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Abstract

Full Text

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TRIETHYLLEAD OXIDE

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Triethyllead oxide $((C_2H_5)_3Pb)_2O$ can be formed as an intermediate product in the oxidation of hexaethyllead by oxygen. As we found earlier (1), the reaction of hexaethyllead with oxygen proceeded with a clearly expressed induction period. If triethyllead oxide had been added beforehand to a solution of hexaethyllead, then in this reaction a sharp shortening of the induction period was observed, up to its complete disappearance.

Figure 1 graphically presents the results of experiments on the oxidation of hexaethyllead by oxygen at a pressure of 300 mm Hg in a solution of *n*-nonane at 60°. Curve 1 shows how oxygen was absorbed by the solution of hexaethyllead with the reaction time. Curve 2 shows how this process proceeded under the same conditions if, before oxidation of the hexaethyllead, triethyllead oxide had been added to its solution in an amount of about 1.3 mole %. The acceleration of the reaction observed in this case is explained by the fact that triethyllead oxide decomposed with formation of free radicals, causing pronounced chain branching.

Fig. 1. Oxidation of hexaethyllead by oxygen. Initial concentration of hexaethyllead 20 mole %.

For a more detailed investigation of triethyllead oxide we carried out its synthesis and studied some of its properties.

Although triethyllead oxide was mentioned in the works of Löwig (2) and Klippel (3), carried out more than one hundred years ago, and also in the recently published work of Gilman et al. (4), in fact this compound was not obtained by them. In carrying out the synthesis these investigators used alcoholic and aqueous solutions in which, as will be shown below, triethyllead oxide is readily hydrolyzed.

Oxides of other trialkyllead compounds had likewise not been synthesized.

Our synthesis of triethyllead oxide is based on the reaction of triethyllead monohydroxide with metallic sodium, carried out at room temperature under a layer of dry benzene. To carry out this reaction, metallic sodium was first dispersed in *n*-nonane, then separated from the hydrocarbon first by decantation of the liquid and then by distillation of its residue at room temperature and reduced pressure (about 0.2–0.5 mm Hg), after which the metal was covered with dry benzene. Into this heterogeneous mixture a definite amount of triethyllead monohydroxide was introduced, calculated so that the metallic sodium was in considerable excess.

In the course of the reaction, triethyllead monohydroxide, which is comparatively sparingly soluble in benzene at room temperature, was converted into readily soluble triethyllead oxide. After 2–3 hours, when the reaction was practically complete, the solid components of the reaction mixture were separated by filtration from the solution, from which benzene was then distilled off at room temperature and reduced pressure. After this distillation, a mobile liquid, faintly colored yellow-green and possessing a sharp characteristic odor, remained in the vessel, along with a small amount of triethyllead monohydroxide that had crystallized during the distillation of the benzene. This mixture was filtered once more through a dense glass filter.

Investigation of the composition and properties of the filtrate showed that this substance is triethyllead oxide. The results of its analysis were: lead content found 68.2 and 68.9% (calculated 68.5%); molecular weight, determined from the depression of the melting point of benzene, 590, 592, 588 (calculated 604).

Triethyllead oxide was very readily hydrolyzed already at room temperature to triethyllead monohydroxide:

$$\left((C_2H_5)_3Pb\right)_2O + H_2O = 2\,(C_2H_5)_3PbOH. \tag{1}$$

In the hydrolysis products, titration with hydrochloric acid solution showed 98–99% of triethyllead monohydroxide relative to the amount calculated theoretically.

