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A STUDY OF THE THERMAL DECOMPOSITION OF SOME TRIPHENYLTIN CARBOXYLATES

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ABSTRACT

The thermal behaviour of some triphenyltin carboxylates has been studied by means of thermogravimetry (TG), differential thermal analysis (DTA), and mass spectrometry. The melting point enthalpies have been determined by means of DTA and found to vary from 17 to 37 kJ mole^{-1}. No distinguishable decarboxylation process is observed, rather the compounds decompose gradually to yield tin(IV) oxide as the final product.

Analysis of the mass spectra of the decomposition products suggests that a phenyl radical is first cleaved, resulting in the formation of a diphenyltin complex with SnO bridging. Successive cleavage finally leaves Sn as the final product.

INTRODUCTION

While the structure and bonding of several organotin carboxylates have been studied by various spectroscopic techniques [1–5], there are only a few studies on their thermal decomposition [6,7]. Even these few studies have been on the thermal decarboxylation of the carboxylates. This is perhaps due to the preparative utility of decarboxylation. The purpose of this study is to investigate systematically the thermal decomposition of organotin carboxylates by means of TG, DTA and mass spectrometry with the hope of obtaining information on the decomposition products and mechanism.

We have earlier reported [8] the preparation and IR spectra of some triphenyltin substituted benzoates. We now report the thermal decomposition of some of these carboxylates by means of TG, DTA and mass spectrometry.

EXPERIMENTAL

The carboxylates were prepared as described elsewhere [8], and characterized by chemical analysis and IR spectroscopy.

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Melting point enthalpy measurements

The DTA measurements were made on a DTA Mettler TA 2000 analyzer using a similar procedure to that of Adeosun and Sime [9], i.e. about 10–20 mg of the sample was weighed on a Cahn electrobalance, sealed into the standard aluminium crucible of the analyzer and scanned at a heating rate of 1°C min^{-1} in flowing N_2 atmosphere. The equipment was calibrated with indium metal. Measurements were made on at least four samples for each compound studied.

Peak areas were measured by cutting and weighing. The enthalpy of transition, ΔH_m, was calculated from the relationship

$$\Delta H_m = MKA/m$$

where A = peak area, K = the calibration coefficient for a given reaction temperature T°C, M = molar mass, and m = sample mass.

TG measurements

The thermogravimetric analyses were carried out on a Stanton-Redcroft TG thermobalance. The sample was placed on an open platinum crucible. The furnace atmosphere was column-dried flowing air (25 cm^3 min^{-1}), sample masses varied from 5–10 mg, the heating rate was 10°C min^{-1}, and the recorder speed was 5 mm min^{-1}.

Mass spectra

The mass spectra were recorded on a Varian Mat-7 mass spectrometer of the Department of Chemistry, University of Guelph, Canada, using an ionizing energy of 70 eV and a temperature of 200°C.

RESULTS AND DISCUSSION

DTA analysis

All the samples exhibit exothermic DTA peaks. The DTA data are summarized in Table 1, which shows that the melting points obtained from the DTA compare favourably with the previously reported values using open-tube capillaries. The melting point enthalpies range from 17 to 37 kJ mole^{-1}. The transition occurred without any decomposition since only one DTA peak was observed for each sample, and the DTA peak temperatures are generally lower than those at the start of decomposition. It was also observed during the melting point determination that the samples had to be heated well above their melting points before effervescence (due to decarboxylation) was observed.

TABLE 1

Differential thermal analysis of $(C_6H_5)_3SnOCOR$ in N_2

Compound R	M.p.(°C) Open tube [8]	 DTA peaks T_m(°C)	M.p. enthalpy, ΔH_m (kJ mole^{-1})
p-CH_3-C_6H_4	99–100	103.7	22.5 ± 0.6
2,4,6-$(CH_3)_3C_6H_2$	111–112	115.3	27.6 ± 0.3
p-CH_3O-C_6H_4	121–122	125.3	17.1 ± 1.0
p-O_2N-C_6H_4	143–144	148.9	37.2 ± 0.8
p-H_2N-C_6H_4	158–160	162.5	32.2 ± 0.3
3,5-$(O_2N)_2$-C_6H_3	163–164	166.9	31.9 ± 0.2

