitative transformation of a diacyl peroxide via the homolytic pathway can be achieved by altering its structure or by subjecting it to photochemical decomposition[64]:



(25)

The high polarity of the medium[65] as well as the electron-donating properties of the migrating group R_i or the electron-accepting properties of R_i' are factors favouring a heterolytic rearrangement.

The above mechanism (22)–(24) takes into account an important factor. It follows from the mechanism that the rearrangement need not necessarily lead initially to the intermediate carbonate $R_iOC(O)OC(O)R_i'$ and only then to the ester $R_iOC(O)R_i'$. There is also a possibility of another pathway, leading to the formation of the ester without the stage involving the formation of the rearrangement product [reaction (22)]. The main cause which makes it necessary to regard the process as one of the radical-ion type is that the majority of the factors (solvent polarity and the influence of substituents) are equally significant for the homolytic and heterolytic reaction pathways[65]. It is known[10], for example, that in certain thermal radical formation reactions the transition state in the homolytic fragmentation of peroxides is stabilised or destabilised by polar substituents or solvents, which have a significant effect on the rate of the process.

The attempts to separate competing homolytic and heterolytic processes with the aid of the ^{18}O oxygen isotope introduced into the carbonyl group of the diacyl peroxide proved unsuccessful[65-68]. In some cases isotope exchange of the oxygen atoms of the carbonyl and peroxy-groups in the rearrangement of a diacyl peroxide was observed[67], while in others the rearrangement took place with retention of ^{18}O in the carbonyl group of the isomeric product and did not entail

a change in the optical activity of the migrating group[68]. It has been shown[67] that carboxy-inversion, radical decomposition, and the isotope exchange between the [^{18}O]carbonyl group and the peroxide oxygen take place at comparable rates, which may be an argument in support of a radical-ion mechanism of the decomposition of diacyl peroxides [reactions (22)–(24)] if one rules out the possibility of a sigmatropic rearrangement[69,70].

The successive transformation of diacyl peroxides into alkyl cyclocarbonates and then into esters is catalysed by Lewis acids[71,72]. The optical properties and isotope composition of the carbonyl oxygen in the diacyl peroxide are fully retained in the rearrangement product when the reaction is catalysed by antimony pentachloride[73]. Together with the detection of the intermediate carboxyanhydride, this is evidence for the similarity of the mechanism of this reaction to the mechanism already discussed [reactions (22)–(24)].

Comparison of kintic data for diacyl peroxides of different structure makes it possible to observe the following feature. In the homolytic propagation of the process the reaction constants ρ have small negative values in the range between -0.2 and -0.9.[74–78] It is believed that the decrease of the dipole–dipole repulsion between the oxygen atoms in the molecule due to electron-accepting substituents reduces the rate of the homolytic decomposition[75]. In the thermal decomposition of substituted benzoyl isobutyryl peroxides a high yield of rearrangement products is observed, which increases after the introduction of electron-accepting substituents ($\rho > 0$); the rate of reaction also increases[70]. This is attributed to the heterolytic propagation of the process. The sign of the reaction constant can apparently serve as a criterion for differentiation between the homolytic and heterolytic reaction pathways in accordance with mechanisms (22)–(24).

Reutov and coworkers[79–81] have shown convincingly that the rearrangement of cyclobutanoyl, acetyl cyclobutyl, and acetyl cyclopropyl peroxides is neither a "purely" homolytic nor a "purely" heterolytic process. On formation of esters as a result of the rearrangement of diacyl peroxides, a radical pair is not produced, as shown by CINP data[80]. Carbonium ions were not formed either, as shown by studies of the thermolysis of acetyl cyclobutyl peroxide labelled with ^{13}C in the methylene group of the side chain[81,82]. Thus the rearrangement of diacyl peroxides must be regarded at the present time as a radical-ion process [reactions (22)–(24)].