Analogously to water, alcohols, as well as tertiary alkyl and aralkyl hydroperoxides, act on triethyllead oxide, giving oxide and peroxide compounds of triethyllead, and also triethyllead monohydroxide:

$$\left((C_2H_5)_3Pb\right)_2O + ROH \rightarrow (C_2H_5)_3PbOH + (C_2H_5)_3PbOR; \tag{2}$$

$$\left((C_2H_5)_3Pb\right)_2O + R'OOH \rightarrow (C_2H_5)_3PbOH + (C_2H_5)_3PbOOR'. \tag{3}$$

Both of these reactions proceeded at high rate already at 10° C below zero. The oxide and peroxide compounds formed in this process hydrolyzed very readily, and at elevated temperature decomposed. For this reason reactions (2) and (3) were carried out at reduced temperature (with gradual raising from −10° to 0° C) and at low initial concentrations (about 0.2 mole/liter) of the reacting substances in hexane solution. The experiments were carried out in an apparatus that made it possible to avoid contact of the reaction mixture with air. Observance of these precautions in carrying out reactions (2) and (3) prevented hydrolysis of the oxide and peroxide lead compounds by water vapor from the air, as well as their oxidation and thermal decomposition.

We studied the reaction of triethyllead oxide with methyl, ethyl, and benzyl alcohols, with dimethylphenylcarbinol, and also with tert-butyl hydroperoxide and α-cumyl hydroperoxide.

As was recently established (5), at room temperature triethyllead monohydroxide is practically completely insoluble in aliphatic hydrocarbons. This made it possible for us, by filtration, to separate the precipitate formed as a result of reactions (2) and (3) from the solution of other organolead compounds and to characterize it qualitatively and quantitatively. In all our experiments carried out for this purpose, the results of such an investigation showed that the indicated precipitate was triethyllead monohydroxide, the amount of which, as a rule, was 95-100% of that calculated theoretically.

In experiments on the interaction of triethyllead oxide with ethyl alcohol, with tert-butyl hydroperoxide, and also with α-cumyl hydroperoxide, the products of reactions (2) and (3) formed together with triethyllead monohydroxide were isolated and characterized. For this purpose

after 5-7 min after mixing the starting substances dissolved in n-hexane, and observing the precautions noted above, the precipitate was separated from the reaction mixture by filtration through a dense glass filter. Then, at a temperature of about 0°C and reduced pressure, the volatile compounds were distilled off from the filtrate. The substance remaining after this was characterized by the content of lead and hydroxyl groups formed after its treatment with water, and also by the molecular weight, determined from the depression of the freezing point of benzene. The results of these determinations are summarized in Table 1.

Table 1

Compound formed	Molecular weight, calculated	Molecular weight, found	Found as percentage of the amount calculated theoretically, %: lead	Found as percentage of the amount calculated theoretically, %: hydroxyl groups after hydrolysis
$(C_2H_5)_3PbOC_2H_5$	339	324; 344	92	94; 99
$(C_2H_5)_3PbO_2C(CH_3)_3$	383	374	–	100

Compound formed	Molecular weight, calculated	Molecular weight, found	Found as percentage of the amount calculated theoretically, %: lead	Found as percentage of the amount calculated theoretically, %: hydroxyl groups after hydrolysis
$(C_2H_5)_3PbO_2C(CH_3)_2C_6H_5$	445	415	99; 101	99

As is seen from Table 1, in our experiments ethoxytriethyllead, tert-butylperoxytriethyllead, and α-cumylperoxytriethyllead, as well as several other analogous compounds, were indeed obtained.

Experiments carried out for the purpose of quantitative determinations showed that per 1 mole of triethyllead oxide that reacted with 1 mole of alcohol or hydroperoxide, 0.9–1.0 mole of triethyllead monohydroxide and 0.9–1.0 mole of the corresponding oxy- or peroxylead-organic compound were formed.

