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OXIDATION OF BIS(TRIETHYLSILYL)MERCURY BY OXYGEN IN THE PRESENCE OF TRIPHENYLPHOSPHINE

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SUMMARY

It has been established that triphenylphosphine is an effective catalyst for the oxidation of bis(triethylsilyl)mercury by oxygen. Some phenomenal features and the final products of oxidation are described, and the mechanism of oxidation is discussed.

INTRODUCTION

It has been established earlier[1] that compounds, containing atoms with electron-donor properties and capable of carrying out the role of ligands for bis(organometallic) derivatives such as $(Alk_3E)_2Hg$, where E = Si or Ge, catalyze oxidation of these compounds by oxygen. In this paper we report the results of more detailed investigation of the oxidation of bis(triethylsilyl) mercury in the presence of triphenylphosphine.

RESULTS AND DISCUSSION

Autooxidation of bis(triethylsilyl)mercury by dry oxygen at temperatures below −10° proceeds with a pronounced and considerable induction period. No induction period is observed in the presence of triphenylphosphine, and the maximum

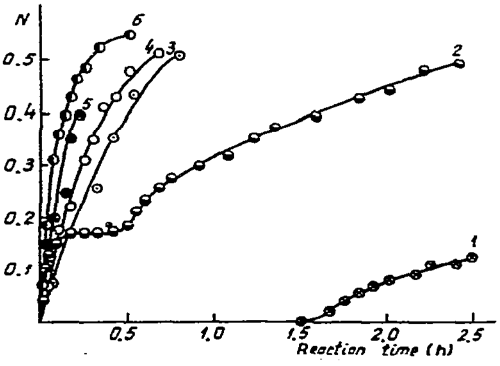

Fig. 1. Bis(triethylsilyl)mercury oxidation in n-octane at −10°. (C_0 = 0.1 mole·l^{-1}; $P(O_2)$ = 300 mm). Curve 1: without additions. Curves 2–6: *n* triphenylphosphine, 0.25; 1.5; 1.0; 0.75; 0.5.

rate of the process (W_{max}) depends on the concentration of additions. These results are illustrated by Fig. 1*.

The oxidation of bis(triethylsilyl)mercury proceeds without the participation of free radicals. This conclusion is drawn from the fact that even large amounts of 2,6-di-tert-butyl-4-methylphenol or *o*-phenylenediamine do not readily retard the rate of oxidation of bis(triethylsilyl)mercury by oxygen in the presence of triphenylphosphine. Analogous results have been obtained earlier[2,3] investigating autooxidation of bis(triethylsilyl)mercury and bis(triethylgermyl)mercury. It is necessary to note that 2,6-di-tert-butyl-4-methylphenol and *o*-phenylenediamine are effective inhibitors of bis(triisopropylgermyl)mercury autooxidation which proceeds according to the free radical mechanism[4].

In the process of the oxidation of bis(triethylsilyl)mercury by oxygen, triphenylphosphine acts as a typical catalyst since it is recovered quantitatively after the reaction.

Catalyzed oxidation of bis(triethylsilyl)mercury in the presence of triphenylphosphine is characterized by a small temperature coefficient. The activation energy of this reaction has a value of 4 kcal·mole^{-1}. The result agrees with those obtained for the catalyzed oxidation of bis(triethylgermyl)mercury[1].

The oxidation of bis(triethylsilyl)mercury in the presence of triphenylphosphine absorbs 0.5 mole of oxygen per mole of the initial bis(organometallic) compound. The final products of this reaction are mercury and hexaethyldisiloxane in quantitative yields.

It has been established in this investigation that the oxidation of bis(triethylsilyl)mercury in the presence of triphenylphosphine is a first order reaction with respect to both the initial bis(organometallic) compound and oxygen. The first is concluded from the fact that the kinetic curves of N *vs.* reaction time coincide (Fig. 2),

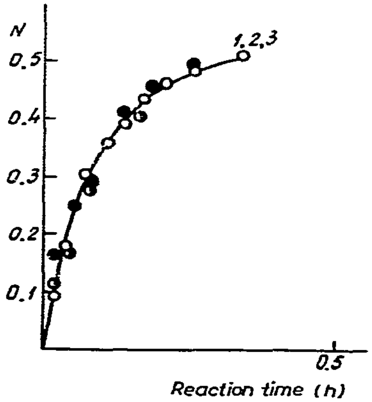

Fig. 2. Bis(triethylsilyl)mercury oxidation in the presence of triphenylphosphine (n=0.5) in n-octane at $-10°$; $P(O_2)$=300 mm; C_0=0.03, 0.05, 0.1 mole·l^{-1}.