V. REARRANGEMENT OF ALKYL(ARYL) PEROXIDES

The rearrangement is not characteristic of symmetrical or asymmetric alkyl peroxides R_iOOR_i' (R_i and R_i' are primary, secondary, and tertiary alkyl groups). Cases are known where the migration of the aryl groups in alkyl aryl peroxides cannot be regarded as intramolecular processes. Kharasch et al.[83] showed that the conversion of triphenylmethyl peroxide into the diphenyl ether of benzopinacol on heating in xylene, described by Wieland[84], is a homolytic reaction:

$$(Ph_3CO)_2 \rightarrow 2Ph_3CO^{\cdot} \rightarrow 2Ph_2\dot{C}OPh \rightarrow Ph_2(PhO)C{-}C(PhO)Ph_2 . \quad (26)$$

The same type of reaction is observed in the thermolysis of t-butyl triphenylmethyl and t-butyl diphenyl-*p*-tolylmethyl peroxides[83]:

$$YC_6H_4Ph_2COOCMe_3 \rightarrow YC_6H_4Ph_2CO^{\cdot} + {}^{\cdot}OCMe_3 \quad (27)$$
$$\swarrow \qquad \searrow$$
$$Ph_2\dot{C}OC_6H_4Y \qquad YC_6H_4(Ph)\dot{C}OPh .$$

Under the influence of protic acids, alkyl aryl peroxides decompose with formation of phenol[85,86]. The bimolecular reaction between the peroxide and the acid probably gives rise to a hydroperoxide, which then undergoes an acid-catalysed rearrangement. Thus organic peroxides R_3COOCR_3 constitute a class of peroxy-compounds for which the homolysis of the O–O bond is most typical[8,9].

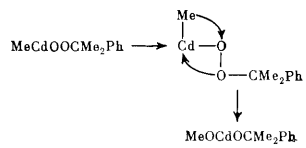
VI. REARRANGEMENT OF ORGANOELEMENTAL PEROXIDES

The monographs and reviews published in recent years[87–92] characterise the field of organoelemental peroxides as one offering promise and developing rapidly. More than five hundred organoelemental peroxides, many of which are capable of rearranging, are now known.

Among organoelemental peroxides of Group II elements rearrangements are known for magnesium and cadmium compounds. When trimethylsilylmethylmagnesium chloride is oxidised by oxygen, the product is a peroxide, which rearranges under the conditions of the synthesis via the reaction[93]

$$Me_3Si{-}CH_2OOMgCl \rightarrow Me_3SiOCH_2OMgCl . \quad (28)$$

Davies and Packer[94,95] pointed out that methylcumenylperoxycadmium, which is stable at room temperature, decomposes at 50 °C with formation of an isomeric compound:



(29)

The reaction of diphenylcadmium with t-butyl hydroperoxide leads to the formation of an intermediate peroxide, which either participates in the disproportionation reaction or rearranges[96]:

$$PhCdOOCMe_3 \xrightarrow{Ph_2Cd} PhCdOCMe_3 + PhCdOPh \quad (30)$$
$$PhCdOOCMe_3 \rightarrow PhOCdOCMe_3 . \quad (31)$$

Among organoelemental peroxides of Group III elements, boron compounds have been studied in greatest detail and to a lesser extent aluminium, thallium, gallium, and indium compounds.

It has been established[97] that the reaction of phenylboronic acid with hydrogen peroxide results in the formation of phenol. The phenol isolated from the reaction mixture did not contain an excess of heavy oxygen[98] when phenylboronic acid $C_6H_5B(^{18}OH)_2$ was oxidised by the peroxide $H_2{}^{16}O_2$ in the presence of $H_2{}^{18}O$. An unstable hydroperoxide is probably formed and then rearranges like organic hydroperoxides.

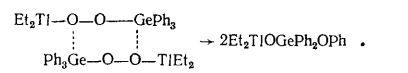
The rearrangement of certain organoboron peroxides take place quantitatively[99] or constitutes an appreciable proportion of the overall process[100–102]. Thus dimethylmethylperoxyboron is converted into a non-peroxide compound of the same molecular weight in the condensed and gas phases via the reaction[99]

$$Me_2BOOMe \rightarrow (MeO)_3BMe. \quad (32)$$

Organoaluminium peroxides are extremely unstable under normal conditions and readily decompose with formation of several products[103]. A rearrangement has been postulated as one of the possible reaction pathways[105,106].

