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Arbuzov Institute of Organic and
Physical Chemistry, USSR Academy
of Sciences, Kazan

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PROGRESS IN THE STUDY OF THE OXIDATION OF ORGANOMETALLIC COMPOUNDS

T. G. Brilkina and V. A. Shushunov

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1. INTRODUCTION

The chemistry of organometallic compounds has a history of more than one hundred years. Various organic compounds of zinc [1,2], boron [3,4], lead [5], and tin [6,7] were prepared as early as the middle of last century. A number of methods have now been developed, for the preparation of a variety of organic derivatives of a given metal, including those containing several atoms of different metals.

Considerable attention has been and is being paid to the study of the properties and reactions of organometallic compounds, since these compounds and their reactions are of considerable theoretical and practical interest. One of the most important reactions of organometallic compounds is their oxidation by oxygen and peroxides. It is well known that certain organometallic compounds, for example those of magnesium, zinc, and boron, are oxidised extremely readily by oxygen, but systematic studies in this direction were begun only in the last ten years.

Recent studies [8-15] have shown conclusively that the reaction of organometallic compounds with oxygen is accompanied by the formation of organometallic peroxides, which subsequently undergo various types of rapid conversion, including reaction with the original organometallic compounds. It has thus become necessary to study the reactions of organometallic compounds with various peroxides.

Systematic studies of the reactions of organometallic compounds with oxygen and peroxides are being carried out successfully in the USSR and abroad. The comprehensive, systematic, and detailed studies of Razuvaev are outstanding.

2. OXIDATION OF ORGANOMETALLIC COMPOUNDS WITH OXYGEN

Organometallic compounds differ extremely widely in their behaviour towards oxygen. Organic compounds of the alkali and alkaline-earth metals, zinc, cadmium, boron, aluminium, and titanium are often spontaneously flammable even at room temperature, whereas organic derivatives of germanium, tin, and lead have a high stability towards oxygen under ordinary conditions; organosilicon compounds are oxidised extremely slowly by oxygen even at elevated temperature.

The reactivity is undoubtedly influenced greatly by the energy of the metal–carbon and metal–oxygen bonds and by the electronic structure of the metal atoms in the organometallic compounds. In the reactions of these compounds with oxygen an important part may also be played by the formation of inorganic and organic peroxides and various complexes and associates, and also by temperature and the nature of the solvent.

It is not yet possible to put forward a fully substantiated single mechanism for the oxidation of all organometallic compounds by oxygen. This is due chiefly to the fact that there are no published data characterising quantitatively the influence of the above factors on the rate of the reaction of organometallic compounds with oxygen. For example, the energy of the metal–carbon bond is known only for a very small number of compounds [16]. Despite the difficulties, however, it is worth summarising the extensive information obtained by many workers on the oxidation of organometallic compounds by oxygen and trying to distinguish the characteristic features of the mechanism of these reactions. No one has yet undertaken this task, although the mechanism of the oxidation by oxygen of the organic compounds of certain metals, chiefly alkali metals, has been examined in a number of papers [17,18].

The oxidation of organometallic compounds by oxygen is a complex process involving several elementary chemical-conversion stages, the number of which depends on the specific conditions under which the reaction is carried out. Various intermediate or final stable products of the chemical transformation of organometallic compounds may be formed, depending on these conditions.

It is appropriate to consider first of all the oxidation by oxygen of those organometallic compounds which undergo this reaction very readily at room temperature or at even lower temperatures. The most characteristic feature of this group of compounds is that the formation of organometallic peroxides is much more rapid than their subsequent transformation. This relationship between the rates

of formation and decomposition of the organometallic peroxides makes it possible to use the reaction of organometallic compounds with oxygen to prepare various organic peroxo-compounds, and this is of interest in preparative chemistry.

It is assumed [14,19-21] that the first elementary step in the reaction of organometallic compounds with oxygen is the formation of an oxygen-containing complex:

$$RM + O_2 \rightleftarrows RM \cdot O_2 \qquad (1)$$

where M is a univalent metal atom and R an alkyl or aryl group.

The assumption that organometallic compounds form an oxygen-containing complex finds considerable justification in the fact that the organic compounds of many metals form stable complexes with ethers, amines, and certain other compounds. Moreover, in many cases very stable complexes consisting of the organic compounds of two different metals are formed.

The stability of the complex formed according to reaction (1) undoubtedly depends on a number of factors, particularly the nature of the original organometallic compounds. It is possible that under appropriate conditions these complexes will be fairly stable, and their dissociation to give the original products will take place slowly, so that their existence may somehow be proved. Some years ago an attempt was made to confirm experimentally the formation of a complex of this type in the oxidation of tri-n-butylboron with oxygen [20]. The results indicated unambiguously that the reaction mixture contained the stable complex $(C_4H_9)_3B \cdot O_2$. More careful experiments by other workers [22] showed convincingly, however, that the earlier results [20] were not reproducible and were therefore erroneous. Thorough examination of the results obtained by other workers in the study of the oxidation of organoboron compounds by oxygen leads to the conclusion that only unstable oxygen-containing complexes are formed in this reaction.

The complex formed may undergo subsequent rearrangement with formation of the corresponding organometallic peroxide [17]:

$$RM \cdot O_2 \rightarrow \begin{matrix} R^{-\delta} & O^{+\delta} & R{-}O \\ | & \cdot\ \| & \rightarrow\ | \\ M^{+\delta} & O^{-\delta} & M{-}O \end{matrix}. \qquad (2)$$

Rearrangement takes place in exactly the same way in the organometallic compounds of bivalent and tervalent metals:

$$R_2M \cdot O_2 \rightarrow RMOOR, \qquad (3)$$

$$R_3M \cdot O_2 \rightarrow R_2MOOR. \qquad (4)$$

We can represent the further oxidation of RMOOR, R_2MOOR, and $RM(OOR)_2$ in analogous fashion, with the formation of $M(OOR)_2$, $RM(OOR)_2$, and $M(OOR)_3$ respectively.

