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## Abstract

## Full Text

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# HOMOLYTIC REACTIONS OF ORGANOTIN COMPOUNDS WITH ALKYL HALIDES, INITIATED BY PEROXIDES

As is known, tetraethyltin is sufficiently inert toward alkyl halides. Additions of anhydrous aluminum chloride, however, cause an exothermic reaction leading to the formation of triethyltin halide ([1,2]). It seemed probable that the reaction could also be initiated in another way, namely with the aid of peroxide compounds. It is known, for example, that under the influence of peroxides aryl derivatives of mercury react with carbon tetrachloride ([3–5]). To confirm this, we investigated the interaction of benzoyl peroxide with binary mixtures of an organotin compound and an alkyl halide in the absence of oxygen. Mixtures of tetraethyltin, dimethyldiethyltin, hexaethyldistannane, and triethyltin chloride with carbon tetrachloride were studied, as well as a mixture of tetraethyltin with propyl bromide. Benzoyl peroxide was taken in the form of small additions (Table 1).

**Table 1**

Reactions of organotin compounds with alkyl halides, initiated by benzoyl peroxide (BP)

| Experiment no. | Taken into the reaction, moles | Temp., °C | Duration, h | Reaction products, moles per 1 mole of peroxide |
|---|---|---|---|---|
| 1 | 0.010 BP0.400 $(C_2H_5)_4Sn$0.470 $CCl_4$ | 75–80 | 12 | 0.53 $CO_2$; 0.95 $C_2H_6$; 13.70 $C_2H_4$; 0.20 *n*-$C_4H_{10}$;28.40 $CHCl_3$; 0.86 $CH_3CH_2CCl_3$; 1.09 $C_6H_5COOH$; 0.34 $C_6H_6$; 29.00 $(C_2H_5)_3SnCl$;3.44 $(C_2H_5)_2SnCl_2$; traces $C_2Cl_6$ |
| 2 | 0.0025 BP0.100 $(C_2H_5)_3SnCl$0.115 $CCl_4$ | 75–80 | 18 | 0.12 $CO_2$; 0.27 $C_2H_6$; 2.60 $C_2H_4$; 0.27 *n*-$C_4H_{10}$;11.50 $CHCl_3$; 6.60 $(C_2H_5)_2SnCl_2$ |
| 3 | 0.0025 BP0.166 $(C_2H_5)_2Sn(CH_3)_2$0.415 $CCl_4$ | 75–80 | 12 | 0.10 $CO_2$; 0.06 $C_2H_6$; 8.80 $C_2H_4$; 0.60 *n*-$C_4H_{10}$;0.06 $CH_4$; 21.00 $CHCl_3$; 16.00 mixture of $(C_2H_5)(CH_3)_2SnCl$ and $(C_2H_5)_2(CH_3)SnCl$ |

| Experiment no. | Taken into the reaction, moles | Temp., °C | Duration, h | Reaction products, moles per 1 mole of peroxide |
|---|---|---|---|---|
| 4 | 0.0025 BP0.050 $(C_2H_5)_6Sn_2$0.150 $CCl_4$ | 90 | 12 | 0.40 $CO_2$; 0.46 $C_2H_6$; 13.90 $C_2H_4$; 1.09 *n*-$C_4H_{10}$;29.40 $CHCl_3$; 15.60 $(C_2H_5)_3SnCl$;8.41 $(C_2H_5)_2SnCl_2$; resin –5.4 g |
| 5 | 0.010 BP0.100 $(C_2H_5)_4Sn$0.244 *n*-$C_3H_7Br$ | 80–85 | 12 | 0.54 $CO_2$; 0.70 $C_2H_6$; 1.10 $C_2H_4$; 1.03 $C_3H_8$;0.70 $C_3H_6$; 0.24 $C_6H_5COOH$; 0.02 $(C_2H_5)_3SnOCOC_6H_5$; 0.19 $(C_2H_5)_2Sn(OCOC_6H_5)_2$;0.68 $(C_2H_5)_3SnBr$ |

It has been established that in all cases at 75–80° a free-radical chain reaction begins. It is natural to suppose that chain initiation occurs as a result of decomposition of the peroxide. The $C_6H_5CO_2\cdot$ and $C_6H_5\cdot$ radicals formed in this process can react both with organotin compounds ([6]) and with haloalkanes ([7]). The interaction of the peroxide with a mixture of tetraethyltin and $CCl_4$ was studied most thoroughly.

