

AUTO-OXIDATION OF ETHYL(TRIETHYLSILYL)MERCURY

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(Received February 9th, 1972)

SUMMARY

The auto-oxidation of ethyl(triethylsilyl)mercury has been investigated. It has been established that auto-oxidation occurs through a free-radical chain process, initiation involving the decomposition of ethyl(triethylsilyl)mercury by means of a bimolecular mechanism with the formation of radicals.

The reaction products have been identified and a mechanism is suggested.

It has been established earlier that the mechanism of the auto-oxidation of symmetrical organic compounds is quite different from that involving organoelement compounds of mercury such as diisopropylmercury and di-n-propylmercury. Alk_2Hg compounds oxidize via a free-radical chain mechanism¹ but the oxidation of bis(triethylgermyl)mercury and bis(triethylsilyl)mercury, $(\text{Alk}_3\text{E})_2\text{Hg}$, proceed without any involvement of free radicals².

It is interesting to study the mechanism of the oxidation of non-symmetrical organomercury compounds thus filling the gap between Alk_2Hg on the one hand and $(\text{Alk}_3\text{E})_2\text{Hg}$ on the other. With this in mind, we have investigated the auto-oxidation of ethyl(triethylsilyl)mercury, Et_3SiHgEt , in n-octane using a vacuum circulatory method and for some runs a static method. The nature of the solvent and the experimental procedure employed were identical to those described earlier¹⁻³.

In comparison with bis(triethylsilyl)mercury, Et_3SiHgEt is more stable to oxygen, the oxidation being accompanied by the absorption of 0.5-0.6 moles of oxygen (*N*) per mole of the initial organomercuric compound. The reaction products have been identified as mercury, ethyl(triethylsiloxy)mercury, triethylsilyl oxide and peroxide, diethylmercury and acetaldehyde (Table 1).

Auto-oxidation of ethyl(triethylsilyl)mercury is quite strongly inhibited by the introduction of agents known to be effective inhibitors of chain oxidation processes of symmetrical organic and organoelement compounds of mercury^{1,3} into the system. This result, which is illustrated in Fig. 1, indicates that a free-radical chain mechanism must also be operative in the auto-oxidation of Et_3SiHgEt .

The mechanism of the initiation (chain origin) reaction in the auto-oxidation of Et_3SiHgEt is of considerable interest. It has been reported earlier that this organomercury compound changes to the symmetrical form on heating (a 70% degree of conversion being achieved after 11 h at 170°) according to the following stoichiometric equation:

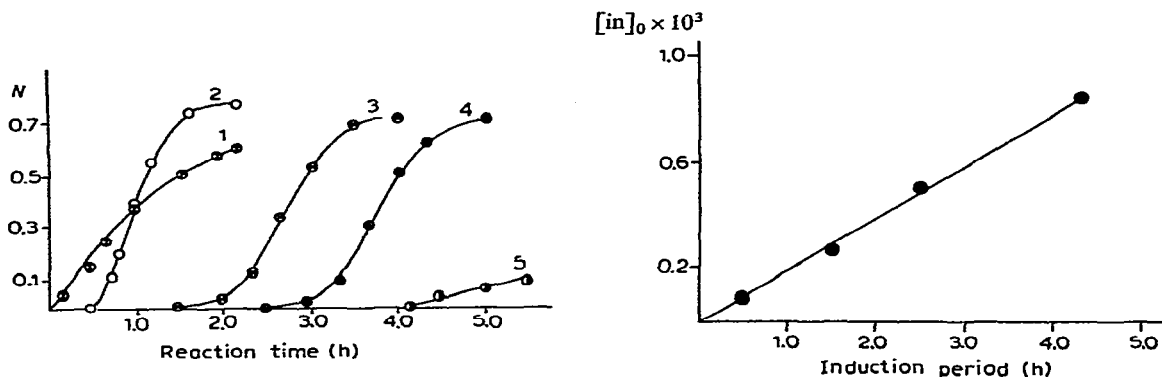


Fig. 1. Oxidation of Et_3SiHgEt in *n*-octane ($c_0 = 0.085 \text{ mol} \cdot \text{l}^{-1}$) in the presence of *o*-phenylenediamine. $T = 60^\circ$: Curve 1: no additions of *o*-phenylenediamine; curves 2-5 obtained with concentrations $n \times 10^3 = 0.085$; 0.252; 0.504; 0.847 of *o*-phenylenediamine respectively present in the system.

Fig. 2. Dependence of the length of the induction period on the inhibitor concentration during the oxidation of Et_3SiHgEt in *n*-octane ($c_0 = 0.085 \text{ mol} \cdot \text{l}^{-1}$) in the presence of *o*-phenylenediamine, $T = 60^\circ$.

TABLE 1

DISTRIBUTION OF Et_3SiHgEt OXIDATION PRODUCTS IN *n*-OCTANE

($c_0 = 0.084 \text{ mole} \cdot \text{l}^{-1}$) at 60° ; $P_{\text{O}_2} = 300 \text{ mmHg}$.

