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SOME ADVANCES IN THE LIQUID-PHASE AUTOXIDATION OF ORGANIC COMPOUNDS OF THE NON-TRANSITIONAL ELEMENTS

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CONTENTS

I. INTRODUCTION

Reactions of organoelement compounds of the non-transition elements (OEC) with oxygen have been known for over a century and were the first reactions of OEC's noted for substances of this class.

However, serious study of OEC oxidation processes began mainly in the early part of this century and in fact most papers relating to OEC autoxidation processes have been published during the last 30–40 years.

For a number of reasons the investigation of OEC oxidation reactions is somewhat complicated experimentally. Thus on the one hand, a detailed mechanism for a given OEC oxidation process is only possible if information is available regarding the importance of quite a number of subsidiary reactions involved in the process *i.e.* spontaneous decomposition and bimolecular reactions with oxygen, homolytic and heterolytic reactions involving intermediate peroxide and non-peroxide oxygen compounds, the influence of catalysts on the products, solvation reactions both of a general and specific nature and so on.

On the other hand, the variety of intermediate products formed and of the intermediate reactions involved during the oxidation of OEC's, together with the considerable influence of the nature and structure of the intermediate products on the route followed by the reaction mechanism under particular experimental conditions and the significant role of solvation effects on the intermediate reactions all play an important part in establishing the sharp distinctions often found between the oxidation mechanisms of even similar OEC analogues.

All of these factors help to make OEC oxidation processes one of the most fascinating fields of chemistry having great theoretical interest.

From the practical viewpoint OEC oxidation reactions have a variety of applications ranging from the preparation of valuable organic oxygen—element compounds and the polymerization of vinyl monomers to the commercial utilization of potentially harmful organometallic compounds in the disposal of waste water and gases.

A knowledge of the exact mechanism of OEC autoxidation processes and of the kinetic nature of their occurrence is vital to the solution of problems related to the correct choice of the optimum conditions for each individual OEC oxidation and for each practical application of the same.

These various problems have stimulated an increasing interest in OEC oxidation processes as reflected by the recent monograph of Brilkina and Shushunov[1] and by the appearance of a number of reviews[2–5] which, to a certain extent, are related to OEC oxidations and problems arising from these processes.

In this review attempts are made to consider the main stages in the OEC autoxidation mechanism: the primary reaction depending on the nature of the OEC, the reaction medium, the electronic state of the oxygen employed and the transformation pathways of intermediate organoelement peroxides and of organic oxygen—element non-peroxide compounds.

In any consideration of the main intermediates and their reactions in the autoxidation of OEC's, account must be taken of the accompanying formation of organoelement peroxide compounds and non-peroxide organic oxygen—element compounds. In addition to the oxidation of organic fragments of OEC's the solvent also sometimes brings about the formation of organic hydroperoxides and non-peroxide oxygen compounds.

Thus in the general case complete account must be taken of these various intermediate reactions and consideration taken of the behaviour of all the above-mentioned substances in the reaction system. Unfortunately, however, it is not possible at present to make such detailed considerations as all the data necessary are not available. In addition, reactions of OEC's with different organic peroxide compounds, of the type considered in detail by Razuvaev, Shushunov, Dodonov and Brilkina[3], have been omitted from some mechanisms since in some autoxidations, especially those in the liquid phase, such reactions are not considered important.

In the latter part of this review some examples are given of the autoxidation reactions of OEC's which demonstrate how the mechanisms and the individual characteristics of OEC autoxiation processes depend to a large extent on the nature of the primary reaction and on the properties of the intermediates formed.

As far as the author is aware no other systematic review such as this has been published. Since the appearance of the results of various OEC autoxidation investigations over the past few years, it has now become possible to make some general observations regarding the mechanisms of the main stages involved in the reaction which could be of use to those interested in controlling the autoxidation of OEC's.

II. PRIMARY REACTIONS IN OEC AUTOXIDATIONS

A. Possible primary reactions

The number of primary reactions and their probability and relative importance is obviously related to the wide range of bonds available in OEC's which in the simplest case consists of element—carbon (E—C), element—element (E—E), carbon—carbon (C—C) and carbon—hydrogen (C—H) bonds.

If primary reactions are confined to those involving the participation of C—C and C—H bonds alone, then the results obtained for hydrocarbon autoxidation reactions should be relevant in this case. In these reactions, it is known[6] that the processes are less likely to occur through the spontaneous first-order fission of C—C or C—H bonds in molecules (bond energy 80—100 kcal·mol^{-1}) than through second-order molecular interactions involving saturated molecules and leading to the formation of free radicals.

$$RH + RH \rightarrow 2R^\bullet + H_2 \quad (1)$$

$$RH + O_2 \rightarrow R^\bullet + HO_2^\bullet \quad (2)$$

$$2RH + O_2 \rightarrow 2R^\bullet + H_2O_2 \quad (3)$$

According to Polanyi and Semenov, the endothermicity (Q) of these reactions may be taken as a measure of the energy necessary for overcoming the activation barriers involved. Thus it is possible that the energy involved is considerable for if reactions (1)—(3) are considered as applying to the alkyl derivatives of non-transition elements of Group IV of the Periodic Table the corresponding endothermicities are $Q_1 \simeq 100$, $Q_2 \simeq 50$ and $Q_3 \simeq 60$ kcal·mol^{-1} respectively.

Bond energies of bonds of the type E—C or E—E depend to a very large extent on the nature of OEC's (see data listed in Table 1).

For this reason, in OEC's with a comparatively low value for the E—C bond energies, the possibility arises of radical generation via spontaneous fission successfully competing with the type of processes depicted in equations (1)—(3), *i.e.*

$$R_mE \rightarrow R_{m-1}E^\bullet + R^\bullet \quad (4)$$

Similar conclusions may be reached when the available data regarding E—E bond energies are considered. Bimolecular reactions are possible between OEC's and oxygen in which the

TABLE 1

Bond energy (Q) of some OEC's

OEC	*Bond*	*Q (kcal·mole⁻¹)*	*References*
$EtLi$	C–Li	47.5 ± 1.5	7
Et_2Hg	C–Hg	41	7
Me_2Hg	C–Hg	51	7
Me_2Zn	C–Zn	47 ± 1	7
Me_2Cd	C–Cd	43.5 ± 1.2	7
Me_3As	C–As	54.6	7
Me_3Sb	C–Sb	57	7
Me_3Bi	C–Bi	44	7
Me_4Si	C–Si	78.8	7
Me_4Ge	C–Ge	61	8
Et_4Sn	C–Sn	50	8
Me_4Pb	C–Pb	34.7	9
Me_4Rb	C–Rb	23.5	7
Et_6Si_2	Si–Si	70 ± 10	8
$(MeO)_6Si_2$	Si–Si	50 ± 20	8
Et_6Ge_2	Ge–Ge	65 ± 5	8
Et_6Sn_2	Sn–Sn	50 ± 10	8
$(EtO)_4Si$	Si–O	106 ± 2	8
$(Et_3Ge)_2O$	Ge–O	91 ± 5	10
$Et_3SnOCOPh$	Sn–O	91 ± 10	10
$Me_3SiOO\text{-}t\text{-}Bu$	O–O	47 ± 4	11

oxygen attack is directed towards the E–C or E–E bond. For example:

$$R_mE + O_2 \rightarrow R_{m-1}EOOR \qquad (5)$$

$$R_{m-1}EER_{m-1} + O_2 \rightarrow R_{m-1}EOOER_{m-1} \qquad (6)$$

$$R_mE + O_2 \rightarrow R_{m-1}EOO^{\bullet} + R^{\bullet} \qquad (7)$$

$$R_{m-1}EER_{m-1} + O_2 \rightarrow R_{m-1}EOO^{\bullet} + R_{m-1}E^{\bullet} \qquad (8)$$

It is rarely possible to directly evaluate the activation energy of the reactions depicted in equations (5)–(8) because of the lack of relevant data. However, in the case of tetraethyltin and hexaethylditin (where such data are available as recorded in Table 1) such calculations lead to a value of Q equal to 40 kcal·mol⁻¹ for reactions (7) and (8).

From this it appears not unreasonable to assume that reactions of the type depicted in equations (5)–(8) can successfully compete with those of the type depicted in (1)–(3).

Two conclusions may be drawn from the above discussion. Firstly, that the primary reactions in OEC autoxidations can differ significantly [reactions (1)–(8)] depending on the nature of the OEC, and secondly that reliable evaluation of the relative importance of the various competing primary reactions is not at present generally possible due to the lack of the required data.

B. Studies of primary reactions in OEC autoxidations neglecting solvent effects or employing indifferent solvents

The results of many studies in which the nature of primary reactions in OEC autoxidation had been investigated have been published. However, in most cases, the conclusions reached regarding the nature of particular primary reactions have been obtained indirectly, direct examination of these reactions being confined to a few isolated examples.

The first discussion of the interaction between oxygen and OEC's dates back to 1909. Thus, in an investigation of the oxidation of ethylmagnesium bromide, Wuyts detected traces of peroxide among the reaction products. On this basis, he put forward his hypothesis regarding the formation of alkylperoxymagnesium halides in this reaction, which apparently results from the interaction of the alkylmagnesium halide with oxygen[12].

$$\mathrm{RMgX} + \mathrm{O_2} \rightarrow \mathrm{ROOMgX} \qquad (9)$$

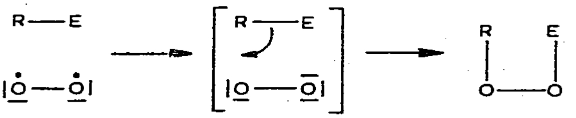
The final products formed in the autoxidation of ethylmagnesium halides were attributed to secondary reactions (*i.e.* interaction of alkylperoxymagnesium halide with initial organomagnesium compound and hydrolysis of the resulting reaction product).

$$\mathrm{ROOMgX} + \mathrm{RMgX} \rightarrow 2\mathrm{ROMgX} \qquad (10)$$

$$\mathrm{ROMgX} + \mathrm{H_2O} \rightarrow \mathrm{ROH} + \mathrm{Mg(OH)X} \qquad (11)$$

In subsequent years, Wuyts mechanism was advanced more than once by other investigators to explain the product composition as arising from the autoxidation of organic compounds of such elements as lithium[13], zinc[14,15], magnesium [16–19], boron [20] and antimony[21].

It was during this period that the mechanism of the interaction of OEC's with oxygen was first discussed[13]. Muller and Töppel suggested that the bimolecular reaction involved proceeds according to the partial ionic mechanism



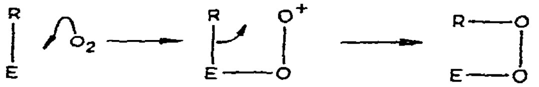
(12)

The formation of such a hetero-organic peroxide during the autoxidation of OEC's was not established experimentally, however, until quite recently. Thus Walling and Buckler[22] in 1955 and Hock and Ernst[23] in 1959 showed that n-butyllithium oxidizes in diethyl ether at −78°, to n-butylperoxylithium. Similarly, oxidation of indenyllithium gives a high yield of the corresponding hetero-organic peroxide. It has also been shown that the oxidation of alkylmagnesium halides leads to the formation of the corresponding alkylperoxymagnesium halides[22–25] as predicted by Wuyts. In this case the reaction was carried out in benzene, diethyl ether or tetrahydrofuran at a temperature within the range –75° to –150°.

Autoxidation of alkylzinc organic compounds proceeds rapidly in organic solvents (ether, benzene, xylene) even at –75° with the formation of organic zinc peroxide[23,24,26]. Similar results have been obtained for completely alkylated cadmium compounds[23,24,27,28], boron compounds[29] and aluminium compounds[24,31–35]. Investigations by these workers of the influence of the reaction temperature, of the ratio OEC/oxygen and of the initial OEC concentration on the yield of peroxide product have convincingly confirmed the correctness of Wuyt's reaction scheme *i.e.* formation of organoelement peroxide as the primary products followed by the alkoxy derivative of the OEC.

Walling and Buckler in their studies not only convincingly confirmed for the first time the formation of organoelement peroxides during the autoxidation but also showed that diphenylamine does not inhibit the autoxidation of alkylmagnesium halides. The latter being oxidized does not induce the oxidation of butaldehyde[22].

