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Abstract

Full Text

Chemistry

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Triethyltin Peroxide

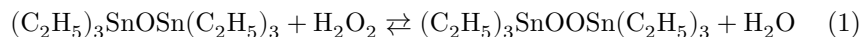
(Presented by Academician B. A. Arbusov on February 25, 1961)

Organometallic peroxide compounds constitute a new class of highly reactive chemical compounds. From a recently published review of methods for the synthesis and reactions of such compounds (¹), it is evident that peroxides of the type R_nMOOMR_n , where R is a hydrocarbon radical and M is a metal, are known only for cadmium, silicon, and germanium. It was of interest to carry out analogous studies of such peroxides of other organometallic compounds.

The present communication contains the results of a study of the triethyltin peroxide synthesized by us— $(C_2H_5)_3SnOOSn(C_2H_5)_3$.

The synthesis of triethyltin peroxide was carried out by mixing equimolecular amounts of triethyltin oxide and anhydrous hydrogen peroxide in a solution of absolute ethyl ether and in the presence of anhydrous sodium sulfate. The reaction was conducted at room temperature in an all-glass apparatus that made it possible to shake the mixture vigorously. After brief (10–15 min) shaking of the reaction mixture, the precipitate was separated from the solution by filtration; a new portion of anhydrous sodium sulfate was introduced into the filtrate, after which the ether was distilled off at room temperature and reduced pressure. Then a small amount of thoroughly dried hexane was added to the residue in the flask, and this mixture was again shaken vigorously for 2–3 min. The residue containing sodium sulfate was separated from the solution by filtration. From the filtrate, the hexane was distilled off at room temperature and reduced pressure. A viscous yellow-golden liquid remained in the flask; investigation of it showed that it was triethyltin peroxide.

The formation of triethyltin peroxide proceeded according to the reaction



Additions of anhydrous sodium sulfate to the reaction mixture were introduced in order to bind the water liberated in reaction (1).

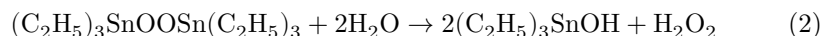
The tin content in the obtained samples of triethyltin peroxide was 53.6% (theoretical value 53.5%); its molecular weight, determined from the depression of the crystallization temperature of benzene, was 443 (theoretical value 443.4).

Fig. 1-3

Figure 1: Fig. 1-3

These experimental values are the averages of three separate determinations, the results of which agreed very closely.

Triethyltin peroxide is very readily hydrolyzed by water without heating according to the reaction



This reaction can be used for analysis of the active-oxygen content in the samples studied by permanganometric titration of the solution. Analysis by this method showed that our preparations were pure triethyltin peroxide (100-101% active oxygen, calculated as triethyltin peroxide).

Triethyltin peroxide is a very unstable compound, and already at a temperature of about 0°C it decomposed completely within twenty-four hours with

with the formation of liquid and solid products. Its decomposition in a sealed glass ampoule at 60° proceeded extremely vigorously, and after only 2-3 min of heating an explosion occurred. If this reaction was carried out in a solution of *n*-nonane, its rate was considerably lower and the process proceeded quietly. It is satisfactorily described by the kinetic equation for a first-order reaction (as determined by active oxygen); this is evident from Fig. 1. These, as well as all subsequent experiments, were carried out in sealed glass ampoules from which the air had first been removed.

In the course of this reaction a white precipitate separated from the solution, insoluble in ordinary organic solvents, which we identified, from its tin content, as diethyltin oxide. The second product of the thermal decomposition of triethyltin peroxide—ethoxytriethyltin—remained in solution. We identified this compound by its boiling point

Fig. 1. Thermal decomposition of triethyltin peroxide in a solution of *n*-nonane at 40°. The straight lines 1, 2, and 3 correspond to initial peroxide concentrations of 0.11, 0.20, and 0.66 mole/liter. $\alpha = C/C_0$

Fig. 2. Thermal decomposition of triethyltin peroxide in *n*-nonane at various temperatures. Curves 1, 2, 3, 4, 5, 6 correspond to temperatures of 20, 30, 40, 50, 60, and 80°. Initial peroxide concentration 0.11 mole/liter

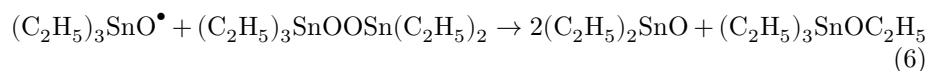
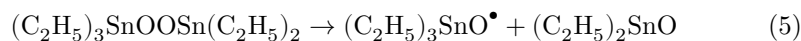
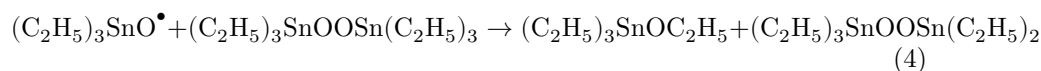
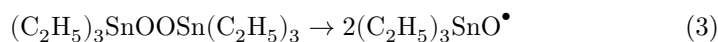
Fig. 3. Oxidation of hexaethyltin with oxygen in a solution of *n*-nonane. Initial hexaethyltin concentration 20 mole %, oxygen pressure 300 mm Hg.

of boiling (190–195°), by its ability to hydrolyze with water to form triethyltin monohydroxide, and by its molecular absorption spectrum. Decomposition of 1 mole of triethyltin peroxide under these reaction conditions was accompanied

by the formation of 0.93 mole (average of two experiments) of diethyltin oxide and 0.98 mole (average of three experiments) of ethoxytriethyltin.

