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Organometallic Peroxy-compounds and Their Reactions

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Experimental studies on the synthesis and reactions of organometallic peroxy-compounds are reviewed and the reactions of organometallic compounds with oxygen and organic peroxides, leading to the formation of both peroxide and non-peroxide products, are considered. The possible modes and mechanisms of the chemical reactions of organometallic peroxy-compounds are discussed.
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I. INTRODUCTION

The advances in the chemistry of organic peroxides have been recently widely described in numerous reviews and monographs and have been discussed at All-Union and International Conferences. On the other hand, the problem of the synthesis of organometallic peroxy-compounds (OMPS) and their chemical reactions have so far been little investigated, although these compounds are of undoubted interest both as regards theoretical research and for practical applications. Much attention has been devoted to these problems at the Gorky Institute of Chemistry from different standpoints: systematic research is being carried out on the synthesis and reactions of OMPS and their role in the autoxidation of organometallic compounds (OMC), the mechanisms of the reactions of OMC with various peroxides are being investigated, and the initiating capacity of OMPC and OMC–oxygen and OMC–peroxide systems in free-radical processes are being elucidated.

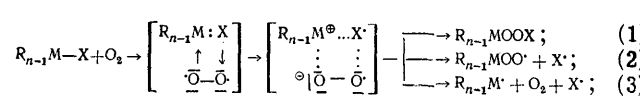
It is useful to examine the fundamental trends in such research, resorting where necessary to data of other investigators. The review does not include information about the peroxy-compounds of boron, phosphorus, and transition metals. There is an extensive literature on these compounds, the consideration of which is impossible within the framework of this article. For boron (R_3B) and phosphorus (R_3P and R_5P) compounds, only the results of a few studies are quoted, confirming the mechanisms of the reactions of their chemical analogues. Attention is concentrated in the review on studies carried out in recent years.

II. REACTIONS OF ORGANOMETALLIC COMPOUNDS WITH OXYGEN AND PEROXY-COMPOUNDS

Many OMC are oxidised by atmospheric oxygen with formation of peroxy-compounds. This process is used as a method of synthesising organic hydroperoxides with primary and secondary organic groups (for example, the oxidation of magnesium and aluminium compounds in ether at a low temperature followed by the hydrolysis of the resulting OMPC). In order to obtain the OMPC in a pure form, the autoxidation of the OMC is not usually employed, since the process is accompanied by secondary molecular and radical reactions of the peroxides.

Some OMC, for example compounds of Group I–III elements, are known to interact readily with oxygen, while others are oxidised only under severe conditions (derivatives of Group IVB elements). Aryl OMC are more resistant to oxygen than the alkyl derivatives. The length and structure of the organic group attached to the metal, the presence of functional groups, etc., are important[1-3]. The oxidation of OMC by oxygen is a complex chemical process. It has now been shown convincingly[4] that the primary reaction in the autoxidation of many OMC is their bimolecular reaction with oxygen. Compounds of Group I–III elements as well as many compounds having an M–M bond react in this way. On the other hand, the autoxidation of the OMC of Group IVB elements[5-7] is initiated by the radicals formed in the spontaneous decomposition of the OMC in the initial stage.

The molecular interaction of OMC with oxygen (or ozone) involves several successive microstages: the coordination of oxygen (or ozone) to the central atom of the OMC via the oxygen p-electrons and the vacant atomic orbitals of the heteroatom and electrophilic attack by the coordinated oxygen on the M–C or M–M bonds followed by electron transfer leading to the formation of either an OMPC or of organic, organometallic, or peroxy-radicals[4,8-12]:

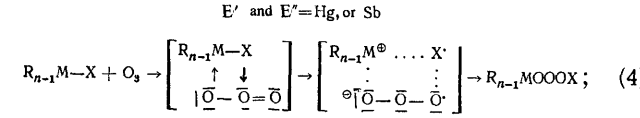


(1) (2) (3)

X=R, E′R_m, E″$(MR_{n-1})_m$;

M=Li, Mg, Zn, Cd, B, Al, Tl, Si Ge, Sn, or Pb;

E′ and E″=Hg, or Sb



(4)

X=R, MR_m, or H; M=Si, Ge, Sn, or Pb.

The high electron affinity of ozone is responsible for the formation of a reactive OMC–ozone complex by compounds which do not enter into similar reaction with oxygen under the usual conditions. The oxidation by ozone of organic derivatives of Group IVB elements, metal alkyls, dimetal hexa-alkyls, halogen-containing derivatives of tin

and lead, trisubstituted organosilanes, and other compounds proceeds at a low temperature (between room temperature and −68° or even −100°C [13-27]).

The OMPC formed via reaction (1) can react under autoxidation conditions with the initial OMC, yielding an alkoxy-derivative or decomposing into radicals with dissociation of O—O or M—O bonds:

$$R_{n-1}MOOR + R_{n-1}MR \rightarrow 2R_{n-1}MOR\ ; \quad (5)$$
$$R_{n-1}MOOR \rightarrow R_{n-1}MO^{\cdot} + {}^{\cdot}OR\ ; \quad (6)$$
$$R_{n-1}MOOR \rightarrow R_{n-1}M^{\cdot} + {}^{\cdot}OOR\ . \quad (7)$$

The radicals formed in the decomposition of the OMC—oxygen complex [Eqns. (2) and (3)] and in the decomposition of the peroxide [Eqns. (5)—(7)] enter into the usual radical reactions in the cage or in the bulk of the solvent. At advanced stages of the autoxidation process, the homolytic substitution of the organic group in the OMC by the peroxy-radical is a very important reaction among these transformations:

$$ROO^{\cdot} + R_nM \rightarrow R_{n-1}MOOR + R^{\cdot}\ .$$

The trioxide formed via reaction (4), in which X is a primary or secondary alkyl group, decomposes to an OMPC and a carbonyl compound:

$$R_{n-1}MOOOCH \rightarrow R_{n-1}MOOH + -C- \ .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

The bimolecular interaction of an OMC with oxygen or ozone [Eqns. (1) and (4)] is very strongly influenced by the specific solvation of the OMC. The reaction may be catalysed by the introduction of a ligand L, which makes the metal more nucleophilic:

$$R_{n-1}M{-}R + O_2 + L \rightarrow \left[\begin{array}{c} L \\ \downarrow \\ R_{n-1}M{-}R \\ \uparrow\ \ \downarrow \\ \cdot\underline{O}{-}\underline{O}\cdot \end{array}\right] \rightarrow \left[\begin{array}{c} (R_{n-1}M{-}L)^{\oplus} \cdots R^{\cdot} \\ \vdots \qquad \cdot \\ {}^{\ominus}|\underline{O}{-}\underline{O}\cdot \end{array}\right] \rightarrow R_{n-1}MOOR + L\ . \quad (8)$$

When the entire coordination capacity of the OMC is saturated by the ligand species, the coordination of O_2 or O_3 to the heteratom becomes impossible and the OMC exhibits an enhanced resistance to oxidation.

The formation of free radicals in the autoxidation of OMC has been demonstrated by employing labelled compounds (using ^{14}C and D). For example, the oxidation of PhLi and phenyl derivatives R_2M (M = Mg, Zn, or Cd) in labelled benzene proceeds with participation of Ph radicals, which react with the solvent and give rise to half-labelled biphenyl. The phenol isolated from the hydrolysis products in the reaction mixture is formed solely from the OMC. [28-32] The reactions of Ph radicals with other solvents (cyclohexane, chloroform, and carbon tetrachloride) [32-35] and the accelerating effect of additives (ethers) [28, 36-39] have also been noted.

In contrast to Ph_2Cd, whose oxidation proceeds wholly via a free-radical mechanism [35], the reaction of Et_2Cd with oxygen (in n-heptane at −80°C) proceeds without the participation of free radicals. This was confirmed by the autoxidation of Et_2Cd in the presence of effective inhibitors (*o*-phenylenediamine, galvinoxyl, and phenothiazine), used previously to demonstrate the free-radical mechanism of the oxidation of dimethylcadmium and organoboron compounds [40]. In the autoxidation of Et_2Cd in heptane, the reversible formation of an OMC—oxygen complex, which is comparatively stable in solution and is subsequently converted into a peroxy-product, was demonstrated experimentally for the first time [41]:

$$Et_2Cd + 2O_2 \rightleftarrows Et_2Cd \cdot 2O_2\ ;$$
$$Et_2Cd \cdot 2O_2 \rightarrow (EtOO)_2Cd\ .$$

The diethylcadmium—oxygen complex is formed over a wide temperature range (between −80° and 20°C). Its slow conversion into the ethylperoxy-derivative of cadmium can be observed even at room temperature. Substances containing atoms with electron-donating properties catalyse the reversible conversion of the complex into a peroxy-compound.

The replacement of one Ph-group in Ph_2Zn or Ph_2Cd by a Ph_3SiO group has a marked influence on the behaviour of the heterosiloxanes $PhMOSiPh_3$ (M = Zn or Cd) towards oxygen. For example, $PhZnOSiPh_3$ [42] and $PhCdOSiPh_3$ [43] are hardly oxidised by molecular oxygen under the usual conditions; the behaviour of $CH_3CdOSiPh_3$ is the same [43]. The alkyl derivative $EtZnOSiPh_3$ slowly absorbs oxygen but is nevertheless more resistant to O_2 than dialkyl- and diphenyl-zinc. On the other hand, $EtCdOSiPh_3$ is oxidised readily in benzene at room temperature, the organocadmium peroxide being formed in 92% yield [43]:

$$EtCdOSiPh_3 + O_2 \rightarrow EtOOCdOSiPh_3\ .$$

Primary alkyl compounds of mercury (Et_2Hg and n-Pr_2Hg) are resistant to oxygen. On the other hand, compounds with secondary (cyclohexyl and isopropyl) and tertiary (t-pentyl) groups undergo autoxidation via a free-radical mechanism including the bimolecular interaction of the OMC with oxygen in the initial stage [Eqn. (1)] and the formation of an unstable peroxide, which reacts further in accordance with Eqns. (5) and (7). [33,44-51]

Alkylperoxy-radicals $RO_2^{\cdot}$ behave as oxidants:

$$RO_2^{\cdot} + R_2Hg \rightarrow ROH + R_{-H}{=}O + RHg^{\cdot}\ .$$

The $RHg^{\cdot}$ radicals, formed both in the initial stage and at advanced stages of the process as a result of the decomposition of RHgOR, [44,52] decompose in their turn into mercury and the alkyl radical or are oxidised to peroxy-radicals [33,44]:

$$RHg^{\cdot} \rightarrow R^{\cdot} + Hg\ ;$$
$$RHg^{\cdot} + O_2 \rightarrow RHgOO^{\cdot}\ .$$

Like the $RO_2^{\cdot}$ radicals, the latter oxidise the OMC with formation of the final products:

$$RHgO_2^{\cdot} + R_2Hg \rightarrow RHgOR + RHgO^{\cdot}\ .$$

The alkoxy-derivatives of mercury thus formed react with oxygen more readily than the initial R_2Hg, but also in accordance with the free-radical chain mechanism [52].

Dicyclohexylmercury is oxidised by air at an appreciable rate even at room temperature. The main oxidation products in isopropyl alcohol at 60°C are cyclohexanol, cyclohexanone, and metallic mercury [49]. The oxidation products of i-Pr_2Hg in cyclohexane, cyclohexene, and benzene at 50°C are mercury, isopropylmercury isopropoxide, isopropylmercury hydroxide, acetone, isopropyl alcohol, propane, and propene. Apart from the above compounds, small amounts (approximately 5%) of phenyl derivatives have been detected in benzene, namely isopropylphenylmercury, Ph_2Hg, biphenyl, and isopropylbenzene [48]. Solvent involvement has been confirmed by isotopic and mass-spectrometric methods using in the oxidation reaction $(CH_3)_2CHOD$, $(CH_3)_2CDOH$, and isopropyl alcohol or R_2Hg labelled with ^{14}C. [45] The formation of free radicals in the autoxidation of R_2Hg [48-50] has been confirmed experimentally also by the inhibitor method [33,44].

Organoboron compounds are known to be readily oxidised by oxygen with formation of a large number of different products, the proportions of which depend very

markedly on the reaction temperature and the solvent. It is suggested [3] that the primary R_3B–oxygen molecular complex is converted into a more or less stable organoboron peroxide in accordance with Eqn. (1). The peroxide is then converted into an alkoxy-derivative in accordance with Eqn. (5) or decomposes with formation of free radicals.

The oxidation of organoaluminium compounds proceeds in the main similarly to the oxidation of boron alkyls. The formation of organoaluminium peroxide was demonstrated for the first time by Sladkov et al. [53] and then confirmed by the low-temperature oxidation of Et_3Al. [54–56] The primary stage of the process is reaction (1). The subsequent interaction of the peroxide with the unoxidised OMC in accordance with Eqn. (5) leads to the formation of the corresponding aluminium alkoxides—the main oxidation products of R_3Al at a moderate temperature. Thus the yield of the peroxy-compound in the oxidation of Et_3Al by dry air in n-heptane at temperatures between −75° and 25°C is higher the lower the initial concentration of Et_3Al and the lower the reaction temperature. In a few instances, the yield of peroxide reaches 50%. At 25°C the peroxide is not detected in the reaction products [55]. As for boron alkyls, there is a succession of stages in the oxidation of the C–Al bond, the rate of oxidation varying appreciably with the number of oxidised alkyl groups. For example, in heptane (at 20–50°C) the ratios of the rates of oxidation of Et_3Al, Et_2AlOEt, and $Et(EtO)_2Al$ are 100 : 25 : 1. [56] Although $Et_3(EtO)Al$ is also oxidised at a high rate, on complete oxidation of Et_3Al under these conditions the yield of $(EtO)_2AlEt$ is low, since the compound exchanges radicals with the initial OMC. This reaction is rapid even at 5–10°C:

$$Et_3Al + (EtO)_2AlEt \rightarrow 2\,Et_2AlOEt\ .$$

In the oxidation of Et_2AlBr (between −30° and 30°C), such exchange does not occur and the reaction is accompanied by the formation of $(EtO)_2AlBr$ only [56].