These results led Walling and Buckler to postulate a molecular mechanism for the interaction of alkylmagnesium halides with oxygen as a consequence of the coordination of oxygen to the metal atom to form an intermediate complex followed by the subsequent 1,3-nucleophilic migration of the alkyl radical to the oxygen.



(13)

A similar mechanism for the primary reactions has been advanced in discussions of the autoxidation of organic derivatives of mercury[36–39], boron[40–46], aluminium[32], lithium[47–49], magnesium[47,49,50], zinc[57] and cadmium[53].

In recent years studies have been made involving the direct examination of primary reactions in the autoxidation of a number of OEC's in hydrocarbons[54–56]. In each case inhibitors were employed in the investigations.

It should be noted that although the use of inhibitors apparently provides a simple method of investigation, it is necessary to treat the conclusions obtained with some care. Thus, for instance, the inability of quinone[40,67], iodine or methylmethacrylate[68], all of which are capable of generating active radicals, to affect the rate of OEC autoxidation led a number of investigators to suggest a molecular mechanism for this process, and as mentioned above, diphenylamine does not inhibit the autoxidation of alkylmagnesium halides[22] despite the reaction being radical in nature.

In subsequent studies Davies and Roberts established that optically active organoboron compounds on autoxidation give organoboron products in which stereospecificity is absent[69–71] and autoxidation processes for a number of OEC derivatives of boron[69,70], aluminium[72], zinc[72], cadmium[72], antimony and bismuth[73] are inhibited by the galvinoxyl radical. These

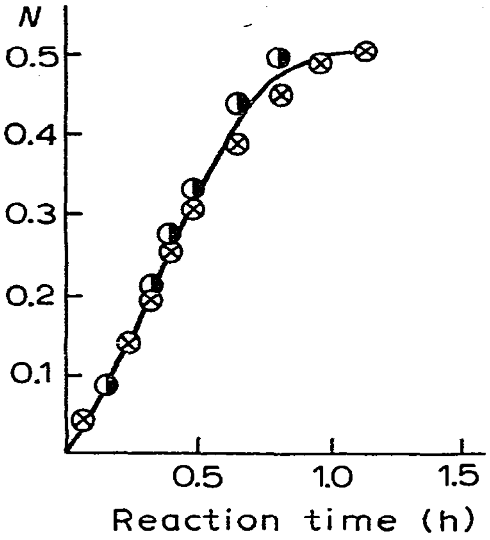


Fig. 1. Oxidation of bis(triethylgermyl)mercury in n-octane (c_0 0.1 mol·l^{-1}) at 0° ◑, without additions; ⊗, in the presence of 2,4-di-t-butyl-4-methylphenol (c_0 0.01 mol·l^{-1})..

results however leave the nature of the mechanism of the primary reaction open to question although they provide convincing proof of the free-radical nature of the mechanism of the liquid-phase autoxidations of the above OEC's under the reaction conditions employed$^{69-72,74-76}$.

The need for care in the use of inhibitors is also dictated by a number of other considerations, *i.e.* dependence of the inhibitor efficiency upon the nature of the inhibitor and OEC, the possibility of the dual function of the inhibitor in the various reactions (both as an inhibitor and as a sensitizer of the OEC oxidation) as well as the possibility that the various reaction systems might be influenced by the concentration of the inhibitor which might induce both positive and negative kinetic effects as a result of its molecular interaction with OEC's in the system.

If all of these various considerations are taken into account, it is possible to discuss the results mentioned above as far as they relate to the nature of the mechanism of the primary reactions in OEC autoxidations.

Razuvaev, Alexandrov, Glushakova and Figurova^{54,55} have shown that the primary reaction in the autoxidation of bis(triethylgermyl)mercury and bis(triethylsilyl)mercury in n-octane is a bimolecular reaction of OEC with oxygen. This conclusion was based on a number of experimental observations. Firstly, autoxidation in the above system is not inhibited by the presence of a great variety of additives (ionol, *o*-phenylenediamine, etc. see Fig. 1)[*]. These materials are, in fact, rather effective inhibitors for the autoxidation of

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[*] In this figure and others, *N* is the number of moles of oxygen absorbed by the reaction mixture per mole of initial OEC.

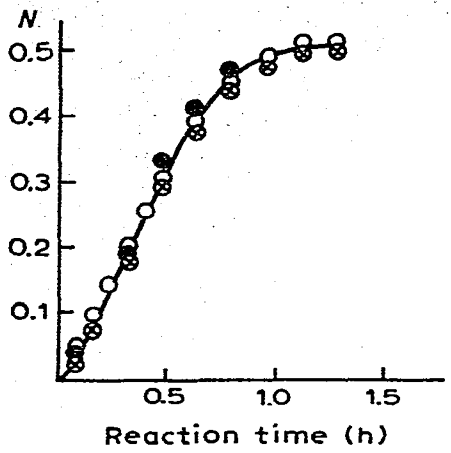

Fig. 2. Oxidation of bis(triethylgermyl)mercury in n-octane at 0°, ●, c_0 0.084; ○, c_0 0.1 and ⊗, c_0 0.2 mol·l^{-1}.

other related OEC's (for example, bis(triisopropylgermyl)mercury, ethyl(triethylsilyl)mercury, diisopropylmercury etc., see below). It should be noted that the addition of small amounts of galvinoxyl* also fails to inhibit the autoxidation of bis(triethylgermyl)mercury and bis(triethylsilyl)mercury.

Secondly, the product composition arising from the autoxidation of bis(triethylgermyl)-mercury or of its silyl analogue points to the absence of initiation involving the oxidation of the solvent (hydrocarbon) as normally should occur in a free-radical mechanism. For example, in the autoxidation of bis(triethylgermyl)mercury at 0° and higher temperatures the reaction products are triethylgermanium oxide and mercury which are produced in quantitative yield[54,55,77,78]. Below −10°, however, the reaction products are triethylgermyl(triethylgermyloxy)mercury, triethylgermanium oxide and mercury with respective yields of 80, 20 and 20%[54,55]. It should also be pointed out that the quantity of oxygen absorbed by the reaction mixture during the oxidation of bis(triethylgermyl)mercury was 0.5 mole per mole of initial bis(triethylgermyl)mercury in all cases.

Thirdly, the autoxidation of bis(triethylgermyl)mercury proceeds as a first-order autocatalytic reaction with respect to initial OEC and as a zero-order reaction with respect to oxygen[55]. The first-order dependence on OEC is clearly demonstrated by the shape of the kinetic curves depicted in Fig. 2, while the zero-order dependence on oxygen is attributed to autocatalysis of the reaction by triethylgermanium oxide and to the spontaneous maintenance of the thermodynamic equilibrium concentration of the complex OEC—triethylgermanium oxide during the reaction.

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* The author thanks Professor A.G. Davies for supplying the samples of galvinoxyl used in these experiments and in those described below.

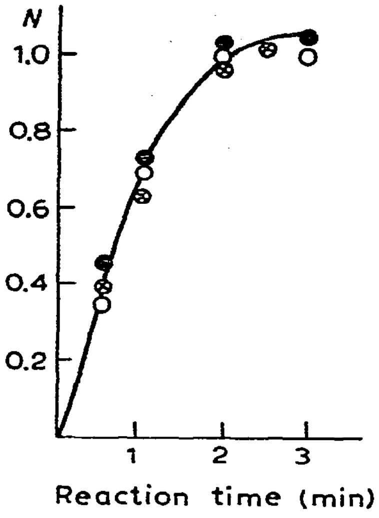

Fig. 3. Oxidation of triethylthallium in n-octane at −50°, ●, c_0 0.03; ○, c_0 0.05 and ⊖, c_0 0.1 mol·l^{-1}.

From these results and on the basis of studies of the chemistry of the reaction[54,55], it is suggested that the autoxidation of bis(triethylgermyl)mercury proceeds by a molecular mechanism involving the bimolecular interaction of OEC with oxygen as a primary reaction.

$$(Et_3Ge)_2Hg + O_2 \rightarrow Et_3GeHgOOGeEt_3 \quad (14)$$

$$Et_3GeHgOOGeEt_3 + (Et_3Ge)_2Hg \rightarrow 2\ Et_3GeHgOGeEt_3 \quad (15)$$

$$Et_3GeHgOGeEt_3 \rightarrow (Et_3Ge)_2O + Hg \quad (16)$$

$$(Et_3Ge)_2Hg + L \rightleftarrows (Et_3Ge)_2Hg \cdot L \quad (17)$$

$$(Et_3Ge)_2Hg \cdot L + O_2 \rightarrow Et_3GeHgOOGeEt_3 + L \quad (18)$$

The autoxidation of triethylthallium in n-octane has also been studied[56]. This reaction proceeds readily even at −70° with ethylperoxydiethylthallium being produced as the sole primary product. Addition of inhibitors which are effective in OEC autoxidations involving free-radical processes to this system (see below) points to the absence of free-radical reactions in the autoxidation of triethylthallium.

This autoxidation is in fact first order with respect to initial OEC (Fig. 3) and first order with respect to oxygen (Fig. 4). This suggests that the reaction in n-octane proceeds via a bimolecular mechanism, *i.e.*

$$Et_3Tl + O_2 \rightarrow Et_3TlOOEt \quad (19)$$

Similar results were obtained in studies of the autoxidation of diethylcadmium in n-octane[57]. In this case ional, *o*-phenylenediamine, galvinoxyl* and phenozianine* were studied

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* Inhibitors kindly supplied by Professor A.G. Davies.

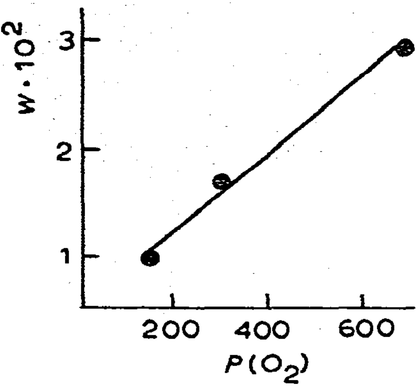

Fig. 4. Dependence of the rate of oxidation (w) of triethylthallium in n-octane at −50° on the pressure of oxygen maintained over the reaction mixture, c_0 0.05 mol·l^{-1}.

as possible inhibitors.

The autoxidations of bis(triisopropylgermyl)mercury[58], tetraethyllead[59–61], hexaethylditin[59,62] and di-n-propylmercury[63] proceed in a somewhat different manner. In these cases the inhibitors studied (*o*-phenylenediamine, ional, etc.) led to the appearance of extended induction periods (see Figs. 5 and 6). That the OEC autoxidation is inhibited by small additions of inhibitors is an indication of a free-radical chain mechanism for the overall process but still leaves the question of the nature of the primary processes involved in this mechanism unanswered.

Information regarding the nature of these processes has, in fact, been obtained through a study of the characteristics of the induction periods observed in these oxidations in the presence of various inhibitors[58–66]. In the presence of inhibitors [IH], the variation in the

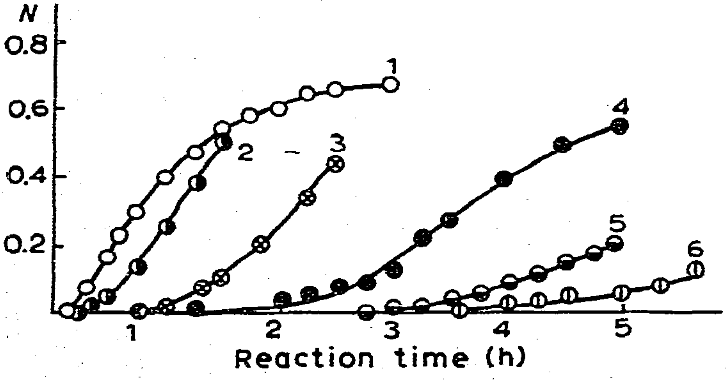

Fig. 5. Oxidation of bis(triisopropylgermyl)mercury in n-decane (c_0 0.07 mol·l^{-1}) at 50°, without additions (○), and with respective additions of *o*-phenylenediamine (in moles per mole of initial OEC) of 0.85 × 10^{-5} (◐), 1.65 × 10^{-5} (⊖), 3.3 × 10^{-5} (●), 5 × 10^{-5} (⊖) and 7 × 10^{-5} (⦶).

