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OXIDATION OF BIS(TRIETHYLGERMYL)MERCURY IN THE PRESENCE OF tert-BUTYL ALCOHOL

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SUMMARY

The oxidation of bis(triethylgermyl)mercury by oxygen in the presence of tert-butyl alcohol has been investigated. It has been shown that the dependence of the rate of oxidation on the value of n* for tert-butyl alcohol within the range n= 0–12 is similar to that for unassociated ligand-catalysts. On increasing n further (from 12 to 60) increasing association of the alcohol causes a drastic increase in the reaction rate relative to the increase in n due to the higher catalytic activity of the high molecular weight associated species.

Autooxidation of bis(triethylgermyl)mercury and bis(triethylsilyl)mercury, which proceeds according to a molecular mechanism[1], is catalyzed by the addition of compounds containing atoms with electron-donor properties[2]. The study of this effect in the oxidation of $(Et_3Si)_2Hg$ using triphenylphosphine as a catalyst has shown[3] that at low values of n* an initial decrease in the effect of the ligand-catalyst $\bar{L}$ occurs as n increases.

It was interesting to study the influence of $\bar{L}$ on the oxidation of $(Et_3Ge)_2Hg$ over a wider range of n values, and in order to do this we have investigated the oxidation of $(Et_3Ge)_2Hg$ in n-octane using tert-butyl alcohol** as the ligand-catalyst $\bar{L}$.

The oxidation of $(Et_3Ge)_3Hg$ was carried out in a circulatory vacuum apparatus, the experimental procedure employed being similar to that described earlier[1].

The oxidation of $(Et_3Ge)_2Hg$ in n-octane in the presence of added tert-butyl alcohol proceeds in a similar fashion to that observed with other ligands[2], without appreciable self-acceleration (Fig. 1) and being accompanied by an oxygen uptake N up to about 0.5 (N=number of oxygen moles absorbed by the reaction mixture, calculated per mole of initial $(Et_3Ge)_2Hg$). The products of this oxidation reaction were hexaethyldigermoxane, triethylgermyl(triethylgermyloxy)mercury and mercury. The yield of triethylgermyl(triethylgermyloxy)mercury was found to be sig-

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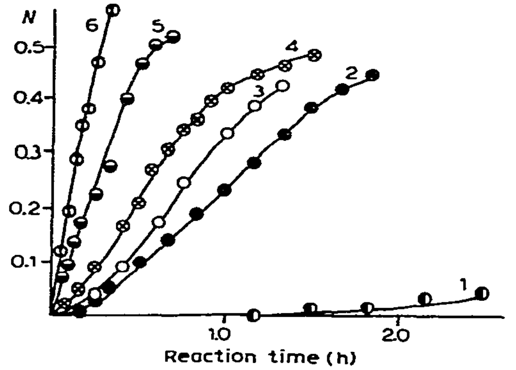
* Here and elsewhere n represents the number of moles of ligand-catalyst $\bar{L}$ per mole of initial $(Et_3Ge)_2Hg$.

** The use of tert-butyl alcohol allows the value of n to be increased up to 60. This is not possible with triphenylphosphine due to its limited solubility in n-octane over the temperature interval studied.



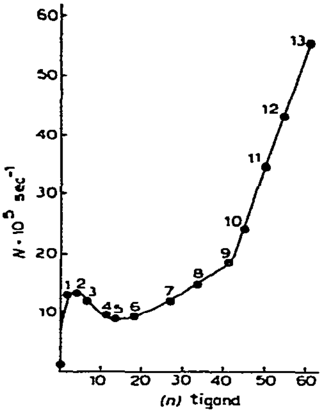


Fig. 1. Oxidation of $(Et_3Ge)_2Hg$ in n-octane with various additions of tert-butyl alcohol, $T=20°$, $P(O_2)=$ 300 mm. The curves illustrated were obtained when the following respective $[OEC]_0$ and n values obtained in the system: 1, 0.0487 mole·l^{-1} and 0; 2, 0.0558 mole·l^{-1} and 2.3; 3, 0.0551 mole·l^{-1} and 4.6; 4, 0.0515 mole·l^{-1} and 18.2; 5, 0.0455 mole·l^{-1} and 45.5; 6, 0.0190 mole·l^{-1} and 60.3.

Fig. 2. The dependence of N_{max} (sec^{-1}) for the catalytic oxidation of $(Et_3Ge)_2Hg$ in n-octane on the n value for tert-butyl alcohol. $T=20°$. $P(O_2)=300$ mm. Points 1, 2, 3, 4, ..., 13 were obtained respectively when $[OEC]_0$ was 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; 0.019 mole·l^{-1} and $[\bar{L}]_0$ was equal to 0.127; 0.252; 0.371; 0.603; 0.718; 0.937; 1.347; 1.630; 1.905; 2.061; 1.630; 1.731; 1.142 mole·l^{-1}.

nificantly dependent on the conditions under which the reaction is allowed to proceed as well as on the time interval allowed to elapse between the termination of oxidation and the analysis of the mixture. This is attributed to the thermal instability of triethylgermyl(triethylgermyloxy)mercury which is present in the final reaction mixture and which, even at room temperature, decomposes to form hexaethyldigermoxane and mercury.