The formation of organometallic peroxides has been observed in the oxidation by oxygen of many organometallic compounds. As early as 1890 it was established that the reaction of diethylzinc with oxygen was accompanied by the formation of a peroxo-compound assumed to have the composition $C_2H_5ZnOOC_2H_5$. [23] In this case, however, the product was definitely not an organometallic peroxo-compound but a peroxo-compound of the diethyl ether used as solvent.

The oxidation by oxygen of the alkyl derivatives of the alkali and alkaline-earth metals, zinc, boron, and aluminium in a number of cases can be carried out in such a way that the yield of the resulting organometallic peroxides reaches 70–90%. [10,11] This makes it possible to use the reaction of organometallic compounds with oxygen to prepare alkyl hydroperoxides, which can be isolated from the reaction mixture after hydrolysis of the organometallic peroxides. This method sometimes has considerable advantages over other methods for the preparation of alkyl hydroperoxides.

Depending on the conditions of oxidation, the organometallic peroxides formed may subsequently undergo various transformations, particularly reaction with the original organometallic compound to form the alkoxide:

$$RM + MOOR \rightarrow 2MOR. \qquad (5)$$

The reaction of organic derivatives of bivalent and tervalent metals is analogous.

Organometallic peroxides may undergo not only intermolecular but also intramolecular reactions:

$$RMOOR \rightarrow M(OR)_2, \qquad (6)$$

$$R_2MOOR \rightarrow RM(OR)_2, \qquad (7)$$

$$RM(OOR)_2 \rightarrow (RO)_2MOOR, \qquad (8)$$

$$R(RO)MOOR \rightarrow M(OR)_3. \qquad (9)$$

It is next necessary to consider the possibility of reaction between the organometallic peroxides and the intermediate or final products of their transformation. Reaction in this case is accompanied by the rupture of carbon–carbon or carbon–hydrogen bonds. Finally, there is a definite probability of reaction between the organometallic peroxides and the solvent.

Thus a high yield of organometallic peroxides in the oxidation of organometallic compounds by oxygen can be obtained only when the reaction is carried out under definite conditions (low temperature, low concentration of oxidisable organometallic compounds, and relatively high oxygen concentration in the solution). These conditions are necessary in order that the rate of formation of the organometallic peroxides may exceed appreciably the rate of their transformation in a given direction.

The elucidation of regularities in the oxidation of organometallic compounds by oxygen might be facilitated considerably by kinetic studies of this reaction. Very few such studies have been made, so that information on the mechanism of the reaction of organometallic compounds with oxygen can be obtained only from papers giving the yields of the compounds formed when the reaction is carried out under certain conditions. In a number of cases these data are undoubtedly insufficiently reliable, since some of the products of the oxidation of organometallic compounds by oxygen, for example organometallic peroxides, are unstable compounds and their yield depends on the duration of the experiment.

The formation of organometallic peroxides in the reaction of the alkyl derivatives of metals with oxygen has been demonstrated by many workers, although in the great majority of cases the peroxo-compounds were not isolated from the reaction mixture. The situation is quite different for the oxidation by oxygen of aryl derivatives of metals. In this case attempts have been made to detect hydroperoxides or peroxides containing a peroxo-group directly attached to an aromatic radical, formed in the oxidation of the corresponding organometallic compounds [10,24]. However, no definite results have been obtained. It has been found [10] that the oxidation of phenylmagnesium halides, *p*-bromophenylmagnesium bromide, and mesitylmagnesium

bromide with oxygen in diethyl ether at -75° gives peroxo--compounds in yields amounting to 1–9% of the calculated quantity, but these compounds were not isolated from the reaction mixture and identified, and their presence was established only by iodometric titration.

Other workers [24] made a more thorough study of the oxidation of aryl compounds of lithium and magnesium, and established that the reaction of phenylmagnesium halides with oxygen in diethyl ether even at -120° takes place without the formation of peroxo-compounds. The oxidation of 9-anthryl-lithium in very dilute solution at -75° was accompanied by the formation of peroxo-compounds, hydrolysis of which gave 9.6 mole % of hydrogen peroxide and 14 mole % of an unidentified organic peroxide. The oxidation of anthrylmagnesium bromide with oxygen led to the formation of peroxo-compounds whose hydrolysis gave only hydrogen peroxide (12.5 mole %). [24]

Thus the results cited are not unambiguous, as the authors themselves point out. It may be suggested that the peroxo-compounds formed are oxidation products of the solvent. This suggestion is supported by the fact that benzoic acid was formed in the reaction of phenylmagnesium halides with oxygen; the benzoic acid is apparently a product of the oxidation of 1-phenylethanol, whose presence in the reaction mixture was also established. Hydrogen peroxide probably results from the hydrolysis of lithium peroxide or magnesium peroxide. The formation of these peroxides in the oxidation of the corresponding aryl derivatives with oxygen is quite possible, although unfortunately this possibility was not investigated in the works cited.