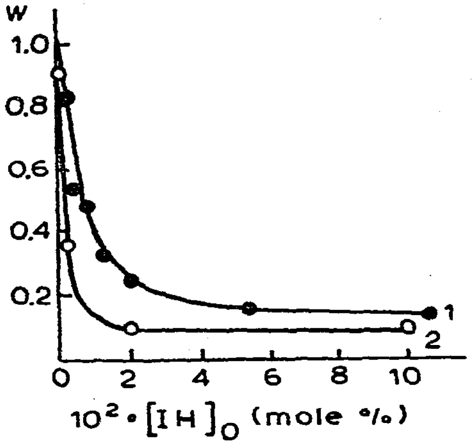

Fig. 6. Dependence of the rate of oxidation (w) of hexaethylditin in n-nonane (c_0 20 mole % and 80° (curve 1)) and hexaethyldilead (c_0 20 mole % and 65° (curve 2)) on the initial concentration of 2,6-di-t-butyl-4-methylphenol.

active radical concentration $[m]$ with time is given by the equation:

$$\frac{d[m]}{dt} = W_0 - (k[\mathrm{IH}] - \varphi)[m] \qquad (20)$$

where W_0 is the rate of initiation, k the rate constant for the destruction of the active radicals by the inhibitor, [IH] and $[m]$ are the concentrations of inhibitor and active centres respectively, and φ is a chain-branching factor.

The critical inhibitor concentration is equal to $[\mathrm{IH}]_{cr} = \varphi/k$; when $[\mathrm{IH}] > [\mathrm{IH}]_{cr}$ the process is stationary and when $[\mathrm{IH}] < [\mathrm{IH}]_{cr}$ such a state is absent from the system.

If the initial inhibitor concentration in a given run is $[\mathrm{IH}]_0 > [\mathrm{IH}]_{cr}$, then during the induction period the inhibitor concentration will drop to the critical value in accordance with the following differential equation:

$$-\frac{d[\mathrm{IH}]}{dt} = k[\mathrm{IH}]\ [m] \qquad (21)$$

Solving this equation for the existence of a stationary state in the system gives

$$[m] = \frac{W_0}{k[\mathrm{IH}] - \varphi}$$

and the boundary conditions $[\mathrm{IH}] = [\mathrm{IH}]_0$ at $t = 0$, and $[\mathrm{IH}] = [\mathrm{IH}]_{cr}$ at $t = t_{ind}$ give rise to the following relationship linking t_{ind} and $[\mathrm{IH}]_0$:

$$([\mathrm{IH}]_0 - [\mathrm{IH}]_{cr}) + \frac{\varphi}{k}\ln\frac{[\mathrm{IH}]_{cr}}{[\mathrm{IH}]_0} = W_0 \cdot t_{ind} \qquad (22)$$

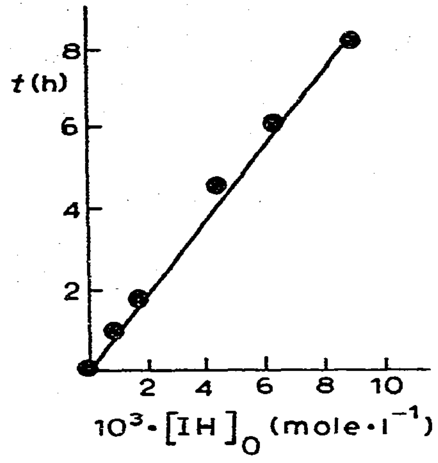

Fig. 7. Dependence of the length of the induction period in the oxidation of tetraethyllead at 100° on the concentration of inhibitor.

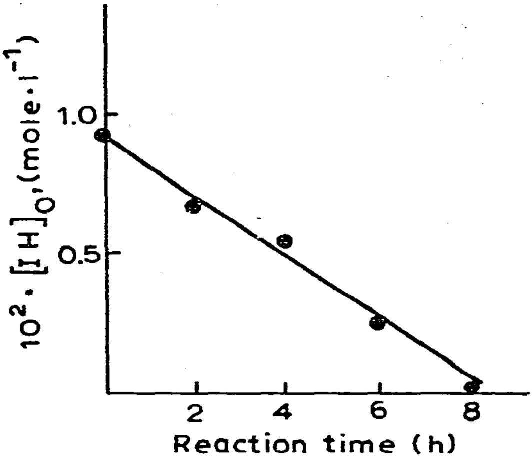

Fig. 8. Consumption of inhibitor during the induction of the oxidation of tetraethyllead at 100°.

In the OEC investigations under discussion, the conditions were chosen so that $[IH]_{cr}$ had a small value (see for example Figs. 7 and 8).

This allows a simplification of equation (22) which, on taking into account the stoichiometric coefficient for inhibition, changes to:

$$W_0 \cdot t_{ind} = f[IH]_0 \qquad (23)$$

Equation (23) links the characteristics of the observed induction period with the type of chain mechanism involved in a given reaction.

With tetraethyllead, it was shown[60,61] that the linear dependence of the length of the induction period on the initial inhibitor concentration (Fig. 7) may be linked with the constant rate of inhibitor consumption during the induction period (Fig. 8). This suggests that stationary conditions are achieved during the induction period and that in this case generation of radicals by means of degenerate branching reactions either does not occur or is not particularly significant. These conclusions thus provide sufficient grounds for assuming that W_0 is the rate of the primary process in this reaction. Further study of the characteristics of the induction period[60,61] indicated that the primary reaction in the autoxidation of tetraethyllead is first order with respect to tetraethyllead, zero order with respect to oxygen and has an activation energy of 44 $\text{kcal}\cdot\text{mol}^{-1}$ (the average bond energy of the lead—carbon bond in tetraethyllead is estimated as 31.5 $\text{kcal}\cdot\text{mol}^{-1}$ [79]).

On the basis of these results, it may be deduced that the primary reaction in the autoxidation of tetraethyllead is the spontaneous decay of the OEC into radicals:

$$Et_4Pb \rightarrow Et_3Pb^{\bullet} + Et^{\bullet} \qquad (24)$$

It should be noted that this conclusion is in agreement with data available for the thermal decomposition of tetraethyllead in the liquid phase[80].

Similar studies of the autoxidations of bis(triisopropylgermyl)mercury[58], hexaethylditin[59-62] and di-n-propylmercury[63] have indicated that in these cases also the primary reactions involved are the spontaneous decay of the initial OEC involving either an element—element bond or an element—carbon bond.

$$(\text{i-Pr}_3\text{Ge})_2\text{Hg} \rightarrow \text{i-Pr}_3\text{GeHg}^\bullet + \text{i-Pr}_3\text{Ge}^\bullet \quad (25)$$

$$\text{Et}_3\text{SnSnEt}_3 \rightarrow 2\ \text{Et}_3\text{Sn}^\bullet \text{ or } \text{Et}_3\text{SnSnEt}_2^\bullet + \text{Et}^\bullet \quad (26)$$

$$\text{n-Pr}_2\text{Hg} \rightarrow \text{n-PrHg}^\bullet + \text{n-Pr}^\bullet \quad (27)$$

It should be noted that the values of the activation energies for reactions (25) and (26) are equal to 16.5 and 50 kcal·mol^{-1}, respectively. The average energy of the germanium—mercury bond in bis(triisopropylgermyl)mercury is 17 ± 3 kcal · mol^{-1} [81], while the energy of the tin—tin bond in hexaethylditin is practically identical with the average energy of the tin—carbon bond in this compound (50 kcal·mol^{-1}, see Table 1).

A more complicated situation exists for the primary reactions involved in the autoxidation of ethyl(triethylsilyl)mercury[64] and tris(triethylgermyl)antimony[65,66]. The autoxidation of ethyl(triethylsilyl)mercury is effectively inhibited by a number of inhibitors. Investigations of the inhibited oxidation of this compound (as in the case of tetraethyllead, see above) have also enabled the nature of the primary reaction process to be deduced from the character of the induction period observed. The results obtained indicated that the primary reaction involved in the autoxidation of ethyl(triethylsilyl)mercury is first order with respect to oxygen and second order with respect to the initial OEC, the activation energy for the reaction being 20 kcal · mol^{-1}.

Ethyl(triethylsilyl)mercury is known[82] to disproportionate on heating in accordance with the following stoichiometric equation.

$$2\text{Et}_3\text{SiHgEt} \rightarrow \text{Et}_2\text{Hg} + (\text{Et}_3\text{Si})_2\text{Hg} \quad (28)$$

On the other hand, it is also known that bis(triethylsilyl)mercury is oxidized by oxygen via a molecular mechanism (see above), and that diethylmercury when studied under conditions identical to those used in the autoxidation of ethyl(triethylsilyl)mercury hardly undergoes any reaction with oxygen. It has also been established that ethyl(triethylsilyl)mercury is not associated in hydrocarbons. On the basis of these data it has been predicted that the initiation process involved in the chain mechanism for the autoxidation of ethyl(triethylsilyl)mercury involves a bimolecular reaction.

$$2\text{Et}_3\text{SiHgEt} \rightarrow \text{Et}_2\text{Hg} + \text{Et}_3\text{SiHg}^\bullet + \text{Et}_3\text{Si}^\bullet \quad (29)$$

In the autoxidation of tris(triethylgermyl)antimony, the process is even more complicated because of the association of the initial OEC. Monomeric tris(triethylgermyl)antimony reacts with oxygen by means of a free-radical chain mechanism[65,66]. In this study, data were also obtained indicating that the primary reaction in the autoxidation of monomeric tris(triethylgermyl)antimony involves the spontaneous fission of the initial OEC into radicals.

Before discussing these results in any detail it is advisable first to consider the influence of specific solvation on the course of OEC interaction with oxygen.

C. The influence of specific solvation on the bimolecular reaction between OEC and oxygen

A considerable amount of data is now available regarding the very considerable influence of the medium on the course of OEC autoxidation. Thus there is evidence of solvent participation in autoxidation reactions of organic compounds of lithium[13], magnesium[83], zinc[51,84], mercury[37–39,87,88] and aluminium[89]. The strong influence of the nature of the solvent on the reaction product ratio has also been demonstrated for oxidation processes involving phenyllithium[13,90], triphenylmethylsodium[91,92], phenylmagnesium bromide[51,83,93,94] and tri-n-butylboron[95].

It has also been established[96] that the rate of autoxidation of 2-phenylbis(diphenylene)-alkylsodium decreases in a series of solvents in relation to the increasing solvation ability of these solvents.

Under ordinary conditions, phenylmagnesium chloride oxidizes slowly in chlorobenzene but additions of anisol or dibutyl ether accelerate the reaction considerably[27]. Similar results have been observed in the oxidation of diphenylmagnesium chloride[98].

Tri-n-butylboron oxidizes at approximately the same rate in anisol, cyclohexane, benzene and isooctane. In dibutyl ether, however, the reaction is slower[95].

A number of workers[20,40,100–103] have studied the influence of water on the oxidation of the trialkylboron compound. It has been shown that the presence of water has no effect on the oxidation of the first boron–carbon bond in tri-n-butylboron but inhibits the further oxidation of the oxy derivatives of the primary reaction[20]. These results have not, however, been subsequently confirmed[40,100,102].

The autoxidation of the trialkylboron compound is retarded on addition of di-t-butyl peroxide[95], ammonia[104–107] and organic nitrogen compounds[40,42,46,100,102,103,106,108,109] to the system.

It has been shown that the oxidation of triethylaluminium is much slower in diethyl ether than in cyclohexane[35].

As far as specific solvation effects on the reactivity of OEC's towards oxygen are concerned, studies of the influence of substances containing atoms with electron-donor properties on the autoxidation of OEC's are of particular interest. In this connection it should be noted that intermolecular reactions involving ligands and OEC's most commonly occur in a specific fashion.

Unfortunately, however, most of the results mentioned above cannot be directly compared since they usually refer to the overall processes involved in the autoxidations. An exception to this is provided by the number of investigations which have been specifically undertaken in an attempt to provide information regarding the influence of specific solvation on bimolecular reactions involving OEC's and oxygen. Among these may be listed the data obtained regarding the relative reactivity of oxygen with respect to coordinatively saturated

OEC complexes with various ligands which are of great interest. Generally, such complexes are quite stable in air. Thus comparison of the non-solvated initial OEC complexes tricyclohexylboron piperidinate[106], trimethylgallium etherate[110,111], trimethylgallium ammoniate[111,112], ammoniates of dimethylgallium chloride and methylgallium dichloride[112] and triethylgallium ammoniate[110] indicates that the latter are more stable towards oxygen.