Analysis of the amount of triethylgermyl(triethylgermyloxy)mercury present in the final reaction mixture in some experiments immediately after the termination of the oxidation process (at −20°) showed that its yield was about 50%. The final products of the oxidation of $(Et_3Ge)_2Hg$ after complete decomposition of triethylgermyl(triethylgermyloxy)mercury are hexaethyldigermoxane and mercury, the yields of these products being close to the quantitative values expected from the following stoichiometric relationship:

$$(Et_3Ge)_2Hg+0.5\ O_2 \overset{\bar{L}}{\longrightarrow} (Et_3Ge)_2O+Hg \qquad (1)$$

Traces of triethylgermyl peroxide have also been detected amongst the products of the reaction. These results are similar to those obtained earlier[2,3] in the presence of other ligand-catalysts.

The oxidation of $(Et_3Ge)_2Hg$ in the presence of tert-butyl alcohol is not a free-radical process. This may be deduced from the fact that the reaction rate is not influenced appreciably by the addition of *o*-phenylenediamine, 2,6-di-tert-butyl-4-methylphenol and other substances known to be effective as inhibitors of oxidation chain reactions of symmetrical organic and organometallic mercury compounds[4,5].

We have found that the dependence of the rate of oxidation of $(Et_3Ge)_2Hg$

($N_{\max}$ (sec^{-1})) on the value of n for tert-butyl alcohol is somewhat complicated (Fig. 2). Over the range $n=0$ to 10–12 the decrease in rate is similar to that observed earlier in the presence of non-associated ligand-catalysts. With these catalysts the decrease in the rate with an increase in n from 10–12 was attributed to the relative lowering of the reactivity of solvated $(Et_3Ge)_2Hg$ as a result of a saturation of the coordination capacity of the compound[3].

Further increase in the value of n led to an increase in the reaction rate which was attributed to association of the ligand-catalyst with different molecular weight associates having different catalytic activity. It is known[6] that association of alcohol leads to the protonization of the hydroxyl group hydrogen and this leads to an increase in the reactivity of the alcohol (as a nucleophilic reagent) as the degree of association increases.

Literature data exist[7] concerning the varying percentage of monomeric tert-butyl alcohol molecules present in the system tert-butyl alcohol–cyclohexane. In this work cryoscopic measurements have been made (in cyclohexane, see Table 1) to establish the percentage of associated tert-butyl alcohol molecules present in the system over various concentration ranges as used during the catalytic oxidation of $(Et_3Ge)_2Hg$. It should, however, be noted that the states of association of tert-butyl alcohol in cyclohexane and in solutions of $(Et_3Ge)_2Hg$ in n-octane (*i.e.* the solutions used in the investigation of the catalytic oxidation of $(Et_3Ge)_2Hg$) are not necessarily identical.

Assuming a molecular mechanism for the oxidation of $(Et_3Ge)_2Hg$ in the presence of tert-butyl alcohol in conjunction with the degrees of association of the ligand-catalyst measured and listed above leads to the reaction scheme 1

SCHEME 1

$$\bar{L}_{i-1}+\bar{L} \rightleftarrows \bar{L}_i \tag{2}$$

$$\bar{L}_i+(Et_3Ge)_2Hg \rightleftarrows (Et_3Ge)_2Hg\cdot\bar{L}_i \tag{3}$$

$$(Et_3Ge)_2Hg\cdot\bar{L}_i+O_2 \rightarrow Et_3GeHgOOGeEt_3\cdot\bar{L}_i \tag{4}$$

$$Et_3GeHgOOGeEt_3\cdot\bar{L}_i \rightarrow Et_3GeOOGeEt_3+Hg+\bar{L}_i \tag{5}$$

$$\begin{aligned}&Et_3GeHgOOGeEt_3\cdot\bar{L}_i+(Et_3Ge)_2Hg \rightarrow\\&\qquad\qquad Et_3GeHgOGeEt_3\cdot\bar{L}_i+Et_3GeHgOGeEt_3\end{aligned} \tag{6}$$

$$Et_3GeHgOGeEt_3\cdot\bar{L}_i \rightarrow (Et_3Ge)_2O+Hg+\bar{L}_i \tag{7}$$

$$Et_3GeHgOGeEt_3 \xrightarrow{\bar{L}_i} (Et_3Ge)_2O+Hg+\bar{L}_i \tag{8}$$

Such a scheme accords reasonably well with the observed chemistry of the oxidation of $(Et_3Ge)_2Hg$ in the presence of tert-butyl alcohol and, in addition, is in agreement with studies of the oxidation of $(Et_3Ge)_2Hg$ in the presence of non-associated ligand-catalysts, carried out earlier[3].