Compound	Yield in moles per mole of mercury compound oxidized
Hg	0.5
$\text{Et}(\text{Et}_3\text{SiO})\text{Hg}$	0.35
$(\text{Et}_3\text{Si})_2\text{O}$	0.13
$(\text{Et}_3\text{SiO})_2$	0.20
Et_2Hg	0.15
CH_3CHO	0.07



It is known² that bis(triethylsilyl)mercury interacts with oxygen according to a molecular mechanism. By special experiments, it has been shown that under identical conditions to those used in studies of the auto-oxidation of Et_3SiHgEt practically no interaction occurs between diethylmercury and oxygen. This suggests that chain initiation in this reaction is due to the decomposition of ethyl(triethylsilyl)mercury with the formation of free radicals [reaction (2)], a reaction which proceeds simultaneously with the symmetrizing process [reaction (1)].



The presence of a homolytic path in the symmetrization of ethyl(triethylsilyl)mercury is confirmed by the range of products obtained when this reaction is carried out in the presence of inhibitors. Thus the decomposition of Et_3SiHgEt has been studied in benzene solution ($c_0 = 50 \text{ vol. } \%$) at 80° in the presence of *o*-phenylenedi-

amine (c_0 inhibitor = 0.7%), the reaction mixture being carefully isolated from oxygen and light. After 100 h, along with compounds described earlier⁴, hexaethyldisilane was detected among the products having a yield of 0.04 mole%. Decreasing the temperature or the length of time for the thermolysis of Et_3SiHgEt caused a decrease in the yield of hexaethyldisilane. Hexaethyldisilane is known⁵ to be a major product arising from the combination of trimethylsilyl radicals which are formed during the initiated homolytic decomposition of bis(trimethylsilyl)mercury.

Additional data concerning the nature of the initiation reaction have been obtained from a study of the oxidation of ethyl(triethylsilyl)mercury in the presence of *o*-phenylenediamine.

It is known⁶ that with strong inhibitors (in) the linear dependence of the length of the induction period (τ_{ind}) on the initial concentration of the inhibitor may be expressed by the equation:

$$\frac{[\text{in}]_0}{\tau_{\text{ind}}} = \frac{f \cdot [\text{in}]_0}{W_0}$$

where f = stoichiometric inhibition factor and W_0 = the rate of initiation. In this case, τ_{ind} may be used as a measure of W_0 .

Since the critical concentration of *o*-phenylenediamine is near zero (Fig. 2) it follows that this material is quite a strong inhibitor of the auto-oxidation of ethyl(triethylsilyl)mercury. For this reason we have investigated the influence of the initial concentration of Et_3SiHgEt , and of the oxygen pressure in the system as well as the influence of the reaction temperature on the value τ_{ind} in the auto-oxidation of Et_3SiHgEt , in the presence of *o*-phenylenediamine. It has been found that increasing the oxygen pressure from 185 up to 400 mmHg has no appreciable effect on the value of τ_{ind} suggesting that the initiation process in this reaction is zero order with respect to oxygen.

When $[\text{in}]_0$ was kept constant the value of τ_{ind} increased as the initial concen-

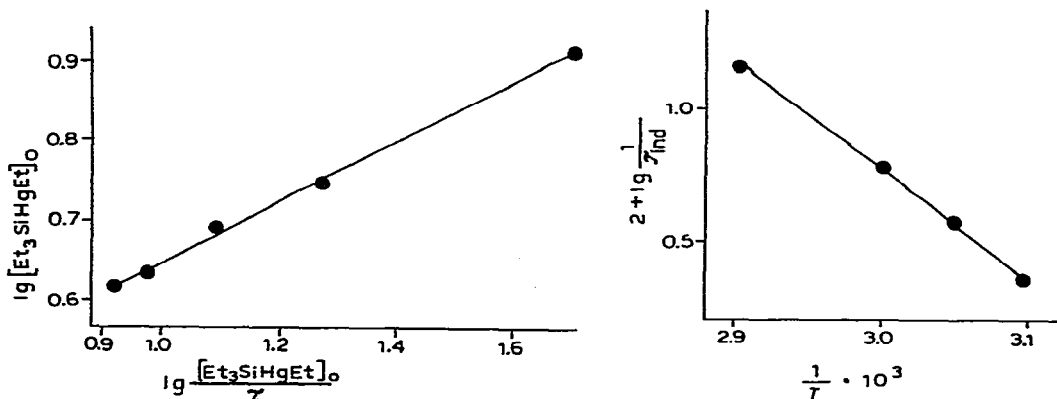


Fig. 3. Dependence of $\lg [\text{Et}_3\text{SiHgEt}]_0 / \tau_{\text{ind}}$ on $\lg [\text{Et}_3\text{SiHgEt}]_0$ for the oxidation of Et_3SiHgEt in *n*-octane ($c_0 = 0.0835 \text{ mol} \cdot \text{l}^{-1}$) in the presence of *o*-phenylenediamine, $n \times 10^3 = 0.0835$.