A number of other papers[46,97–99,113–115] give more detailed accounts of kinetic investigations of the influence of ligands on the reactivity of OEC's towards oxygen. Thus it has been established[113–115] that the reactions of bis(triethylgermyl)mercury and bis(triethylsilyl)mercury with oxygen, which as mentioned above normally proceed by a molecular mechanism, are effectively catalyzed by small additions of different compounds such as ammonia, amines, pyridine, alcohols, ethers, triphenylphosphine, water and hexaalkyldimetaloxanes of silicon, germanium, tin, etc.

All these compounds can function as ligands as they contain atoms possessing electron-donor properties and they presumably act as such in oxidation processes since autoxidation of bis(triethylgermyl)mercury in the presence of a number of potential ligands (triphenylphosphine, hexaethyldigermanoxane, etc.) indicates that the ligand is unchanged chemically during the reaction[113,114].

This result provides convincing evidence that these ligands play an important role as catalysts, and indeed by use of the inhibitor method it has been shown that these catalytic processes proceed without the participation of free radicals[113,114].

The kinetic characteristics of autoxidations undertaken in the presence of potential ligands are of interest.

Thus, it has been shown[113–115] that the catalytic oxidation of bis(triethylgermyl)mercury in the presence of a number of ligands (triethylamine, pyridine, ammonia, triethylgermanium oxide, t-butyl alcohol) over small values of n^* for the ligand follows first-order kinetics with respect to the initial OEC, first-order kinetics with respect to oxygen and first-order kinetics with respect to the ligand.

Examples of such kinetic data are provided in Figs. 9–11 respectively.

This kinetic behaviour suggests that the catalytic activity of the ligand involves the formation of an OEC–ligand (L) complex under such conditions that a thermodynamic equilibrium is maintained between its concentration and those of the initial reactants *i.e.*

$$(Et_3Ge)_2Hg + L \rightleftarrows (Et_3Ge)_2Hg\cdot L \qquad (30)$$

$$(Et_3Ge)_2Hg\cdot L + O_2 \rightarrow Et_3GeHgOOGeEt_3 + L \qquad (31)$$

Studies of the catalytic oxidation of bis(triethylgermyl)mercury and its silyl analogue indicated the absence of peroxides similar to those depicted in reaction (31) amongst the reaction products. However, there was sufficient evidence to indicate that such compounds are formed as intermediates in the reaction. The fact that such peroxides are not amongst the final products of the reaction must be attributed to their high reactivity towards the initial OEC.

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[*] Here and elsewhere n represents the number of moles of ligand (catalyst), L, per mole of initial OEC.

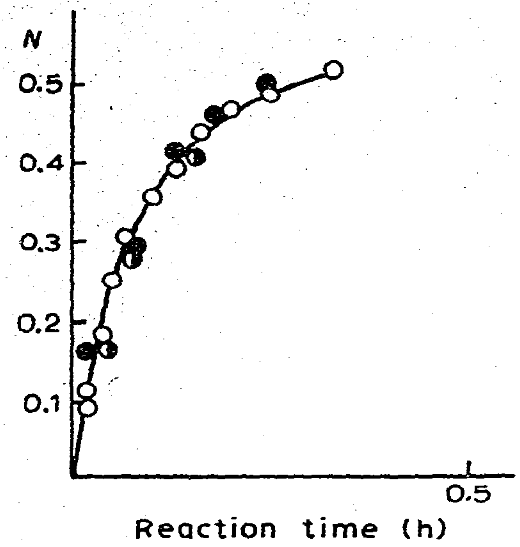


Fig. 9. Oxidation of bis(triethylsilyl)mercury in the presence of triphenylphosphine ($n = 0.5$) in n-octane at -10° c_0^{OEC} 0.03 (○); 0.05 (◐) and 0.1 (●) mol·l^{-1}; $P(O_2)$ 300 mmHg.

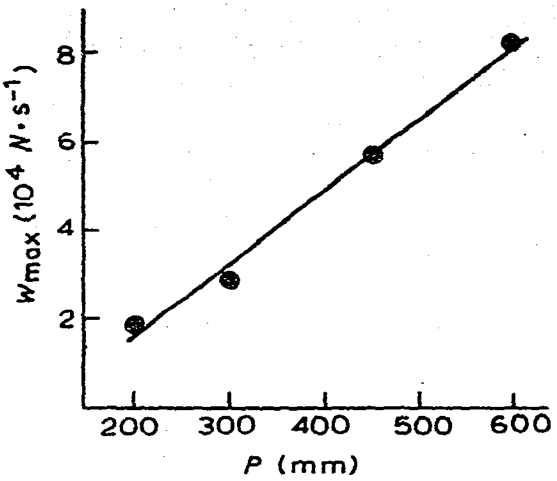


Fig. 10. Effect of oxygen pressure on the oxidation of bis(triethylsilyl)mercury in the presence of triphenylphosphine ($n = 1.5$) at -10°.

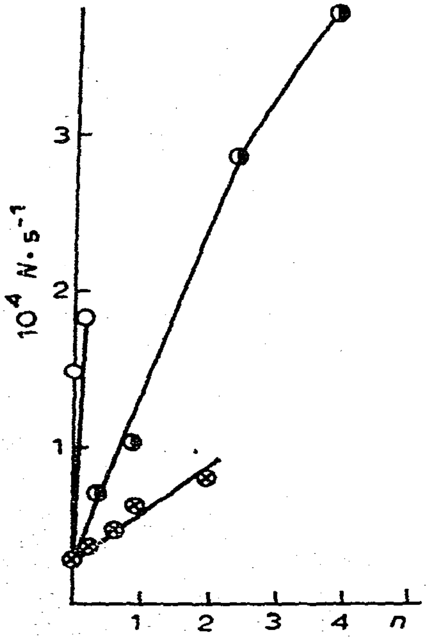


Fig. 11. Dependence of rate of catalytic oxidation of bis(triethylgermyl)mercury in n-octane (c_0 0.1 mol·l^{-1}) at -20° on the presence of additives, ○, pyridine; ◐, triethylamine, ○ triethylgermanium oxide.

$$Et_3GeHgOOGeEt_3 + (Et_3Ge)_2Hg \rightarrow 2Et_3GeHgOGeEt_3 \qquad (32)$$

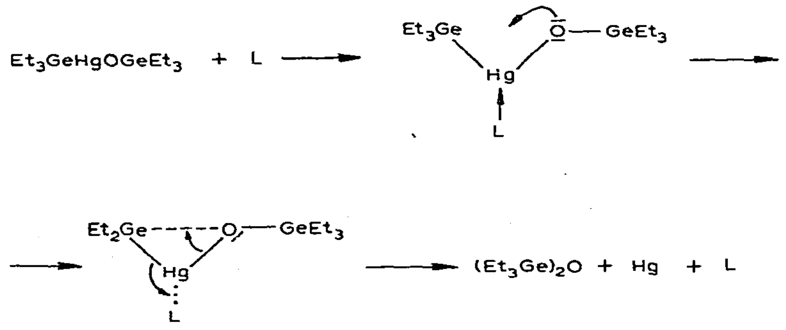
Triethylgermyl(triethylgermyloxy)mercury is the main product of the autoxidation of bis(triethylgermyl)mercury at temperatures below 0° [54]. The addition of potential ligand catalysts to the oxidations of bis(triethylgermyl)mercury and its silyl analogue complicates both processes since this leads to the induced decomposition of the triethylgermyl(triethylgermylperoxy)mercury and triethylgermyl(triethylgermyloxy)mercury present in the system.

$$Et_3GeHgOOGeEt_3 \xrightarrow{L} (Et_3GeO)_2 + Hg \qquad (33)$$

$$Et_3GeHgOGeEt_3 \xrightarrow{L} (Et_3Ge)_2O + Hg \qquad (34)$$

It has been established[116] that the catalytic decomposition of triethylgermyl(triethylgermyloxy)mercury in the presence of a number of ligands (ammonia, triethylamine, triethylphosphine, water, t-butyl alcohol) is first order with respect to the initial dimetaloxane and to the ligand added to the system. Thus, the use of the inhibitor method indicates the absence of free-radical initiation in this reaction.

On the basis of these results it has been proposed that the mechanism of the catalytic action of ligands in reactions such as those depicted in equations (33) and (34) is similar to the internal nucleophile effect[117] on the intermolecular nucleophilic coordination of oxygen to the germanium atom.



(35)

During the catalytic oxidation of bis(triethylgermyl)mercury and its silyl analogue, increasing competition of reactions such as (32), (33) and (34) (depending on the reaction conditions) has an appreciable effect on the respective yields of triethylgermanium peroxide and triethylsilicon peroxide (Table 2).

The use of ligands as catalysts in the oxidation of OEC's is accompanied by a decrease in the activation energy of the process in comparison to that of the uncatalyzed autoxidation. For example, the oxidation of bis(triethylgermyl)mercury in the presence of ammonia ($n = 0.25$) exhibits an activation energy of 6.8 kcal·mol^{-1} as against a value of 13.7 kcal·mol^{-1} for the uncatalyzed autoxidation of this OEC[113].

Reports have been published[98,99] presenting data related to the catalytic effect of ethers

TABLE 2

Yield of $(Et_3E)_2$ (E = Ge, Si) obtained during the oxidation of $(Et_3Ge)_2Hg$ or $(Et_3Si)_2Hg$ in the presence of ligands c_0^{OEC} 0.1 mol·l^{-1}

Initial OEC	*L*	*n*	*Reaction temperature (°C)*	*Yield (mol.%)*
$(Et_3Ge)_2Hg$	NH_3	10	−50	81
$(Et_3Ge)_2Hg$	NH_3	4	−21	19
$(Et_3Ge)_2Hg$	NH_3	0.1	−20	traces
$(Et_3Si)_2Hg$	C_5H_5N	17	−20	10–30
$(Et_3Si)_2Hg$	C_5H_5N	1	−20	traces
$(Et_3Si)_2Hg$	t-C_4H_9OH	17	−20	traces

(over the region $n = 0$ to 1) on the oxidation of unsolvated organomagnesium compounds. In this case it has been shown that the initiation reaction in the catalyzed oxidation is free radical in nature. However, this does not affect the rate-determining stage in the reaction which corresponds to the bimolecular reaction of the initial OEC with oxygen[98].

These same authors have shown that the oxidations of diphenylmagnesium in chlorobenzene and of diphenylmagnesium–phenylmagnesium bromide in toluene are catalyzed by a variety of ethers added to the systems. The influence of these catalysts was shown to decrease in the order: $(n\text{-}C_4H_9)_2O > Et_2O >$ 1,2-dimethoxyethane > tetrahydrofuran > $PhOCH_3 > (i\text{-}Pr)_2O > PhOEt$.

This sequence does not correspond to any decrease in the basicity of the ethers and the authors attribute the effect to steric reasons.

These investigators also showed that the catalytic action of the ethers studied is only effective up to an n value of 0.5 or 1 depending on the nature of the ether. This behaviour is associated with the formation of OEC–ligand complexes with a definite composition.

It is interesting to note that in addition to the formation of OEC–ether complexes whose reactivity towards oxygen is greater than that of the unsolvated OEC, magnesium halides and oxidation products containing magnesium have an inhibiting effect on the rate of interaction of diphenylmagnesium with oxygen[99].

In a similar manner the rate of oxidation of the diphenylmagnesium complex in the presence of phenylmagnesium bromide is less than that of unsolvated diphenylmagnesium.

Data concerning the catalytic oxidation of bis(triethylgermyl)mercury in the presence of a number of ligands and over a wide range of n have also been reported[114,115]. As mentioned above, when n is small (over the range 0.5–2, depending on the nature of the ligand) the oxidation of this OEC proceeds via the formation of an OEC–ligand complex such that a thermodynamic equilibrium is maintained between the concentration of the complex and those of the initial reactants. Further increase of ligand content (increasing n from 0.5 up

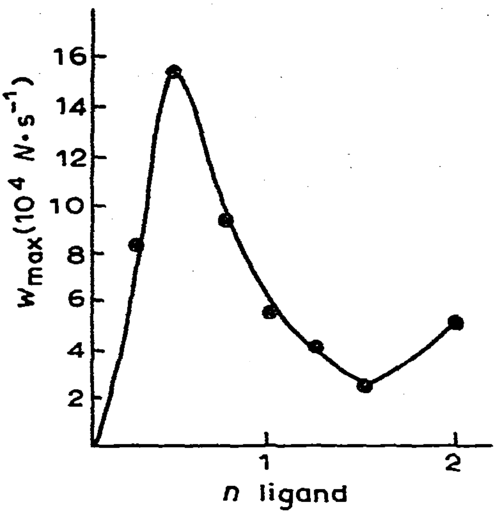


Fig. 12. Influence of *n* triphenylphosphine on the rate of catalytic oxidation of bis(triethylsilyl)mercury in n-octane (c_0 0.1 mol·l^{-1}) at −10°.