The rate of thermal decomposition of triethyltin peroxide in a solution of *n*-nonane increased with increasing temperature. The value of the apparent activation energy of this reaction, estimated from the experimental data presented in Fig. 2 in the form of kinetic curves, proved to be 14 kcal. Additions of triethyltin peroxide initiated the polymerization of methyl methacrylate, as well as the polymerization of acrylonitrile, which indicates the free-radical character of its decomposition. This conclusion is also confirmed by the presence of induced decomposition, manifested in an increase in the rate constant of this reaction with increasing initial concentration of the starting compound, as is evident from Fig. 1.

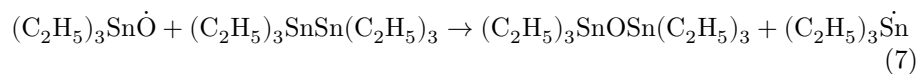
The mechanism of the thermal decomposition of triethyltin peroxide can therefore be represented in the form of the following scheme:

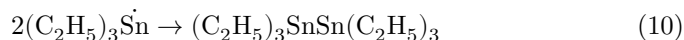
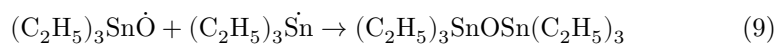
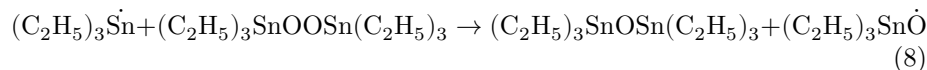


Under the quasi-stationary condition for the concentration of radicals, their consumption by reaction (6) ensures first order of the reaction with respect to triethyltin peroxide.

Triethyltin peroxide, even at room temperature, reacted at a high rate with hexaethyldistannoxane. The sole product of this reaction was triethyltin oxide, identified by us by its boiling point, by its ability to be hydrolyzed by water with formation of triethyltin monohydroxide, and by its molecular absorption spectrum. Decomposition of one mole of triethyltin peroxide in hexaethyldistannoxane was accompanied by the formation of two moles of triethyltin oxide.

The mechanism of this reaction may be represented in the form of the following scheme:





Triethyltin peroxide may be formed as an intermediate compound in the reaction of hexaethyldistannoxane with oxygen. An attempt to detect this compound in the reaction mixture after partial oxidation of hexaethyldistannoxane was unsuccessful, which may be due to the high rate of interaction of triethyltin peroxide with hexaethyldistannoxane. However, it turned out that additions of triethyltin peroxide substantially accelerated the oxidation of hexaethyldistannoxane by oxygen. The results of such experiments are presented in Fig. 3. Curve 1 in this figure refers to a reaction carried out at 50°, while curve 2 gives the results of an analogous experiment, but in which, 45 min after the start of the reaction, an addition of triethyltin peroxide in an amount of about 0.4 mole of peroxide per mole of hexaethyldistannoxane was introduced into the reaction mixture. Curves 3 and 4 give the results of analogous experiments carried out at 60°. All these experiments were performed according to the procedure described earlier (², ³).

It had previously been established (³) that oxidation of hexaethyldistannoxane by oxygen was accompanied by the formation of diethyl- and triethyltin oxides. Specially designed experiments showed that diethyl- and triethyltin oxides, as well as ethoxytriethyltin, did not affect the oxidation of hexaethyldistannoxane by oxygen and themselves were not oxidized in the process. Consequently, the acceleration in the oxidation of hexaethyldistannoxane by oxygen observed upon introduction of additions of triethyltin peroxide into the reaction mixture was due only to this peroxide, or to radicals formed during its transformation, but not to the final products of its transformation. In addition, this acceleration indicated that the reaction occurring here between triethyltin peroxide and hexaethyldistannoxane was accompanied by the formation of radicals initiating the oxidation of hexaethyldistannoxane by oxygen, the chain mechanism of which had been established by us earlier.

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REFERENCES

¹ T. G. Brilkina, V. A. Shushunov, *Proceedings on Chemistry and Chemical Technology*, Gorky, 1960, p. 505. ² V. A. Shushunov, T. G. Brilkina, Yu. A. Aleksandrov, *ibid.*, 1959, p. 329. ³ Yu. A. Aleksandrov, B. A. Radbil, V. A. Shushunov, *ibid.*, 1960, p. 381.

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

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