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Short communication

THERMAL DECOMPOSITION OF $Me_3SnO_2PCl_2$, $Me_2Sn(O_2PCl_2)_2$ AND $Ph_3SnO_2PCl_2$

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Abstract

TG and DTA studies on $Me_3SnO_2PCl_2$, $Me_2Sn(O_2PCl_2)_2$ and $Ph_3SnO_2PCl_2$ were carried out under dynamic argon atmosphere. The results show that the decomposition proceeds in different stages leading to the formation of $Sn_3(PO_4)_2$ as a stable product. This compound was characterized by IR spectroscopy. Decomposition schemes involving reductive elimination reactions were proposed.

Keywords: IR, $Me_2Sn(O_2PCl_2)_2$, $Me_3SnO_2PCl_2$, $Ph_3SnO_2PCl_2$, TG-DTA

Introduction

There has been considerable interest in the chemistry of organotin compounds as a result of the variety of their industrial applications [1]. However, the literature contains few reports on the thermal decomposition of these compounds. In a recent study the thermal decomposition of Me_2SnSnF_6 and $Me_2Sn(SbF_6)_2$ has been discussed [2]. The thermal decomposition of Me_2SnX_2 (X = SO_3F, SO_3CF_3) was described as involving first the cleavage of a tin-oxygen bond followed by the cleavage of a tin-carbon bond [3].

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$Me_3SnO_2PCl_2$ and $Me_2Sn(O_2PCl_2)_2$ were prepared by the reaction of $P_2O_3Cl_4$ with Me_3SnCl and Me_2SnCl_2, respectively [4]. The reaction of $POCl_3$ with $(Ph_3Sn)_2O$ and with Me_2SnO leads to $Ph_3SnO_2PCl_2$ and $Me_2Sn(O_2PCl_2)_2$ respectively [5].

According to spectroscopic studies, the organotin dichlorophosphates have been assigned a polymeric structure in which the O_2PCl_2 groups function as bidentate bridge ligands through both oxygen atoms [4–6]. $Me_3SnO_2PCl_2$ has been shown by single crystal X-ray diffraction to have polymeric chains of Me_3Sn groups linked by O_2PCl_2 bridges [7].

In this paper, the thermal decomposition of $Me_3SnO_2PCl_2$, $Me_2Sn(O_2PCl_2)_2$ and $Ph_3SnO_2PCl_2$ is described.

Experimental

$Me_3SnO_2PCl_2$ [4], $Me_2Sn(O_2PCl_2)_2$ [5], $Ph_3SnO_2PCl_2$ [5] and $Sn_3(PO_4)_2$ [8] were prepared according to published methods.

Thermogravimetry (TG) and differential thermal analysis (DTA) of the compounds were carried out using a Shimadzu computerized thermal analysis system DT-40. The system includes programs which process data from the thermal analyzer with the chromatopac C-R3A. The rate of heating was kept at 5 deg·min^{-1} using Ar atmosphere (40 ml·min^{-1}). In the DTA studies α-alumina powder standard material was applied as a reference. IR spectra of the thermal decomposition products of the compounds were recorded using a PYE Unicam spectrophotometer model (SP3-300) in the range of 4000–200 cm^{-1} and a KBr disc technique.

Results and discussion

Thermogravimetry (TG) and differential thermal analysis (DTA) curves of $Me_3SnO_2PCl_2$, $Me_2Sn(O_2PCl_2)_2$ and $Ph_3SnO_2PCl_2$ are shown in Figs 1, 2 and 3, respectively. Figure 1(a) shows the DTA curve of $Me_3SnO_2PCl_2$ which exhibits three decomposition steps with maxima at 137, 158 and 181°C. The TG curve (b) indicates two steps corresponding to mass loss in the temperature range 100–250°C. The first sharp and strong endothermic peak starting at 124°C and extending to 142°C, involving a mass loss of about 11%, is probably due to the melting of this compound [4] together with its decomposition, the evolution of volatile fragments and the formation of intermediates. The second endothermic peak extending from 142 to 175°C and accompanied by 53% mass loss corresponds to the decomposition of the intermediate formed in the first step. The third small endothermic peak associated with 5% loss in mass may correspond to the decomposition of a stable fragment formed in the second step.