If the formation of organometallic peroxides took place only by reactions (1)–(4) and their transformation only by reactions (5)–(9), formation of hydrocarbons should not be observed in the oxidation of organometallic compounds by oxygen or air. However, the formation of hydrocarbons R–R and R–H has been observed repeatedly in these processes. For example, in the oxidation of phenyl-lithium with oxygen in benzene, biphenyl and lithium phenoxide were isolated in approximately equal quantities as the chief reaction products [25]. The oxidation of tolyl-lithium with oxygen in diethyl ether was accompanied by the formation of a number of compounds, including toluene and products of the dimerisation of tolyl radicals [26]. The formation of biphenyl was also observed in the oxidation by oxygen of phenylmagnesium bromide [27-29], diphenylmagnesium [30], diphenylzinc [30,31], diphenylmercury [32], and triphenylaluminium [33]. The yield of biphenyl depended to a marked extent on the reaction conditions, chiefly the nature of the solvent used. In the oxidation of phenylmagnesium bromide with oxygen in diethyl ether, benzene was formed in 10.6% yield. The oxidation of diphenylzinc with oxygen at room temperature was also accompanied by the formation of benzene, in 28% and 32% yield in cyclohexane and chloroform respectively. When the reaction was carried out in carbon tetrachloride, the product was not benzene but chlorobenzene, in 58% yield [31].

The formation of hydrocarbons in the oxidation of various organometallic compounds in the liquid phase by oxygen can readily be explained if we assume that this reaction takes place partly or entirely by a free-radical mechanism. Such a mechanism may involve the following elementary stages:

$$RM \cdot O_2 \longrightarrow R^{\cdot} + MOO^{\cdot}, \quad (10)$$

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}, \quad (11)$$

$$RM + ROO^{\cdot} \longrightarrow MOOR + R^{\cdot}, \quad (12)$$

$$RM + MOO^{\cdot} \longrightarrow MOOM + R^{\cdot}, \quad (13)$$

$$SH + R^{\cdot} \longrightarrow RH + S^{\cdot}, \quad (14)$$

$$R^{\cdot} + R^{\cdot} \longrightarrow R_2, \quad (15)$$

$$R^{\cdot} + R^{\cdot} \longrightarrow RH + R_{-H}, \quad (16)$$

$$R^{\cdot} + S^{\cdot} \longrightarrow RS, \quad (17)$$

$$S^{\cdot} + S^{\cdot} \longrightarrow S_2. \quad (18)$$

Here SH represents the solvent or another compound present in the reaction mixture.

When R is an alkyl radical, reaction (11) takes place very readily with a low activation energy, so that in the oxidation of alkyl derivatives of metals, reactions (14)–(18) play a significant part only at very low concentrations of oxygen in the reaction mixture. Chain termination in the oxidation of alkyl derivatives of metals with oxygen takes place chiefly with the participation of peroxy-radicals.

If the rate of reaction (12) is much greater than the rate of reaction (13), the oxidation of an organometallic compound by oxygen gives chiefly the organometallic peroxide, not the metal peroxide.

The peroxo-compounds formed in reactions (12) and (13) may interact with the original organometallic compounds by reactions (5) and (19).

$$RM + MOOM \rightarrow MOM + ROM. \quad (19)$$

The situation is quite different when R is an aryl radical. Oxygen does not add on to aryl radicals with the formation of peroxy-radicals, so that reactions (14), (15), (17), and (18) play an important part in this case. The oxidation of these organometallic compounds by oxygen may involve the elementary stages (10), (13), and (20)–(27).

$$RM + MOO^{\cdot} \longrightarrow MOM + RO^{\cdot}, \quad (20)$$

$$RM + RO^{\cdot} \longrightarrow MOR + R^{\cdot}, \quad (21)$$

$$MOOM + R^{\cdot} \longrightarrow MOR + MO^{\cdot}, \quad (22)$$

$$RM + MO^{\cdot} \rightarrow MOM + R^{\cdot}, \quad (23)$$

$$MOO^{\cdot} + R^{\cdot} \longrightarrow RO^{\cdot} + MO^{\cdot}, \quad (24)$$

$$MO^{\cdot} + R^{\cdot} \longrightarrow MOR, \quad (25)$$

$$MO^{\cdot} + MO^{\cdot} \longrightarrow MOOM, \quad (26)$$

$$RO^{\cdot} + R^{\cdot} \longrightarrow ROR. \quad (27)$$

Chain termination in this case takes place by reactions (15) and (25)–(27), and may also take place by reactions (17) and (18), depending on the nature of the solvent. Confirmation of our assumption that reaction (17) is possible is provided by the formation of phenyltrichloromethane in the oxidation of diphenylzinc with oxygen in chloroform or carbon tetrachloride [31].

When a mixture of alkyl and aryl derivatives of a given metal is oxidised with oxygen, it is necessary to make allowance not only for the above stages but also for the possibility of reaction of the aryl organometallic compounds with an alkyl organometallic peroxide, and also with alkylperoxy-radicals. This is shown, for example, by the fact that the addition of alkylmagnesium halides to solutions of phenylmagnesium halides leads to a sharp increase in the yield of phenol in the oxidation of a mixture of these organometallic compounds with oxygen [34,35].

Reactions (19), (22), and (26) are characteristic only of the case where more or less stable metal peroxides are formed in the oxidation of aryl organometallic compounds by oxygen. In other cases, however, when these peroxides

are not formed, reactions (19), (22), and (26) must be excluded from the above scheme for the oxidation mechanism. This may be the case, for example, in the reaction of oxygen with aryl derivatives of boron and aluminium.