Quantitative calculations of the influence of catalysts on the oxidation of $(Et_3Ge)_2Hg$ especially when these catalysts are associated tert-butyl alcohol molecules present in varying ratios, leads, in the general case, to a complicated expression

TABLE 1

DATA OF CRYOSCOPIC MEASUREMENTS FOR tert-BUTANOL IN CYCLOHEXANE

ROH (*mole*·l^{-1})	$\alpha = \frac{\textit{apparent mol.wt.}}{\textit{monomer mol.wt.}}$
0.11	3.9
0.41	4.24
0.69	4.46
0.98	4.76
1.32	5.19
1.56	5.29
1.94	5.41

for the rate *W*. This expression may, however, be simplified if it is assumed that reaction with oxygen in the system is a zero order process*.

$$W = \Sigma\, k_{3i}\,[\text{OEC}]\,\frac{\left(\prod_i k_{2i}\right)\cdot[\text{L}]^i}{\prod_i (k'_{2i}+k_{3i})[\text{OEC}]} \tag{9}$$

where [OEC], [L], k_{2i}, k'_{2i} and k_{3i} represent the concentrations of $(Et_3Ge)_2Hg$ and the ligand-catalyst, the rate constant for the formation and decomposition of *i*-meric associate according to reaction (2) and the rate constant for the interaction of the *i*-meric associate with $(Et_3Ge)_2Hg$ according to reaction (3), respectively.

From such an analysis of the results, as depicted graphically in Fig. 2, it may be seen that the value of N_{max} (sec^{-1}) for the catalytic oxidation of $(Et_3Ge)_2Hg$ at values of $n > 12$ is solely dependent on the value of *n*.

As *n* increases N_{max} (sec^{-1}) also increases independently of the magnitudes of the initial concentrations of $(Et_3Ge)_2Hg$ and $\bar{L}$. This result suggests that under the experimental conditions employed

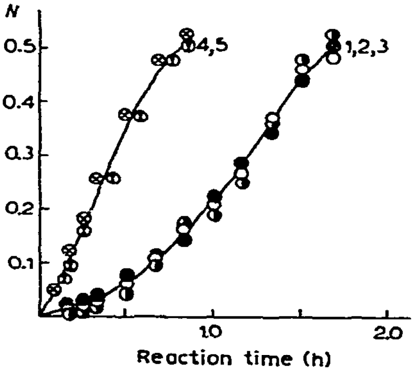


Fig. 3. The oxidation of $(Et_3Ge)_2Hg$ in n-octane with various additions of tert-butyl alcohol. $T = -20°$, $P(O_2) = 300$ mm. The curves illustrated were obtained when $[\text{OEC}]_0$ was respectively equal to: 1, 0.0257; 2, 0.0504; 3, 0.0744 mole·l^{-1} and $n = 22.75$; and 4, 0.0393; 5, 0.0464 mole·l^{-1} and $n = 41.1$.

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* It has been established in this work that the oxidation of $(Et_3Ge)_2Hg$ in the presence of tert-butyl alcohol is zero order with respect to oxygen when $n > 12$.

$$k_{3i}[\text{OEC}] \gg k_{2i}$$

Under these conditions, and assuming that the extent of the reaction is not too great ($[\text{OEC}] \approx [\text{OEC}]_0$) and that the change of $[\bar{\text{L}}]_0$ is small for the interval of concentration values employed (*i.e.* $[\bar{\text{L}}] = \alpha[\bar{\text{L}}]_0$ where $\alpha \approx$ constant.), the expression for the relative reaction rate for the oxidation of $(\text{Et}_3\text{Ge})_2\text{Hg}$ may be written as

$$N = \sum_i a_i \cdot n_i$$

where

$$a_i = k_i \left(\frac{\prod_i k_{2i}}{\prod_i k_{3i}} \right) \alpha^i \qquad (10)$$

Equation (10) provides a quantitative expression for the observed dependence of the relative rate of oxidation of $(\text{Et}_3\text{Ge})_2\text{Hg}$ on the n value of the ligand-catalyst (Fig. 2, $n > 12$).

It has also been established that the rate of oxidation of $(\text{Et}_3\text{Ge})_2\text{Hg}$ with increasing amounts of tert-butyl alcohol ($n > 12$) may be satisfactorily described by a first-order kinetic equation dependent solely on the initial concentration of the bimetallic organic compound. This is demonstrated in Fig. 3 where plots of N *versus* time for various initial $(\text{Et}_3\text{Ge})_2\text{Hg}$ concentrations lie on the same curve provided that n remains constant. This result is also in agreement with the predictions of Eqn. (10).

EXPERIMENTAL

Bis(triethylgermyl)mercury was synthesized by the hydride method[8] and purified by re-condensation under reduced pressure. The fraction with b.p. 123.5°/1 mm was used. tert-Butyl alcohol used was of "Chem. pure" grade of m.p. 25°, $n_d^{20} = 1.3876$.

Generally the initial oxygen pressure over the reaction mixture was 300 mm with the exception of experiments in which the influence of the initial oxygen pressure on the rate of oxidation was investigated. The following methods were used in the analysis of the products of the reaction. Hexaethyldigermoxane was identified and analyzed quantitatively by GLC, mercury was estimated by the method used earlier[1-5], while an iodometric technique was used for the analysis of triethylgermyl peroxide[1].

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