TG analysis

The TG data are summarized in Table 2 and the curves are shown in Fig. 1. The observed overall mass loss (%) is generally in good agreement with the calculated values, which correspond to the decomposition reaction

$$(C_6H_5)SnOCOR \rightarrow Sn + \text{volatile or gaseous products}$$

We believe that during the decomposition process the organic moieties were oxidized to gaseous products like CO_2, H_2O. The residue on the Pt crucible was yellow while hot and white when cold. This was attributed to SnO_2 which must have been formed by the oxidation of the tin. As can be seen from the TG curves in Fig. 1, the decomposition appears to be a multi-step process but the absence of clearly defined end-plateaux makes the step-wise decomposition analysis and hence the assignment of decomposition stages to specific fragments difficult.

It was hoped that the decarboxylation process

$$(C_6H_5)_3SnOCOR \rightarrow (C_6H_5)_3SnR + CO_2$$

would constitute one of the decomposition steps. The mass loss (%) corre-

TABLE 2

Thermogravimetric analysis of $(C_6H_5)_3SnOCOR$ in air

Compound R	Temp. range (°C)	Overall mass loss(%) Found	 Calcd.
p-CH_3-C_6H_4	192–503	75.6	75.5
2,4,6-$(CH_3)_3$-C_6H_2	223–435	78.0	76.9
p-CH_3O-C_6H_4	94–423	71.0	76.3
p-O_2N-C_6H_4	183–503	80.0	77.0
p-H_2N-C_6H_4	142–479	74.0	75.6
2,5-$(O_2N)_2$-C_6H_3	196–512	79.0	78.8

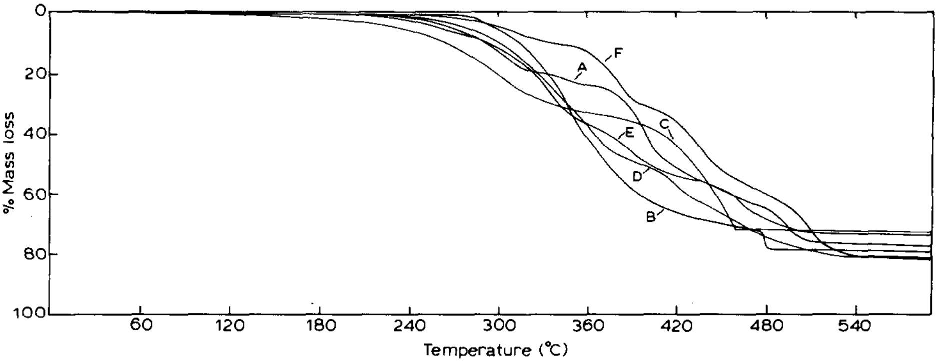


Fig. 1. TG curves for triphenyltin carboxylates. A, $Ph_3SnOCOC_6H_4CH_3$; B, $Ph_3SnOCOC_6H_2(CH_3)_2$; C, $Ph_3SnOCOC_6H_4OCH_3$; D, $Ph_3SnOCOC_6H_4NO_2$; E, $Ph_3SnOCOC_6H_4NH_2$; and F, $Ph_3SnOCOC_6H_3(NO_2)_2$.

sponding to this process varies from 7.8 to 9.1%. This did not agree with any observed distinguishable mass-loss step, and is difficult to explain because several stable organotin compounds have been prepared by the thermal decarboxylation of appropriate organotin carboxylates. Even cyanomethyl triphenyltin has been prepared by thermal decarboxylation under partial vacuum of triphenyltin cyanoacetate [8]. We therefore decided to run the TG curve of triphenyltin cyanoacetate with the hope of detecting the decarboxylation process. A two-step process was observed as shown in Fig. 2 but none corresponds to the decarboxylation process. The step-wise mass losses (%) shown in Table 3 are attributed to the processes:

$$\text{(i)}\ (C_6H_5)_3SnOCOCH_2CN \rightarrow (C_6H_5)_3Sn^{\bullet} + \begin{array}{c} CNCH_2COO^{\bullet} \\ \downarrow [O] \\ \text{volatile products} \end{array}$$

$$\text{(ii)}\ (C_6H_5)_3Sn^{\bullet} \rightarrow Sn + \begin{array}{c} \text{gaseous products} \\ (CO_2,\ H_2O) \end{array}$$

We believe that the organic moieties were oxidized to volatile or gaseous products and were carried away in the air flow.