Ph_3Al is oxidised in benzene, n-hexane, n-nonane, and ethyl ether more slowly and the solvent is involved in the oxidation [30,57,58]. Thus phenol (after hydrolysis) and biphenyl were found in the oxidation of Ph_3Al in benzene, and phenol, acetophenone, acetaldehyde, and alumina were found after the reaction in ether.

Et_3Tl is oxidised without the formation of free radicals. The peroxide produced via reaction (1) shows a smaller capacity for decomposition and isomeric transformations than the aluminium analogue. It was therefore possible to obtain the peroxide $Et_2TlOOEt$ in the oxidation of Et_2Tl in n-octane at −70°C. [59]

The organic compounds R_4M (where M = Si, Ge, Sn, or Pb, and R = alkyl) are in most cases highly resistant to oxygen. They react appreciably with oxygen at a fairly high temperature. The primary reaction in the autoxidation of such OMC as well as symmetrical organobimetallic compounds $R_3M–MR_3$ is homolytic decomposition of the initial compound at the metal–carbon or metal–metal bond, for example:

$$Et_4M \rightarrow Et_3M^{\cdot} + Et^{\cdot}\ ;$$

$$Et_3M–MEt_3 \rightarrow 2\,Et_3M^{\cdot}\ (\text{or}\ \ Et_3M–\dot{M}Et_2 + Et^{\cdot})\ ;$$

M=Sn, or Pb.

The development of the free radical chain process is due to the formation and further interactions of the peroxy-radicals:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}\ ;$$

R=Et, Et_3Sn, or Et_3Pb .

In the case of Et_4Pb (80–130°C, without solvent or in alkanes), degenerate chain branching by the peroxy-product and a number of other side reactions of the latter take place in addition to the reactions of the $RO_2^{\cdot}$ radicals with the initial OMC and their decomposition reactions [6,7,60–62]:

$$EtO_2^{\cdot} + Et_4Pb \rightarrow Et_3PbOOEt + Et^{\cdot}\ ;$$

$$Et_3PbOO^{\cdot} \rightarrow Et_2PbO + EtO^{\cdot}\ .$$

A characteristic feature of the autoxidation of Et_6Sn_2 (60–90°C, without solvent or in alkanes) is the absence of degenerate branching, owing to the high reactivity of the peroxy-compound with respect to the initial OMC: [60,61,63,64]

$$RO_2^{\cdot} + Et_3SnSnEt_3 \rightarrow Et_3SnOOSnEt_3 + R^{\cdot}\ ;$$

$$Et_3SnOOSnEt_3 + Et_3SnSnEt_3 \rightarrow 2\,Et_3SnOSnEt_3\ ,$$

$$RO_2^{\cdot} \rightarrow \text{products}\ ,$$

R=Et, or Et_3Sn .

The formation of the peroxide in small amounts in the oxidation of Et_6Sn_2 has been demonstrated by infrared spectroscopy [63].

The autoxidation of Et_6Pb_2 (40–90°C, without solvent, in hydrocarbons, or in Et_4Pb) proceeds in the initial stages similarly to the oxidation of Et_6Sn_2 with the preferential dissociation of the Pb–Pb bond [60,61,63–65]. The kinetic process characteristics are more complex, since, as the process proceeds, "limiting" behaviour due to the influence of the reaction products is observed. Nor can one rule out the role of steric factors. For example, the latter explains the higher reactivity of Ph_6Pb_2 with respect to $t\text{-}BuO_2^{\cdot}$ radicals compared with that of Ph_6Sn_2. [66]

The photoinitiated oxidation of the compounds R_4M (M = Sn or Pb) with the same and different alkyl groups [67–69] as well as the oxidation of $(Et_3Sn)_2O$ [70] proceeds comparatively rapidly at room temperature, while Et_6Sn_2 is oxidised [71] even at temperatures in the range between −30° and 0°C. In the free-radical chain process involving the conversion into peroxy-radicals of the radical pairs formed in the photolysis of the M–C or M–M bonds, there is competition with the photosensitised oxidation of the OMC, the primary product of which is the corresponding OMPC. In many cases, the yield of peroxide reaches 15–25%. [68,69] The radicals are formed as a result of the photochemical dwcomposition of the peroxides at the O–O bond.

An increase of reactivity of the OMC of Group IVB metals towards oxygen is observed when the organic group in R_4M is replaced by groups derived from organic derivatives of the elements of the type EMR_3, where E is an element of Group II or V. [7,61,64,65,72,73] The reactions of such compounds with oxygen proceed under very mild conditions via a bimolecular mechanism without the participation of free radicals [74–79]. Dimetalloxanes are formed in accordance with Eqns. (1) and (5), for example:

$$\begin{gathered}(R_3M)_2Hg + O_2 \rightarrow R_3MHgOOMR_3\ ;\\ R_3MHgOOMR_3 + (R_3M)_2Hg \rightarrow 2R_3MHgOMR_3\ ;\\ R_3MHgOMR_3 \rightarrow Hg + R_3MOMR_3\ ;\\ \text{M=Si, or Ge; R=Et, or Ph.}\ .\end{gathered} \qquad (9)$$

When R = Et, the dimetalloxanes produced are responsible for the autocatalytic oxidation of the OMC. However, in the autoxidation of $(Ph_3Ge)_2Hg$, hexaphenyldigermanoxane is catalytically inactive [80].

The interaction of $(Et_3Ge)_2Hg$ and $(Et_3Si)_2Hg$ (0°C, alkanes) with oxygen is accelerated by small amounts of added ligands (NH_3, amines, pyridine, Ph_3P, etc.) [74–77]. The nature of the process and the kinetic parameters correspond to a catalytic reaction with formation of an

OMC–ligand complex [Eqn. (8)]. The peroxide formed is involved in competing catalytic decomposition reactions with the ligand L [Eqn. (10)] and reactions with the initial OMC [Eqn. (9)]:

$$Et_3MHgOOMEt_3 \xrightarrow{L} Et_3MOOMEt_3 + Hg \ . \qquad (10)$$

There is also a possibility of the catalytic decomposition of the hydroxy-derivative formed under these conditions [79]:

$$Et_3MHgOMEt_3 \xrightarrow{L} Et_3MOMEt_3 + Hg \ .$$

Under certain conditions (high ligand concentration), the reaction proceeds wholly in accordance with the Eqn. (10).[76]

In the oxidation of $(Et_3Ge)_3Sb$ in n-octane at 18°C in accordance with the equation

$$2(Et_3Ge)_3Sb + 3O_2 \rightarrow 3(Et_3Ge)_2O + Sb_2O_3 \ ,$$

the autoxidation mechanism varies as a function of association of the initial compound from a reaction without the formation of free radicals (for polyassociated species) to a free-radical chain process [for the monomeric form $(Et_3Ge)_3Sb$].[81,82]

$[(i\text{-}Pr)_3Ge]_2Hg$ oxidises via a free-radical mechanism, which distinguishes this compound from the ethyl analogue. The comparatively high oxidation temperature (approximately 50°C) creates conditions for the thermal homolysis of the peroxy- and hydroxy-derivatives formed in the initial stage [83,84]:

$$i\text{-}Pr_3Ge\,HgOOGe(Pr\text{-}i)_3 \rightarrow i\text{-}Pr_3GeHg^{\cdot} + i\text{-}Pr_3GeOO^{\cdot} \ ;$$
$$i\text{-}Pr_3GeHgOGe(Pr\text{-}i)_3 \rightarrow i\text{-}Pr_3GeHg^{\cdot} + {}^{\cdot}OGe(Pr\text{-}i)_3 \ .$$

The addition of an inhibitor reduces sharply the rate of oxidation of the initial OMC.

The formation of triethylsilyl peroxide in the autoxidation of ethyl(triethylsilyl)mercury is explained by radical reactions [85]:

$$2Et_3SiHgEt \rightarrow Et_2Hg + Et_3SiHg^{\cdot} + Et_3Si^{\cdot} \ ;$$
$$Et_3Si^{\cdot} + O_2 \rightarrow Et_3SiO_2^{\cdot} \ ;$$
$$Et_3SiO_2^{\cdot} + Et_3SiHgEt \rightarrow \begin{cases} \rightarrow Et_3SiOHgEt + Et_3SiO^{\cdot} \\ \rightarrow Et_3SiOOSiEt_3 + EtHg^{\cdot} \end{cases} .$$

A wide variety of products, due to different intermediate and side reactions, are frequently formed in the autoxidation of OMC; particular mention should be made of the processes caused by the reactions of peroxides with OMC. Evidently the knowledge of the nature of these reactions is important for a general understanding of the mechanism of the formation and chemical reactions of OMPC. It is therefore useful to consider in greater detail the reactions of OMC with organic peroxides and the peroxides of organo-element derivatives.

Depending on the nature of the initial compounds and the reaction conditions, the nature of the interaction of OMC with peroxides may vary markedly, the reaction can proceed with or without the formation of OMPC. The mechanism of these processes can be both heterolytic and homolytic and is frequently very complex. An interesting heterolytic reaction of OMC with organic peroxides and peroxides of organo-element derivatives is nucleophilic substitution. It takes place with retention of the O–O bond and is therefore the basis of the principal method for the synthesis of OMPC. The reaction proceeds in accordance with the general equation

$$R_{n-1}MX + R'OOY \rightarrow R_{n-1}MOOR' + XY \ , \qquad (11)$$

where $n \geq 1$, M = metal, R = alkyl or aryl, R′ = metal, hydrogen, or alkyl, X = OH, NH_2, NR_2, halogen, alkyl, aryl, alkoxy-group, aryloxy-group, or another substituent, and Y = metal or hydrogen. In many cases, reaction (11) is reversible and, in order to displace its equilibrium in the required direction, is carried out in the presence of bases (NH_3, amine, pyridine, etc.) or dehydrating agents (anhydrous sodium or magnesium sulphates).

A wide variety of OMPC have been obtained by reaction (11). For example, when organic peroxides were allowed to interact with lithium, sodium, and potassium halides, the pure peroxides of the alkali metals of the type ROOM [R = t-Bu, $(CH_3)_2PhC$, $(CH_3)Ph_2C$, or Ph_3C] were obtained in a crystalline state, which cannot be achieved in their synthesis by other methods [86–90].

Fully alkylated or arylated organocadmium and organomercury compounds react with hydroperoxides and the hydrocarbon group is substituted. The reactions are complicated both by the ready oxidation of the peroxide derived from the initial OMC, which failed to react, and by the peroxide decomposition reactions. In the case of organocadmium compounds, there is a possibility of the formation of mono- and di-peroxy-derivatives, for example PhCdOOBu-t and $Cd(OOBu\text{-}t)_2$.[91] The mercury compounds R_2Hg (R = n- and i-Pr or Ph) react with t-BuOOH to form the monoperoxy-compound only, which cannot be isolated owing to its further reactions under the conditions of the synthesis (at 70–100°C) in accordance with Eqns. (5) and (7).[92–96] Analogous reactions of the intermediate peroxy-compound occur when $RHgCCl_3$ (R = n- and i-Pr or Ph) reacts with t-BuOOH (80°C).[46] Fairly stable organomercury peroxides were obtained from the sodium salt of cumenyl hydroperoxide and ethyl- or phenyl-mercury chloride [97,98] or the derivatives of the latter XC_6H_4HgCl (X = *p*-Cl or *p*-CH_3O) in toluene solution [99]. The less stable compound $PhCH_2HgOOC(CH_3)_2Ph$ [98] and the mercury diperoxide $[Ph(CH_3)_2COO]_2Hg$ were obtained similarly [100].

