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ON THE INFLUENCE OF TRIS(TRIETHYLGERMYL)STIBINE ASSOCIATION ON ITS OXIDATION BY OXYGEN

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SUMMARY

It has been established that tris(triethylgermyl)stibine associates under the influence of temperature, light and in contact with triphenylphosphine or triethylamine.

It is shown that association of tris(triethylgermyl)stibine leads to a change in the nature of the process of autooxidation from a chain free-radical (for monomeric forms) to one taking place without the participation of free radicals (for polyassociates).

The yields and some phenomenal features of autooxidation of tris(triethylgermyl)stibine at different multiple associations are studied.

INTRODUCTION

As a further development of research[1,2] concerning the kinetics of the mutual reaction of oxygen with biorganoelement compounds, we studied the autooxidation of tris(triethylgermyl)stibine, $(Et_3Ge)_3Sb$, in n-octane.

RESULTS AND DISCUSSION

Tris(triethylgermyl)stibine is a relatively mobile colorless liquid gradually turning to a yellow-orange color even at room temperature due to its association. Monomeric tris(triethylgermyl)stibine [preparation (I)] is colorless. An increase of temperature, exposure to dispersed sun rays and contact with triphenylphosphine or triethylamine enhances the appearance of the color. During this process there are no noticeable amounts of gaseous products nor sediment of reaction. After exposure of preparation (I) to room temperature during several hours and during a week the average molecular weight of the colored tris(triethylgermyl)stibine was determined to be 1960 and 3200, respectively.

The reactivity of tris(triethylgermyl)stibine towards oxygen depends on its degree of association. This is graphically illustrated in Fig. 1*, where curves 1 and 2 were obtained for tris(triethylgermyl)stibine having an average molecular weight of

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* In this Fig. and further N is number of moles of oxygen absorbed by the reaction mixture calculated to one mole of initial tris(triethylgermyl)stibine assuming it to be in a monomeric.

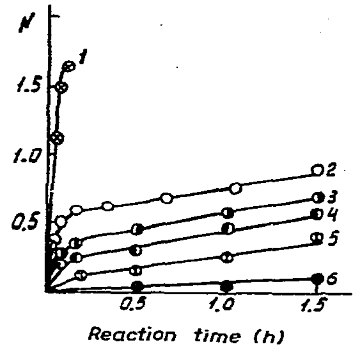


Fig. 1. Tris(triethylgermyl)stibine oxidation in n-octane (C_0=0.039–0.042 mole·l^{-1}) at 18°. Curve 1: preparation (IIa) without addition; curve 2: preparation (IIb) without addition; curves 3–6: preparation (IIb) with addition of *o*-phenylenediamine with 100 C_0(*o*-Phen)/C_0=1, 2, 4 and 6 or 8, respectively.

three times [preparation (IIa)] or five times [preparation (IIb)] to that of the monomeric form.

In connection with this data it is necessary to note that a further increase in the degree of association of preparation (II) decreases its reactivity towards oxygen, and as for the remains, after recondensation of preparation (I) (see above), no oxidation was observed in the course of several days when exposed to air.

We carried out detailed study regarding autooxidation of preparations (IIa) and (IIb).

Autooxidation of preparation (IIa) takes place according to a chain free-radical mechanism. This conclusion is drawn from the fact, that addition of *o*-phenylenediamine (an effective inhibitor of free-radical processes of autooxidation of organic derivatives of non-transition elements of group IV[3]) sharply inhibits the oxidation of preparation (IIa) (Fig. 2, curves 4 and 4′). In the case of preparation (IIb) the influence of this inhibitor is observed only at the beginning of the process. The settled reaction rate practically does not depend on the inhibitor concentration (Fig. 1, curves 2–6). Such influence of the inhibitor on autooxidation of preparation (IIb) may be explained by the circumstances that during the initial stage of the process non-associated tris(triethylgermyl)stibine or its low molecular associates "burn away". During the

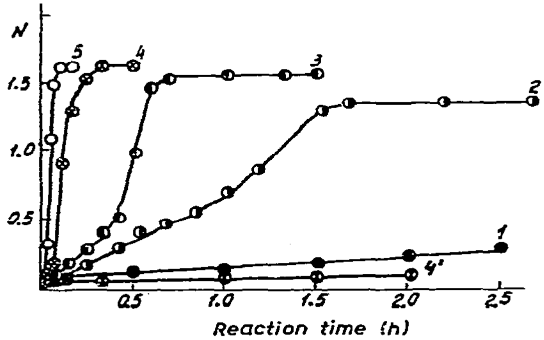


Fig. 2. Oxidation of preparation (IIa) in n-octane (C_0=0.043 mole·l^{-1}) at −10°, −7.5°, −5°, 0° and 18° (curves 1–5, respectively). Curve 4′ corresponds to 0° and C_0(*o*-Phen)=0.003 mole·l^{-1}.

following stage high molecular associates are oxidized without free radicals participating in the reaction.