Some workers[18] conclude that the formation of hydrocarbons in the oxidation of organometallic compounds by oxygen results from the termolecular reaction

$$ROOM + 2RM \rightarrow ROM + MOM + R{-}R, \qquad (28)$$

but the following objections may be made to this conclusion. Firstly, there are no sufficiently convincing data on the formation of peroxides of the type ROOM in the oxidation of aryl organometallic compounds. Secondly the termolecular reaction (28) cannot explain the formation of hydrocarbons RH, although in a number of cases the formation of such compounds is an extremely characteristic feature. Thirdly and finally, reaction (28) makes no allowance for the participation of the solvent, despite the fact that a considerable number of studies have now established directly or indirectly that the solvent takes part in these processes. Thus the oxidation of tolyl-lithium with oxygen in diethyl ether leads to the formation of toluene and 1-tolylethanol[26]. In the case of phenylmagnesium bromide, formation of 1-phenylethanol was observed[27]. Phenol and biphenyl, formed in the oxidation of diphenylmagnesium with oxygen in deuterated benzene, contain deuterated phenyl radicals[30]. Similarly the oxidation of diphenylzinc in deuterated benzene gives deuterated biphenyl[30]. The same reaction in deuterated chloroform was accompanied by the formation of benzene containing 60% of deuterium[31].

These data indicate that in the oxidation of organometallic compounds by oxygen, hydrocarbons are formed not by reaction (28) but as a result of the formation of free radicals. An analogous conclusion was reached in a study of the products of the oxidation of trialkylborons in the liquid phase[36].

Kinetic studies of the oxidation of dimethylzinc, diethylzinc[37,38], triethylboron, and tri-n-propylboron[39] by oxygen in the gaseous phase also indicate a free-radical mechanism for this reaction.

The above chain mechanism for the oxidation of organometallic compounds by oxygen makes it possible to explain the fact that the alkyl derivatives of metals are more readily oxidised than the aryl derivatives. This difference is due chiefly to the marked tendency of alkyl radicals to react with oxygen with formation of the corresponding peroxy-radicals, and the complete absence of this tendency in aryl radicals. Therefore the oxidation of the readily oxidised alkyl organometallic compounds by oxygen takes place with the formation of a smaller number of reaction products than in the oxidation of the corresponding aryl organometallic compounds. Thus in the oxidation of dibutylzinc with oxygen in diethyl ether at 0° the yield of organometallic peroxide reached 90% of theoretical[11]. The oxidation of diphenylzinc with oxygen in cyclohexane, however, gives chiefly benzene, phenol, and biphenyl[31].

It is quite possible that the process may take place with the participation of free radicals or by molecular rearrangement of an oxygen-containing complex, depending on the specific conditions of the reaction. The ratio of the rates of these two processes may vary over a very wide range.

Papers dealing with the oxidation of organotitanium compounds by oxygen are particularly noteworthy. The chemistry of organotitanium compounds is still in the initial stage of its development (see, for example, a recently published review[40]). Systematic studies in this field are being successfully carried out by Razuvaev and his coworkers. It has been found that dicyclopentadienyltitanium[41], cyclopentadienylphenyltitanium[42], diphenyltitanium[43], and dicyclopentadienyldiphenyltitanium[41] are extremely readily oxidised by oxygen. It is significant that the rate of oxidation of dicyclopentadienyldiphenyltitanium depends to a marked extent on the nature of the solvent in which the reaction is conducted[41,44].

Other authors have also noted the extremely ready reaction of oxygen with dicyclopentadienyltitanium[45], trimethylcyclopentadienyltitanium[46,47], methyltitanium trichloride[48], ethyltitanium trichloride[48,49], and tetramethyltitanium[50].

The mechanism of the oxidation of organic compounds of mercury, silicon, tin, and lead differs significantly from that examined above. Here it should first of all be noted that the rate of oxidation of the organic compounds of these metals by oxygen depends to a very marked extent on the nature of the organic radicals present and also on the valency state of the metal atom. For example, the dialkyl and diaryl derivatives of tin[51-62] and lead[63-65], and the alkylated and arylated silanes[66-72] and stannanes[41,54,73-76], are readily oxidised by oxygen. The tetra-alkyl and more particularly the tetra-aryl derivatives of silicon, tin, and lead in most cases have a high stability towards oxygen, which decreases appreciably on going from the organic derivatives of silicon to the corresponding lead compounds. For example, tetraphenylsilicon is not oxidised appreciably when heated in air to 400°,[77] whereas tetraphenyl-lead inflames in air at a much lower temperature[78].

The influence of the nature of the organic radicals in the tetra-alkyl compounds of silicon, tin, and lead on the rate of the reaction of these compounds with oxygen is extremely marked. Replacement of primary alkyl radicals in a tetra-alkyl-lead by secondary alkyl radicals is accompanied by a significant increase in the rate of oxidation of these organolead compounds by oxygen[79,80]. Tetrabenzyl-lead is particularly readily oxidised by oxygen[81].

The oxidation of organomercury compounds by oxygen is of considerable interest. With a very early exception[82], no papers on these reactions have appeared until recently, since the opinion has long been held[83] that the organic compounds of mercury have a high stability towards oxygen. This incorrect opinion is convincingly refuted by the work of Razuvaev and his coworkers, which shows that in a number of cases organomercury compounds are very readily oxidised by oxygen. For example, dicyclohexylmercury in isopropyl alcohol is oxidised at a considerable rate even at room temperature[84]. Di-isopropylmercury[85-87], di-t-pentylmercury[86], and dibenzylmercury[86] show analogous behaviour.

A characteristic feature of the oxidation of dialkylmercury compounds by oxygen is the formation of a complex mixture of reaction products. For example, the oxidation of di-isopropylmercury by oxygen in carbon tetrachloride gave isopropylmercuric chloride, acetone, isopropyl chloride, chloroform, carbon monoxide, carbon dioxide, and metallic mercury[86]. This led to the suggestion that an organomercury peroxo-compound is formed[84,86] and that free radicals take part in the reaction of dialkylmercury with oxygen[86]. The suggestion that free radicals

are involved in the reactions of certain organomercury and organolead compounds with oxygen is confirmed by the results of a study of the nature of this process. The oxidation with oxygen of di-isopropylmercury[87] or tetraethyl-lead[88] shows a clearly defined induction period. Moreover, the addition of inhibitors decreases considerably the rate of reaction of di-isopropylmercury with oxygen[87].