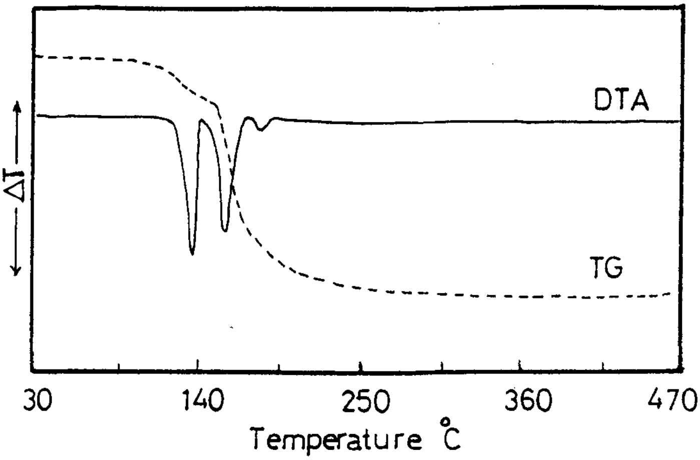

Fig. 1 DTA and TG curves of $Me_3SnO_2PCl_2$

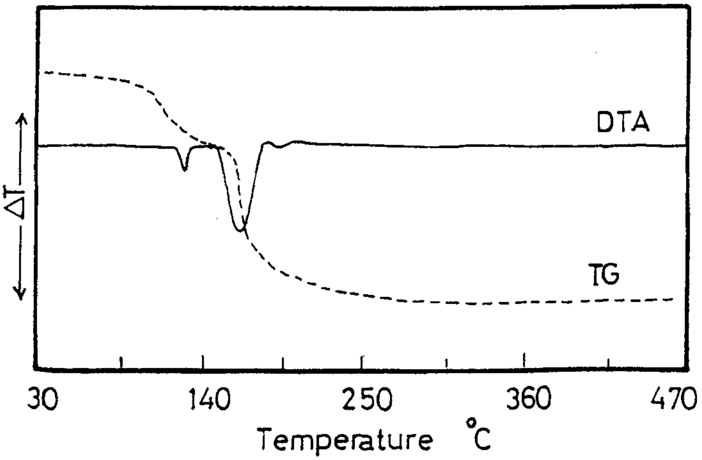

Fig. 2 DTA and TG curves of $Me_2Sn(O_2PCl_2)_2$

Figure 2, curve (a) of $Me_2Sn(O_2PCl_2)_2$ shows that the thermal decomposition proceeds in three stages with maxima at 130, 169 and 195 °C. The TG curve (b) exhibits a total mass loss of 52.5%. The first small endothermic peak starting at 127°C and extending to 135°C which is accompanied by about 14% mass loss may be attributed to the melting and decomposition processes. This step is similar to the first step observed in the case of $Me_3SnO_2PCl_2$, except that the peak has a small area. This behaviour is probably due to the transformation of a part of $Me_2Sn(O_2PCl_2)_2$ to $Me_3SnO_2PCl_2$ according to the following equation:

$$2Me_2Sn(O_2PCl_2)_2 \rightarrow Me_3SnO_2PCl_2 + MeSn(O_2PCl_2)_3$$

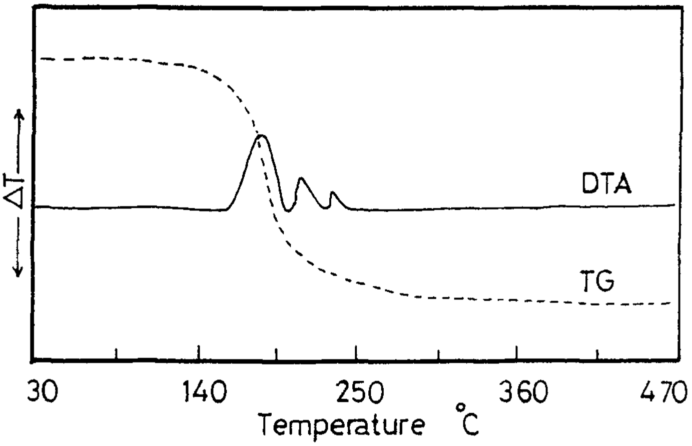

Fig. 3 DTA and TG curves of $Ph_3SnO_2PCl_2$

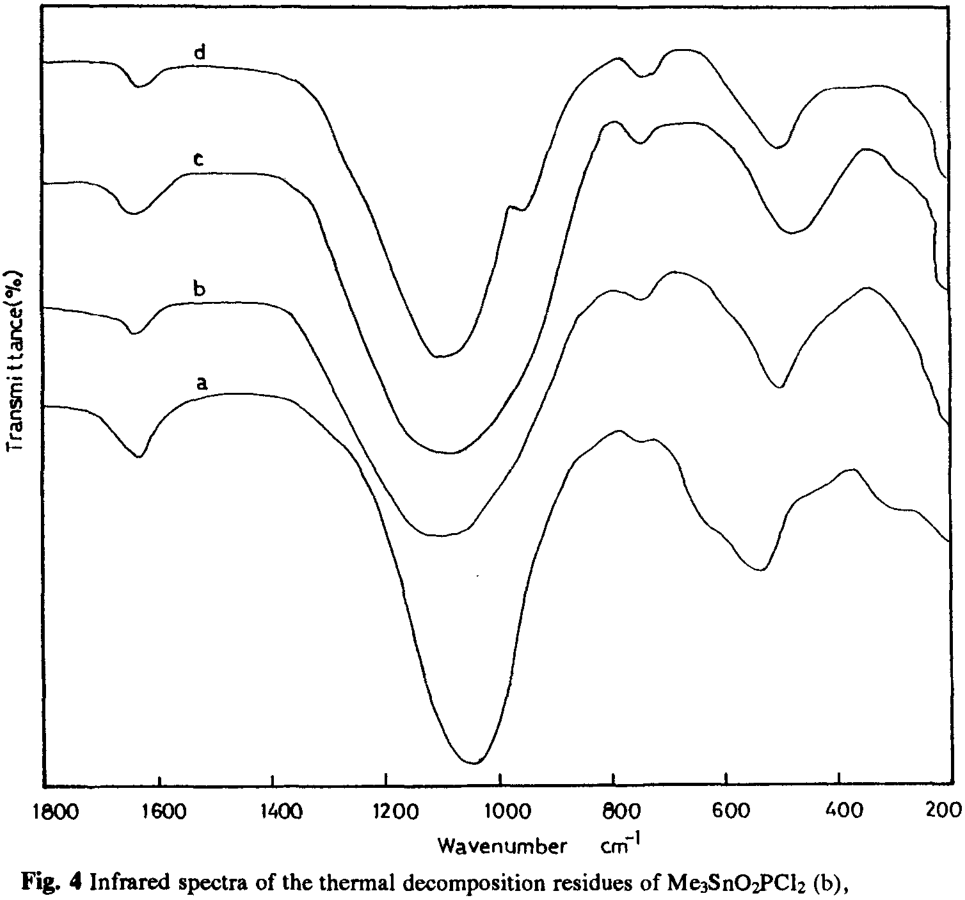

Fig. 4 Infrared spectra of the thermal decomposition residues of $Me_3SnO_2PCl_2$ (b), $Me_2Sn(O_2PCl_2)_2$ (c) and $Ph_3SnO_2PCl_2$ (d); (a) IR spectrum of prepared $Sn_3(PO_4)_2$

The second endothermic peak starting at 150°C and extending to 180°C which is accompanied by about 33.5% mass loss may correspond to the main decomposition stage. The third small endothermic peak associated with about 5% mass loss indicates the decomposition of a stable fragment formed in the second step. It is worth noting that the similarity in the thermal behaviour of $Me_2Sn(O_2PCl_2)_2$ and $Me_3SnO_2PCl_2$ suggests that the mechanism of their decomposition is also similar.

Figure 3(a) shows that the DTA curve of $Ph_3SnO_2PCl_2$ displays three decomposition stages with maxima at 184, 210 and 230°C, while the TG curve (b) exhibits one decomposition step involving 75% mass loss. The first main exothermic peak starting at 160°C and extending to 197°C is due to the main decomposition step. The second and third exothermic peaks having relatively small peak areas may be related to the decomposition of two fragments formed during the thermolysis.

Figure 4 shows the IR spectra of the residues of the three compounds and that of $Sn_3(PO_4)_2$, prepared according to the literature [8]. These spectra are identical and closely resemble the previously published IR spectrum of $Sn_3(PO_4)_2$ [9]. In addition, the IR spectra of the residues show the absence of any organic species. The formation of $Sn_3(PO_4)_2$ indicates that the reduction of tin is a major process during the thermal decomposition of organotin dichlorophosphates. The reduction of Sn(IV) to Sn(II) was also observed in the thermal decomposition of Ph_3SnOH. Continuous heating of Ph_3SnOH in N_2 atmosphere to 400°C produced tin oxides residue in which the $SnO:SnO_2$ ratio was approximately 5:1. The reduction of tin takes place by the elimination of Ph-Ph [10].

On the basis of all these results, the following scheme is proposed for the decomposition of $Me_3SnO_2PCl_2$, $Me_2Sn(O_2PCl_2)_2$ and $Ph_3SnO_2PCl_2$ in argon atmosphere:

$$6Me_3SnO_2PCl_2 \rightarrow Sn_3(PO_4)_2 + 3Me_4Sn + 4POCl_3 + 3Me_2 \qquad (1)$$

$$3Me_2Sn(O_2PCl_2)_2 \rightarrow Sn_3(PO_4)_2 + 4POCl_3 + 3Me_2 \qquad (2)$$

$$6Ph_3SnO_2PCl_2 \rightarrow Sn_3(PO_4)_2 + 3Ph_4Sn + 4POCl_3 + 3Ph_2 \qquad (3)$$

Other volatile products might be formed as a result of a simultaneous cleavage of tin-carbon and tin-oxygen bonds. Moreover, the formation of Me_4Sn and Ph_4Sn has been previously observed in the thermal decomposition of $(Me3Sn)_2PO_3H\cdot 2H_2O$ [11] and Ph_3SnNO_3 [12], respectively.

The calculated overall mass loss for the decomposition of $Me_3SnO_2PCl_2$ according to Eq. 1 is 69.5% which is consistent with the experimental value 69%.

The TG curves show an overall mass loss of about 53% for $Me_2Sn(O_2PCl_2)_2$ and 75% for $Ph_3SnO_2PCl_2$. These values are close to the calculated mass losses of 56% and 81% expected from Eqs (2) and (3) respectively.

The thermal decomposition of organotin dichlorophosphates leads to a tin phosphate residue, while the thermal decomposition of $Me_2Sn(SO_3F)_2$ gives SnO_2. This behaviour can be attributed to the higher volatility of the sulphur oxides relative to the phosphorus oxides. The loss of SO_3 and a small amount of SO_2 by the pyrolysis of $Me_2Sn(SO_3F)_2$ has been observed [3].

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