The products of autooxidation of preparations (IIa) and (IIb) are hexaethyldigermoxane and antimony trioxide in the ratio given by the equation:

$$2\,(Et_3Ge)_3Sb+3\ O_2 \rightarrow 3\,(Et_3Ge)_2O+Sb_2O_3$$

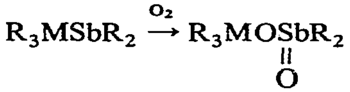
The periods of self acceleration and of sharp deceleration of kinetic curves 2 and 3 (see Fig. 2) coincide with the time of sedimentation of antimony trioxide. At a higher temperature (curves 4 and 5) the reaction solution remains homogeneous till the end of the reaction. However, soon after a sediment of antimony trioxide settles down from these solutions. An analysis of these reactive mixtures, before a sediment settles, as to active oxygen or to the contents of pentavalent antimony gives negative results. These results show that the oxidation of preparation (IIa) at temperatures above zero yields an intermediate organoelement compound not containing peroxide of oxygen or pentavalent antimony. A further resolution of this product yields hexaethyldigermoxane and antimony trioxide. One may assume the intermediate to be tris(triethylgermoxy)stibine.

In this case the ratio of tris(triethylgermyl)stibine and oxygen as well as the resulting products of the reaction are in accord with the following consistent stoichiometric equations:

$$2\,(Et_3Ge)_3Sb+3\ O_2 \rightarrow 2\,(Et_3GeO)_3Sb$$
$$2\,(Et_3GeO)_3Sb \rightarrow 3\,(Et_3Ge)_2O+Sb_2O_3$$

It is necessary to note that autooxidation of tris(triethylsilyl)stibine[4] also did not yield any peroxide or derivatives of pentavalent antimony. The only product of this reaction was determined to be bis(triethylsiloxy)(triethylsilyl)stibine, $(Et_3SiO)_2$-$SbSiEt_3$.

It is interesting to note that the organoelement derivatives of antimony of the type R_3MSbR_2 or R_3MOSbR_2, where R is the organic radical and M the nontransition element of group IV, are not stable in the presence of oxygen. Oxidation of these compounds results in derivatives of pentavalent antimony[5]:



$$R_3MSbR_2 \xrightarrow{O_2} R_3MO\underset{\underset{O}{\|}}{S}bR_2$$

We have established that antimony peroxide is indifferent to the process of autooxidation of tris(triethylgermyl)stibine while hexaethyldigermoxane effects the rate of oxidation of non-associated tris(triethylgermyl)stibine or its low molecular associates. The character of this influence is determined by the amount of hexaethyldigermoxane (*n*, in moles per mole of biorganoelement compound calculated to a monomeric form). From Fig. 3 it may be seen that when *n* is equal to about 1 digermoxane accelerates the oxidation of preparation (IIa), and as *n* increases in value as a result of oxidation of preparation (IIa) a deceleration action of this addition may be noticed. A similar effect (but more sharply manifested) is observed on the addition of triphenylphosphine and triethylamine during the autooxidation of preparation (IIa) (Fig. 3, curves 2 and 3). In this case to a certain extent the process is retarded also due to the association of monomeric tris(triethylgermyl)stibine by

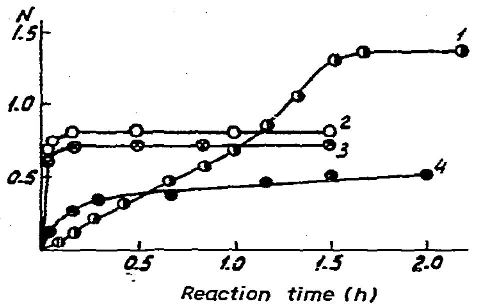


Fig. 3. Oxidation of preparation (IIa) in n-octane ($C_0 = 0.043$ mole·l^{-1}) at –7.5°. Curve 1: without addition; curves 2–4: with addition of triethylamine, triphenylphosphine and hexaethyldigermanoxane respectively; n (see text) equal to one in all cases.

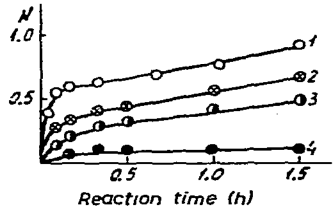


Fig. 4. Oxidation of preparation (IIb) in n-octane ($C_0 = 0.039$ mole·l^{-1}) at 18°. Curve 1: without addition; curves 2–4: with addition of triphenylphosphine, n equal to 0.3, 1 and 2, respectively.

triphenylphosphine or triethylamine. The dual nature of the influence of hexaethyldigermoxane on the rate of oxidation of preparation (IIa) determines the kinetic curves 2 and 3 (Fig. 2) being complicated.