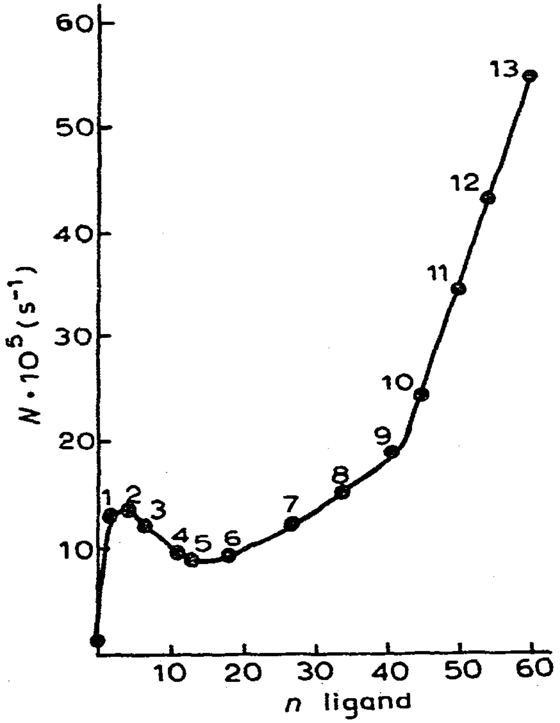


Fig. 13. Dependence of $N_{max.}$ (s^{-1}) for the catalytic oxidation of bis(triethylgermyl)mercury in n-octane on the value of *n* t-butyl alcohol *t* −20°, $P(O_2)$ 300 mmHg. The points 1, 2, 3, 4, ... 13 have been obtained with $(OEC)_0$ respectively equal to 0.0558, 0.0551, 0.0545, 0.0533, 0.0527, 0.0515, 0.0493, 0.034, 0.0464, 0.0455, 0.0323, 0.0318 and 0.019 mol·l^{-1} and $(L)_0$ respectively equal to 0.127, 0.252, 0.371, 0.603, 0.718, 0.937, 1.347, 1.63, 1.905, 2.061, 1.630, 1.731 and 1.142 mol·l^{-1}.

to 1.5 and from 2 up to 15 when triphenylphosphine and t-butyl alcohol are used respectively as ligands) leads to a negative kinetic effect[114,115].

The results depicted in Figs. 12 and 13 are the first examples described which illustrate the change in the catalytic effect when the *n* value of the ligand is increased.

The negative effect of the ligand may be associated with the decrease in the coordination capacity of the heteroatom in the OEC towards specific ligand solvation[114,115].

In the oxidation of bis(triethylgermyl)mercury in the presence of t-butyl alcohol[115], the rate of the reaction of OEC with oxygen continues to increase even at *n* values greater than 12. This behaviour is due to the tendency for the ligand to associate at increasing values of *n* and for the catalytic activity of the associates to increase with increasing molecular weight.

Data have also been reported[72] regarding the autoxidation of dimethylcadmium. The results obtained for this compound suggest that in this case the primary reaction involves bimolecular reaction between the OEC and oxygen. In this connection it is interesting that pyridine catalyzes the oxidation of dimethylcadmium in isooctane[72]. Unfortunately, however, the results reported do not extend over a particularly wide range of *n* values.

D. The mechanism of the primary reaction in OEC autoxidation. The influence of the nature of the OEC, the reaction medium and the electronic state of the oxygen added

The results of the experimental investigations considered above indicate that the nature of the OEC plays an important role in the mechanism of the primary reaction involved in the autoxidation of these compounds.

A comparison of the possible primary reactions involved suggests that the bimolecular heterolytic nature of this reaction involving direct interaction between the OEC and oxygen, as opposed to the spontaneous fission of the OEC into radicals, should increase as the effective electronegativity (χ) of the OEC heteroatom decreases and as the value of χ for oxygen increases (as occurs for example when oxygen is substituted for ozone). That such behaviour does occur is demonstrated by a comparison of the results of studies of the primary reactions which occur during the autoxidation and ozonization of a given OEC.

The great affinity of ozone for an electron (2.89 eV in comparison with 0.87 eV for oxygen[7]) gives rise to a heterolytic mechanism for the ozonolysis reaction of OEC's[118], which does not occur during the corresponding reaction with oxygen.

It is well known[119,120] that the mechanism of the reaction of an OEC with ozone may be represented as a succession of individual steps.

(i) Coordination of ozone to the OEC heteroatom involving interaction between the electrophilic centre of ozone and the vacant atomic orbitals of the heteroatom.

(ii) Electrophilic attack on the element—carbon bond by the coordinated ozone.

(iii) Transformation of the intermediate trioxide. For example, with ethyl derivatives of the non-transition elements of Group IV the reaction mechanism involved may be depicted by the following scheme[119,120]:

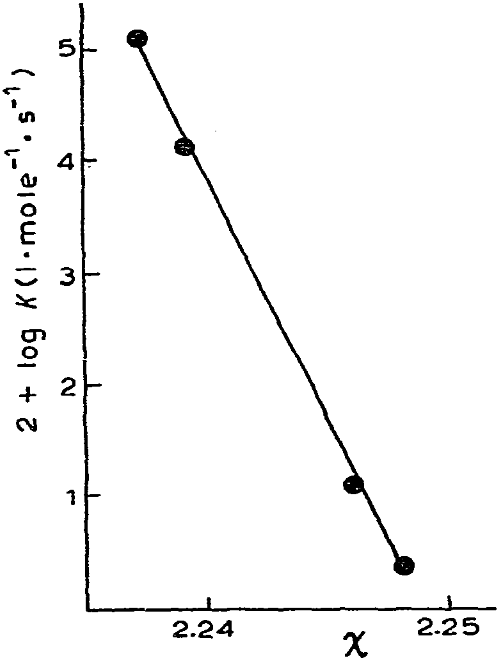


Fig. 14. Dependence of log K for the ozonolysis of Et_4E (where E = Si, Ge, Sn or Pb) on the χ value of the heteroatom.

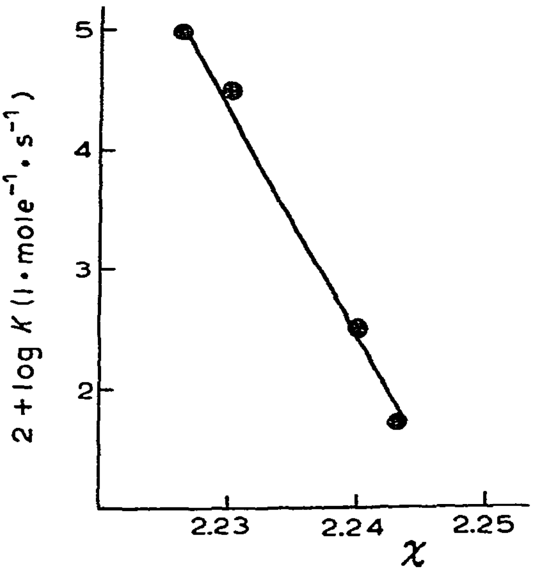
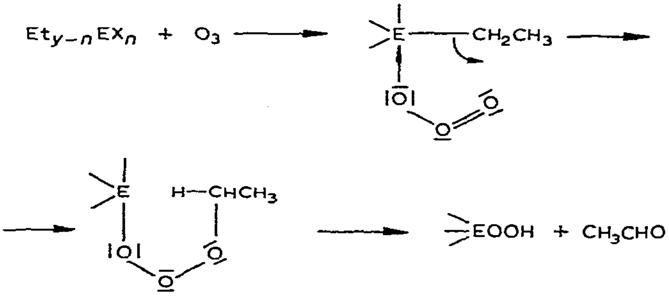


Fig. 15. Dependence of log K for the ozonolysis of Et_3EEEt_3 (where E = Si, Ge, Sn or Pb) on the χ value of the heteroatom.



(36)

From such a mechanism it follows that the relative reactivity of ozone towards OEC's which are equivalent with respect to available vacancies in heteroatom coordination capacity may be related to the χ* value for the OEC heteroatom. The presence of such a correlation which may be expressed by an equation similar to the Hammett–Taft equation has been

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* The χ value for a given OEC heteroatom (general formula $E_bC_mH_k$) may be calculated through use of the equation $\chi = b + m + k\sqrt{\chi_E^b\chi_C^m\chi_H^k}$ (Sanderson's method[121]) using elements in accordance with Gordy's system[122].

TABLE 3

The dependence of the mechanism of the primary reaction in the autoxidation of OEC on the χ value of the OEC heteroatom

OEC	χ^a	*Nature of primary reaction mechanism*	*Reference*
Et_2Cd	2.162	Bimolecular reaction with oxygen	57
$(Et_3Ge)_2Hg$	2.205	Bimolecular reaction with oxygen	54, 55
$(Et_3Si)_2Hg$	2.207	Bimolecular reaction with oxygen	54, 55
Et_3Tl	2.211	Bimolecular reaction with oxygen	56
$Et_3SiHgEt$	2.196	Spontaneous fission of OEC	64
$n\text{-}Pr_2Hg$	2.195	Spontaneous fission of OEC	63
$(i\text{-}Pr_3Ge)_2Hg$	2.226	Spontaneous fission of OEC	58
$Et_3SnSnEt_3$	2.230	Spontaneous fission of OEC	59
$(Et_3Ge)_3Sb$	2.232	Spontaneous fission of OEC	65, 66
Et_4Pb	2.236	Spontaneous fission of OEC	60

[a] The χ value of the OEC heteroatom has been calculated in the same way as that employed for the data relating to the ozonolysis of OEC (see Figs. 14 and 15).

established for Et_4E[123,124] and Et_6E_2 [124] where E = Si, Ge of Pb (Figs. 14 and 15). This relationship is only broken down on successive substitution of ethyl radicals by halide or oxygen fragments, a process which disturbs the d_π–p_π conjugation in the molecule[126,127].

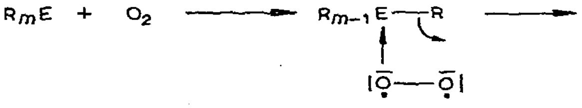
These results suggest that the nature of the mechanism involved in the primary reaction for the autoxidation of OEC may also depend on the χ value of the OEC heteroatom. The results reported in Table 3 support this suggestion.

From the table it may be seen that a change in the mechanism of the primary reaction occurs as the χ value of the OEC heteroatom increases, bimolecular interaction with oxygen occurring at low χ values while spontaneous fission of OEC into radicals occurs at high χ values. This means that the probability of bimolecular interaction of OEC's with oxygen increases as the effective electronegativity of the OEC heteroatom decreases (electronegative effect).

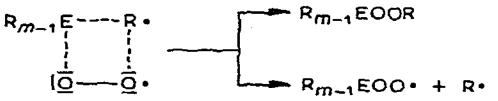
The χ value at which the change in mechanism occurs, obviously varies when different OEC's are compared. This follows from the possible appearance of steric effects, from differences in the bond energies of the E–C bond depending on the nature of the OEC (see Table 1) as well as on other factors (thus in the autoxidation of ethyl(triethylsilyl)mercury, for example, the mechanism of the primary reaction is complicated by an intermolecular reaction involving the initial OEC).

The heterolytic molecular reaction of OEC's with oxygen apparently proceeds in successive stages which in accordance with the autoxidation and ozonolysis data available for these compounds are (a) coordination of oxygen to the OEC heteroatom via the *p* electrons of the oxygen and the vacant atomic orbitals of the heteroatom and (b) electrophilic attack on the element–carbon bond by the coordinated oxygen.

This mechanism may be depicted by the following scheme:



(37)



(38)

Specific solvation of OEC by compounds containing atoms with electron-donor properties decreases the effective electronegativity of the heteroatom through the formation of complexes containing a donor-accpetor heteroatom–ligand bond. In this way OEC–ligand complexes are formed which have higher reactivities towards oxygen than the initial OEC.