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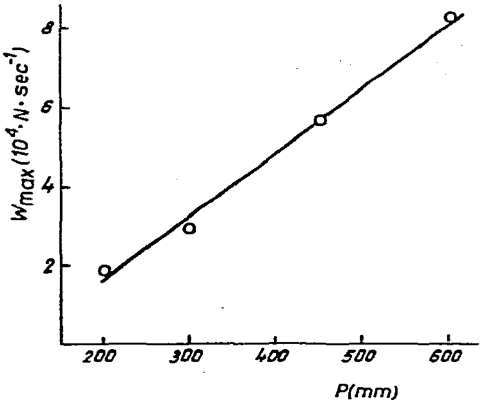
* In this figure and further N is the number of moles of oxygen absorbed by the reaction mixture calculated to one mole of initial bis(triethylsilyl)mercury, n is the number of moles of triphenylphosphine in the reaction mixture to one mole of initial bis(triethylsilyl)mercury.



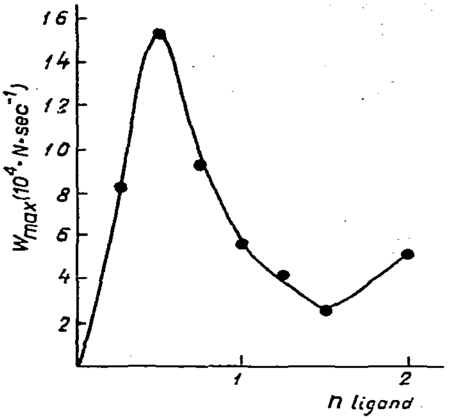


Fig. 3. The influence of initial oxygen pressure on the maximum rate of oxidation of bis(triethylsilyl)-mercury in the presence of triphenylphosphine ($n = 1.5$) at −10°.

Fig. 4. The influence of relative triphenylphosphine concentration on the maximum rate of catalytic oxidation of bis(triethylsilyl)mercury in n-octane at −10°.

and the second is illustrated by the results shown in Fig. 3 (curve of dependence of W_{max} on the value of the oxygen pressure above the reaction mixture).

The dependence of W_{max} on the value of n for triphenylphosphine is complex (Fig. 4). This influence of the same ligand-catalyst, depending on its concentration, is recorded for the first time.

It is known[1], that the oxidation of bis(triethylgermyl)mercury by oxygen in the presence of some ligands-catalysts is a first order reaction with respect to the catalyst. The same result has been obtained during the oxidation of bis(triethylsilyl)mercury with small amounts of triphenylphosphine ($n = 0.5$). In this case the reaction kinetic characteristics (the first order with respect to each reaction component and to the catalyst) correspond to the case of catalyst interaction in the condition of spontaneous support of thermodynamic equilibrium concentration of the intermediate complex of bis(triethylsilyl)mercury–triphenylphosphine.

$$(Et_3Si)_2Hg + L \rightleftarrows (Et_3Si)_2Hg \cdot L \qquad (1)$$

$$(Et_3Si)_2Hg \cdot L + O_2 \rightarrow Et_3SiHgOOSiEt_3 + L \qquad (2)$$

It is possible to predict the secondary reactions from the results of investigation of the oxidation of bis(triethylgermyl)mercury and the oxidation of intermediate products of this process[1–3,5]. It is concluded from these studies that bis(triethylsilyl)mercury easily yields to the following transformations: interaction with initial bis(organometallic) compound or to catalyzed decomposition to ligands.

$$Et_3SiHgOOSiEt_3 + (Et_3Si)_2Hg \rightarrow 2\ Et_3SiHgOSiEt_3 \qquad (3)$$

$$Et_3SiHgOOSiEt_3 \xrightarrow{L} Et_3SiOOSiEt_3 + L \qquad (4)$$

We expect, based on results of ref. 3, that bis(triethylsilyl)mercury must be stable to triethylsilyl peroxide at comparatively "mild" temperature conditions. The absence of triethylsilyl peroxide among catalyzed bis(triethylsilyl)mercury oxidation products shows the advantageous proceeding of reaction (3) in comparison with reaction (4).