In case of the oxidation of preparation (IIb) the effective value of n, an active addition, for instance triphenylphosphine (Fig. 4) is greater than would be expected because of high molecular associates prevailing in the preparation, and also because of the association of the monomeric form of tris(triethylgermyl)stibine by triphenylphosphine. This is the cause of the high retardation of the process of autooxidation of preparation IIb at the initial stage by additions of triphenylphosphine (Fig. 4).

Previously it has been shown[2] that hexaethyldigermoxane, triphenylphosphine and triethylamine under certain conditions are effective ligands-catalysts for oxidation of bis(triethylgermyl)mercury and similar compounds. During the present investigation it has been established that the above mentioned compounds, being introduced into n-octane solution of tris(triethylgermyl)stibine, remain unchanged during the oxidation of the latter.

We also studied the oxidation of tris(triethylgermyl)stibine in the presence of *o*-phenylenediamine in an amount sufficient to suppres the free-radical path of the reaction. The results indicate that the inhibited oxidation of preparation (IIa), in case of a zero order of the process relative to the inhibitor, is a reaction of the zero order with respect to oxygen and of the first order with respect to the initial biorganoelement compound. Similar results were obtained during inhibited oxidation of preparation (IIb).

EXPERIMENTAL

The production and purification of oxygen, the purification of the solvent, and the experimental techniques were identical to those described previously[6]. The pressure of the oxygen above the reaction mixture, as a rule, was set at about 300 mm.

Tris(triethylgermyl)stibine was obtained by the reaction of triethylgermane with triethylstibine[4]. The coloured liquid was purified by means of recondensation at a temperature of about 100°/0.1–0.2 mm to give monomeric tris(triethylgermyl)-stibine, a mobile colorless liquid. (Found: C, 36.17; H, 7.66; Ge, 36.07; Sb, 19.93; mol.wt. cryoscopic in cyclohexane, 590. $C_{18}H_{45}Ge_3Sb$ calcd.: C, 35.94; H, 7.61; Ge, 36.21; Sb, 20.24%; mol.wt., 601.5.)

To analyze the products of the reaction the mixture was separated from the antimony trioxide sediment by filtration. The filtrate was analyzed for hexaethyldigermoxane (UV-spectrometric and chromatographic methods). The yield of antimony trioxide was determined by weight and by titration with $KBrO_3$ in a hydrochloric (muriatic) acid medium[7].

A qualitative analysis of this product was performed to determine its chemical composition and the amount of trivalent antimony.

Oxidation of 2.22×10^{-4} mole of tris(triethylgermyl)stibine [preparation (IIa)] in n-octane ($C_0 = 0.043$ mole·l^{-1}) at 18° gave 1.14×10^{-4} mole of antimony trioxide. (Found: Sb, 82.80 calcd.: Sb, 83.54%.) The reaction for pentavalent antimony was found to be negative. The UV-spectrum of the filtrate is identical to the UV-spectrum of the n-octane solution of hexaethyldigermoxane.

Oxidation of preparation (IIa) under similar conditions gave a homogeneous solution without a sediment. Evaporating the solvent under reduced pressure gave a viscous colorless liquid, which on standing gave antimony trioxide sediment. Contact with humid air sharply accelerates this process. This unstable product analyzed correctly for tris(triethylgermoxy)stibine. (Found: C, 32.93; H, 6.86; Ge, 33.22; Sb, 18.57. $C_{18}H_{45}Ge_3O_3Sb$ calcd.: C, 33.31; H, 6.99; Ge, 33.55; Sb, 18.79%.

Oxidation of 1.55×10^{-4} mole of tris(triethylgermyl)stibine (preparation IIb) in n-octane ($C_0 = 0.039$ mole·l^{-1}) at 18° gave 2.4×10^{-4} mole of hexaethyldigermoxane and 0.78×10^{-4} mole of antimony trioxide. (Found: Sb, 83.50. Calcd.: Sb, 83.54%.) The reaction for pentavalent antimony was found to be negative.

2.02×10^{-4} mole of tris(triethylgermyl)stibine [preparation (IIb)] in n-octane ($C_0 = 0.039$ mole·l^{-1}) at 18° was oxidised in the presence of 0.58×10^{-4} mole of triphenylphosphine. Filtration and subsequent evaporation of the solvent and hexaethyldigermoxane at room temperature and reduced pressure gave triphenylphosphine (0.57×10^{-4} mole), m.p. 78°, (the melting point of triphenylphosphine being 78.5° [8]).

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