The heterolytic mechanism for the interaction between OEC's and oxygen or ozone (reactions such as those depicted in equations (36), (37) and (38) suggests that the extent to which catalysis of oxidation or ozonolysis reactions occurs through addition of ligands is also dependent on the availability of vacant coordination sites on the OEC heteroatom (coordination capacity effect).

Results which provide convincing evidence for the existence of this effect have been obtained during investigations of the catalytic effect of ligands on the bimolecular reaction between OEC's and oxygen as well as from studies of the ozonolysis of OEC's.

It has been noted[114,115] that the filling of vacant coordination sites in the heteroatom of a given OEC by ligands leads to a negative kinetic effect. This also provides a possible reason for the relatively greater stability towards oxygen of OEC complexes which are coordinately saturated with ligands in comparison to unsolvated OEC's[106,110–112].

The formation of the coordinately saturated complexes on ozonolysis of triethyltin chloride ($EtClSnO \cdot Et_3SnCl \cdot O_3$ and $EtClSnO \cdot Et_3SnCl$[128]) and diethyltin dichloride ($EtCl_2SnOOH \cdot Et_2SnCl_2$[129]) is responsible for the high stability of organotin fragments containing one, two and even three tin–carbon bonds towards ozone.

A similar result has been obtained from an investigation of the ozonolysis of a number of other ethyl-lead and -tin derivatives[130–131].

In the heterolytic reaction between OEC's and oxygen (or ozone), the coordination capacity effect and the electronegativity effect appear in successive stages. Hence despite a high value for the effective electronegativity of a given OEC heteroatom, on coordination to the heteroatom oxygen (or ozone) may be unable to undergo rapid electrophilic attack on the heteroatom–carbon bond and this would lead to the second stage in the process being very slow.

In this case, an accumulation of the reversible OEC–oxygen (or OEC–ozone) complex would occur in the system. This behaviour has been observed for chelates of the transi metals[134], but a similar situation reported earlier for tri-n-butylboron complexes[135] h subsequently been disproved[95]. More recently, however, fairly convincing evidence of formation of a reversible OEC—oxygen complex has been obtained in a study of the au dation of diethylcadmium[137].

The autoxidation of diethylcadmium in paraffin hydrocarbons proceeds readily at t atures above −80°, with up to two moles of oxygen being absorbed per mole of initial depending on the initial concentration (c_0) of diethylcadmium and the reaction tempe For example, at −40° and c_0 0.04 mol·l^{-1} two moles of oxygen were absorbed per mo initial OEC ($N = 2$)[137].

Immediately after uptake of oxygen the reaction mixture consists of a homogeneou solution which precipitates a solid on standing. At $N = 2$, this solid is diethylperoxycad Before the formation of the solid diperoxide, it has been shown that the diethylcadmiu forms a reversible complex with oxygen. This is supported by the following observation if oxygen is pumped out of such a reaction mixture, free OEC is obtained once more wl is capable of recombining with oxygen to form a complex in which the ratio of OEC/ox lies in the range up to 1/2. Using the same solution of diethylcadmium, this procedure c be repeated successively several times.

The resulting 1/2 diethylcadmium—oxygen complex exhibits a sharp absorption banc 276 nm which disappears either on "pumping" out the oxygen from the system or on co version of the complex to the diperoxide (precipitation).

From the kinetics of the transformation of the complex to the diperoxide (the experi being conducted in quartz reaction vessels), it appears likely that this reaction is heterog and occurs on the walls of the reaction vessel. The activation energy obtained for the rearrangement was 9 kcal·mol^{-1} and quite small additions of substances containing atoms electron-donor properties catalyze the process. It should be noted that the formation of similar reversible OEC—ozone complex had been established earlier during the ozonolysis of triethyltin chloride[128].

From this it appears that the mechanism of the primary reaction in the autoxidation c OEC is dependent on the nature of the OEC, the electronic state of the oxygen added to system and the nature of the medium. Other things being equal the probability of a bimolecular heterolytic interaction between the OEC and oxygen increases as the electrone tivity of the heteroatom in the OEC decreases or on an increase in the electronegativity o oxygen (*i.e.* replacing oxygen with ozone).

Specific solvation of OEC's by ligands leads to the successive appearance of positive an negative kinetic effects, the first being caused by a decrease in the electronegativity of the OEC heteroatom while the second is attributable to the influence of the ligand on the coo dination capacity of the heteroatom.

III. THE PRINCIPAL INTERMEDIATE PRODUCTS FORMED DURING THE AUTOXIDATION OF OEC's

A. *Organoelement peroxides*

Organoelement peroxides are found amongst the autoxidation products both when the primary reaction proceeds heterolytically and homolytically.

If the primary reaction proceeds heterolytically and reaction (37) is the principal reaction then the corresponding organoelement peroxide is the major molecular product after the reversible OEC—oxygen complex of the reaction.

If the primary reaction proceeds homolytically, or if this reaction is heterolytic and reaction (38) is the principal reaction, the formation of organoelement peroxides is governed by the considerable tendency of OEC's to undergo bimolecular homolytic substitution reactions with peroxy radicals. Such free-radical substitution reactions have been reviewed previously by Ingold and Roberts[5].

The nature of the overall process in the autoxidation of OEC's is very dependent on the properties of the organoelement peroxides formed as intermediates. In this connection it is interesting to consider the possible transformation routes of organoelement peroxides in the autoxidation of OEC's.

The most common organoelement peroxides known to date are those of the type $R_{m-x}E(OOR')_x$ where m is the valency of the heteroatom.

The route by which these peroxides are transformed depends both on their nature and on the medium. In hydrocarbon solvents and when R′ is a tertiary radical, the corresponding peroxides decompose by homolytic breakage of the oxygen—oxygen bond*. This fact has been established through studies of both the kinetics and the products of the thermal decomposition of peroxide derivatives of silicon[138–145], germanium[141], tin[141,146–148], lead[141], mercury[149] and phosphorus[186].

Recently, data have been reported[150] which suggest that the homolytic decomposition reactions of these peroxides are in competition with bimolecular reactions between the peroxides and the solvent. Thus the primary reactions involved in the thermal decomposition of such peroxides (for example, those of the non-transition metals in Group IV of the Periodic Table) in hydrocarbons are thought to involve the following[150]:

$$R_3EOOR' \longrightarrow R_3EO^{\bullet} + R'O^{\bullet} \tag{39}$$

$$R_3EOOR + R''H \longrightarrow R'OH + \{R_3EO^{\bullet},\ \dot{R}''\} \tag{40}$$

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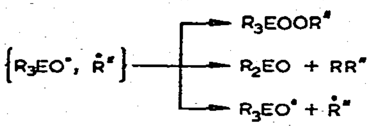
* This mode of decomposition for OEC peroxides has been assumed by a large number of investigators on the basis of indirect data. In the discussion below, however, only studies in which the mechanism of the decomposition of the peroxide OEC has been specifically investigated, are considered.



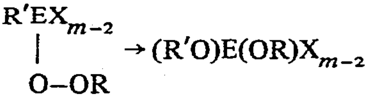
$$\{R_3EO^\bullet, \dot{R}''\} \rightarrow R_3EOOR'' \quad (41)$$

$$\{R_3EO^\bullet, \dot{R}''\} \rightarrow R_2EO + RR'' \quad (42)$$

$$\{R_3EO^\bullet, \dot{R}''\} \rightarrow R_3EO^\bullet + \dot{R}'' \quad (43)$$

With the organosilicon peroxides $(CH_3)_3Si{-}OOC(CH_3)_n(C_6H_5)_{3-n}$ it has been established[144] that the magnitude of the rate constant for the homolytic decomposition of the peroxide increases as the value of n increases and also increases in the series of solvents n-nonane < toluene < isopropylbenzene < anisole < dioxane.

In addition to reactions (39) and (40), the peroxides are also capable of intermolecular rearrangement to form isomeric products which do not contain active oxygen.



$$\begin{array}{l} R'EX_{m-2} \\ | \\ O{-}OR \end{array} \rightarrow (R'O)E(OR)X_{m-2} \quad (44)$$

Such rearrangements have been observed in studies of the decomposition of peroxides of boron[29,40,42,136,151], aluminium[35,152], silicon[140,145], tin[147] and antimony[152–154].

The presence of intramolecular rearrangements in some cases does not exclude the simultaneous homolytic decomposition of the peroxide. In this respect the results obtained from investigations of the thermal decomposition of t-butylperoxydiethylphosphate, t-butylperoxyphenylethylphosphate, t-butylperoxydibutylphosphate and t-butylperoxydiethylphosphate in n-nonane are of interest[156–158]. In all these cases it has been shown that the organophosphorus peroxides simultaneously undergo homolytic decomposition and heterolytic rearrangement to isomeric products which do not contain peroxo groupings.

If the t-butylperoxy radicals are replaced by cumylperoxy or s-butylperoxy and if n-nonane is replaced with a solvent capable of dipole–dipole interactions, this leads to an increasing tendency for heterolytic rearrangements to occur.

Peroxide derivatives where R′ is either a primary or a secondary radical are also of interest. From studies of the behaviour of ethylperoxydiethylthallium[56] and s-butylperoxytriethyltin[159], it has been shown that in this case intramolecular rearrangement occurs involving interaction with the hydrogen of the α-carbon atom.

$$Et_2TlOOEt \rightarrow Et_2TlOH + CH_3CHO \quad (45)$$

$$Et_3SnOOCH(CH_3)C_2H_5 \rightarrow Et_3SnOH + C_2H_5COCH_3 \quad (46)$$

Decomposition of the corresponding peroxides in the original OEC as the solvent medium is also particularly interesting.

As mentioned above, it has been widely held[13–21] that interaction between the intermediate organoelement peroxide and the OEC from which it is derived proceeds during autoxidation by a mechanism similar to that proposed by Wuyts[12]

$$R_{m-1}EOOR + R_mE \rightarrow 2R_{m-1}EOR \qquad (47)$$

More recently, however, data have been reported which indicate that the interaction is somewhat more complicated. Thus Hansen and Hamann[68,160] have suggested that the interaction of triethylboron with ethylperoxydiethylboron involves the formation of a radical couple which is capable of reacting via two routes.

$$Et_3B + Et_2BOOEt \longrightarrow Et_2BOEt + \{Et^\bullet, Et_2BO^\bullet\} \qquad (48)$$

$$\{Et^\bullet, Et_2BO^\bullet\} \longrightarrow Et_2BOEt \qquad (49)$$

$$\{Et^\bullet, Et_2BO^\bullet\} \longrightarrow Et^\bullet + Et_2BO^\bullet \qquad (50)$$

This suggestion has been supported by a number of other investigations[46,161,162]

It has been shown[163] that the decomposition of t-butylperoxytriethyltin in tetraethyltin is not complicated by reactions such as that depicted in (47) but that on replacing tetraethyltin by hexaethylditin as a solvent such a reaction occurs.

Elsewhere[164] it has been shown that reactions such as (48)–(50) occur when t-butylperoxytriethyltin is decomposed in the presence of diethyltin oxide.

The results of a recent study indicate that the peroxide products of the autoxidation of OEC are capable of producing self-inhibition of the reaction between the initial OEC and oxygen through the formation of donor–acceptor type complexes with the initial OEC. Such behaviour has been observed in an investigation of the autoxidation of diethylcadmium in hydrocarbon solvents[175].