Fully alkylated or arylated derivatives of aluminium and thallium also readily undergo the substitution of the organic group for the peroxy-group. In the reaction of Ph_3Al with t-butyl or cumenyl hydroperoxides (at room temperature in toluene), the peroxide Ph_2AlOOR was not isolated, since it is readily converted into the aryloxy-derivative [101]. In the reaction of $(EtO)_3Al$ with $Ph(CH_3)_2.COOH$ or of the diethoxy-derivative $(EtO)_2AlCl$ with the salt of this hydroperoxide, the peroxide $(EtO)_2AlOOC.(CH_3)_2Ph$ was isolated and characterised [54,102]. When alkoxy- and alkyl groups are attached to an aluminium atom simultaneously, the alkyl group is substituted by the peroxy-group in the reaction with ROOH:

$$(EtO)_2AlEt + n\text{-}C_8H_{17}CHOOH \rightarrow (EtO)_2AlOOCHC_8H_{17}\text{-}n + EtH \ .$$
$$\qquad\qquad\qquad\quad | \qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\quad OH \qquad\qquad\qquad\quad OH$$

Under the reaction conditions, the peroxide formed is converted into the unstable polymeric peroxide $[-Al(O-)OOCH.(C_8H_{17}O-)]_n$.[103]

Fairly stable peroxides with a Tl–C bond have been obtained from organothallium compounds by nucleophilic substitution reactions. Depending on the reactant ratio, the reaction of Et_3Tl with pure H_2O_2 can give rise to both Et_2TlOOH (in 50% yield), which exists for several hours at 0–5°C, and the organothallium peroxide $Et_2TlOOTlEt_2$, which is stable at room temperature [104]. The peroxides Et_2TlOOR' [R′ = t-Bu or $Ph(CH_3)_2C$], which are stable under the usual conditions, are formed in high yields (60 to 80%) in the reaction of Et_3Tl with the corresponding hydroperoxides (at 0°C in benzene) [105]. The analogous reaction

with triphenylgermyl hydroperoxide gave the organobimetallic peroxide $Et_2TlOOGePh_3$ (80% yield)[104,106]. The hydroperoxide Ph_3SiOOH reacts with Et_3Tl, but the peroxide formed under such conditions rearranges to $Et_2TlOSi(PhO)Ph_2$.[106]

Nucleophilic substitution reactions [Eqn.(11)] have been used particularly successfully for the synthesis of peroxy-compounds of Group IVB elements having the structure R_3MOOR' and the organometallic peroxides $R_3M-OOM'R'_3$, both symmetric and asymmetric, with identical and different central metal atoms. Tertiary hydroperoxides and R_3SiX (X = Cl, Br, or NEt_2) gave, in the presence of bases at temperatures between 0° and −5°C, the stable organosilicon peroxides $R_3SiOOCR'R''R'''$ (R = CH_3, Et, or Ph and R', R'', and R''' = CH_3 or Ph),[107-111] while secondary hydroperoxides gave $R_3MOOCH(CH_3)Ph$ (M = Si, Ge, or Sn; R = CH_3, Et, or n-Pr).[112] Hydrogen peroxide and chlorosilanes react in the presence of ammonia to form symmetrical organosilicon peroxides with identical and different groups attached to the silicon atom, namely $R_3SiOOSiR_3$ (R = CH_3, Et, n-Pr, or Ph)[113,114] and $R_2R'SiOOSiR'R_2$ (R = CH_3 or Ph; R' = CH_3Ph, p-BrC_6H_4, or p-$CH_3OC_6H_4$).[115-117] The asymmetric organosilicon peroxides $Ph_3SiOOSiR_3$ (R = CH_3, Et, n-Pr, n-Bu, n-C_5H_{11}, n-C_6H_{13}, or Ph),[110,118,119] and $Ph_3SiOOSi(CH_3)_2R$ (R = n-Bu, Ph, p-BrC_6H_4, p-$CH_3C_6H_4$, or p-$CH_3OC_6H_4$),[115,120] and the organo-dimetallic peroxides R'R''R'''$SiOOGePh_3$ (R', R'', R''' = CH_3, Ph, Et, n-Pr, n-Bu, or n-C_5H_{11})[118,121,122] have been synthesised by reaction (11) from hydroperoxides of organic derivatives of the elements and alkyl(aryl)silicon halides.

A series of stable dialkyl(aryl)-t-alkylperoxychlorosilanes have been obtained recently by a novel procedure[123]. They are synthesised by the reaction of $RR'SiCl_2$ with t-alkylperoxymagnesium chlorides in molar proportions of 1:1:

$$RR'SiCl_2 + R''OOMgCl \rightarrow RR'Si(OOR'')Cl + MgCl_2\ ;$$

R and R' = CH_3, Et, $CH=CH_2$, CH_2Cl, or Ph;

R'' = t-C_4H_9, or t-C_5H_{11}.

The substitution of the second chlorine atom takes place with difficulty even in the presence of a considerable excess of R''OOMgCl. Peroxides having the structure $RR'Si(OOR'')_2$ are obtained in small amounts under these conditions (approximately 6%). On the other hand, when chloroperoxysilanes are acted upon by alkyl hydroperoxides in the presence of ammonia or pyridine at 0°C, it is easy to obtain diperoxy-compounds derived from silicon and containing identical or different alkylperoxy-groups at the silicon atom[123]:

$$RR'Si(OOR'')Cl + R'''OOH \xrightarrow[(C_5H_5N)]{NH_3} RR'Si(OOR'')(OOR''') + HCl\ ;$$

R and R' = CH_3, Et, or Ph; R'' = t-C_4H_9;

R''' = t-C_4H_9, t-C_5H_{11}, or $C(CH_3)_2C_6H_{11}$.

The reaction of the hydroperoxides Ph_3SiOOH and Ph_3GeOOH with the methyl hemiacetal of chloral (at room temperature in CH_2Cl_2 or $CHCl_3$ as solvent) is also interesting from the synthetic standpoint. The reaction gives fairly satisfactory yields of organosilicon and organogermanium peroxy-compounds containing functional groups in the alkylperoxy-group[124]:

$$R_3MOOH + CH_3OCHCCl_3 \rightarrow R_3MOOCHCCl_3 + CH_3OH\ .$$

(OH on the first CH; OH on the second CH)

When alkoxy or hydroxy-derivatives of alkyltin were used as the starting materials with the corresponding hydroperoxides, the organotin peroxides Et_3SnOOR' [R' = t-Bu or $Ph(CH_3)_2C$] were obtained by reaction (11) and isolated in high yields (approximately 90%)[125]. The peroxide $Et_3SnOOBu$-s was obtained by the same method[126].

The nucleophilic substitution of an isocyanato-group linked to a Group IV element by an alkylperoxy-group has been demonstrated in the reaction of $n\text{-}Bu_3MNCO$ and $n\text{-}Bu_2M(NCO)_2$ (M = Ge or Sn) with t-butyl and cumenyl hydroperoxides. The reaction proceeds readily at room temperature, but is complicated by the side reaction of the hydroperoxides with HNCO.[127]

The lead peroxides Et_3PbOOR' [R' = t-Bu or $Ph(CH_3)_2C$], whose thermal stability is low, are formed from alkoxy-, hydroxy-, or oxo-derivatives of lead and hydroperoxides[128-130]. The solid peroxide $[Et_3PbOO(CH_3)_2C]_2C_6H_4$ was isolated in a fairly pure state after the reaction of Et_3PbOH with the dihydroperoxide derived from p-di-isopropylbenzene[128].

OMPC are not formed in the reactions with hydroperoxides of organolead and organotin compounds having M−M bonds. The metal−metal bond is dissociated, for example[131]:

$$(n\text{-}Bu_2Sn)_n + nt\text{-}BuOOH \rightarrow (n\text{-}Bu_2SnO)_n + nt\text{-}BuOH\ .$$

In the analogous reaction with cumenyl hydroperoxide (at 15−20°C in n-hexane or n-nonane), hexaethyldilead is readily converted into $Et_3PbOC(CH_3)_2Ph$ and Et_3PbOH, which undergo the substitution of their functional groups by the peroxy-group in the presence of an excess of the hydroperoxide[128].

Phenylderivatives of phosphorus(V) and antimony(V) undergo the substitution of one Ph group for the alkylperoxy-group in reactions with hydroperoxides. Pentaphenylantimony (Ph_5Sb) reacts with t-BuOOH and $Ph(CH_3)_2$.COOH at room temperature in absolute pyridine giving a quantitative yield of the stable peroxides Ph_4SbOOR',[132] which can also be obtained in high yields from the hydroperoxide salts R'OOM [M = Na or Li; R' = t-Bu, Ph $Ph(CH_3)_2C$, $Ph_2(CH_3)C$, or Ph_3C] and tetraphenylstibonium halides[133]. The reaction of Ph_5P with t-BuOOH in pyridine, dioxan, or ether proceeds in a more complex manner, but its main pathway (80−85%) also involves the formation of an intermediate peroxide which immediately decomposes[132]:

$$Ph_5P + t\text{-}BuOOH \xrightarrow{-PhH} [Ph_4POOBu\text{-}t] \rightarrow Ph_3PO + PhOH + (CH_3)_2C{=}CH_2\ .$$

In the reactions of Ph_5P or benzyloxytetraphenylphosphorus with Ph_3SiOOH and Ph_3GeOOH, peroxy-compounds were not isolated either, because they isomerised to non-peroxy-products at the instant of formation[134]:

$$Ph_4PR + Ph_3MOOH \xrightarrow{-RH} [Ph_4POOMPh_3] \rightarrow Ph_3P(OPh)OMPh_3\ ;$$

R = Ph, or OCH_2Ph; M = Si, or Ge.

The same hydroperoxides and Ph_3SnOOH react with Ph_4SbBr in the presence of triethylamine to form the organobimetallic peroxides $Ph_4SbOOMPh_3$ (M = Si, Ge, or Sn), which were isolated in a pure form[135]. The mixed diperoxide of antimony and silicon $Ph_3Sb(OOSiPh_3)_2$ can be obtained by treating a mixture of t-butyl hydroperoxide and Ph_3SiOOH with Ph_3Sb:[136]

$$Ph_3Sb + t\text{-}BuOOH + 2Ph_3SiOOH \xrightarrow{-H_2O} Ph_3Sb(OOSiPh_3)_2 + t\text{-}BuOH\ .$$

The attempts to synthesise compounds of the peroxyester type by the nucleophilic substitution of alkyl or functional groups in OMC by acyl hydroperoxides were unsuccessful. The peracyl compounds obtained via the reaction

$$R_{n-1}MX + R'CO_3H \rightarrow R_{n-1}MOOC(O)R' + HX\ ,$$

(M = Hg, Sn, or Ph; R and R' = alkyl or aryl, and X = OH, OR'', or $OCOCH_3$; M = Tl, R = Et, R' = alkyl, and X = Et or OH).

either decompose immediately with liberation of oxygen (organomercury and organothallium derivatives) [104,137-139] or rearrange (organotin and organolead derivatives) [140-143]. Depending on the nature of the group R, for the latter compounds these two pathways can compete [143-146]:

$$R_3MOOC(O)R' \begin{cases} \longrightarrow R_3MOC(O)R' + 0{,}5\,O_2 \\ \longrightarrow R_2(RO)MOC(O)R' \end{cases}.$$

and, for the diperacyl derivative of diphenyltin, they are equally probable [147]. The intermediate diperoxides formed in the reaction of $Et_2Pb(OH)_2$ and $Et_2Sn(OH)_2$ with percapric acid decompose quantitatively to oxygen and the diethylmetal dicaprate [147,148]. Thus the reactions of OMC with peroxides containing an acid hydrogen atom (with hydroperoxides and peracids) lead to the formation of more or less stable OMPC. The reactions of OMC with other peroxy-compounds—alkyl and acyl peroxides and peroxyesters—are more varied. These reactions are not usually accompanied by the formation of OMPC. Depending on the nature of the peroxy-compound and the metal in the OMC, they can proceed either heterolytically or with intermediate formation of reactive OMC–peroxide complexes, which subsequently undergo both heterolytic and homolytic reactions. Such a mechanism is characteristic of the reactions of peroxides with electron-deficient compounds (those of Groups II and III). Many reactions of OMC with peroxides proceed as free-radical chain processes. In the first stage, the peroxide decomposes to free radicals, which then react with the OMC. The reactions of the above peroxides with OMC of Group IV elements takes place in this way. The peroxides can also act as oxidants, for example, in reactions with organic compounds of metals with free electron pairs [phosphorus(III) and antimony(III)]. The reactions of OMC with peroxy-compounds have been examined fairly completely in our previous reviews [2,149] and here we shall therefore merely give a brief survey of the results of studies by the Gorky group of chemists.

The reactions of organolithium compounds with alkyl peroxides involve the heterolysis of the peroxy-group and depend significantly on the nature of the organic group in the OMC and the peroxide. Alkyl-lithium compounds interact with alkyl peroxides to form asymmetric ethers and lithium alkoxides in accordance with the equation

$$RLi + R'OOR' \rightarrow R'OLi + ROR'. \qquad (12)$$

Kinetic studies on the reactions of RLi (R = Et or n-Bu) with t-butyl and cumenyl peroxides [150,151] confirm the earlier hypothesis [152] that the OMC of Group I metals react with alkylperoxides via an S_N2 mechanism:

$$R^{\ominus} \curvearrowright \underset{R'}{O}\!-\!OR' \longrightarrow ROR' + OR'^{\ominus}. \qquad (13)$$

However the interpretation of the mechanism of reaction (12) from the standpoint of one-electron transfer and the formation of a radical pair, reacting both within and outside the solvent cage [153], is also supported by some evidence, for example:

$$EtLi + t\text{-}BuOOBu\text{-}t \rightarrow [Et^{\cdot}, t\text{-}BuO^{\cdot}] + t\text{-}BuOLi.$$

In view of the foregoing, the results obtained in the study of the reactions of compounds of the type R_3MLi with organic peroxides and peroxides of organic derivatives of the elements are of interest [154]. In the series of organobimetallic compounds having an M–M bond, the compounds R_3MLi exhibit the greatest polarity of this bond and behave at the same time as weaker nucleophiles than RLi. The reactions of R_3MLi [M = Ge or Sn; R = Et or $(CH_3)_3SiCH_2$] with t-butyl peroxide, benzoyl peroxide, dicyclohexyl percarbonate, and peroxides of organic derivatives of the elements and organometallic compounds proceed under mild conditions and involve nucleophilic attack by the R_3M anion on one of the peroxide oxygen atoms. In asymmetric peroxides of organic derivatives of the elements, the nature of the nucleophilic cleavage of bonds depends on the nature of the nucleophile, the steric effects of the substituents at the peroxy-group, and other factors.