A reliable demonstration of the rearrangement of organothallium peroxides has been achieved by Razuvaev et al.[106], who showed that, on heating diethylthalliumperoxy (triphenyl)

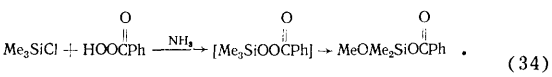
germane in an inert solvent at 80 °C, the rearrangement product is formed quantitatively via the second-order reaction



(33)

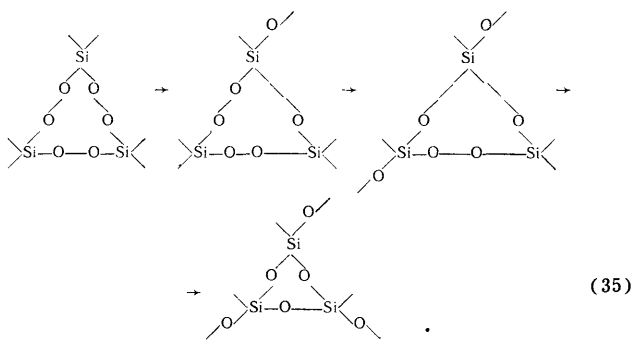
The syntheses of organogallium and organoindium peroxides have been achieved in recent years[107]. The products of the thermal decomposition reaction indicate that their rearrangement takes place simultaneously with homolytic decomposition[107].

The possibility of the rearrangement of peroxide compounds of Group IV elements was first pointed out by Buncel and Davies[108,109]. When an attempt was made to synthesise trimethylsilyl peroxybenzoate, the product isolated was dimethylmethoxysilyl benzoate, which the authors believe to be the product of the rearrangement of an intermediate peroxide:



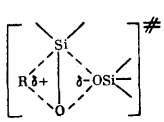
(34)

Approximately at the same time Jenkner[110] reported that dialkyldihalogenosilanes react with H_2O_2 to form cyclopolysiloxanes containing the Si–O–O–Si, Si–O–Si, and Si–O–C groups. The presence of the Si–O–C group was explained erroneously by the oxidation of the Si–C bond. It has been shown[111], that hexamethylcyclotrisilperoxane, which is the first representative of cyclic silyl peroxides, rearranges with contraction of the ring and migration of the methyl group:

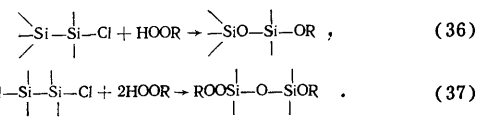


(35)

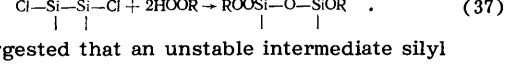
X-Ray diffraction studies have shown that the average value of the Si–O–O–Si torsional angle is 135.6°, i.e. peroxide bridges have a nearly *trans*-conformation. The negative entropy $\Delta S^{\#} = -13.7$ e.u. and the spatial disposition of the atoms indicate a cyclic transition state:



Kawazumi and Murai[112] observed that siloxanes are formed in the synthesis of t-butylperoxypentamethyldisilane and 1,2-di-t-butylperoxytetramethyldisilane:

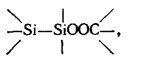


(36)

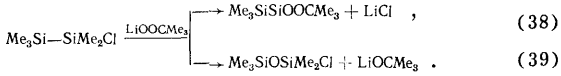


(37)

It has been suggested that an unstable intermediate silyl peroxide is formed:



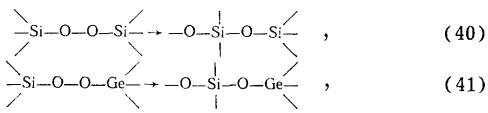
which rearranges under the conditions of the synthesis. However, Razuvaev and coworkers[113–115] established that chlorine-containing di- and tri-silanes are oxidised at the Si–Si bond by the hydroperoxide or its lithium salt before the silyl peroxide is formed:



(38)

(39)

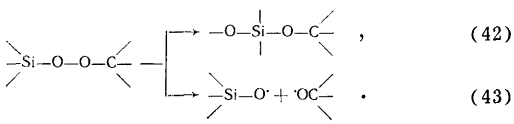
In the thermal and catalytic decomposition of the organoelemental peroxides R_3EOOH [116–120] a rearrangement is observed when E = Si or Ge.[116–118] Silicon and silicon-germanium peroxides rearrange quantitatively to the isomeric siloxanes[121–124]:



(40)

(41)

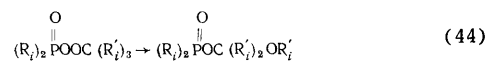
while organosilicon peroxides decompose via two parallel reactions[125]:



(42)

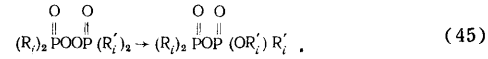
(43)

Peroxide compounds of Group V elements are capable of rearranging with migration of an alkyl or aryl group from a tertiary carbon atom[126–128]:



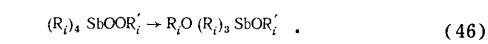
(44)

or from a phosphorus atom[129,130]:



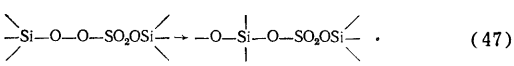
(45)

Such reactions are also characteristic of antimony derivatives[131–134]:



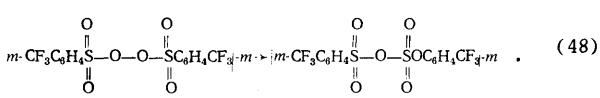
(46)

Bressel and Blaschette[135] observed a rearrangement of bis-(trimethylsilyl) peroxomonosulphate in methylene chloride at a temperature below 0 °C:



(47)

The decomposition of *m*-trifluoromethylbenzenesulphonyl peroxide in ethylbenzene and in cumene and also in the absence of a solvent is, according to the authors[136], an ionic reaction and involves the migration of the aryl group:



(48)

In essence, the consideration of the mechanism of the rearrangement of organoelemental peroxides involves the study of compounds of Group IV elements and in the first place silicon compounds. There is as yet no unanimous view concerning the mechanism of the rearrangement of organoelemental peroxide compounds. Some authors tend to regard the rearrangement as one occurring in a radical pair, while others treat it as a heterolytic process. The results of experimental studies do not provide an unambiguous answer. Investigators have frequently observed that the same factors, which had been believed earlier to be features of either heterolytic or homolytic processes, have the same influence on on both processes.

Dannley suggested that the rearrangement of organoelemental hydroperoxides has a free-radical mechanism[116,118,121]. The author believes that the radicals $\rangle EO^{\cdot}$ (E = Si or Ge), formed as a result of the homolysis of the peroxide linkage, rearrange in a solvent cage or are liberated into space and participate in radical reactions:

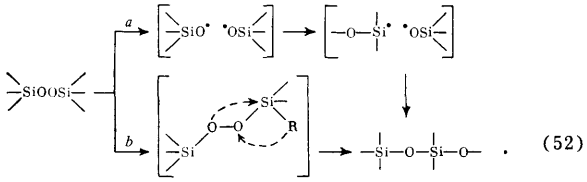
$$(R_i)_3EOOH \rightarrow (R_i)_3EO^{\cdot} + {}^{\cdot}OH\ ; \qquad (49)$$

$$(R_i)_3EO^{\cdot} \xrightarrow{SH} (R_i)_3EOH + S^{\cdot}\ , \qquad (50)$$

$$(R_i)_3EO^{\cdot} \rightarrow R_iO(R_i)_2E^{\cdot} \xrightarrow{{}^{\cdot}OH} R_iO(R_i)_2EOH \rightarrow R_iOH + [(R_i)_2EO]_x\ . \qquad (51)$$

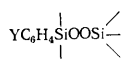
A study of the decomposition of triphenylsilyl hydroperoxide[116] established that the reaction is insensitive to a change in the polarity of the solvent (nitrobenzene, methyl benzoate, anisole, *o*-dichlorobenzene), is accelerated on irradiation with ultraviolet light, and is not catalysed by acids (monochloro- and trichloro-acetic acids in *o*-dichlorobenzene).

In contrast to silyl hydroperoxide, the silyl peroxides $\rangle SiOOSi\langle$ rearrange quantitatively to isomerise siloxanes; the liberation of siloxy-radicals into space is not observed. In order to account for the mechanism of his process, Shubber and Dannley[121] were forced to assume that the rearrangement has a latent radical mechanism [reaction (52), pathway *a*], although they do not rule out the possibility of a concerted rearrangement of the bonds [reaction (52), pathway *b*] without the formation of free radicals:



(52)

The principal argument in support of the rearrangement in a radical pair reduces to the fact that in the silyl peroxides



a relatively slight increase of the capacity for the migration of the aryl groups is observed in the sequence phenyl (1.0) < *p*-tolyl (1.1) < anisyl (6.0), which is more likely to be a property of homolytic than heterolytic processes[121].