In comparison with the above-mentioned peroxides, those of the general formulae $R_{m-1}EOOER_{m-1}$ and $R_{m-1}EOOE'R_{m-1}$ have been less well studied. The kinetics and products of the thermal decomposition of triethyltin peroxide in n-nonane, as well as in a mixture of hexaethyltin with n-nonane, have been studied in an attempt to assess the ability of this peroxide as an initiator in radical processes, *i.e.* the polymerization of methylmethacrylate, autoxidation of hexaethylditin, etc. It has been found that the thermal decomposition of this peroxide proceeds via two routes; spontaneous homolytic fission and rearrangement into non-peroxide products

$$Et_3SnOOSnEt_3 \longrightarrow 2Et_3SnO^\bullet \qquad (51)$$

$$Et_3SnOOSnEt_3 \longrightarrow Et_3SnOEt + Et_2SnO \qquad (52)$$

In the presence of hexaethylditin, interaction of peroxide with the organotin compound occurs both by a molecular and a radical mechanism.

$$\mathrm{Et_3SnOOSnEt_3 + Et_3SnSnEt_3} \rightarrow \mathrm{2(Et_3Sn)_2O} \tag{53}$$

$$\mathrm{Et_3SnOOSnEt_3 + Et_3SnSnEt_3} \rightarrow \mathrm{(Et_3Sn)_2O + Et_3SnO^{\bullet} + Et_3Sn^{\bullet}} \tag{54}$$

$$\mathrm{Et_3Sn^{\bullet} + Et_3SnOOSnEt_3} \longrightarrow \mathrm{(Et_3Sn)_2O + Et_3SnO^{\bullet}} \tag{55}$$

$$\mathrm{Et_3SnO^{\bullet} + Et_3SnSnEt_3} \longrightarrow \mathrm{(Et_3Sn)_2O + Et_3Sn^{\bullet}} \tag{56}$$

$$\mathrm{Et_3SnO^{\bullet} + Et_3Sn^{\bullet}} \longrightarrow \mathrm{(Et_3Sn)_2O} \tag{57}$$

Thermal decomposition of trimethylsilylperoxy(triphenyl)silane involves isomerization to form a non-peroxide product[169].

$$\mathrm{Ph_3SiOOSi(CH_3)_3 \rightarrow (PhO)Ph_2SiOSi(CH_3)_3} \tag{58}$$

Increasing the dielectric constant of the solvent increases the rate of the reaction and decreases its activation energy (see Table 4).

In the series $\mathrm{Ph_3GeOOSiPh_x(CH_3)_{3-x}}$, the value of the rate constant for isomerization which occurs via a reaction similar to (58) increases linearly as x increases[170].

Hydroperoxides of organoelement compounds have been the least studied of all OEC peroxides. It has been pointed out[171] that trimethylsilyl hydroperoxide disproportionates even under normal conditions to form trimethylsilyl peroxide and hydrogen peroxide.

$$\mathrm{2(CH_3)_3SiOOH \rightarrow (CH_3)_3SiOOSi(CH_3)_3 + H_2O_2} \tag{59}$$

Elsewhere[172] it has been shown that triethyltin hydroperoxide may be stabilized as the perhydride.

$$\mathrm{2Et_3SnOOH + H_2O_2 \rightarrow (Et_3SnOOH)_2 \cdot H_2O_2} \tag{60}$$

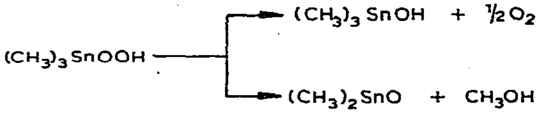
Results of studies of the thermal decomposition of trimethyltin hydroperoxide[173] indi-

TABLE 4

The influence of the dielectric constant (ϵ) of the solvent (RH) on the rate constant for the isomerization of $\mathrm{Ph_3SiOOSi(CH_3)_3}$[169]

RH	*ϵ(20°)*	*$k \times 10^5$ (s^{-1})*	*E(kcal·mol^{-1})*
Heptane	1.92	26.6	28
Isopropylbenzene	2.38	31.6	27.6
Anisol	4.33	35.7	27.1

cate that this hydroperoxide may transform in two ways, one involving the liberation of oxygen and the other not.



$$(CH_3)_3SnOOH \rightarrow (CH_3)_3SnOH + \tfrac{1}{2}O_2 \qquad (61)$$

$$(CH_3)_3SnOOH \rightarrow (CH_3)_2SnO + CH_3OH \qquad (62)$$

The decomposition of triphenylsilicon hydroperoxide is assumed to proceed via a radical mechanism[174].

$$Ph_3SiOOH \rightarrow Ph_3SiO^{\bullet} + HO^{\bullet} \qquad (63)$$

$$Ph_3SiO^{\bullet} \rightarrow Ph_2\dot{S}iOPh \qquad (64)$$

$$Ph_2\dot{S}iOPh + HO^{\bullet} \rightarrow Ph_2Si(OPh)OH \qquad (65)$$

Thus, organoelemental peroxide compounds formed as intermediates during the autoxidation of OEC's are able to transform either by means of a homolytic or a heterolytic mechanism depending on the nature of the peroxides, the nature of the initial OEC and on the solvent.

B. Oxygen-containing non-peroxide OEC's

From general considerations it is possible to arrive at some conclusions regarding the influence of oxygen-containing non-peroxide organoelemental reaction products on the rate of autoxidation of the initial OEC.

To date, however, reliable data are only available regarding two possible influences of these products.

Firstly, these materials should be capable of specifically solvating the initial OEC and thereby influencing its subsequent autoxidation and secondly these materials may be capable of interaction with any free radicals which may be generated during the reaction.

The influence of solvation on the reactivity of OEC's towards oxygen has been considered above. Here only data relating to the interaction of oxygen-containing non-peroxide organoelemental compounds with free radicals in the autoxidation of OEC will be considered.

It has been shown[166] that differences between the kinetic features of the autoxidation of hexaethyldilead in comparison with that of hexaethylditin may be associated with the distinctive role of triethyllead oxide which is formed as an intermediate in the first reaction.

It has been established[176,177] that the influence of triethyllead oxide on the autoxidation of hexaethyldilead involves disproportionation of the oxide.

Investigation of the products and of the kinetics of the thermal decomposition of triethyllead oxide[177,178] enables the following scheme to be suggested for the mechanism for this reaction.

$$2(Et_3Pb)_2O \rightarrow Et_4Pb + Et_3PbOPbEt_2OPbEt_3 \tag{66}$$

$$(Et_3Pb)_2O + Et_3PbOPbEt_2OPbEt_3 \rightarrow Et_4Pb + Et_3Pb(OPbEt_2)_2OPbEt_3 \tag{67}$$

$$(Et_3Pb)_2O + Et_3Pb(OPbEt_2)_2OPbEt_3 \rightarrow Et_4Pb + Et_3Pb(OPbEt_2)_3OPbEt_3 \tag{68}$$

etc.

$$\sim\sim(OPbEt_2)_i\sim\sim \rightarrow \sim\sim(OPbEt_2)_{i-1}\ OPbEt\sim\sim + Et^{\bullet} \tag{69}$$

Generation of free radicals by the disproportionation of triethyllead oxide leads to degenerate branching of the chains during the autoxidation of hexaethyldilead.

It has been shown[179] that ethyllead hydroxides formed as the products of the autoxidation of tetraethyllead considerably accelerate this free-radical chain process.

Examination of these hydroxides has established[180] that their effectiveness as accelerators may be attributed to their readiness to disproportionate and to generate free ethyl radicals.

$$2Et_3PbOH \rightarrow Et_4Pb + Et_2Pb(OH)_2 \tag{70}$$

$$2Et_2Pb(OH)_2 \rightarrow Et_4Pb + EtPb(OH)_3 \tag{71}$$

$$EtPb(OH)_3 \rightarrow C_2H_4 + 2H_2O + PbO \tag{72}$$

$$2Et_2Pb(OH)_2 \rightarrow PbO_2 + Et_4Pb + 2H_2O \tag{73}$$

$$Et_2Pb(OH)_2 \rightarrow Et_2PbO + H_2O \tag{74}$$

$$Et_2PbO \rightarrow PbO + 2Et^{\bullet} \tag{75}$$

$$2Et^{\bullet} \rightarrow C_2H_4 + C_2H_6 \tag{76}$$

$$2Et^{\bullet} \rightarrow C_4H_{10} \tag{77}$$

From an investigation of the autoxidation of di-isopropylmercury it has been established[38,39] that degenerate branching in this system may be attributed to isopropylmercury isophosphate which is formed as an intermediate. In fact, data available regarding the thermal decomposition of this compound indicate that isopropylmercury isophosphate also functions through the generation of free radicals[181].

IV. PECULIAR FEATURES OF THE AUTOXIDATION OF OEC's

A. Processes which proceed according to a molecular mechanism

A molecular mechanism for the liquid-phase autoxidation of the OEC concerned has been established in the oxidation of diethylcadmium[57], bis(triethylgermyl)mercury[54,55], bis(triethylsilyl)mercury[54,55], triethylthallium[56] and bis(triphenylgermyl)mercury[182].

In all these cases the influence of ligands in the specific solvation of the OEC is very pronounced[114,115].

A general scheme for the autoxidation of OEC's via a molecular mechanism may be illustrated by considering the case of bis(triethylgermyl)mercury.

$$(Et_3E)_2Hg + O_2 \underset{k_1''}{\overset{k_1'}{\rightleftarrows}} [(Et_3E)_2Hg \cdot O_2] \rightarrow Et_3EHgOOEEt_3 \tag{78}$$

$$Et_3EHgOOEEt_3 + (Et_3E)_2Hg \rightarrow 2Et_3EHgOEEt_3 \tag{79}$$

$$Et_3EHgOEEt_3 \rightarrow (Et_3E)_2O + Hg \tag{80}$$

$$(Et_3E)_2Hg + L \underset{k_2''}{\overset{k_2'}{\rightleftarrows}} [(Et_3E)_2Hg \cdot L] \tag{81}$$

where L is $(Et_3E)_2O$ or any aother active additive.

$$[(Et_3E)_2Hg \cdot L] + O_2 \xrightarrow{k_3} Et_3EHgOOEEt_3 \cdot L \tag{82}$$

$$Et_3EHgOOEEt_3 \cdot L + (Et_3E)_2Hg \rightarrow Et_3EHgOEEt_3 \cdot L + Et_3EHgOEEt_3 \tag{83}$$

$$Et_3EHgOOEEt_3 \cdot L \rightarrow Et_3EOOEEt_3 + Hg + L \tag{84}$$

$$Et_3EHgOEEt_3 \cdot L \rightarrow Et_3EOEEt_3 + Hg + L \tag{85}$$

$$Et_3EHgOOEEt_3 \xrightarrow{L} Et_3EOOEEt_3 + Hg + L \tag{86}$$

$$Et_3EHgOEEt_3 \xrightarrow{L} Et_3EOEEt_3 + Hg + L \tag{87}$$

The rate of oxygen uptake may be expressed by an equation of the form:

$$w = k_1' [OEC] [O_2] + k_3 [O_2] \frac{k_2' [OEC] [L]}{k_2'' + k_3 [O_2]} \tag{88}$$

where k_1', k_2', k_2'' and k_3 are the rate constants for the interaction of oxygen with the OEC, for the formation and decomposition of the complex OEC · L and for the interaction of oxygen with this complex, respectively; [OEC], $[O_2]$ and [L] are the concentrations of the initial OEC, oxygen and the ligand catalyst.

In the absence of catalytic processes involving the ligands the rate equation takes the form:

$$w = k_1' [OEC] [O_2] \tag{89}$$

An example of this state of affairs occurs in the autoxidation of bis(triphenylgermyl)-mercury[182].

When considerable autocatalysis as well as catalysis involving additives occurs the rate equation may be written as

$$w = k_3 [O_2] \frac{k_2' [OEC] [L]}{k_2'' + k_3 [O_2]} \tag{90}$$

If $k_2'' \gg k_3 [O_2]$, the concentration of the complex OEC · L may be put equal to the thermodynamic equilibrium value and $w = k_3 \cdot k_2'/k_2'' \cdot [OEC] [L] [O_2]$.

An example of this occurs in the catalytic autoxidation of bis(triethylgermyl)mercury in the presence of a number of ligands[113, 114].

If $k_2'' \ll k_3[O_2]$, the concentration of the complex OEC · L is not the thermodynamic equilibrium value and $w = k_2'[\text{OEC}][\text{L}]$.

This occurs in the autoxidation of bis(triethylgermyl)mercury (where autocatalysis occurs via triethylgermanium oxide[54,55]).

Various complications arise in the kinetic treatment if association of the OEC or the ligand occurs or if the degree of association influences the catalytic activity of the ligand.