A characteristic feature of the reaction of oxygen with alkyl compounds of mercury and metals in Group IVB of the Periodic System is the large temperature coefficient of reaction rate[87-90]; thus at low temperatures these reactions take place very slowly, and with increase in temperature several parallel and successive chemical processes take place simultaneously. With rise in temperature the peroxo-compounds formed undergo rapid reaction with the original organometallic compounds or with products of their transformation, so that it is very difficult to detect compounds containing peroxide oxygen in the reaction mixture.

If the organometallic compounds contain metal–metal bonds in addition to metal–carbon bonds, there is a marked increase in their reactivity. The rate of the reaction of these compounds with oxygen varies over a very wide range, depending on the nature of the metals forming the metal–metal bond. The reactions of this type of compound, including the reactions with oxygen, have been reviewed in detail[91].

3. OXIDATION OF ORGANOMETALLIC COMPOUNDS WITH PEROXIDES

The reactions of organometallic compounds with organic and inorganic peroxides are extremely numerous and varied, and in the past ten years a very large number of papers have been devoted to their study. The greatest contribution to the study of the reactions of organometallic compounds with peroxides has been made by Razuvaev and his coworkers, who have published a large number of papers reporting a systematic study of the reaction of the organic compounds of several metals with alkyl and acyl peroxides.

The character of the reaction of organometallic compounds with peroxides is influenced by the nature of the original compounds and the reaction conditions. These processes may take place by homolytic or heterolytic mechanisms. In a number of cases the mechanism is extremely complex.

The most characteristic heterolytic reaction of organometallic compounds with peroxides is nucleophilic substitution:

$$R_{n-1}MX + R'OOZ \rightarrow R_{n-1}MOOR' + XZ, \qquad (29)$$

where $n \geq 1$, M = metal, R = alkyl or aryl, R′ = metal, hydrogen, alkyl, or aryl, X = OH, NH_2, halide, alkyl, aryl, alkoxyl, aryloxy-radical, or some other substituent, and Z = metal or hydrogen. In a number of cases reaction (29) is reversible.

If M = mercury, silicon, germanium, tin, or lead and X = alkyl or aryl, reaction (29) takes place with great difficulty and extremely slowly. If the temperature is raised in order to increase the reaction rate, the organic compounds of these metals react with peroxides chiefly by a homolytic mechanism with rupture of the oxygen–oxygen bond.

Reaction (29) can be used to obtain a wide variety of organometallic peroxo-compounds, i.e. compounds containing both metal and peroxide oxygen. For example, the reaction of hydroperoxides with the oxides, hydroxides, alkoxides, hydrides, or amides of alkali and alkaline-earth metals gives the corresponding organometallic peroxides[92-102]. Peroxo-compounds are formed also by the reaction of hydroperoxides with dialkylzinc[12], dialkylcadmium[103], and trialkylaluminium[15]. Organometallic peroxides of boron[104], silicon[105-112], germanium[113,114], tin[114-116], and lead[114] are obtained by the reaction of hydroperoxides with organometallic compounds containing halogeno-, hydroxo-, or amino-groups joined to the metal.

If anhydrous hydrogen peroxide is used instead of hydroperoxides, it is possible to obtain metallo-organic peroxides. The difference between organometallic and metallo-organic peroxides is that the former contain a "carbon–peroxide oxygen" bond and the latter a "metal–peroxide oxygen–metal" bond.

All organometallic peroxo-compounds exhibit a number of common properties. In most cases they readily undergo hydrolysis and decompose rapidly in reactions with compounds containing labile hydrogen. All organometallic peroxo-compounds are powerful oxidising agents and very readily oxidise, for example, the organic compounds of a large number of metals, as noted in the first part of the present review.

A very interesting heterolytic reaction of organometallic peroxides is the intramolecular rearrangement of some of them:

$$R_3MOOCOR' \rightarrow R_2(RO)MOCOR'. \qquad (30)$$

There are sufficient grounds for assuming that the rearrangement takes place by a mechanism analogous to the familiar heterolytic rearrangement of peroxy-esters. This assumption is confirmed fairly convicingly by the results of a kinetic study of the heterolytic rearrangment of a number of acylperoxy-compounds of triphenyltin.

It was established that the product of reaction (30) in the case which we studied is readily hydrolysed by water:

$$C_6H_5O(C_6H_5)_2SnOCOR + H_2O \longrightarrow HO(C_6H_5)_2SnOCOR. \qquad (31)$$

The acyloxyhydroxydiphenyltin readily undergoes further transformation, owing to the ready disproportionation of the corresponding organotin compounds:

$$2 \cdot HO(C_6H_5)_2SnOCOR \longrightarrow (C_6H_5)_2Sn(OH)_2 + (C_6H_5)_2Sn(OCOR)_2, \qquad (32)$$

$$(C_6H_5)_2Sn(OH)_2 \longrightarrow (C_6H_5)_2SnO + H_2O, \qquad (33)$$

$$2 \cdot (C_6H_5)_2Sn(OCOR)_2 \longrightarrow (C_6H_5)_3SnOCOR + C_6H_5Sn(OCOR)_3, \qquad (34)$$

$$3 \cdot C_6H_5Sn(OCOR)_3 \longrightarrow (C_6H_5)_2SnOCOR + 2Sn(OCOR)_4. \qquad (35)$$

The assumption that these disproportionations take place is convincingly confirmed by the results of a study of the composition of the reaction mixture formed under various hydrolysis conditions. Thus triphenyltin acetate was detected and isolated when aqueous diethyl ether was used for the hydrolysis of phenoxydiphenyltin acetate, which is in turn a product of the rearrangement of triphenyltin peracetate.