The reactions of R_3MLi with t-butyl peroxide in tetrahydrofuran (THF) proceed in accordance with Eqn. (13) and the products are t-BuOLi and $R_3MOBu\text{-}t$ [M = Sn or Ge; R = Et or $(CH_3)_3SiCH_2$]. When M = Ge and R = Et, the yield of $Et_3GeOBu\text{-}t$ is low (11%), since the alkoxy-derivative enters in its turn into a nucleophilic substitution reaction with the initial OMC:

$$Et_3GeOBu\text{-}t + Et_3GeLi \rightarrow Et_3Ge\text{—}GeEt_3 + t\text{-}BuOLi. \qquad (14)$$

The compounds R_3MLi ($R_3M = Et_3Ge$), $[(CH_3)_3SiCH_2]_3Ge$, and $[(CH_3)_3SiCH_2]_3Sn$ are involved in reactions (13) and (14) with bis(trimethylsilyl) peroxide, which is known to be more reactive in relation to nucleophiles than t-butyl peroxide.

In the reaction of $[(CH_3)_3SiCH_2]_3SnLi$ with t-butylperoxytrimethylsilane and t-butylperoxytriphenylgermane, the R_3Sn anion attacks the oxygen atom linked to the t-butyl group in the peroxide [154,156]:

$$R_3SnLi + R'_3MOOBu\text{-}t \xrightarrow{THF} R_3SnOBu\text{-}t + R'_3MOLi$$
$$R = (CH_3)_3SiCH_2;\ R'_3M = (CH_3)_3Si,\ \text{or}\ Ph_3Ge.$$

On the other hand, in the reaction of the germyl analogue R_3GeLi with a silyl peroxide, products, the formation of which is probably due to the metallation of the t-butyl group of the peroxide in the initial stage followed by the elimination of isobutene, were obtained in high yields. The oxygen–oxygen bond does not dissociate under these conditions [154]:

$$R_3GeLi + (CH_3)_3SiOOBu\text{-}t \longrightarrow (CH_3)_3SiOOC(CH_3)_2CH_2Li + R_3GeH;$$

$$(CH_3)_3SiO\text{—}\overset{CH_3}{\overset{|}{C}}\text{—}CH_3 \longrightarrow (CH_3)_3SiOOLi + CH_2{=}C(CH_3)_2;$$
$$Li\text{—}CH_2$$

$$R = (CH_3)_3SiCH_2.$$

The reactions of R_3GeLi with $Ph_3GeOOBu\text{-}t$ and $Ph_3GeOOSi(CH_3)_3$ proceed in accordance with Eqn. (13), the R_3Ge anion attacking the oxygen atom linked to the Ph_3Ge fragment of the peroxide, for example:

$$R_3GeLi + Ph_3GeOOSi(CH_3)_3 \rightarrow R_3GeOGePh_3 + (CH_3)_3SiOLi; \qquad (15)$$
$$R = (CH_3)_3SiCH_2.$$

The reaction of the tin analogue with the latter peroxide leads to the formation of the phenylation product:

$$R_3SnLi + Ph_3GeOOSi(CH_3)_3 \longrightarrow \left[\begin{array}{c} Ph \quad Ph \\ | \quad | \\ Ph\text{—}Ge\text{—}O \\ \diagdown \quad \diagup \\ R_3Sn\text{—}Li \quad O\text{—}Si(CH_3)_3 \end{array}\right] \longrightarrow$$

$$\longrightarrow R_3SnPh + Ph_2GeO + (CH_3)_3SiOLi;$$
$$R = (CH_3)_3SiCH_2.$$

The reaction with the symmetric peroxide $Ph_3GeOOGePh_3$ does not involve phenylation and proceeds in accordance with mechanism (15).

Acyl peroxides (benzoyl peroxide and dicyclohexyl percarbonate) and t-butyl perbenzoate interact with R_3SnLi,

the process likewise involving the heterolysis of the peroxy linkage[154]:

$$R_3SnLi + PhC(O)OOR' \xrightarrow{-R'OLi} R_3SnOC(O)Ph \xrightarrow{R_3SnLi} R_3SnSnR_3 + PhC(O)OLi;$$

$R=(CH_3)_3SiCH_2$; $R'=PhC(O)$, t-Bu.

$$R_3SnLi + [C_6H_{11}OC(O)O]_2 \rightarrow R_3SnOC(O)OC_6H_{11} + C_6H_{11}OC(O)OLi$$

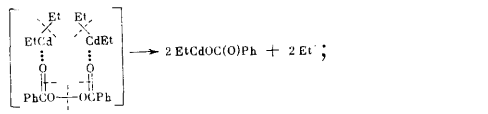
$$R_3SnOC_6H_{11} \xrightarrow{-CO_2} \xrightarrow{R_3SnLi} R_3SnSnR_3 + C_6H_{11}OLi$$

$$C_6H_{11}OC(O)OLi \xrightarrow{H_2O} C_6H_{11}OC(O)OH \rightarrow C_6H_{11}OH + CO_2.$$

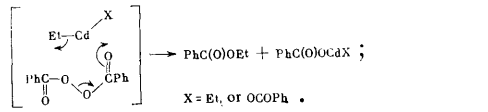
In the similar reactions of R_2Mg (R = Ph or n-C_5H_{11}) with alkyl peroxides, only one Mg–C bond undergoes heterolytic cleavage[61,157-159]:

$$R_2Mg + R'OOR' \rightarrow RMgOR' + ROR'.$$

A characteristic feature of the reactions of organocadmium and organomercury compounds R_2M (M = Cd and R = Et or Ph; M = Hg and R = Ph) with benzoyl peroxide is the formation of 1 : 1 and 2 : 1 donor–acceptor complexes, in which there is a possibility of both heterolytic and homolytic cleavage of bonds[91,160]. The reactions involving the 1 : 1 complex take place without the formation of free radicals, while the M–C and O–O bonds undergo homolytic dissociation in the decomposition of the 2 : 1 complex. For example, in the case of cadmium we have



$\rightarrow$ 2 EtCdOC(O)Ph + 2 Et$^{\cdot}$;



$\rightarrow$ PhC(O)OEt + PhC(O)OCdX;

X = Et, or OCOPh.

$Ph_3SiOCdR$ (R = CH_3 or Et) react similarly with benzoyl peroxide in benzene. The Cd–C and O–O bonds are dissociated in the coordination complexes formed, while the Si–O–Cd linkage persists[43].

The reactions of the dialkylmercury compounds R_2Hg with benzoyl peroxide lead to the formation of a more complex mixture of products. Free-radical processes also play a significant role in the reaction[96,160,161]. Thus, in the reaction of i-Pr_2Hg, benzoic acid, propane, propene, CO_2, and mercury were isolated in addition to isopropylmercury benzoate.

Organomercury compounds react with alkyl peroxides also via OMC–peroxide complexes, which decompose with formation of radicals, initiating the subsequent decomposition of the initial OMC in the reactions of the latter with the solvent[92-94,162]:

$$R_2Hg + \text{t-BuOOBu-t} \rightarrow \left[\begin{array}{c} R-Hg-R \\ \uparrow \\ \text{t-Bu}-\overline{O}-\overline{O}\text{Bu-t} \end{array}\right] \rightarrow RHgOBu\text{-t} + R^{\cdot} + \text{t-BuO}^{\cdot};$$

R=n- or i-Pr.

The reactivity of organic derivatives of Group III elements in relation to alkyl and acyl peroxides is in many respects determined by the nature of the metal. Thus Et_3Al reacts with t-butyl peroxide similarly to organocadmium compounds[163,164]:

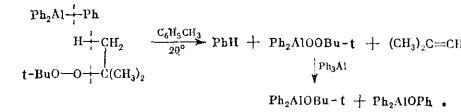
$$2\,Et_3Al + \text{t-BuOOBu-t} \xrightarrow[C_6H_6]{20^\circ} \left[Et_2Al(Et)(AlEt_2)(\text{t-BuO})(OBu\text{-t})\right] \rightarrow 2\,Et_2AlOBu\text{-t} + 2\,Et^{\cdot}.$$

The formation of ether is due to a side reaction involving a heterolytic transformation of the 1 : 1 complex:

$$\left[Et_2Al(Et)(\text{t-BuO})(OBu\text{-t})\right] \rightarrow Et_2AlOBu\text{-t} + EtOBu\text{-t}.$$

The etherate of triethylaluminium and the complex $Et_3Al.Ph_3P$ do not interact with t-butyl peroxide at room temperature[165]. The low reactivity of the Al–C bond in etherates persists also in the compound $(Ph_3Si)_2AlEt$ with the Si–Al bond[166].

In contrast to alkyl derivatives, Ph_3Al reacts with t-butyl peroxide with the intermediate formation of an organoaluminium peroxide, which then reacts with the initial OMC:[101,163]



$Ph_2AlOBu\text{-t} + Ph_2AlOPh$.

Organoaluminium compounds react with acyl peroxides more vigorously than with alkyl peroxides. The reaction of benzoyl peroxide with Et_3Al in solution proceeds even below 0°C.[164,167,168] As for t-butyl peroxide, the reactions proceed with the intermediate formation of donor–acceptor complexes having OMC : peroxide ratios of 2 : 1 and 1 : 1 and decomposing homolytically and heterolytically respectively.

When the alkyl group in an organoaluminium compound is substituted by an alkoxy-group, the probability of heterolytic processes is enhanced. Such behaviour has been noted, for example, in the reaction of dicyclohexyl peroxydicarbonate with $Et_2AlOC_6H_{11}$ and Et_2AlOBu-n and also in the reactions of benzoyl and acetylbenzoyl peroxides with $EtAl(OEt)_2$.[169] However, the reactions of Et_2AlOCH_3 and Et_2AlOBu-s with benzoyl peroxide involve mainly the formation of a 2 : 1 complex, which decomposes homolytically[170]. On the other hand, when aluminium tri-isopropoxide reacts with benzoyl peroxide, the intermediate peroxy-compound is formed[171,172]:

$$(i\text{-PrO})_3Al + [PhC(O)O]_2 \rightarrow [(i\text{-PrO})_3Al \cdot (PhCOO)_2] \rightarrow PhC(O)OAl(OPr\text{-i})_2 + PhC(O)OPr\text{-i}$$

$$\rightarrow PhC(O)OAl(OPr\text{-i})_2 + 0.5O_2. \quad (16)$$

In the reactions of acyl peroxides with the etherate of Et_3Al or the complex $Et_3Al.Ph_3P$ at room temperature, the donor is displaced in the first stage and intermediate 2 : 1 and 1 : 1 complexes are then formed. The ratio of the products of the homolytic and heterolytic decomposition of these complexes depends on the nature of the ligand. Thus $Et_3Al.Ph_3P$ reacts with benzoyl peroxide mainly homolytically, while in the reaction of the etherate the two pathways compete[165]. The complex $(Ph_3Si)_2AlEt.2LiBr.2THF$ reacts with benzoyl peroxide in the same way as with t-butyl peroxide, the process involving the preferential cleavage of the Si–Al bond[166].

Triethylindium and triethylthallium have a reduced electron-accepting capacity. Their reaction with t-butyl peroxide therefore proceeds with much greater difficulty than the reaction of Et_3Al. The reaction of Et_3In with the peroxide begins only at 50°C and Et_3Tl reacts at a still higher temperature (100°C).[173] A complex, which can subsequently decompose heterolytically and homolytically, is also formed in the first stage, for example:

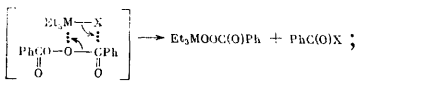
$$Et_3In + \text{t-BuOOBu-t} \rightarrow [Et_3In \cdot \text{t-BuOOBu-t}] \rightarrow \begin{cases} \rightarrow Et_2InOBu\text{-t} + EtOBu\text{-t} \\ \rightarrow Et_2InOBu\text{-t} + Et^{\cdot} + \text{t-BuO}^{\cdot}. \end{cases}$$

The mechanism of the reaction of Et_3Tl with acyl peroxides is analogous to that of the reaction of Et_3Al.[167,174,175]

When one ethyl group in Et_3Tl is substituted by an isopropoxy-group, the reaction with benzoy peroxide (at approximately 20°C) involves the heterolytic cleavage of the Tl–O bond in the organothallium compound and the C–O bond in the peroxide. As in reaction (16), the perbenzoate formed decomposes with liberation of oxygen[176]. The reaction of benzoyl peroxide with a siloxy-derivative of diethylthallium (at 40–50°C) involves the heterolytic dissociation of the Si–O bond in the OMC–peroxide complex with formation of a peracyl derivative of silicon, which rearranges[176]:

$$Et_2TlOSiPh_3 + (PhCOO)_2 \rightarrow Ph_3SiOOC(O)Ph + Et_2TlOCOPh \quad (17)$$
$$\downarrow$$
$$Ph_2(PhO)SiOC(O)Ph .$$

There is a wide variety of reactions of organic compounds of Group IV elements with alkyl and acyl peroxides. The nature of the reactions is determined both by the nature of the heteroatom and by the structure of the organometallic and peroxy-compounds. There is a possibility of reactions involving the intermediate formation of a reactive complex and, as in the alkoxy-derivatives of aluminium and thallium discussed above, in this complex the heterolytic transformations can occur with retention of the O–O bond and the formation of OMPC:[108,177,178]



$$\rightarrow Et_3MOOC(O)Ph + PhC(O)X ;$$

M=Sn; X=OCH_3, OEt, OC_6H_{11}-cyclo, OPh, or OCH_2Ph .

M=Si; X=NEt_2 .

Peresters of organic derivatives of the elements undergo a heterolytic rearrangement (M = Sn or Si) via mechanism (17) and decompose to a slight extent with liberation of oxygen (M = Si). There is also a possibility of the dissociation of the O–O bond in the reaction complex, for example in the reaction of Et_3SnNEt_2 with benzoyl peroxide[108].