This finding can hardly be regarded as sufficient justification for a radical mechanism of the rearrangement. The sequence in which the capacity for migration of the aryl groups YC_6H_4 varies is different in radical reactions and in the rearrangements. It is known[83,137] that, following the rearrangement in an alkoxy-radical,

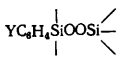


(53)

the capacity for migration of the YC_6H_4 group increases after the introduction of electron-accepting substituents Y. The same behaviour has been observed in isomerisation in an alkyl radical[138]:

$$YC_6H_4CMe_2\dot{C}H_2 \rightarrow Me_2\dot{C}CH_2C_6H_4Y\ , \qquad (54)$$

while in rearrangements of silyl peroxides

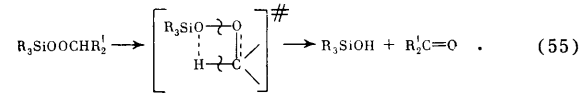


the rate of reaction diminishes after the introduction of an electron-accepting substituent Y.[21] Furthermore, it has been shown that siloxy- and germyloxy-radicals do not isomerise[139,140].

Experimental data indicating a heterolytic mechanism of the rearrangement show that the reactions involved in the rearrangement of silyl peroxides are sensitive to changes in solvent polarity[141] and are accelerated under the influence of nucleophiles such as F^- and CN^-.[142] An increase of pressure to several thousand atmospheres increases the rate of rearrangement of silyl peroxides severalfold[143]. If the rearrangement occurred in a radical pair, the opposite relation would have been observed.

Silyl peroxides $R_3SiOOSiR_3$ do not rearrange quantitatively via reaction (40) in solution alone. For example, in the gas phase there is no solvent cage effect. However, even in this case it has been established that the rearrangement of $Me_3Si.OOSiMe_3$ takes place quantitatively, which indicates a non-radical mechanism of the process. The only difference between the gas-phase and liquid-phase reactions consists in the difference between the rates of the process[144].

Organosilicon peroxides containing an α-hydrogen atom at a silicon or carbon atom undergo thermolysis with migration of the hydrogen atom to one of the peroxide oxygen atoms. It has been shown that the migration of hyrogen constitutes an intramolecular rearrangement, which takes place simultaneously with the radical decomposition[145,146]:



(55)

The rearrangement of silyl peroxides in which there is an α-hydrogen atom at the silicon atom is of special interest[145,146]:



(56)

Reaction (56) makes it possible to generate silanones in different solvents at 160–180 °C.

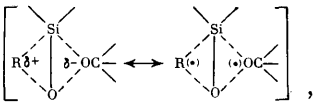
Since 1977 systematic studies have begun on the structure of organoelemental peroxides by electron diffraction[147] and X-ray diffraction[111,148–150]. The results of the studies on silyl peroxides agreed with the concept of rearrangement in a "rigid" cyclic complex.

In analysing the arguments for and against the homolytic and heterolytic mechanisms of the rearrangements of silyl peroxides one should probably not pose the question unduly categorically and one should postulate, for example, that "in the same reacting system some of the bonds undergo homolytic dissociation, while another fraction of the same bonds... are ruptured heterolytically".[151] It is quite probable that the elementary reaction in the rearrangement of the molecular skeleton is preceded by electron transfer. For example, two parallel reactions are observed in the thermolysis of cumenylperoxy(triphenyl)silane:

$$Ph_3SiOOCMe_2Ph \xrightarrow[\text{anisole}]{160^\circ} \begin{cases} \rightarrow PhOPh_2SiOCMe_2Ph \\ \quad (\Delta G^{\#} = 138\ \text{kJ mol}^{-1}; & (57) \\ Ph_3SiO^{\cdot} + {}^{\cdot}OCMe_2Ph \\ \rightarrow (\Delta G^{\#} = 142\ \text{kJ mol}^{-1}\ . & (58) \end{cases}$$

The values of $\Delta G^{\#}$ calculated by Yablokov et al.[123] are the same, within the limits of the error of the measurement (±4 kJ), for the rearrangement and the homolytic reaction

and are consistent with the hypothesis of a radical-ion mechanism of thermolysis in an activated state:



which is analogous to that proposed by Leffler and More[61] for the rearrangement of diacyl peroxides.

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