It might be suggested that the organotin compound formed by reaction (30) should react further with the peroxy-acid:

$$C_6H_5O(C_6H_5)_2SnOCOR + RCO_3H \rightarrow RCOO(C_6H_5)_2SnOOCOR + C_6H_5OH. \qquad (36)$$

The organotin peroxo-compound newly formed by reaction (36) should, by analogy with reaction (30), have undergone transformation with the loss of peroxide oxygen. It was established, however, that this did not take place, and the yield of phenol never exceeded 1 mole per mole of original organotin compound.

Depending on the nature of the original organotin compound and the experimental conditions, the rate of formation of acylperoxytriphenyltin by the reaction

$$(C_6H_5)_3SnX+RCOOOH \rightarrow (C_6H_5)_3SnOOCOR+HX, \quad (37)$$

may be greater or less than the rate of reaction (30). The difference in the molecularities and hence in the orders of these reactions makes it possible to establish, from kinetic data, which of these processes is the slower.

If in the original organotin compound $(C_6H_5)_3SnX$ the substituent X is a hydroxo-, methoxy-, or nitrophenoxy--group, reaction (37) takes place very rapidly, and the rate of formation of the organotin compound $C_6H_5OSn(C_6H_5)_2OCOR$, containing no peroxo-group, is determined by the rate of reaction (30). On the other hand, if the substituent X in the original organotin compound is a chloro- or acyloxy--group, reaction (37) takes place much more slowly than the rearrangement of the organotin peroxo-compound formed from the starting materials. In this case the rate of formation of the acyloxyphenoxydiphenyltin, and hence the rate of decrease in the concentration of peroxo-compounds in the reaction mixture, is determined by the rate of reaction of the starting materials.

The rearrangement of organotin peroxo-compounds containing an acylperoxy-radical is a first-order reaction. The rate of this reaction depends to a marked extent on the nature of the organotin peroxo-compound, the nature of the solvent, and the temperature.

The rate of rearrangement of these compounds in anhydrous methanol increases with change in the radical R in $(C_6H_5)_3SnOOCOR$ in the sequence

$$CH_3 < n\text{-}C_9H_{19}C_6H_5 < C_6H_4NO_2\text{-}m\ (p) < C_6H_4NO_2\text{-}o.$$

The replacement of methanol by toluene leads to an increase in the rate of rearrangement of the acylperoxytriphenyltin. In methanol this reaction takes place at a high rate in the temperature range from -20° to 10°, whereas in toluene it takes place at approximately the same rate in the range from -30° to 0°.

In the reaction of triphenyltin acetate with peracetic acid in toluene, reaction (37) is much slower than reaction (30). This is quite understandable, since in the formation of triphenyltin peracetate a weak acid is displacing a stronger acid from its salt. The rate of decrease in the concentration of peroxo-compounds in the reaction mixture in this case is determined by the rate of the bimolecular reaction (37).

Acetic acid is liberated in the reaction of triphenyltin acetate with peracetic acid. It was found that the addition of acetic acid decreases considerably the rate of the reaction of peracetic acid with triphenyltin acetate in toluene. Study of the kinetics of this reaction shows that the free energy of activation increases regularly, while the entropy of activation decreases, with increase in the concentration of acetic acid in the reaction mixture.

It should be noted that the reaction of peracetic acid with triphenyltin acetate in toluene takes place at a measurable rate in the range 5–30°, where thermal decomposition of peroxycarboxylic acids is quite insignificant.

The rearrangement of various organic compounds of silicon[105], germanium[113], and lead[117] takes place in analogous fashion.

Interesting results were obtained in a study of the reaction of ethoxytriethyltin with benzoyl peroxide[118,119]. In an inert solvent, e.g. benzene, ethoxydiethyltin benzoate and ethyl benzoate are formed in 80–90% yield. It is suggested[118,119] that in this case the initial product is triethyltin perbenzoate, which subsequently undergoes the heterolytic rearrangement (30).

The spontaneous decomposition of organometallic peroxo-compounds by a homolytic mechanism is often accompanied by the formation of a complex mixture of chemical compounds. These compounds are products of the interaction of primary and secondary radicals with the solvent or with other substances present in the reaction mixture. The formation of free radicals during the spontaneous decomposition of organometallic peroxo-compounds is proved by the initiation of the polymerisation of various monomers as a result of the addition of, for example, organosilicon[105,106] and organotin[120–122] peroxides.

The reactions of organometallic compounds with organic peroxides in many cases also involves the participation of free radicals. The most interesting results on this type of reaction have been obtained by Razuvaev and his coworkers, who began to investigate the reactions of organometallic compounds more than thirty years ago. Even at that early date, in a study of the thermal decomposition of organic compounds of mercury, Razuvaev obtained the first evidence of the formation of free aryl radicals in solution[123–125]. Subsequent work proved the formation of free radicals in the thermal and photochemical decomposition of a number of organometallic compounds, for example in the thermal decomposition of diphenylmercury[123–127], tetraethyl-lead[128], and hexaethyldiplumbane[128], and also in the photochemical decomposition of dimethylmercury[129,130], diphenylmercury[21,131–135], and various other organic compounds of mercury[136–139].