The kinetic analysis of the catalysis of the oxidation of bis(triethylgermyl)mercury by t-butyl alcohol, present as associates in different ratios, leads to the following scheme for the process[115].

$$L_{i-1} + L \rightleftarrows L_i \tag{91}$$

$$L_i + (Et_3Ge)_2Hg \rightleftarrows [(Et_3Ge)_2Hg \cdot L_i] \tag{92}$$

$$[(Et_3Ge)_2Hg \cdot L_i] + O_2 \rightarrow Et_3GeHgOOGeEt_3 \cdot L_i \tag{93}$$

$$Et_3GeHgOOGeEt_3 \cdot L_i + (Et_3Ge)_2Hg \rightarrow Et_3GeHgOGeEt_3 \cdot L_i + Et_3GeHgOGeEt_3 \tag{94}$$

$$Et_3GeHgOOGeEt_3 \cdot L_i \rightarrow Et_3GeOOGeEt_3 + Hg + L_i \tag{95}$$

$$Et_3GeHgOGeEt_3 \cdot L_i \rightarrow Et_3GeOGeEt_3 + Hg + L_i \tag{96}$$

$$Et_3GeHgOGeEt_3 \xrightarrow{L_i} Et_3GeOGeEt_3 + Hg \tag{97}$$

In the general case, the above scheme leads to a very complicated expression for the overall rate (w). However, if reaction with oxygen is assumed to be zero order*, the resulting expression for w is relatively simple.

$$w = \Sigma k_{3i}[\text{OEC}] \frac{(\prod\limits_i k_{2i}) \cdot [\text{L}]^i}{\prod\limits_i (k'_{2i} + k_{3i}[\text{OEC}])} \tag{98}$$

where [OEC], [L], k_{2i}, k'_{2i} and k_{3i} are respectively the concentrations of bis(triethylgermyl)-mercury and the ligand catalyst and the rate constants for the formation and decomposition of i-meric associates as depicted in equation (91) and for the interaction of i-meric associates with bis(triethylgermyl)mercury as depicted in equation (92).

Recently, results have been reported[115] suggesting that under the above conditions $k_{3i}[\text{OEC}] \gg [k'_{2i}]$ in this system. Under these conditions and also assuming that the reaction has not proceeded to any great extent ($[\text{OEC}] \approx [\text{OEC}]_0$), if the concentration of ligand employed is a simple multiple of the initial ligand concentration ($[\text{L}] = \alpha[\text{L}]_0$; α = constant) then the expression for the relative rate of oxidation of bis(triethylgermyl)mercury takes the form:

$$N = \Sigma a_i n_i$$

---

* It has been established[115] that the oxidation of bis(triethylgermyl)mercury in the presence of t-butyl alcohols zero order in oxygen when the degree of association of the alcohol is greater than unity.

where $$a_i = k_{3i}\left(\frac{\prod_i k_{2i}}{\prod_i k_{3i}}\right)\alpha^i \qquad (99)$$

Equation (99) corresponds to the relationship established experimentally for the dependence of the relative rate of oxidation of bis(triethylgermyl)mercury on the ratio of ligand catalyst, n, in the system[115].

B. Processes which proceed by means of a free-radical mechanism

Detailed data are now available for the free-radical chain processes involved in the liquid-phase autoxidation of tetraethyllead[60,61,179], hexaethyldilead[179], hexaethylditin[183] and a number of organoboron compounds[44,46].

The formal kinetic characteristics of these processes are similar to those described in the literature for the liquid-phase autoxidation of hydrocarbons[6].

The autoxidation of tetraethyllead, at least in the early stage, proceeds[60,61] according to the relation

$$N = a \cdot e^{\varphi t} \qquad (100)$$

where a is a proportionality constant, φ is an autocatalysis factor and t is the time of reaction.

The temperature dependence of the autocatalysis factor may be depicted by the equation

$$\varphi = 6.3 \times 10^{11} \cdot \exp\{-25500/RT\}\ (\mathrm{s}^{-1}) \qquad (101)$$

The factor φ at the temperature normally employed for the autoxidation of tetraethyllead (80–100°) has an average value of 10^{-4} s^{-1} which is similar in magnitude to the value of the autocatalysis factors for the degenerate branched-chain processes involved in the autoxidation of hydrocarbons[184].

Degenerate chain branching occurs in the early stages of the autoxidation of tetraethyllead and results in the formation of the peroxide product found in this reaction[179].

Davies and co-workers[46] have made a detailed study of the kinetics of the free-radical chain processes involved in the autoxidation of some organoboron compounds (tri-t-butyl-, tri-s-butyl- and tri-n-butylboron, di-n-butyl (alkoxy)boranes, n-butyl(dialkoxy)boron, etc.) in isooctane in the absence and in the presence of pyridine as a ligand capable of complexing with organoboron compounds.

For those organoboron compounds whose kinetic behaviour has been studied adequately, it has been established that the basic reaction scheme involves free-radical chain interaction with oxygen

Initiation: $\mathrm{R}^{\bullet}$ (rate R_i) (102)

Chain propagation: $\mathrm{R}^{\bullet} + \mathrm{O}_2 \rightarrow \mathrm{ROO}^{\bullet}$ (103)

$\mathrm{ROO}^{\bullet} + \mathrm{BR} \xrightarrow{k_p} \mathrm{ROOB} + \mathrm{R}^{\bullet}$ (104)

Chain termination: $2\mathrm{ROO}^{\bullet} \xrightarrow{2k_f}$ unactive products (105)

In this reaction scheme, the following designations are employed: BR depicts the organoboron compound, k_p and k_f are the rate constants for propagation and termination and R_i is the rate of the chain-initiation process.

From the reaction scheme outlined in equations (102)–(105), the general expression for the rate of autoxidation of the organoboron compounds investigated may be obtained as:

$$w = \frac{k_p}{(2k_f)^{\frac{1}{2}}} [\mathrm{BR}] \cdot R_i^{\frac{1}{2}} \qquad (106)$$

The theoretical relationship is identical to the classic expression for the rate of autoxidation of hydrocarbons where quadratic chain termination via peroxy radicals occurs[6].

As has been shown previously[62,183], the autoxidation of hexaethylditin also proceeds in accordance with a mechanism similar to that depicted in equations (102)–(105), with the rate of the reaction being expressed by an equation identical to (106).

The kinetic features of the autoxidation of hexaethyldilead, which is the nearest analogue of hexaethylditin, are also of interest. Unlike the autoxidation of hexaethylditin, that of hexaethyldilead is characterized by pronounced autocatalysis[179] (Fig. 16) which appears to exhibit some characteristic features[185]. Thus, if the autoxidation of hexaethyldilead is carried out over a range of different temperatures, but with the same initial concentration of the lead compound, considerable changes in the maximum rate of the process occur over a relatively small range of temperatures (Fig. 17). A similar effect is observed if the tempera-

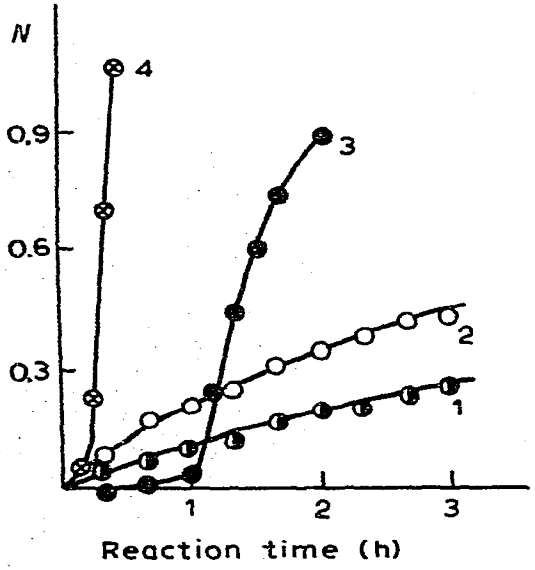


Fig. 16. Oxidation of hexaethylditin (curves 1 and 2) and hexaethyldilead (curves 3 and 4) in n-nonane (1 and 3 at 60°; 2 and 4 at 70°; c_0^{OEC} 20 mole % and $P(\mathrm{O_2})$ 300 mmHg).

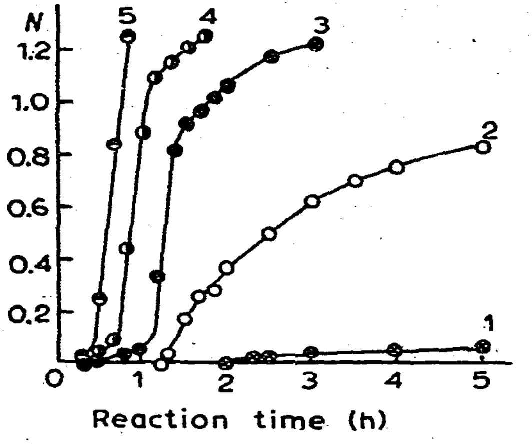


Fig. 17. Oxidation of hexaethyldilead in tetraethyllead at 60(1), 62.5(2), 65(3), 67.5(4) and 70°(5), respectively.

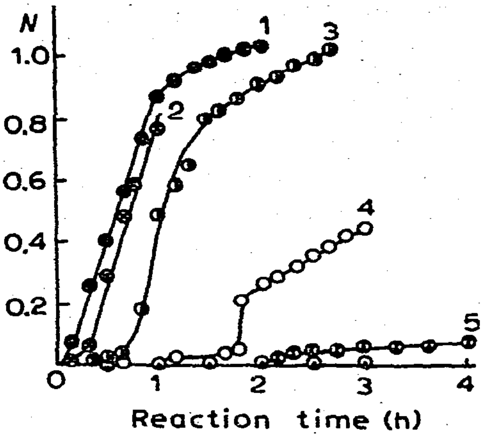


Fig. 18. Oxidation of hexaethyldilead at c_0 100(1), 50(2), 30(3), 22.5(4) and 20(5) mole % in tetraethyllead as a solvent. Temperature 70°, $P(O_2)$ 300 mmHg.

ture of the reaction is kept constant but if the initial concentration of hexaethyldilead is changed (Fig. 18). These effects are observed both in the absence of solvent and in the presence of the solvents used in this study (tetraethyllead, n-nonane and trichlorobenzene).

If the values of the temperatures and of the initial concentrations of hexaethyldilead over which the variations of the maximum rate of autoxidation are observed are plotted against each other, as depicted in Fig. 19, then a smooth curve may be drawn through the

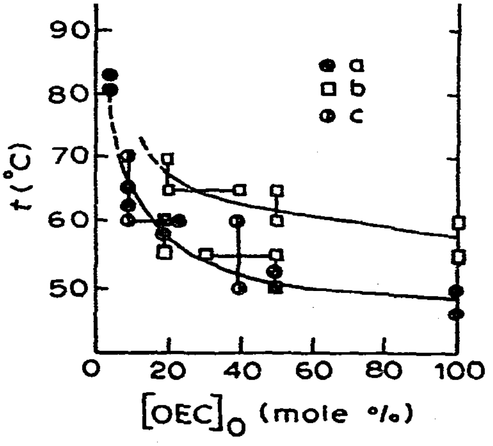


Fig. 19. The temperature dependence of the maximum rate of the autoxidation of hexaethyldilead as a function of the initial reactant concentration when the solvent was tetraethyllead(a), n-nonane(b) and trichlorobenzene(c) ($P(O_2)$ 300 (1) and 500 mmHg (2)).

resulting points as shown. The results depicted in this figure also show that if a constant pressure of oxygen is maintained over the reaction mixture, decreasing the initial concentration of hexaethyldilead in all the solvents employed shifts the maximum rate of the autoxidation towards higher temperatures. On the other hand, if the oxygen pressure over the reaction mixture is decreased (keeping the initial concentration of hexaethyldilead in the system constant), this shifts the temperature at which a maximum rate of autoxidation is observed towards lower values. The latter observation is a consequence of the fact that the rate of autoxidation of hexaethyldilead decreases as the oxygen pressure over the reaction mixture increases.

Investigation of the mechanism of the autoxidation of hexaethyldilead has shown[166,176-178] that the formation of triethyllead oxide is responsible for the above effects. This oxide, which is formed as an intermediate during the autoxidation is unstable and decomposes via two parallel routes: generation of free radicals (leading to degenerate branching) and oxidation to inactive products.

V. CONCLUSIONS

It is now possible to arrive at certain conclusions regarding the dependence of the mechanism of primary reactions involved in the autoxidation of OEC's on the nature of these compounds, on the nature of the medium and on the electronic state of the oxygen employed.

The probable manner in which the intermediate peroxide and oxygen-containing non-peroxide OEC's formed during the process may also be predicted. The results obtained may be considered as providing a basis for a general theory of the autoxidation of OEC's.

If this theory is to be developed further, it will be necessary to establish in a quantitative fashion the exact dependence of the mechanism of the primary reaction on the nature of the OEC, of the medium and of the electronic state of the oxygen employed as well as to investigate quantitatively the nature of the intermediate reactions and of the general and specific solvation effects observed.

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