The hydrides of Group IV elements having organic substituents (R_3MH) do not react with benzoyl or t-butyl peroxide at room temperature. Their interaction is observed only at the temperature corresponding to the decomposition of the peroxide into radicals. For example, benzoyl peroxide reacts with Et_3SiH in the presence of oxygen and a solvent at 95–97°C. The main reaction products are triethylsilyl benzoate, benzoic acid, and carbon dioxide[179]. Benzoyloxy-radicals decompose or abstract hydride hydrogen from the OMC, forming triethylsilyl radicals $Et_3Si^{\cdot}$:

$$Et_3SiH + PhC(O)O^{\cdot} \rightarrow PhC(O)OH + Et_3Si^{\cdot} ;$$
$$Et_3Si^{\cdot} + PhC(O)OOC(O)Ph \rightarrow Et_3SiOC(O)Ph + PhC(O)O^{\cdot} .$$

The formation of free organosilyl radicals $R_3Si^{\cdot}$ (R = alkyl or aryl) in reactions of silicon hydrides with t-butyl peroxide has been noted[180,181]. Using ESR, it has recently been possible to demonstrate the formation of triorganogermyl radicals R_3Ge in the reaction of R_3GeH (R = alkyl or phenyl) with t-BuO$^{\cdot}$ radicals obtained on photolysis of t-butyl peroxide[182]. The radical mechanism of the reactions of organotin hydrides with alkyl and acyl peroxides has been confirmed by the use of labelled peroxides. It has been established that the reaction involving diacyl peroxide has a chain mechanism and that stannyl radicals ($R_3Sn^{\cdot}$) initiate the decomposition of the peroxide. The reaction of organotin hydrides with t-butyl or t-butyl-cumenyl peroxide has a radical but non-chain mechanism and organometallic radicals do not initiate the decomposition of the peroxide even at a fairly high temperature (130°C).[183,184]

Tetra-alkyl compounds R_4M (M = Si, Ge, Sn, or Pb) also react with t-butyl, benzoyl, or acetylbenzoyl peroxides and with peresters only at the temperature corresponding to the decomposition of the peroxy-compounds into free radicals[179,185–190]. In these reactions, Et_4Si and Et_4Ge behave as hydrogen donors:

$$Et_4M + R^{\cdot} \rightarrow RH + Et_3M\dot{C}_2H_4 ;$$
M=Si, Ge, Sn; R=CH_3, Ph, t-BuO, RC(O)O .

The radicals derived from the peroxides behave in the same way in the reaction with hexaethyldisilane. The Si–Si bond is not dissociated under these conditions[191]:

$$R^{\cdot} + Et_3Si{-}SiEt_3 \rightarrow RH + Et_3Si{-}SiEt_2\dot{C}_2H_4 .$$

Secondary organosilicon radicals recombine, while $Et_3Ge\dot{C}_2H_4$ radicals undergo slight decomposition at the M–C bond in addition to dimerisation[185]:

$$Et_3M\dot{C}_2H_4 \rightarrow C_2H_4 + Et_3M^{\cdot} ;$$
M=Ge, Sn.

The radical $Et_3Sn\dot{C}_2H_4$ does not dimerise and merely decomposes in accordance with the last equation[185,188–190].

The radicals derived from the peroxide do not behave merely as hydrogen acceptors and are capable also of displacing ethyl radicals from the molecule. Only this reaction proceeds with Et_4Pb:[189,190]

$$Et_4M + R^{\cdot} \rightarrow Et_3MR + Et^{\cdot} ; \quad (18)$$
M=Sn, Pb; R=t-BuO, PhC(O)O .

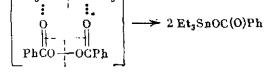
Ethyl radicals disproportionate or react with the initial OMC.

The replacement of the ethyl group in Et_4Sn by a halogen or the benzoyloxy-group does not alter significantly the nature of the interaction with benzoyl peroxide. The formation of all the products detected can be readily accounted for by the free-radical reaction (18). However, this is accompanied by a cryptoradical transformation in the cyclic complex[178,179]. Similar results have been obtained in the reactions of peroxides with tetrapropyl- and tetraisopropyl-tin and in the reaction of t-butyl peroxide with Et_6Sn_2.[189,191]

The reactions of phenyl derivatives of Group IV elements have been hardly investigated. In one of the first studies on these lines[192], it was established that Ph_4Pb does not react with acetyl peroxide, which decomposes and interacts with the solvent. However, in the reaction of $(CH_3)_3SnPh$ with benzoyl peroxide, the bond between the metal and the benzene ring undergoes homolytic cleavage[190]:

$$PhC(O)O^{\cdot} + (CH_3)_3SnPh \rightarrow (CH_3)_3SnOC(O)Ph + Ph^{\cdot} .$$

The reactions of acyl peroxides with organic derivatives of Group IV metals having metal–metal bonds differ markedly from the reactions of R_4M. Thus the interaction of Et_6Sn_2 with benzoyl and acetylbenzoyl peroxides and dicyclohexyl percarbonate proceeds under very mild conditions and is not characterised by the wide variety of products usually observed in free-radical processes. According to some workers[189,193–197], the reaction proceeds via a stage involving the formation of an unstable cyclic complex, for example:



$$\rightarrow 2\,Et_3SnOC(O)Ph ,$$

in which the Sn–Sn and O–O bonds dissociate homolytically without the formation of free-radicals. The absence of any other parallel reactions was confirmed by the determination of the heat of reaction, which proved to be 108 kcal.[198] The cryptoradical mechanism has also been confirmed by the formation of the acetate derivative of the OMC in the reaction with acetylbenzoyl peroxide[195]. Et_6Pb_2 [128,195] and organotin compounds having chains of tin atoms[196,199–202] react similarly with benzoyl peroxide. Polymeric dibutyltin reacts exothermically with benzoyl peroxide, but under these conditions the Sn–Sn bond does not dissociate regardless of the reactant ratio, 1,2-dibenzoyloxy-1,1,2,2-tetrabutyldistannane being formed instead[131].

In the studies on the properties of organobimetallic compounds with M–M′–M groups (M is a Group IVB metal and M′ a metal belonging to another Group), reactions with organic peroxides are also widely investigated in order to be able to compare the behaviour of such compounds and OMC having an M–M bond.

The interaction of $(Et_3Ge)_2Cd$ with t-butyl hydroperoxide in hexane solution (at 0–5°C) proceeds with evolution of heat. The main reaction pathway is the oxidation of the OMC with a side process involving the selective alcoholysis of the OMC by the carbinol formed[203]:

$$(Et_3Ge)_2Cd + t\text{-BuOOH} \rightarrow Et_3GeCdOGeEt_3 + t\text{-BuOH},$$
$$(Et_3Ge)_2Cd + t\text{-BuOH} \rightarrow Et_3GeCdOBu\text{-}t + Et_3GeH.$$

Since $Et_3GeHgOGeEt_3$ is extremely unstable[79] even at temperatures below −20°C, free mercury $(Et_3Ge)_2O$, and t-BuOH were isolated in the analogous reaction of $(Et_3Ge)_2Hg$ with t-BuOOH. The reaction of t-butyl peroxide with $(Et_3Ge)_2Cd$ (at approximately 20°C) led to the isolation of a complex mixture of products, the formation of which can be explained by a mechanism involving one-electron transfer in the complex, where OMC behaves as the electron donor[203]:

$$(Et_3Ge)_2Cd + t\text{-BuOOBu-}t \rightarrow \left[\begin{matrix} Et_3GeCd^{\oplus} \cdot GeEt_3 \\ t\text{-BuO}^{\ominus} \cdot OBu\text{-}t \end{matrix}\right] \rightarrow Et_3GeCdOBu\text{-}t + t\text{-BuO}^{\cdot} + Et_3Ge^{\cdot}.$$

Triethylgermyl radicals dimerise and recombine with t-BuO· radicals. Apart from recombining, decomposing, and abstracting hydrogen, the latter induce the decomposition of the initial OMC:

$$(Et_3Ge)_2Cd + t\text{-BuO}^{\cdot} \rightarrow Et_3GeCdOBu\text{-}t + Et_3Ge^{\cdot}.$$

In contrast to the compound examined, its mercury analogue does not react even under the conditions of the photochemical decomposition of the peroxide[72].

Compounds of the type $[R_3M]_nM'$, where M is a Group IV element and M′ a Group II–VI element, react with acyl peroxides vigorously at room temperature, evolving heat, as in the case of Et_6Sn_2, and involving the intermediate formation of active cyclic complexes, decomposing via a cryptoradical mechanism[149,204,205].

The reactions are described by simple stoichiometric equations. When M′ = Cd, the corresponding metal benzoates are formed[206,207]:

$$(Et_3M_2)Cd + 2\,(PhCOO)_2 \rightarrow Cd\,(OCOPh)_2 + 2\,Et_3MOCOPh$$
$$M=Si \text{ or } Ge.$$

Compounds with Ge–Zn bonds react similarly[208]. In a study of the reaction of bis(triethylgermyl)cadmium with asymmetric peroxides, it was established that the formation of the activated transition complex is preceded by the orientation of the peroxide molecules relative to the polarised Ge–Cd bond[203]:

$$(Et_3Ge)_2Cd + PhC(O)OOR \rightarrow \left[\begin{matrix} Et_3GeCd-GeEt_3 \\ \vdots \quad \vdots \\ PhC(O)O-O-R \end{matrix}\right] \rightarrow Et_3GeCdOC(O)Ph + Et_3GeOR;$$
$$R=CH_3C(O) \text{ or } t\text{-Bu}.$$

The mercury analogues $(Et_3M)_2Hg$ (M = Si or Ge) react in the same way with benzoyl peroxide and dicyclohexyl percarbonate[72,73,209,210]. The intermediate $Et_3MHgOC(O)R$ decomposes quantitatively under these conditions to metallic mercury and the corresponding derivative $Et_3MOC(O)R$:

$$(Et_3M)_2Hg + (RCOO)_2 \rightarrow Et_3MHgOC(O)R + Et_3MOC(O)R$$
$$Hg + Et_3MOC(O)R \leftarrow$$
$$R=Ph \text{ or } OC_6H_{11}\text{-cyclo}.$$

In the analogous reaction of the thallium compound $(Et_3Ge)_3Tl$, the free metal is not liberated and, as for the cadmium compound, the products are the metal benzoates—thallium benzoate and triethylgermanium benzoate[211,212]. The metal M′ is liberated in a free state in the reactions of $(Et_3M)_nM'$ (where M = Si, Ge, or Sn and M′ = Sb, Bi,[213–215] or S, Se, Te [216]) with benzoyl peroxide, the products being the triethylmetal benzoates in accordance with the equations

$$2\,(Et_3M)_3M' + 3\,(PhCOO)_2 \rightarrow 2M' + 6Et_3MOC(O)Ph;$$
$$M=Si, Ge \text{ or } Sn;\ M'=Sb \text{ or } Bi.$$
$$(Et_3M)_2M' + (PhCOO)_2 \rightarrow M' + 2\,Et_3MOC(O)Ph;$$
$$M=Si, Ge \text{ or } Sn;\ M'=S, Se \text{ or } Te.$$

Acetyl peroxide reacts with $(Et_3Si)_2Te$, giving a quantitative yield of elemental tellurium and triethylsilicon benzoate and acetate[216].

The interaction of benzoyl peroxide with ethyl(triethylsilyl)mercury, having a single Si–Hg bond, is described by simple equations[72]:

$$2\,EtHgSiEt_3 + (PhCOO)_2 \rightarrow Et_2Hg + Hg + 2Et_3SiOCOPh.$$

This also applies to the reaction with compounds having several atoms of different metals linked to one another, for example $Et_3GeHgSiEt_3$ and $Et_3GeHgSiEt_2SiEt_3$,[73] and with compounds of the type R_3SiSeH.[217]

The reactions of alkyl derivatives of Group V elements with organic hydroperoxides are regarded as oxidation-reduction processes accompanied by the transition of the central element to the highest valence state and the reduction of the hydroperoxides to the corresponding alcohols. The reaction mechanism involves nucleophilic attack on peroxide oxygen by the OMC with the intermediate formation of an ion pair, for example:

$$R_3Sb: \rightarrow \underset{H}{O}\text{–}OBu\text{-}t \rightarrow \left[R_3\overset{+}{S}bOH\ \ \overset{-}{O}Bu\text{-}t\right] \rightarrow R_3SbO + t\text{-BuOH}.$$

The deprotonation of the 'onium cation in the ion pair leads to the formation of the oxide of the trialkyl derivative of the element (R_3SbO).[218]

In the reactions of trialkylbismuth R_3Bi (R = CH_3 or Et) with t-BuOOH, an ion pair is also formed in the initial stage. However, since the bismuth(V) state is less stable than the anitmony(V) state, the carbon atom attached to the bismuth atom and not hydrogen is subjected to nucleophilic attack in the bismuthonium ion $R_3\overset{+}{B}iOH$. Ultimately the organobismuth compound is dealkylated without a change in the valence of bismuth. When $R_3\overset{+}{B}iOH$ is attacked by

the strongly nucleophilic peroxy-anion formed in the reversible reaction

$$t\text{-BuO}^- + t\text{-BuOOH} \rightleftarrows t\text{-BuOH} + t\text{-BuOO}^-,$$

an asymmetric dialkyl peroxide is produced:

$$t\text{-BuOO}^- + R\text{–}\overset{+}{B}i(OH)R_2 \longrightarrow t\text{-BuOOR} + R_2BiOH.$$

An ether and a carbinol are formed via similar reactions of alkoxide and hydroxide anions. It has also been established that the heterolytic process is accompanied to a slight extent by a homolytic reaction involving the homolysis of bonds induced by the molecules [218]:

$$R_3Bi + O(H)\text{–}OBu\text{-}t \rightarrow [R_3Bi \leftarrow O(H)\text{–}OBu\text{-}t] \rightarrow R^{\cdot} + R_2BiOH + {}^{\cdot}OBu\text{-}t.$$

Phenyl derivatives of phosphorus(III), arsenic(III), and antimony(III) are readily oxidised by t-butyl hydroperoxide to the corresponding oxides Ph_3EO, like the alkyl compounds. The rates of oxidation of Ph_3P and Ph_3Sb are approximately the same, while Ph_3As reacts with the hydroperoxide approximately sixty times more slowly. Such a change in rate has been explained by the presence of two opposed factors: the ability of *d* orbitals to form π bonds with the peroxy-group and the E–O bond energy [219].