Proof of the formation of free radicals in the thermal or photochemical decomposition of organometallic compounds was obtained using tracer atoms[21,126,127,133,134]. This method also provided proof that organic radicals of the organometallic compounds underwent exchange with the solvent.

Subsequently, Razuvaev and his coworkers found that oxygen and organic peroxides increase considerably the rate of decomposition of organometallic compounds and their exchange of organic radicals with the solvent[21,126]. This established the interrelationship of the thermal and photochemical decomposition of organometallic compounds with their oxidation by oxygen and peroxides.

Of the large number of homolytic reactions of organometallic compounds with peroxides, only those of alkyl and acyl peroxides with organic compounds of mercury[140], silicon[141–143], germanium[144], tin[142,143], and lead[141,142,145] have been studied in detail.

Benzoyl peroxide reacts with diethylmercury, di-isopropylmercury, and diphenylmercury[140] with the formation of a complex mixture of products, probably resulting from simultaneous molecular and free-radical processes.

The reaction of di-isopropylmercury with t-butyl hydroperoxide takes place fairly readily. It is suggested

that this reaction involves the intermediate formation of an organomercury peroxo-compound.

Tetra-alkyl derivatives of silicon, germanium, tin, and lead react readily at 80–95° with acyl peroxides, the direction of the reaction depending to a marked extent on the metal. Thus in the reaction of benzoyl peroxide with tetraethylsilane[141,142] and hexaethyldisilane[143] no rupture of the Si–C bond is observed, whereas the reaction with tetraethylgermanium gives products which indicate rupture of the Ge–C bond[144]. This is shown to an even greater extent in the reactions of acyl peroxides with tetraethyltin[142] and tetraethyl-lead[141,142], and also with hexaethyldistannane[142] and hexaethyldiplumbane[145]. The reaction at 130–150° of t-butyl peroxide with tetraethylgermanium[144], tetraethyltin[142], and hexaethyldistannane[143] is to some extent analogous.

The experimental results indicated that the reactions of acyl and alkyl peroxides with alkyl derivatives of mercury, silicon, germanium, tin, and lead take place either completely or partly by a free-radical mechanism.

The formation of free radicals in the oxidation of organometallic compounds by oxygen or peroxides can be used to initiate various chain reactions. Among these reactions, radical polymerisation is of particular interest. The most important results in this connection have been obtained in the study of polymerisation initiated by organoboron and organoaluminium compounds in the presence of oxygen or peroxides.

It is now firmly established that trialkylborons in the presence of oxygen are powerful initiators of the radical polymerisation of many unsaturated compounds. The first papers on the study of organoboron compounds as initiators for the polymerisation of unsaturated compounds were published in 1957[146–149]. These were followed by others[150–158] containing more or less detailed information on the initiating power of various trialkylborons and the mechanism of the reactions taking place.

It was first found that tributylboron initiates the polymerisation of acrylonitrile[146,149], methyl methacrylate[147,149], ethylene[148], styrene[147,149], vinyl chloride, vinyl acetate, and n-butyl vinyl ether[149]. It was established that the emulsion polymerisation of acrylonitrile at 20° and 50° in the presence of tributylboron takes place only if oxygen is also present[150]; it was shown that peroxo-compounds of the type R_2BOOR, $RB(OOR)_2$, or $B(OOR)_3$ are formed. The addition of isobutyldi-isobutylperoxyboron to acrylonitrile brings about polymerisation of the latter[159], indicating homolytic dissociation of this organoboron peroxo-compound.

It has been suggested[153,155–158] that the mechanism of polymerisation initiation is more complex than oxidation of the trialkyborons by oxygen to the corresponding peroxides followed by their homolytic dissociation. It was first suggested that a complex $R_3B.O_2$ is formed and acts as polymerisation initiator[155], but, as already noted, if this complex is formed at all, it may well undergo rapid rearrangement to a more stable peroxo-compound or decompose to the original components.

Published data on the part played by organoboron peroxides in the initiation of radical polymerisation are contradictory. It has been shown[159] that the initiating power of isobutyldi-isobutylperoxyboron is the same as that of tri-isobutylboron in the presence of air, yet it has also been stated[156] that neither tri-n-butylboron nor its peroxide is by itself an effective initiator for the polymerisation of methyl methacrylate, but that when taken together these compounds are extremely active. On this basis it was suggested that the initiation involves the stages

$$R_3B+M \rightleftarrows R_3B\cdot M, \quad (38)$$

$$R_3B\cdot M+R_2BOOR \rightarrow R_3B\cdot M\cdot RO^{\cdot}+R_2BO^{\cdot}, \quad (39)$$

where M represents a molecule of the monomer.

Study of the influence of the $[R_3B]:[O_2]$ ratio on the degree and initial rate of polymerisation showed that the process takes place most readily when this ratio is close to unity[158]. When $[R_3B] \ll [O_2]$, all the organoboron compound is converted into the peroxide, whereas when $[R_3B] \gg [O_2]$ the peroxide formed is very rapidly used up in the reaction with R_3B, so that the polymerisation is rapidly quenched. Here, as before[156], it is suggested that the formation of radicals takes place readily only by reaction of the trialkylboron with its peroxide.