Fig. 4. Dependence of $\lg 1/\tau_{\text{ind}}$ on $1/T$ for the oxidation of Et_3SiHgEt in *n*-octane ($c_0 = 0.0835 \text{ mol} \cdot \text{l}^{-1}$) in the presence of *o*-phenylenediamine.

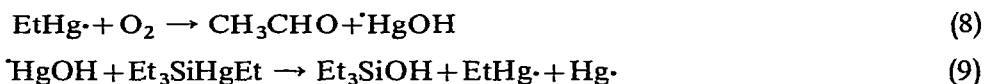
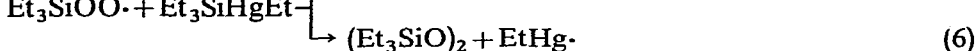
tration of Et_3SiHgEt decreased. This suggests (Fig. 3) that the order of the initiation process with respect to Et_3SiHgEt is close to two.

The temperature dependence of τ_{ind} during the auto-oxidation of ethyl(triethylsilyl)mercury in the presence of an inhibitor is adequately given by the Arrhenius equation (Fig. 4). The calculated value of the activation energy for initiation is 19.7 kcal/mol which is approximately equal to the known value of the mercury-silicon bond energy for bis(trimethylsilyl)- and bis(triethylsilyl)-mercury* (13.6 kcal/mol⁷ and 20 kcal/mol⁸) respectively.

From the basis of the results obtained it is believed that initiation occurs as a result of the bimolecular reaction** :



Chain propagation then probably proceeds according to the following scheme:



It is assumed that the auto-oxidation of Et_3SiHgEt is not influenced by the interaction of triethylsilyl peroxide with diethylmercury, as we have established by special experiments that these compounds do not react in *n*-octane ($c_0 = 0.04 \text{ mol} \cdot \text{l}^{-1}$ and $0.07 \text{ mol} \cdot \text{l}^{-1}$ respectively) on heating for a period of one day at room temperature or for two hours at 60° .

EXPERIMENTAL

Ethyl(triethylsilyl)mercury was prepared by the hydride method⁹ and purified by two recondensations under reduced pressure in an inert atmosphere. The fraction with b.p. $80^\circ/1 \text{ mmHg}$ was used in the present studies.

Usually the initial oxygen pressure in contact with the reaction mixture was maintained at 300 mmHg except for runs in which the influence of the initial oxygen pressure on the rate of Et_3SiHgEt oxidation was investigated.

* The value of the bond energy of the mercury-silicon bond was calculated from the kinetic data for the thermolysis of bis(trimethylsilyl)mercury in ref. 7 and equated with the energy necessary to effect the cleavage of the first mercury-silicon bond.

In ref. 8 the mean value of the energy of the mercury-silicon bond as calculated from thermochemical data is given.

** Cryoscopic measurements in cyclohexane indicate that no association of Et_3SiHgEt occurs.

The analysis of the reaction products was carried out in the following manner. After oxidation the reaction mass was separated from residual mercury by filtration, the resulting filtrate (1) treated with water and the aqueous layer titrated with 0.01 N HCl in the presence of methyl orange in order to estimate the ethylmercury hydroxide formed during the hydrolysis of ethyl(triethylsiloxy)mercury.

Equal quantities of a solution of iodine in tetrachloromethane were added to two equal volumes of filtrate (1), washed with water and then after 1.5 h (this length of time being required for complete interaction between diethylmercury and iodine to occur) 2 ml of a saturated solution of sodium iodide, acetic acid and sodium carbonate was added to one of the samples. After 30 min* the quantity of free iodine in both samples was determined and from their difference the yield of diethylmercury and triethylsilyl peroxide formed during oxidation was calculated.

Triethylsilyl peroxide was analysed by infrared spectroscopy and by the formation of hydrogen peroxide during the hydrolysis of the reaction mixture by sulphuric acid solution after oxidation. The amount of hydrogen peroxide determined by cerimetric and iodometric methods was found to correspond to the amount of peroxidating oxygen determined iodometrically as described above.

Triethylsilyl oxide was identified by GLC. Hydrolysis of the oxidized mixture in the presence of HCl (1/1) led to a 2.3 fold increase in the yield of triethylsilyl oxide indicating that ethyl(triethylsiloxy)mercury also occurs in the mixture obtained after oxidation.

Mercury was analysed by the method used earlier^{2,3}, whilst acetaldehyde was identified through its reaction with 2,4-dinitrophenylhydrazine. Hexaethyldisilane was analysed by GLC.

Cryoscopic measurements were undertaken on cyclohexane solutions of $\text{Et}_3\text{Si-HgEt}$ after the complete exclusion of oxygen.

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* This reaction time was determined by special separate experiments.