In similar reactions with the hydroperoxides Ph_3SiOOH and Ph_3GeOOH, the peroxide oxygen is subjected to nucleophilic attack by triphenylphosphine or triphenylantimony, but, in contrast to alkyl hydroperoxides, the 'onium cation is not deprotonated, a new element–oxygen–element bond being formed [136]:

$$Ph_3E\text{–}O(H)\text{–}OE'Ph_3 \longrightarrow [\overset{+}{Ph_3E}OH \quad \overset{-}{O}E'Ph_3] \longrightarrow Ph_3E(OH)OE'Ph_3;$$

E = P or Sb; E' = Si or Ge.

The symmetrical t-butyl peroxide is less reactive as an oxidant for Ph_3E. Whereas Ph_3P can be nevertheless converted into Ph_3PO at an elevated temperature (110° to 120°C) with formation of di-t-butyl ether, Ph_3As, Ph_3Sb, and Ph_3Bi do not react with t-butyl peroxide under these conditions [155]. Compared with the latter, bis(trimethylsilyl) peroxide is a more powerful oxidant. In the reaction with Ph_3P, Ph_3PO is formed quantitatively after a short time at a temperature as low as 25–60°C. [134,155,220] Ph_3As and Ph_3Sb react just as easily, but with a somewhat lower yield of the oxide product. However, triphenylbismuth is inert with respect to the action of this peroxide too [155]:

$$Ph_3E + (CH_3)_3SiOOSi(CH_3)_3 \rightarrow \left[Ph_3E\begin{matrix}OSi(CH_3)_3\\ OSi(CH_3)_3\end{matrix}\right] \rightarrow Ph_3EO + (CH_3)_3Si\text{–}O\text{–}Si(CH_3)_3;$$

E = P or Sb.

The organometallic peroxide $Ph_4SbOOGePh_3$ reacts similarly with Ph_3P [134] and Ph_3Sb, forming two final products:

$$Ph_3E + Ph_4SbOOGePh_3 \rightarrow \left[Ph_3E\begin{matrix}OSbPh_4\\ OGePh_3\end{matrix}\right] \rightarrow Ph_3EO + Ph_4SbOGePh_3;$$

E = P or Sb.

The foregoing data have shown that the reactions of OMC with oxygen and various peroxides proceed with formation of kinetically independent species having an unpaired electron. Because of this, the OMC–oxygen or OMC–peroxide systems can initiate various chain processes. The initiating capacity of such systems has been studied both in the polymerisation reactions of alkenes and their derivatives and in the reactions of OMC with various substrates. It is impossible to discuss this problem in detail in the present review. As an example, one may quote the initiation of the polymerisation of certain monomers by dialkylmercury or trialkylaluminium in the presence of oxygen [55,221–223] or by a trialkylboron–peroxide system [224] and the initiation of the oxidation of the solvent in the autoxidation of OMC, for example the oxidation of isopropyl alcohol or n-nonane in the reaction involving the oxidation of $i\text{-Pr}_2Hg$. [33,44,45,50] The initiation of the reactions of organomercury compounds of the type R_2Hg (R = alkyl or aryl) with polyhalogenomethanes by oxygen [47], perbenzoic acid [225], t-butyl hydroperoxide and peroxide [93,94], benzoyl peroxide [162,226], and peroxides obtained from cyclohexanone [227] has been noted. Acyl peroxides initiate the reactions of CCl_4 with tetraethylsilane [2,194,228], various organotin derivatives [192,194,195,229–231], and tetraphenyllead [192,230]. The conversion of mercury carboxylates into organomercury compounds, initiated by peroxides, is of interest from the preparative standpoint [232–234].

III. REACTIONS OF ORGANOMETALLIC PEROXY-COMPOUNDS

Organometallic peroxy-compounds are highly reactive. Their chemical reactions can occur in different ways, including both heterolytic and homolytic dissociation of the bonds in the molecule. In many cases, these reaction pathways operate simultaneously. For some peroxy-compounds, the reaction pathway can vary sharply as a function of conditions.

Heterolytic dissociation of the M–O bond in OMPC has been observed in their reactions with H_2O, HCl, and H_2SO_4. Peroxy-compounds of Group I–III elements are very readily hydrolysed by atmospheric moisture [59,88,90,98–100,104,106,235]. Hydroperoxides and organometallic peroxides give rise to the quantitative formation of H_2O_2 in this reaction, for example we have for thallium derivatives [104,106]:

$$\begin{aligned} &Et_2TlOOH + H_2O \rightarrow Et_2TlOH + H_2O_2;\\ &Et_2TlOOTlEt_2 + 2H_2O \rightarrow 2Et_2TlOH + H_2O_2. \end{aligned} \qquad (19)$$

Alkylperoxy-derivatives gives rise to the corresponding hydroperoxides:

$$R_mMOOR' + H_2O \rightarrow R_mMOH + R'OOH, \qquad (20)$$

where M is a Group I–III element. The reaction with hydrogen chloride or its alcoholic solution results in the formation of the corresponding alkyl(aryl) metal halides.

The sensitivity of the peroxides of Group IV elements to hydrolysis depends on the nature of the central metal atom and increases from silicon to lead. The compound Ph_3SiOOH is insensitive to hydrolysis under the usual conditions. In aqueous dioxan in the presence of sulphuric acid, the M–O bond is protolysed both in Ph_3SiOOH [236] and in Ph_3GeOOH and Ph_3SnOOH: [237]

$$Ph_3MOOH + H_2O \xrightarrow{H^+} Ph_3MOH + H_2O_2;$$

M = Si, Ge or Sn.

The acid hydrogen atom in R_3MOOH may be substituted by a fragment comprising an organic derivative of the element in reactions with compounds such as Et_3Tl, [106] Ph_5P, and Ph_4POCH_2Ph, [134] and with Group IV and V metal halides [110,118–122,135,238]. The proton-donating capacity of hydroperoxides decreases in the sequence $Ph_3SiOOH > Ph_3GeOOH > Ph_3COOH > Ph_3SnOOH$ [239] and for triorganosilyl hydroperoxides the sequence is $Ph_3SiOOH > Ph_3COOH > (CH_3)_3SiOOH$. [240]

Organosilicon peroxides of the type R_3SiOOR' and symmetrical and asymmetric peroxides of the type $R_3SiOOSiR'_3$ are fairly resistant to atmospheric moisture. The peroxide

$Et_3SiOOBu\text{-}t$ is slowly hydrolysed by water to silanol and t-BuOOH,[107] while in the presence of acids the hydrolysis is faster.

The reaction of $Ph_3SiOOSbPh_4$ with HCl in benzene differs from the usual heterolysis of the Si–O bond[135]:

$$Ph_3SiOOSbPh_4 + HCl \rightarrow Ph_3SiOOH + Ph_4SbCl .$$

When this peroxide as well as its germyl and stannyl analogues interact with sulphuric acid, both M–O bonds are cleaved and H_2O_2 is formed[135].

All organotin and organolead peroxides are readily hydrolysable. When R_3MOOR' and R_3MOOMR_3 react with H_2O, acetic acid, or HCl, the Sn–O and Pb–O bonds are heterolysed and organic hydroperoxides or H_2O_2 are formed[23,71,128,129,237,241–244], as in reactions (19) and (20). There are isolated examples of the heterolysis of the O–O bond in certain organometallic compounds. Such cleavage of the O–O bond in organosilicon peroxides has been achieved under the influence of nucleophiles [RLi, EtONa, RMgX, and Ph_3E (E = P, As, or Sb)][155].

More typical reactions of OMPC involving the dissociation of the O–O bonds are the homolytic reactions occurring under the influence of heat, light, or radical initiation. The formation of radicals has been demonstrated in the thermal decomposition of the peroxy-compounds of the elements of all the Groups examined. In n-nonane, *m*-xylene, cumene, and t-butylbenzene solutions, Group I metal peroxides decompose at 80–130°C.[86–89,235,245,246] Thus $Ph(CH_3)_2COOLi$ decomposes to the extent of 80% in 3 h at 90°C [235] and the sodium derivative decomposes to the extent of 35% in 1 h at 80°C. The complex $Ph(CH_3)_2.COONa.Ph(CH_3)_2COOH$ is less stable, losing 80% of peroxide oxygen in 1 h at a temperature as low as 65°C.[89] The complex of potassium cumenyl peroxide with cumenyl hydroperoxide is also relatively unstable[245]. The thermal stability of alkali metal arylalkyl peroxides diminishes with increase of the number of phenyl groups. The peroxides decompose with homolysis of the O–O bond in the initial stage:

$$\underset{M=Li,\ Na\ or\ K;\quad R=t\text{-}Bu,\quad Ph(CH_3)_2C\ or\ Ph_2(CH_3)C,\ Ph_3C.}{MOOR \rightarrow MO^{\cdot} + {}^{\cdot}OR ;} \qquad (21)$$

The radicals formed dehydrogenate the solvent:

$$MO^{\cdot} + SH \rightarrow MOH + S^{\cdot} ; \qquad (22)$$

$$RO^{\cdot} + SH \rightarrow ROH + S^{\cdot} . \qquad (23)$$

The tertiary RO· radicals decompose via the usual mechanism:

$$\begin{matrix} R' \\ R''—CO^{\cdot} \\ R''' \end{matrix} \rightarrow R'—\underset{\underset{O}{\|}}{C}—R'' + R'''^{\cdot} \qquad (24)$$

and can give rise to ketones, which in their turn enter into a molecular reaction with the initial OMPC. For example, potassium cumenyl peroxide decomposes to the extent of 60–80% via mechanism (21) and reacts to the extent of 20–40% in accordance with the equation

$$\underset{\underset{O}{\|}}{PhCCH_3} + 3\,Ph(CH_3)_2COOK \rightarrow PhC(O)OK + HC(O)K + 2\,Ph(CH_3)_2COH + Ph(CH_3)_2COK .$$

The thermal stability of mercury monoperoxides $RHgOOR'$ [R' = t-Bu or $Ph(CH_3)_2C$] decreases in the series $R = p\text{-}ClC_6H_4 > Ph > PhCH_2 > p\text{-}CH_3OC_6H_4 > Et > i\text{-}Pr$.[98,247,248] t-Butylperoxy-derivatives of alkyl- and arylmercury are thermally less stable than the corresponding cumenylperoxy-derivatives. The peroxides decompose above 90°C with homolytic dissociation of the O–O bond and the formation of the oxy-radicals R'O· and RHgO·, which, apart from their involvement in reactions (22) to (24), can also initiate the decomposition of the peroxide, for example, we have for $EtHgOOC(CH_3)_2Ph$:[97,248]

$$\begin{matrix} R'O^{\cdot} + EtHgOOC(CH_3)_2Ph \rightarrow R'OH + \\ + {}^{\cdot}C_2H_4HgOOC(CH_3)_2Ph \\ \qquad\qquad \big| \longrightarrow C_2H_4 + HgO + Ph(CH_3)_2CO^{\cdot} ; \\ R' = Ph(CH_3)_2C \text{ or } EtHg . \end{matrix}$$

Apart from dehydrogenating the solvent, the alkylmercuroxy-radicals decompose via the mechanism

$$EtHgO^{\cdot} \rightarrow Et^{\cdot} + HgO .$$

Alkyl radicals recombine and abstract hydrogen from the solvent. Dicumenylperoxymercury decomposes similarly (at 130°C in toluene)[100].

The radical decomposition of OMPC is frequently accompanied by a rearrangement of the peroxides, which can take place at the metal atom or at a tertiary carbon atom in the alkylperoxy-group. The isomeric transformation of the latter type with simultaneous homolytic decomposition has been observed in the photolysis of $EtHgOOC(CH_3)_2Ph$ (λ = 366 nm)[247]:

$$EtHgOOC(CH_3)_2Ph \xrightarrow{h\nu} EtHgOC(CH_3)_2OPh .$$

As already noted, organoaluminium peroxy-compounds, formed in the autoxidation of the alkyl derivatives R_3Al, are very readily converted into the isomeric alkoxy-derivatives when the molecule contains unoxidised groups. Such a possibility is ruled out in the absence of alkyl groups from the aluminium compound.

The compound $(EtO)_2AlOOC(CH_3)_2Ph$ is relatively stable at room temperature. After the hydrolysis of the decomposition products (at 90°C in xylene), $Ph(CH_3)_2COH$, $PhC(O)CH_3$, α-methylstyrene, ethyl alcohol, and aluminium hydroxide were found. It is suggested that these products are formed as a result of a radical reaction of the peroxide[102].