Freshly prepared ethoxytriethyllead $(C_2H_5)_3PbOC_2H_5$ is a colorless crystalline substance, melting at a temperature of about 20° into a liquid that fumes in air. This is in agreement with the data of Gilman and Abbott cited in the review (^{6}). Methoxytriethyllead $(C_2H_5)_3PbOCH_3$ is a cream-colored crystalline substance, decomposing without melting upon heating to 60–70°. α-Cumyloxytriethyllead $(C_2H_5)_3PbOC(CH_3)_2C_6H_5$ is a liquid of low mobility at room temperature, having a faint yellow-green color. tert-Butylperoxytriethyllead $(C_2H_5)_3PbO_2C(CH_3)_3$ and α-cumylperoxytriethyllead $(C_2H_5)_3PbO_2C(CH_3)_2C_6H_5$ are viscous liquids of pale golden color.

All the oxy- and peroxylead-organic compounds obtained by us are unstable and, in sealed ampoules, decomposed slowly even at room temperature, acquiring a reddish-brown color that intensified with time.

Triethyllead oxide reacted very vigorously with acetone at room temperature. Thus, when this reaction was carried out in a dilute hexane solution with an equimolecular ratio of triethyllead oxide and acetone, an immediate separation occurred of a colorless crystalline precipitate, which, by its content of lead and hydroxyl group, was identified by us as triethyllead monohydroxide.

When triethyllead oxide was mixed with a large excess of acetone, formation of a colorless crystalline product was likewise observed. The solution above the precipitate gradually, already at room temperature, turned dark brown. In this case, as reaction products we established the formation of mesityl oxide, which was isolated as a fraction during distillation of the reaction mixture and by reaction with 2,4-dinitrophenylhydrazine, as well as of a small amount of an intensely dark-brown resinous higher-boiling product, which we did not inves-

Fig. 2. Decomposition of triethyllead oxide at different temperatures. Curves 1, 2, and 3 were obtained at 70, 80, and 90°

Figure 2: Fig. 2. Decomposition of triethyllead oxide at different temperatures. Curves 1, 2, and 3 were obtained at 70, 80, and 90°

tigate further. The interaction of triethyllead oxide similarly proceeded with triethyl-

lead with acetaldehyde. In this case, the reaction mixture above the precipitated sediment gradually changed from a mobile, colorless liquid into a viscous pale-yellow mass.

Triethyllead oxide decomposed slowly at room temperature and comparatively rapidly on heating, with the formation of a gas, a liquid, and a solid. Figure 2 shows three kinetic curves indicating how gas evolution proceeded with time in this reaction at different temperatures. By the chromatographic method we established that the gas evolved in this process consisted of an equimolecular mixture of ethane and ethylene containing about 1 vol.% butane. The reaction products remaining after removal of the gas consisted of a mixture of a transparent liquid and a cream-colored precipitate. This liquid was distilled off from the precipitate under reduced pressure and identified by reaction with monochloroacetic acid as tetraethyllead (7), the yield of which reached 0.97 mole per mole of decomposed triethyllead oxide. We did not study the solid reaction product in detail, but found that it contained lead (87.5%), an organic residue, probably an ethyl radical, and was practically insoluble in ordinary organic solvents.

Fig. 2. Decomposition of triethyllead oxide at different temperatures. Curves 1, 2, and 3 were obtained at 70, 80, and 90°.

The thermal decomposition of triethyllead oxide may be represented by the following reaction scheme:

$$((C_2H_5)_3Pb)_2O \rightarrow (C_2H_5)_4Pb + C_2H_6 + C_2H_4 + (C_2H_5)_xPbO. \qquad (4)$$

The formation of ethane and ethylene in this reaction is explained by disproportionation of ethyl radicals, the presence of which, in our opinion, is the reason for the accelerating effect, noted above, of additions of triethyllead oxide on the oxidation of hexaethyllead by oxygen. If water had been added beforehand to the hexaethyllead solution and its oxidation by oxygen was carried out, the triethyllead oxide formed in this process as an intermediate product was instantaneously hydrolyzed to triethyllead monohydroxide, and the oxidation reaction proceeded very slowly. Curve 3 (Fig. 1) shows how oxygen absorption proceeded during the oxidation of HEL in the presence of water additions.

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Note: Figure translations are in progress. See original paper for figures.