The decarboxylation of triphenyltin cyanoacetate observed earlier [8] could therefore be explained by the step-wise process in which the carboxylate radical, $CNCH_2COO^{\bullet}$, is formed. The radical degrades further to the cyanomethyl radical, $CNCH_2^{\bullet}$ and CO_2, and then reacts with the triphenyltin radical, $(C_6H_5)_3Sn^{\bullet}$, to give the decarboxylation product, $(C_6H_5)_3SnCH_2CN$, i.e.

$$(C_6H_5)_3SnOCOCH_2CN \rightarrow (C_6H_5)_3Sn^{\bullet} + CNCH_2COO^{\bullet}$$

$$CNCH_2COO^{\bullet} \rightarrow CNCH_2^{\bullet} + CO_2$$

$$CNCH_2^{\bullet} + (C_6H_5)_3Sn^{\bullet} \rightarrow (C_6H_5)_3SnCH_2CN$$

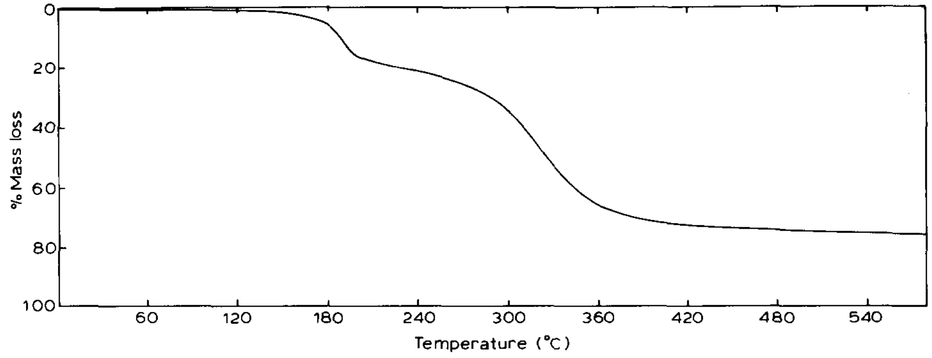


Fig. 2. TG curve for triphenyltin cyanoacetate, $Ph_3SnOCOCH_2CN$.

TABLE 3

TG analysis of $(C_6H_5)_3$ $SnOCOCH_2CN$ in air

Temp. range (°C)	Overall mass loss(%)	Step-wise mass losses (%)	
		Temp. range (°C)	Mass loss (%)
32–343	73.0(72.6)	32–152	19.0(19.4)
		152–343	54.0(53.2)

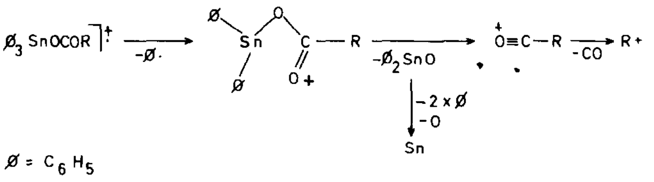
Figures in parentheses represent calculated values.

Mass spectra

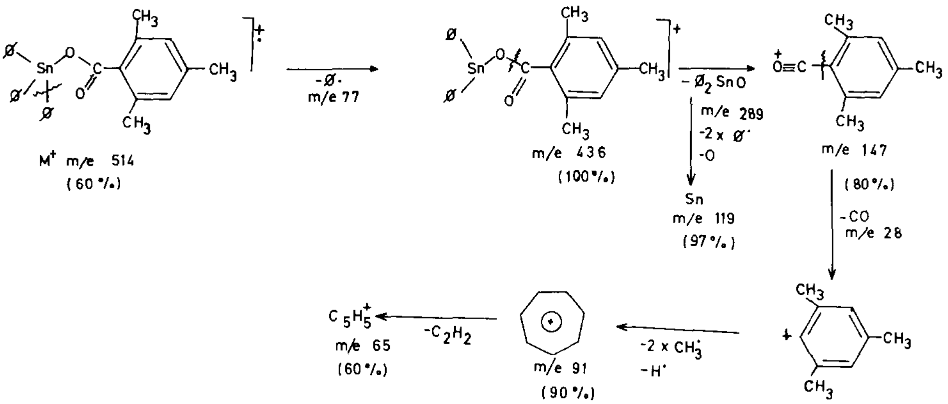
Since the TG measurements provided very little information on the decomposition products and mechanisms, mass spectra of the samples were run. The fragmentation patterns are discussed here.