We have established that triethylsilyl(triethylsiloxy) mercury decomposes easily in the presence of triphenylphosphine according to the equation:

$$\mathrm{Et_3SiHgOSiEt_3} \xrightarrow{\mathrm{Ph_3P}} (\mathrm{Et_3Si})_2\mathrm{O}+\mathrm{Hg} \tag{5}$$

Reaction (5) is in accordance with earlier investigations of catalyzed decomposition of triethylgermyl(triethylgermoxy)mercury to ligands[5]. The composition of the final oxidation products of bis(triethylsilyl)mercury in the presence of triphenylphosphine show the process to be a combination of reactions (1), (2), (3) and (5).

It is interesting to note that $W_{\max}$ decreases as n of triphenylphosphine increases from the value of 0.5 (Fig. 4). This result may be explained on the basis of the influence of ligand on bimolecular reaction of bis(organometallic) compounds with oxygen. Ligand coordination to the heteroatom of organometallic compound leading the intermediate [reaction (1)], causes a decrease in the effective electronegativity of the heteroatom. The latter enhances organometallic interaction with oxygen which takes place according to the heterolytic mechanism. The catalysis of the oxidation of organometallic compounds to ligands is stipulated by these circumstances[6]. However, besides the effect due to the decrease in the heteroatom electronegativity on the rate of interaction of organometallic compounds with oxygen, the coordinate capacity saturation of the heteroatom also has a considerable effect. A number of cases have been reported[7] where the ligand saturation of the coordinate capacity of the heteroatom of organometallic compounds of high reactive capabilities stabilizes it against oxidation by oxygen. From this standpoint the reason for the dependence of bis(triethylsilyl)mercury catalytic oxidation $W_{\max}$ on the value of ligand-catalyst n (Fig. 4) can easily be understood.

We have assumed that triphenylphosphine coordinates to the mercury atom of the bis(organometallic) compound, as the formation of complexes of ligands with trialkylsilyl derivatives is not a characteristic feature[8].

The formation of a bis(triethylsilyl)mercury–triphenylphosphine complex is

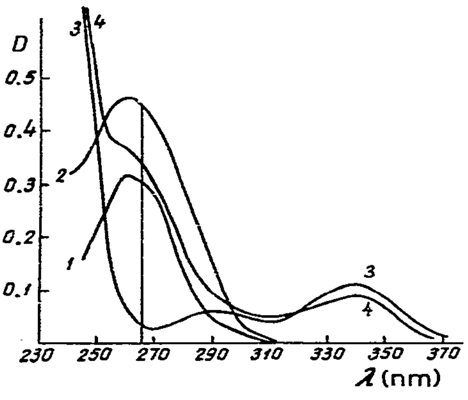


Fig. 5. Electron absorbtion spectra in n-octane: 1: triphenylphosphine solution (C_0=0.0019 mole·l^{-1}); 2: triphenylphosphine solution (C_0=0.0023 mole·l^{-1}); 3: bis(triethylsilyl)mercury solution (C_0=0.023 mole·l^{-1}); 4: solution containing bis(triethylsilyl)mercury (C_0=0.023 mole·l^{-1}) and triphenylphosphine (C_0=0.0023 mole·l^{-1}).

confirmed by comparing UV spectra of n-octane solutions of individual compounds and their mixtures (Fig. 5). This is evident from decreasing triphenylphosphine-band intensity (260 nm) caused by the *n*-transition due to the participation of a free pair of electrons of the phosphorous atom in the presence of bis(triethylsilyl)mercury. In the case investigated the characteristic absorption band for the donor–acceptor bis(triethylsilyl)mercury complex could not be observed. This might be caused by initial bis(organometallic) compound "shading".

EXPERIMENTAL

Experimental procedure was identical to that in ref. 3. Oxygen was dried over "molecular sieve" at low temperature.

Bis(triethylsilyl)mercury was synthesized by the hydride method.

Triphenylphosphine was purified by recrystallization from an alcohol/ether mixture. M.p. 78.5° (ref. 10 gives also m.p. 78.5°).

Hexaethyldisiloxane was identified and analysed quantitatively by GLC. Triphenylphosphine was determined either by the weight method (after evaporating the solvent at reduced pressure and washing the residue with alcohol), or by its reaction with tertbutyl peroxide. In the first case as much as 96% of it was determined (m.p. and mixed m.p. 78.5°). In the second case 100% of initial triphenylphosphine was determined and triphenylphosphine oxide was isolated as a reaction product of triphenylphosphine with tert-butyl peroxide. M.p. and mixed m.p. 153–154°, ref. 10 gives 152–153°.

UV spectra of triphenylphosphine, bis(triethylsilyl)mercury and their mixtures were taken in n-octane solutions under complete exclusion of oxygen.

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