The role of oxygen in polymerisation initiated by a trialkylboron can be played by various other oxygen-containing compounds — hydrogen peroxide, manganese dioxide, copper(II) oxide, etc.[153]

Organoaluminium compounds, like organoboron compounds, initiate radical polymerisation in the presence of oxygen or peroxides. The initiation of the polymerisation of various monomers by a trialkylaluminium has been studied by a number of workers[160–167]. It has been established[161] that the polymerisation of vinyl chloride, initiated by triethylaluminium in the presence of oxygen, involves an induction period. The existence of the induction period was attributed to preliminary oxidation of the original organoaluminium compound by oxygen. This reaction gives compounds containing oxide and peroxide oxygen, introduced at the "aluminium–carbon" bond. These organoaluminium peroxo-compounds react more or less readily with organoaluminium compounds still containing unoxidised "aluminium–carbon" bonds. This stage[161] also determines the initiating power of the "trialkylaluminium–oxygen" system. Instead of trialkylaluminium compounds, it is possible to use for this purpose alkylalkoxyaluminium compounds with varying degrees of replacement of alkyl radicals by alkoxy-radicals. Study of the initiating power of these compounds for the particular case of ethyl derivatives of aluminium showed that, in the presence of oxygen, diethylaluminium ethoxide is a most active initiator for the polymerisation of vinyl chloride.

The influence of the nature of the alkyl radicals in trialkylaluminium on the initiating power in the presence of oxygen has also been studied[163]. It was concluded that the organoaluminium compounds bring about radical polymerisation only under conditions which ensure their conversion into corresponding peroxo-compounds.

The initiating activity of trialkylaluminium compounds in the presence of organic peroxides has been studied[162,163,168].

Triethylaluminium reacts vigorously even at 0° with cumenyl hydroperoxide[163] with the liberation of ethane and the formation of an organoaluminium peroxo-compound, which undergoes further transformation more or less rapidly depending on the reactant concentrations.

The "triethylaluminium–cumenyl hydroperoxide" system does not effectively initiate the polymerisation of vinyl acetate. If diethylaluminium ethoxide is used instead of triethylaluminium, the system is an effective initiator for

the polymerisation of this monomer. If ethylaluminium diethoxide is used instead of diethylaluminium ethoxide, a considerable decrease in initiating power is observed.

The systems formed by triethylaluminium and tri-isobutylaluminium with benzoyl peroxide are effective initiators for the radical polymerisation of vinyl acetate, methyl methacrylate, and acrylonitrile[162,168]. It was found that these initiators bring about polymerisation of the monomers even at -30°. Replacement of an alkyl derivative of aluminium by an alkoxy-derivative is accompanied by complete loss of initiating power in the presence of benzoyl peroxide.

A kinetic study has been made[168] of the polymerisation of vinyl acetate initiated by triethylaluminium in the presence of benzoyl peroxide.

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Gorky State University

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TRANSESTERIFICATION OF PHOSPHITES AND PHOSPHONITES WITH MONOHYDRIC AND POLYHYDRIC ALCOHOLS AND PHENOLS

K.A. Petrov and R.G. Gol'tsova

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I. INTRODUCTION

Twenty years ago the chemistry of the organic compounds of phosphorus entered a period of vigorous development. About a hundred years were required, after the first organophosphorus compounds had been prepared, for sufficient experimental results to accumulate and for the theoretical and practical value of certain compounds to be assessed, which determined the further development of this branch of organic chemistry. The most important work, which provided a foundation for further investigations, was undertaken by Michaelis, Arbuzov, and their many students.

At the present time the practical application of organophosphorus compounds is being continually extended. Because of their high thermal and chemical stability they are successfully employed as plasticisers for synthetic resins, on which they confer non-flammability, resistance to frost[1-3], and sometimes stability towards radiation[4]. The use of organic compounds of phosphorus as extractants[5,6] and flotation agents[7] is no less valuable. Substances containing phosphorus have proved to be valuable additives for lubricating oils, giving to the latter durability and several other desirable properties[8]. Polymers and oligomers containing phosphorus are used for the manufacture of ion-exchange resins, surface-active agents, adhesives, glasses with unique optical properties, etc.[9]

A large number of physiologically active substances of practical interest have been found among organophosphorus compounds. The chemistry of phosphorus occupies a primary place in the number and variety of pesticides. The products Thiophos, Chlorophos, Carbophos, Octamethyl, Butaphos, Ragor, Systoxes, etc. have received wide publicity, and are used in large quantities in agriculture.

Organophosphorus poisons, discovered during recent decades, are more toxic than all hitherto known poisons, and in this respect approach the most virulent compounds of vegetable and animal origin.

Organophosphorus compounds are used also as drugs, e.g. in the treatment of glaucoma (Phosarbin, Armin, Fosfakol)[10], tumours (TEPA, Thio-TEPA, DIPIN, etc.)[11,12], and cardiovascular diseases (hydrazides and amides of thiophosphates)[13]. Natural substances containing phosphorus — nucleic acids, phosphatides, coenzymes, glycopyrophosphates, and many others — are extremely important for the vital activity of organisms[14].

The organophosphorus compounds which find practical use or which are of importance in biochemical processes are mainly esters and amide–esters of phosphoric, phosphorothioic, and pyrophosphoric acids, derivatives of alkylphosphonic acids, and phosphine oxides. It is essentially the chemistry of phosphates and pyrophosphates which is of concern to industry and biochemistry. The importance of phosphates, phosphorothioates, and pyrophosphates is determined not only by their usefulness but also by their availability.

A common feature of several methods of obtaining these compounds is the use of acid and normal phosphorous esters as intermediates in their synthesis. Thus various phosphates are obtained by oxidising phosphites by the addition of sulphur to them, chlorination, reaction with sulphur chlorides, disulphides, thiocyanates, sulphenyl chlorides, chloramines, etc. The alkylation of sodium phosphites by Michaelis' method and of normal phosphites by Arbozov's method or the addition of dialkyl phosphites to unsaturated compounds, etc. yields phosphonates.

Thus phosphites, while being of intrinsic value in their use as such, possess high reactivity, and are therefore