Each compound was heated to an average temperature of 200°C. For all compounds, it is observed that a phenyl radical is first cleaved, most probably resulting in the formation of a diphenyl complex with Sn–O bridging. From the observed metastable peaks, it is clear that this initial phenyl radical cleavage is followed by homolytic fission of a benzoyl cation [except $(C_6H_5)_3SnOCOCH_2CN$]. Carbon monoxide is subsequently cleaved and diphenyl tin oxide in all cases further fragments to phenyl radicals, tin and oxygen. The peak at m/e 119 assigned to the residual Sn is observed as the most prominent peak in all the spectra [Scheme 1]. A representative fragmentation pattern is shown for $(C_6H_5)_2$ SnOCO C_6H_2 $(CH_3)_2$ [Scheme 2].

Triphenyltin cyanoacetate, $(C_6H_5)_3$ $SnOCOCH_2CN$, fragments slightly differently from all the others. A distinct peak corresponding to $M+1$ is

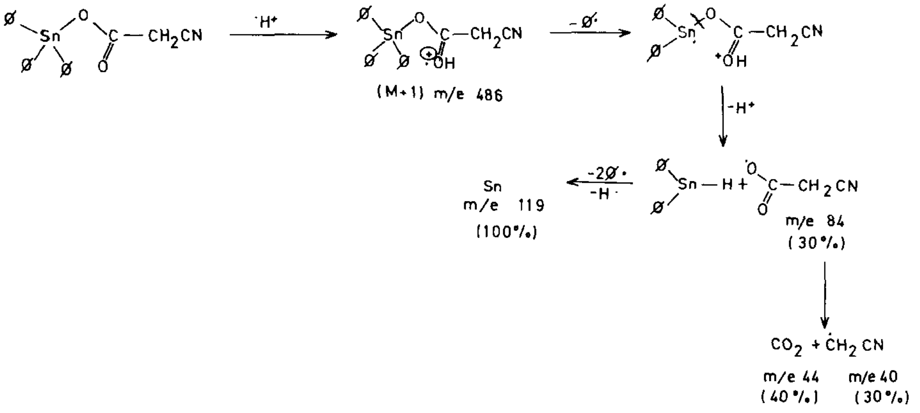


Scheme 1. General fragmentation pattern of $(C_6H_5)_3SnOCOR$.



Scheme 2. Fragmentation pattern of $(C_6H_5)_3SnOCOC_6H_2(CH_3)_2$.

observed and is attributed to intermolecular proton transfer rather than to isotopic phenomenon. Furthermore, $(C_6H_5)_3SnOCOCH_2CN$ fragmentation seems to favour cleavage of CO_2. This is most likely due to the absence of an aryl group which would make the general scheme operative. Consequently, a peak at *m/e* 84 (30%) is observed corresponding to the radical $NCCH_2COO^\cdot$ which further fragments to $NCCH_2^\cdot$ and CO_2 (*m/e* 44; 40%). This process is



Scheme 3. Fragmentation pattern of $(C_6H_5)_3SnOCOCH_2CN$.

also supported by the fact that the compound $Ph_3Sn\ CH_2CN$ has been synthesized by the decarboxylation of $(C_6H_5)_3\ SnOCOCH_2CN$ under partial vacuum whereas attempts to synthesize corresponding compounds from the other carboxylates have not been successful. The fragmentation pattern of $(C_6H_5)_3\ SnOCOCH_2CN$ is shown in Scheme 3.

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