Thallium peroxides constitute an example of OMPC for which the influence of the peroxide structure on the nature of its reaction is a maximum. The decomposition of diethylthallium hydroperoxide is an example of the decomposition of a peroxide with evolution of oxygen. The hydroperoxide, which can be stored at 0–5°C for several hours, decomposes rapidly at room temperature[104]:

$$Et_2TlOOH \rightarrow Et_2TlOH + 0.5O_2 .$$

Peracyl derivatives of thallium also decompose with evolution of oxygen and the formation of the corresponding diethylthallium carboxylates[137,139,249,250]:

$$\underset{R=CH_3,\ n\text{-}C_9H_{19} .}{Et_2TlOOC(O)R \rightarrow Et_2TlOC(O)R + 0.5O_2 ;}$$

The peroxides R_2TlOOR' [R = Et or Ph; R' = t-Bu or $Ph(CH_3)_2C$] decompose in solution in n-nonane, toluene, cumene, and chlorobenzene at 100°C and above with dissociation of the O–O bond and the formation of radicals which are then involved in competing solvent decomposition and dehydrogenation reactions[105,249,250]:

$$R_2TlOOR' \rightarrow R_2TlO^{\cdot} + {}^{\cdot}OR' . \qquad (25)$$

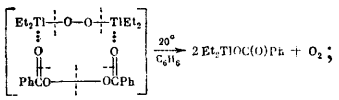
The rate of decomposition increases with the initial concentration, which indicates the presence of an induced decomposition stage in the breakdown process. Apart from spontaneous homolysis via mechanism (25), autocatalytic decomposition of alkylperoxy-derivatives of diphenylthallium by one of the decomposition products (phenylthallium oxide) has been noted[249,250]. In contrast

to tertiary alkylperoxy-derivatives of thallium, $Et_2TlOOEt$ undergoes molecular decomposition in solution in n-octane above 50°C:[59]

$$Et_2TlOOEt \rightarrow Et_2TlOH + CH_3CHO .$$

This results in the formation of diethylthallium hydroxide in a high yield (75–80%) and acetaldehyde (30%), which largely condenses under the influence of thallium hydroxide.

The organothallium peroxide $Et_2TlOOTlEt_2$ and the mixed peroxide of thallium and germanium, which are stable at room temperature, undergo an interesting reaction with benzoyl peroxide[104]:



$$\xrightarrow[C_6H_6]{20^\circ} 2\,Et_2TlOC(O)Ph + O_2 ;$$

$$Et_2TlOOGePh_3 + (PhCOO)_2 \rightarrow Et_2TlOC(O)Ph +$$
$$+ Ph_3GeOC(O)Ph + O_2 .$$

The study of the thermal transformation of the latter peroxide showed that it rearranges but only at the germanium atom and not at the thallium atom. It is interesting that, according to kinetic data, the reaction is bimolecular[106]:

$$Et_2TlOOGePh_3 \xrightarrow[80^\circ]{C_6H_5CH(CH_3)_2} Et_2TlOGe(OPh)Ph_2 \xrightarrow{H^+,H_2O} Et_2TlOH + Ph_2Ge(OH)OPh .$$

The silyl analogue rearranges similarly already during its preparation from Et_3Tl and $Ph_3SiCOOH$.[106]

For the peroxy-compounds of Group IVB elements as well as thallium peroxides, there is a possibility of all types of reactions: spontaneous free-radical decompositions, including radical-induced stages, rearrangement at the central metal atom, and molecular decomposition, which is comparatively uncommon among OMPC.

The thermolysis of Ph_3SiOOH is known[251] to proceed with the homolysis of the O–O bond in the initial stage:

$$Ph_3SiOOH \xrightarrow[>100^\circ]{C_6H_5OCH_3} \left.\begin{array}{l} Ph_3SiO^\cdot + {}^\cdot OH \\ \rightarrow Ph_2(PhO)Si^\cdot \end{array}\right\rightarrow (PhO)Ph_2SiOH . \qquad (26)$$

The formation of phenol among the products is explained by the rearrangement of the $Ph_3SiO^\cdot$ radical.

The decomposition of Ph_3SiOOH in chlorobenzene is catalysed by cobalt(II) salts (the stearate and abietate). The reaction proceeds under conditions where the thermal decomposition via mechanism (26) hardly occurs. The decomposition products are Ph_3SiOH, H_2O, and O_2 and there is no phenol[252]. Kinetic data for the influence of inhibitors and spectroscopic study of the valence transformations of the catalyst established that the decomposition under these conditions proceeds via a radical non-chain mechanism, similar to that of the catalytic decomposition of organic hydroperoxides. Cobalt stearate also catalyses the radical decomposition of Ph_3GeOOH, the rate of which is comparable to the rates of decomposition of the silicon analogue and Ph_3COOH.[253] In contrast to these hydroperoxides, the thermolysis of the least stable Ph_3SnOOH in benzene, toluene, dioxan, or acetonitrile at 10–40°C proceeds via two competing pathways:

$$Ph_3SnOOH \left\{\begin{array}{l} \xrightarrow{k_1} (Ph_2SnO)_x + PhOH \\ \xrightarrow{k_2} Ph_3SnOH + 0.5\,O_2 . \end{array}\right.$$

The ratio of the rates of decomposition varies little in different solvents and the reaction mixture does not catalyse the polymerisation of olefinic monomers[237].

Alkyl triorganosilyl peroxides R_3SiOOR' (R and R′ are alkyl groups) undergo homolytic decomposition on heating to a high temperature (170–200°C).[109,254–256] The dissociation energies of the O–O bond in a series of OMPC, including peroxy-compounds of silicon, have been determined by a thermochemical method[257]. The decomposition of $(CH_3)_3SiOOBu\text{-}t$ in anisole, isopropylbenzene, n-nonane, and decane is described by the equation for first-order kinetics[254,256] and the rate of decomposition of the compounds $(CH_3)_3SiOOR'$, where R = $Ph(CH_3)_2C$, $Ph_2(CH_3)C$, or Ph_3C, increases steadily with increase of the number of phenyl groups[109,256]. The initial stage of the decomposition is homolysis of the O–O bond:

$$(CH_3)_3SiOOR' \rightarrow (CH_3)_3SiO^\cdot + {}^\cdot OR' . \qquad (27)$$

Tertiary alkoxy-radicals react via mechanisms (23) and (24). The radicals $Ph_3CO^\cdot$ and $Ph_2(CH_3)CO^\cdot$, formed via reaction (27) from the corresponding arylalkylperoxysilanes, are not only involved in these reactions but also undergo rearrangement:

$$2\,Ph_3CO^\cdot \rightarrow 2\,(PhO)Ph_2C^\cdot \rightarrow [(PhO)Ph_2C—]_2$$

In contrast to the tertiary alkoxy-radicals $RO^\cdot$, $(CH_3)_3SiO^\cdot$ radicals do not decompose and merely dehydrogenate the solvent:

$$(CH_3)_3SiO^\cdot + SH \rightarrow (CH_3)_3SiOH + S^\cdot . \qquad (28)$$

The decomposition of $Et_3SiOOBu\text{-}t$ in hydrocarbons (nonane, decane) proceeds via a radical mechanism above 140°C, the decomposition products being C_2H_6, C_2H_4, t-BuOH, Et_3SiOH, Et_3SiOR, EtOH, and siloxane[107,258–260]. At 170° to 200°C, the process is complicated by the induced decomposition stage[258,259]. The decomposition of $Et_3GeOOBu\text{-}t$ proceeds similarly[254].

The thermal stability of organosilicon peroxides R_3SiOOR' depends on the nature of the group R. In the series $(CH_3)_3SiOOCH(Ph)CH_3$, $Et_3SiOOCH(Ph)CH_3$, and $n\text{-}Pr_3SiOOCH(Ph)CH_3$, the thermal stability is a maximum for the first peroxide and a minimum for the last (in nonane at 180°C).[112] The thermal stability of the germyl analogues $(CH_3)_3GeOOCH(Ph)CH_3$ and $Et_3GeOOCH(Ph)CH_3$ is higher, the methyl derivative being the most stable[112]. According to kinetic data and the structure of the decomposition products, silyl peroxides incorporating a secondary alkylperoxy-group react simultaneously via three pathways. Apart from the homolytic decomposition in accordance with mechanism (27) and the subsequent reactions of the radicals via mechanisms (23), (24), and (28), the peroxide undergoes a rearrangement at the silicon atom with a synchronous redistribution of bonds in the active cyclic complex:

$$R_3SiOOCH(Ph)CH_3 \rightarrow (RO)R_2SiOCH(Ph)CH_3 ; \qquad (29)$$

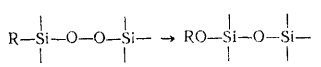
the peroxide also undergoes molecular decomposition to a ketone and silanol[261]:

$$R_3SiOOCH(Ph)CH_3 \rightarrow R_3SiOH + PhC(O)CH_3 ;$$
$$R=CH_3,\ Et,\ n\text{-}Pr.$$

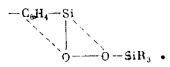
The possibility of the last pathway in the decomposition of the above peroxides has been confirmed by the formation of acetophenone.

The thermal stability of the compounds $Ph_3SiOOCPh_n.(CH_3)_{3-n}$ as well as that of their ethyl analogues decreases as the phenyl groups accumulate in the peroxy-component[110,111]. The peroxide reacts via two simultaneous pathways in accordance with Eqns. (27) and (29); reaction (24) does not occur for $Ph_3SiOOCPh_3$.

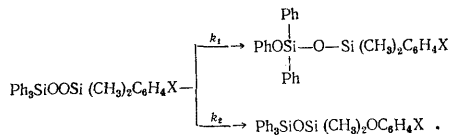
The rearrangements of the OMPC of Group IV elements have been investigated in detail for symmetric and asymmetric organosilicon peroxides and mixed OMPC: $(R_3SiO-)_2$ (R = CH_3, Et, or n-C_6H_{13});[114] $[Ar_n(CH_3)_{3-n}SiO-]_2$ (Ar = Ph, *p*-$CH_3OC_6H_4$, or *p*-BrC_6H_4);[113,115-117] $Ph_3SiOOSiR_3$ (R = CH_3, Et, n-Pr, n-Bu, n-C_5H_{11}, or n-C_6H_{13});[113,118,119,262,263] $Ph_3SiOOSi(CH_3)_2R$ (R = n-Bu, Ph, $CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, or *p*-BrC_6H_4);[113,115,262,264] $R_3SiOOGePh_3$ (R = alkyl or aryl)[118,121,122]. The thermal decomposition of these peroxides has been investigated in the temperature range 70–100°C and in different solvents. In inert solvents, the peroxides are converted into isomeric non-peroxy-compounds—aryl(alkyl)oxydisiloxanes:



The rearrangement is accompanied by the migration of the aryl or alkyl group from the silicon atom to the oxygen atom. The yield of rearrangement products is quantitative. The rate of rearrangement of the peroxides $[Ph_n(CH_3)_{3-n}SiO-]_2$ increases with increase of the number of phenyl groups. The results of kinetic measurements indicate a heterolytic mechanism of the rearrangement. One of the causes of the rearrangement is the effect of the $d\pi-p\pi$ conjugation between the silicon atom and the peroxide oxygen. The electron density deficit at the oxygen atoms increases following the introduction of electron-accepting groups into the moiety attached to silicon. It is noteworthy that the CH_3O and CH_3 groups in the *p*-position in the benzene ring of the peroxides $[p\text{-}XC_6H_4(CH_3)_2SiO-]_2$ increase the rate constants for the rearrangement, the aryl group migrating, which is due to the more effective interaction of the π-electron cloud of the benzene ring with the *p* electrons of the oxygen atom in the cyclic transition complex:

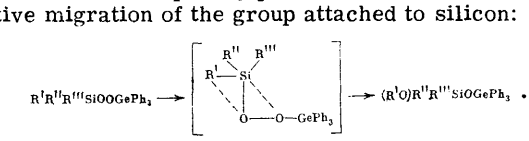


The rearrangement of the peroxides $p\text{-}XC_6H_4(CH_3)_2SiOOSiPh_3$ is a complex reaction proceeding via two pathways[113,264]:



The relative capacities for migration of the aryl groups attached to different silicon atoms were determined by a kinetic method[113]. The rearrangement of the peroxides $Ph_3SiOOSiAlk_3$ proceeds exclusively via the migration of the Ph group from the silicon to the oxygen atom[113,119,262,263], the thermal stability decreasing with increase of the *I* effect of the alkyl groups in the sequence CH_3 > Et > n-Pr > n-Bu.[119]

On heating in the solid state or in solution above 100°C, the mixed organosilicon organogermanium peroxides $R_3SiOOGePh_3$ (R = CH_3, Et, n-Pr, n-Bu, n-C_5H_{11}, or Ph)[118,121,122] and $(CH_3)_2PhSiOOGePh_3$ [121] are quantitatively converted into a non-peroxy product. This involves the selective migration of the group attached to silicon:



The rate of rearrangement increases with increase of solvent polarity and the number of phenyl groups attached to the silicon atom[118,121]. In terms of the rate of isomerisation, the compounds $Alk_3SiOOGePh_3$ can be arranged in the sequence CH_3 < Et < n-Pr < n-Bu < n-C_5H_{11} < Ph.[122] The factors which determine the pathway and rate of the rearrangement are as follows, as in the case of organosilicon peroxides: (1) electron density deficit at the peroxide linkage; (2) nucleophilic properties of the groups attached to silicon; (3) favourable energy of the cyclic transition state.

The relative basicities of peroxides of the type $R_3MOOM'R_3$ (M and M' = Si or Ge; R = alkyl or aryl) and the relative migration capacities of the groups have been estimated spectroscopically[265,266] and the different pathways of the rearrangements undergone by these peroxides have been studied.