The main products of this reaction are triethyltin chloride, ethylene, and chloroform (Table 1, experiment No. 1), which can be explained by the following scheme:

$$R^{\bullet} + (C_2H_5)_4Sn \rightarrow RH + (C_2H_5)_3Sn\dot{C}_2H_4, \quad \text{where R} = C_6H_5COO \text{ and } C_6H_5; \tag{1}$$

$$(C_2H_5)_3SnC_2H_4 \rightarrow (C_2H_5)_3Sn^{\bullet} + C_2H_4. \quad (2)$$

Reaction (1) is confirmed by the presence of benzoic acid and benzene among the products. The resulting $(C_2H_5)_3Sn$-radicals react with $CCl_4$, giving triethyltin chloride and trichloromethyl radicals. The latter, judging from the high yield of chloroform, actively participate in the chain process

$$(C_2H_5)_3Sn^{\bullet} + CCl_4 \rightarrow (C_2H_5)_3SnCl + CCl_3^{\bullet}; \quad (3)$$

$$CCl_3^{\bullet} + (C_2H_5)_4Sn \rightarrow CHCl_3 + (C_2H_5)_3SnC_2H_4 \quad \text{etc.} \quad (4)$$

Triethylstannyl radicals may apparently also be formed by another route:

$$CCl_3^{\bullet} + (C_2H_5)_4Sn \rightarrow CH_3CH_2CCl_3 + (C_2H_5)_3Sn^{\bullet}. \quad (5)$$

As A. E. Borisov showed [4], a reaction similar to (5) is the principal one in the interaction of $R_2Hg$ with $CCl_4$ initiated by peroxides. In our case reaction (5) plays a subordinate role; therefore the yield of 1,1,1-trichloropropane is low. In addition to the substances named, the reaction mixture contains ethane and traces of butane. These compounds (together with ethylene) are normal products of disproportionation and dimerization of ethyl radicals. The latter probably arise by reaction (6), which, as shown earlier [6], usually accompanies (1),

$$C_6H_5COO^{\bullet} + (C_2H_5)_4Sn \rightarrow (C_2H_5)_3SnOCOC_6H_5 + C_2H_5^{\bullet}. \quad (6)$$

Traces of hexachloroethane, detected in the mixture, are formed as a result of recombination of trichloromethyl radicals (chain termination). Finally, along with $(C_2H_5)_3SnCl$, we isolated diethyltin dichloride. Consequently, triethyltin chloride can undergo the same transformations as the initial tetraethyltin. This is confirmed by the reaction of benzoyl peroxide with a mixture of $(C_6H_5)_3SnCl$ and $CCl_4$ (experiment No. 2). In this case as well, the chain character of the process is preserved, although the yield of the main products decreases.

Conversely, during decomposition of benzoyl peroxide in a mixture of tetramethyltin and carbon tetrachloride it is not possible to observe a chain process. It might therefore have been expected that the chain reaction of diethyldimethyltin with $CCl_4$ (experiment No. 3) would proceed only at the expense of its ethyl groups. However, the tin-containing product is not pure dimethyltin dichloride and, judging from the analysis (as well as from the analysis and melting point of the acetate obtained from it), contains a considerable impurity of diethylmethyltin chloride.

The peroxide-initiated interaction of hexaethyldistannane with carbon tetrachloride proved unexpectedly complex (experiment No. 4). As is known, in benzene medium the peroxide reacts with hexaethyldistannane already at room temperature

$$(C_6H_5COO)_2 + (C_2H_5)_6Sn_2 \rightarrow 2\,(C_2H_5)_3SnOCOC_6H_5. \quad (7)$$

In carbon tetrachloride, along with triethyltin benzoate, its chloride is formed [(8)].

