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ACTION OF THIONYL CHLORIDE ON ORGANOTIN OXIDES

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SUMMARY

Reactions between bis(trialkyltin) oxides or dialkyltin oxides and thionyl chloride give the corresponding organotin chlorides and sulphur dioxide in almost quantitative yields. A mechanism involving a cyclic transition state is proposed.

INTRODUCTION

Several reactions between organotin oxides and various metallic and organometallic halides have previously been investigated[1-4], but there seems to be no report on the reactions of acid halides with these oxides. Those between thionyl chloride and some bis(trialkyltin) oxides and dialkyltin oxides are described below, and a mechanism is proposed.

EXPERIMENTAL

Bis(tri-n-propyltin) oxide (b.p. 195–196°/20 mmHg), bis(tri-n-butyltin) oxide (b.p. 225–227°/10 mmHg), di-n-propyltin oxide and di-n-butyltin oxide were used as supplied by M/S Pure Chemicals Ltd., Kirby (U.K.). Molecular weights were determined cryoscopically in benzene. Molar conductances of the reactants, and of their mixtures either neat or in nitrobenzene, were measured at $25 \pm 0.5°$ by use of a conductivity bridge (Toshniwal CL 01/01). Infrared spectra were recorded on a Perkin–Elmer Model 337 Spectrometer, using sodium chloride optics. The spectra of liquids were recorded with thin films and those of solids with KBr pellets.

Reactions between organotin oxides and thionyl chloride

Bis(tri-n-propyltin) oxide (2.55 g, 5 mmole), bis(tri-n-butyltin) oxide (2.97 g, 5 mmole), di-n-propyltin oxide (1.10 g, 5 mmole) or di-n-butyltin oxide (1.19 g, 5 mmole) in carbon tetrachloride (25 ml) was placed in a three-necked flask (100 ml), which was connected with an external trap containing 0.5 *M* NaOH solution, a nitrogen inlet tube, and a dropping funnel. Thionyl chloride (1.29 g, 10 mmole) was added dropwise until sulphur dioxide was no longer evolved. The flask was heated on a water bath for 1–3 h to complete the reaction. The sulphur dioxide evolved was absorbed by NaOH solution and estimated by the usual method. After the reaction, the solvent and unreacted thionyl chloride were removed by distillation and identified

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR ORGANOTIN CHLORIDES PRODUCED

Compound	*Yield* (%)	*M.p.* (°C) *or* *b.p.* (°C/mmHg)	*Analytical data, found (calcd.)*		
			Sn (%)	*Cl* (%)	*Mol.wt.*
Tri-n-propyltin chloride	90	122/13	39.0 (39.7)	12.7 (13.0)	280 (273)
Tri-n-butyltin chloride	88	104/0.7	35.9 (36.5)	10.5 (10.8)	305 (315)
Di-n-propyltin dichloride	87	80–81	41.0 (40.9)	13.1 (13.40)	260 (265)
Di-n-butyltin dichloride	85	42–43	39.1 (39.1)	23.4 (23.6)	300 (293)

by infrared spectroscopy. Physical and analytical data of the products are listed in Table 1. The recovery of sulphur dioxide was 90–95% in each case. Bands at 776 and 564 cm^{-1} which are associated with Sn–O bonds in bis(trialkyltin) oxides and dialkyltin oxides respectively[5] were absent from the IR spectrum of the product, showing the conversion to the chloro compound to be complete.

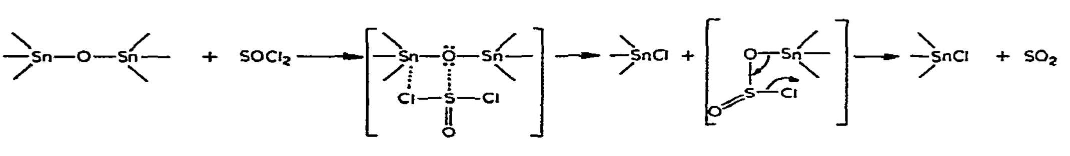
DISCUSSION

The reactions between the bis(trialkyltin) oxides or dialkyltin oxides and thionyl chloride can be represented by the equations:

$$R_3Sn\text{–}O\text{–}SnR_3 + SOCl_2 \rightarrow 2\,R_3SnCl + SO_2$$

$$R_2SnO + SOCl_2 \rightarrow R_2SnCl_2 + SO_2$$

The bis(trialkyltin) oxides are monomeric, whereas the dialkyltin oxides are polymeric with Sn–O–Sn bonds. Mössbauer spectroscopy[6] has shown that the tin atoms in the latter group of oxides have a coordination number of five[7]. The most probable mechanism for the attack of the Sn–O–Sn bond by thionyl chloride is one involving a cyclic transition state, as shown below:



An analogous mechanism has been proposed for the reaction between bis(triphenyltin) oxide and mercury(II) chloride[4]. An alternative would be an ionic mechanism involving solvolysis of the oxide by thionyl chloride. However, both reactants are non-conducting, and there is no evidence from conductivity determinations for the formation of a conducting species when they are mixed neat or dissolved together in nitrobenzene. Moreover, the infrared spectra of organometallic alkoxides and oxides of Group IV elements in methanol and pyrrole[8], provide evidence for the donor properties of the oxygen atom of the linkage –Sn–O–Sn–, which is consistent with the mechanism proposed.

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