Peroxy-compounds of tin, such as the organotin peroxides R_3SnOOR' and the organostannyl peroxides $R_3SnOOSnR_3$, are less stable than the corresponding silicon and germanium peroxides. The nature of the group R' in the peroxide has an appreciable influence on the decomposition of Et_3SnOOR'. When R' = Et, the peroxide decomposes comparatively rapidly in solution at room temperature[69,242,260]. The peroxides $(CH_3)_3SnOOBu\text{-}t$ and $Et_3SnOOBu\text{-}t$ are stable under the same conditions[254,259,260,267]. The main decomposition products of $Et_3SnOOBu\text{-}t$ (in n-dodecane at 170°C) are $(Et_2SnO)_x$, $(Et_3Sn)_2O$, $Et_3SnOH.0.5H_2O$, t-BuOH, CH_3COCH_3, CH_4, C_2H_6, C_2H_4, and the dimerisation product of the dodecyl radical. The decomposition proceeds via radical and induced mechanisms: the initial stage involves the homolysis of the O–O bond:

$$Et_3SnOOBu\text{-}t \rightarrow Et_3SnO^{\cdot} + {}^{\cdot}OBu\text{-}t \quad (30)$$

This is followed by the competing decomposition reactions and the reactions of the radicals with the solvent and the peroxide. Apart from the radical process, the peroxide also undergoes a molecular transformation to $Et_2(EtO)SnOBu\text{-}t$ similar to the rearrangement undergone by silyl peroxides and there is a competing molecular interaction of the initial peroxide with the solvent[268]:



The peroxide decomposition products at low initial concentrations indicate the absence of free $Et_3SnO^{\cdot}$ radicals. With increase of the concentration of the peroxide and temperature, the yield of products resulting from the radicals formed via mechanism (30) increases. The thermolysis of the peroxide is accelerated by the addition of $(Et_2SnO)_x$ and $(Et_3Sn)_2O$, which are involved in the radical reaction[269].

In connection with the possible formation of peroxides on oxidation of Et_4Sn and Et_6Sn_2, the influence of these compounds on the decomposition of organotin peroxides was studied. The addition of Et_4Sn to a solution of $Et_3SnOOBu\text{-}t$ in n-decane (at 160°C) hardly alters the rate of decomposition of the peroxide, while the addition of Et_6Sn_2 greatly accelerates the decomposition. The reaction products are the same as in the decomposition of the peroxides in pure decane, but their proportions are altered[267]. In the presence of Et_6Sn_2, the compound $Et_3SnOBu\text{-}t$ is formed in addition. The reaction has a radical chain mechanism with initial decomposition via mechanism (30). The radicals attack both the solvent and the OMC molecules, $Et_3SnO^{\cdot}$ radicals reacting preferentially with Et_4Sn, displacing Et· radicals, rather than abstracting hydrogen:

$$Et_3SnO^{\cdot} + Et_4Sn \rightarrow Et_3SnOSnEt_3 + Et^{\cdot}.$$

In the decane–Et_6Sn_2 system, the radical decomposition is accompanied by the molecular interaction of the peroxides with the OMC:

$$Et_3SnOOBu\text{-}t + Et_3SnSnEt_3 \rightarrow Et_3SnOSnEt_3 + Et_3SnOBu\text{-}t .$$

The tin peroxide $Et_3SnOOBu$-s, containing a secondary group, is less stable than the t-butylperoxy-derivative [126] and also less stable than its germanium and silicon analogues. In solution in n-dodecane, the decomposition is a first-order reaction with formation of $(Et_2SnO)_x$, $(Et_3Sn)_2O$, $CH_3C(O)Et$, and C_2H_6. A kinetic study showed that, in n-nonane, isopropylbenzene, and anisole (at 150° to 200°C), a rearrangement and molecular decomposition take place in addition to radical decomposition:

$$Et_3SnOOBu\text{-}s \rightarrow (EtO)\,Et_2SnOBu\text{-}s ,$$
$$Et_3SnOOBu\text{-}s \rightarrow Et_3SnOH + CH_3C(O)Et .$$

Molecular decomposition has also been suggested for the tin peroxide $Et_3SnOOCH_2Ph$ with a primary alkylperoxy-group, formed in solution on photochemical oxidation of Et_3SnCH_2Ph by oxygen [67]:

$$Et_3SnOOCH_2Ph \rightarrow Et_3SnOH + PhCHO .$$

Organotin peroxides with tertiary and secondary arylalkyl groups attached to peroxide oxygen, $Et_2SnOOC(CH_3)_2Ph$ and $Et_3SnOOCH(CH_3)Ph$, are less stable than the corresponding silicon and germanium derivatives [112,269]. The decomposition of the first peroxide (in octane at 140–170°C) is a first-order reaction. The products are determined by the reactions of the $Et_3SnO^{\cdot}$ and arylalkoxy-radicals formed via mechanism (30). The peroxide also undergoes the decomposition induced by the solvent radicals [125,260,267,270], for example:

$$Et_3SnOOC(CH_3)_2Ph + S^{\cdot} \xrightarrow{-SH} CH_3\dot{C}HSnEt_2OOC(CH_3)_2Ph \rightarrow$$
$$\rightarrow C_2H_4 + Et_2SnO + Ph(CH_3)_2CO^{\cdot} .$$

The thermal stability of the phenyl derivative $Ph_3SnOOC(CH_3)_2Ph$ is also lower than that of the germanium and silicon analogues. The peroxide decomposes at a measurable rate at a temperature as low as 130°C. Whereas homolytic decomposition of $Ph_3MOOC(CH_3)_2Ph$ (where M = Si or Ge) at the O–O bond is accompanied by the simultaneous isomeric transformation into the phenoxy-derivative $(PhO)Ph_2MOC(CH_3)_2Ph$, the organotin peroxide does not react under comparable conditions in anisole at 130°C. The radical mechanism includes the formation of $Ph(CH_3)_2CO^{\cdot}$ and $Ph_3SnO^{\cdot}$ radicals, the former giving rise to the induced decomposition of the peroxide:

$$Ph_3SnOOC(CH_3)_2Ph + Ph(CH_3)_2CO^{\cdot} \rightarrow Ph_3SnO^{\cdot} + Ph(CH_3)_2COOC(CH_3)Ph ,$$

and the latter being capable of decomposition with ejection of the Ph$^{\cdot}$ radical, instead of the $Ph_3SiO^{\cdot}$ and $Ph_3GeO^{\cdot}$ radicals [271]:

$$x\,Ph_3SnO^{\cdot} \rightarrow (Ph_2SnO)_x + x\,Ph^{\cdot} .$$

The organostannyl peroxides $R_3SnOOSnR_3$ are thermally less stable than the peroxides of the type R_2SnOOR'. For example, $Et_3SnOOSnEt_3$ [61,63,241,243,244,272] decomposes at 0°C in the course of one day and explodes at 60°C. The decomposition in solution in n-nonane (at 20–80°C) proceeds with the quantitative formation of Et_2SnO and $EtOSnEt_3$ as the final products. The reaction follows first-order kinetics and is induced by the radicals derived from the peroxide:

$$Et_3SnOOSnEt_3 \rightarrow 2\,Et_3SnO^{\cdot} ;$$
$$Et_3SnOOSnEt_3 + Et_3SnO^{\cdot} \rightarrow Et_3SnOEt + Et_3SnOO\dot{S}nEt_2 ;$$
$$Et_3SnOO\dot{S}nEt_2 \begin{cases} \rightarrow Et_2SnO + Et_3SnO^{\cdot} \\ \xrightarrow{Et_3SnO^{\cdot}} 2\,Et_2SnO + Et_3SnOEt \end{cases} .$$

The peroxide gives rise to the polymerisation of acrylonitrile and methyl methacrylate.

Among all the peroxides of Group IVB elements, the thermal stability of the organolead peroxides is lowest. Thus $Et_3PbOOBu$-t and $Et_3PbOOC(CH_3)_2Ph$ decompose slowly even at room temperature and rapidly with evolution of a gas on heating [69,128,129,243]. The decomposition has a radical mechanism and the reaction mixtures catalyse the polymerisation of olefins [69]. The autocatalytic decomposition of $Et_3PbOOBu$-t has been noted (in hydrocarbons at 90–120°C), the rate of reaction increasing with increase of the initial concentration of the peroxide [254].

The peroxide $Ph_3PbOOC(CH_3)_2Ph$ is the least stable of the compounds obtained in the $Ph_3MOOC(CH_3)_2Ph$ series (M is a Group IV element) [271]. Very little benzene has been found in the autocatalytic decomposition products, since the $Ph_3PbO^{\cdot}$ radicals do not decompose like the $Ph_3SnO^{\cdot}$ radicals, giving rise to Ph_3PbOH as a result of the dehydrogenation of the solvent. The autocatalysis is due to the presence of diphenyl-lead oxide, formed as a result of the reactions of the hydroxide:

$$2\,Ph_3PbOH \rightarrow (Ph_3Pb)_2O + H_2O ;$$
$$x\,(Ph_3Pb)_2O \rightarrow x\,Ph_4Pb + (Ph_2PbO)_x .$$

The addition of the oxide not only shortens the induction period, but also accelerates the decomposition of the peroxide owing to the formation of the less stable oxoperoxide [271]:

$$Ph_3PbOOC(CH_3)_2Ph + (Ph_2PbO)_x \rightarrow Ph_3Pb(OPbPh_2)_xOOC(CH_3)_2Ph .$$

Radical and heterolytic reactions are characteristic of the peroxy-compounds of Group V elements, as for the peroxides of Group IV elements already mentioned. The homolytic decomposition of organoantimony peroxides Ph_4SbOOR' (R' is a tertiary group) has been achieved under the influence of ultraviolet light [273], for example:

$$Ph_4SbOOBu\text{-}t \xrightarrow{h\nu} Ph_4SbO^{\cdot} + {}^{\cdot}OBu\text{-}t ;$$
$$Ph_4SbO^{\cdot} \rightarrow Ph_3SbO + Ph^{\cdot} .$$

In their interaction with the solvent (toluene and chlorobenzene) via a radical substitution mechanism, the Ph$^{\cdot}$ and t-BuO$^{\cdot}$ radicals give rise to benzene, a carbinol, and a mixture of isomeric methylbiphenyls or chlorobiphenyls. The decomposition of the peroxide induced by the solvent radicals has been noted in chlorobenzene as a side reaction. In chloroform, the stages involving the induced decomposition and photolysis of the peroxide at the O–O bond compete: in carbon tetrachloride, the induced decomposition is the main reaction pathway:

$$CCl_4 \xrightarrow{h\nu} Cl^{\cdot} + {}^{\cdot}CCl_3 ;$$
$$Ph_4SbOOR' + Cl^{\cdot} \rightarrow Ph_4SbCl + [{}^{\cdot}OOR'] .$$

The $^{\cdot}CCl_3$ radicals frequently recombine and frequently interact with the peroxide:

$$Ph_4SbOOR' + {}^{\cdot}CCl_3 \rightarrow Ph_4SbCCl_3 + [{}^{\cdot}OOR']$$
$$\rightarrow Ph_4SbCl + :CCl_2 .$$

The addition of cyclohexene to $CHCl_3$ or CCl_4 lowers the contribution of the induced decomposition.

Under thermal decomposition conditions (in polar and non-polar solvents at 100°C), the peroxides Ph_4SbOOR' [R' = t-Bu, $Ph(CH_3)_2C$, $Ph_2(CH_3)C$, or Ph_3C] isomerise quantitatively to a non-peroxy product with migration of one phenyl group from the antimony atom to the oxygen atom [133]:

$$Ph_4SbOOR' \rightarrow Ph_3Sb(OPh)OR' \xrightarrow{2HCl} Ph_3SbCl_2 + PhOH + R'OH .$$

The solvent is not involved in this reaction.

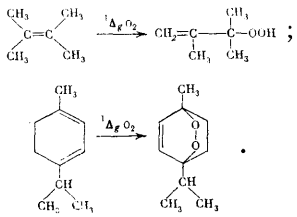
The mixed peroxides involving antimony and a Group IV element behave similarly on heating to 100°C in the solid state or in solution. The rearrangement again takes place at the antimony atom [135]:

$$Ph_4SbOOMPh_3 \xrightarrow{100^\circ} Ph_3Sb(OPh)OMPh_3 \rightarrow Ph_3SbO + Ph_3MOPh\ ;$$
$$M=Si,\ Ge\ or\ Sn.$$

Molecular decompositions are also possible for the peroxy-compounds of antimony. Bis(triphenylbromo-antimony) peroxide $Ph_3(Br)SbOOSb(Br)Ph_3$ is fairly stable at room temperature in the crystalline state, but decomposes rapidly in solution. Two independent reactions then occur: molecular decomposition with elimination of oxygen and a rearrangement with simultaneous cleavage of the O–O bond and the migration of the Ph group from antimony to oxygen:

$$Ph_3(Br)SbOOSb(Br)Ph_3 \rightarrow Ph_3(Br)SbOSb(Br)Ph_3 + 0.5\ O_2\ ;$$
$$Ph_3(Br)SbOOSb(Br)Ph_3 \rightarrow Ph_2(PhO)(Br)SbOSb(Br)Ph_3\ .$$

The contribution of the decomposition of the peroxide via mechanism (31) is greater the higher the concentration of the peroxide in solution. It is of interest that the oxygen evolved is in an excited state and enters into reactions typical of singlet oxygen. In the decomposition of the peroxide in chlorobenzene with added tetramethylethylene or α-terpinene at 70°C, oxygen is hardly evolved, the product being 3-hydroperoxy-2,3-dimethylbut-1-ene or ascaridole respectively [274]:



The above brief review shows that OMPC constitute a very interesting class of compounds. However, in contrast to their formation and thermal decomposition reactions, the chemical reactions of the peroxides have been little investigated. One can state with confidence that new data will be obtained in the immediate future on the reactivities, structures, and the analysis of these compounds, and that practical applications will be suggested.

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