It therefore seemed likely that the chain reaction of hexaethyldistannane with $CCl_4$ would also proceed through homolytic cleavage of the tin–tin bond. However, the unexpectedly high yield of chloroform and ethylene indicates attack by trichloromethyl radicals on the ethyl groups of hexaethyldistannane. If the attack proceeded according to reactions similar to (1) and (2), one could expect the formation of pentaethylchlorodistannane. Instead, triethyltin chloride and diethyltin dichloride are formed. Consequently, in the course of the reaction the metal–metal bond is nevertheless destroyed, and additional studies are required in order to decide whether this process is homolytic.

Finally, in studying the interaction of benzoyl peroxide with a mixture of tetraethyltin and propyl bromide, it was possible to show that not only $CCl_4$ can participate as the alkyl halide in the chain reaction (experiment No. 5). The identified products of the process are ethane, ethylene, propane, propylene, carbon dioxide, benzoic acid, triethyltin bromide, triethyltin benzoate, and diethyltin dibenzoate. This permits the assertion that equations (1), (2), and (6) are also valid for the present case.

The triethylstannyl radicals arising according to equation (2) react with propyl bromide:

$$(C_2H_5)_3Sn^{\bullet} + BrCH_2CH_2CH_3 \rightarrow (C_2H_5)_3SnBr + C_3H_7{}^{\bullet}. \quad (8)$$

Propyl and ethyl radicals (see reactions (6) and (8)) then disproportionate. Since the encounter of two radicals in the liquid phase is unlikely, disproportionation apparently takes place in the course of a chain process:

$$R^{\bullet} + (C_2H_5)_4Sn \rightarrow RH + (C_2H_5)_3Sn^{\bullet} + CH_2{=}CH_2, \quad (9)$$

$$R^{\bullet} + CH_3CH_2CH_2Br \rightarrow RH + CH_3\dot{C}HCH_2Br, \quad (10)$$

$$CH_3\dot{C}HCH_2Br \rightarrow CH_3{-}CH{=}CH_2 + Br^{\bullet}, \quad (11)$$

where R = $C_2H_5$ and $C_3H_7$. Reaction (9), as was shown above, proceeds with the intermediate formation of $(C_2H_5)_3SnC_2H_4$ radicals. The validity of equations (10) and (11) has been confirmed by us through a study of the decomposition of peroxidic compounds in propyl bromide, which is the subject of another paper.

## Experimental Part

### Interaction of benzoyl peroxide with a mixture of tetraethyltin and $CCl_4$

A mixture of 0.010 mole of benzoyl peroxide, 0.400 mole of tetraethyltin, and 0.470 mole of $CCl_4$ is heated for 12 hours to 75–80° under nitrogen in a flask fused to a reflux condenser connected with carbon dioxide absorbers and a gas meter. From the increase in weight of the absorbers, the formation of 0.53 mole of $CO_2$ is established (here and below, yields are given per 1 mole of peroxide). The gaseous products are analyzed by a chromatographic method. The formation of 0.95 mole of ethane, 13.70 moles of ethylene, and 0.20 mole of butane is demonstrated. The reaction mixture is fractionated. In the fraction with b.p. 66–80°, chloroform is demonstrated by the isonitrile reaction. Its amount is determined by comparing the refractive indices of the isolated fraction and an artificially prepared mixture of $CHCl_3$ and $CCl_4$. The yield is 28.40 moles. In the fraction with b.p. 80–110°, 0.34 mole of benzene is detected spectrophotometrically (*m*-dinitrobenzene, m.p. 80–81°), and 1,1,1-trichloropropane is identified by saponification to propionic acid [9], *S*-benzylisothiuronium propionate, m.p. 150°. According to data [10]: m.p. 153–154°.

The fraction with b.p. 180–200° is analyzed by the procedure [11]. 29.00 moles of triethyltin chloride and 3.44 moles of diethyltin dichloride are isolated.

Concentrated $H_2SO_4$ is added to the non-distillable residue, and the mixture is heated. Traces of hexachloroethane sublime. M.p. 183° without depression when mixed with the pure substance.

In a parallel experiment, the presence of 1.09 mole of benzoic acid in the mixture is demonstrated by the Chugaev–Tzerevitinov method.

The procedure for carrying out the other experiments (see Table 1) and for identifying the products was the same as that described above.

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