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A thermal analytical study of some mono- and di-organotin oxides and carboxylates

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Simultaneous thermogravimetry and differential thermal analysis studies on a variety of mono- and di-organotin oxides and carboxylates were performed; for the carboxylates, these studies followed ^{119}Sn NMR spectroscopic investigation. All the organotin compounds thermally degrade to tin(IV) oxide (SnO_2) in either air or oxygen, as was confirmed by Mössbauer spectroscopy in the cases of RSn(O)OH (R = butyl, octyl) and Bu_2SnO.

The organotins are less stable than previously believed since evidence for degradation was obtained in many cases at approximately 160–170 °C.

In addition it was found that oxygen influences the thermal stability of the organotins, since Bu_2SnO did not degrade when heated for 1 h at 280 °C under nitrogen, yet readily broke down at 170 °C in air. Furthermore, pure oxygen had the effect of lowering reaction temperatures by approximately 10–12°C compared with those in air.

Keywords: Organotin, thermal analysis, decomposition, Mössbauer, NMR

1 INTRODUCTION

Thermogravimetric (TG) or differential thermal analytical (DTA) techniques are useful in the study of the thermal stability of chemicals. However, to date there are few such reports[1–4] relating to organotin compounds and it is generally believed that the Sn–C bond is stable[5] at temperatures up to 200 °C. We therefore describe herein details of simultaneous TG and DTA investigations of a range of mono- and di-organotin oxides and carboxylates.

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Table 1 ^{119}Sn NMR data

Compound	Concentration (M)[a]	δ^{119}Sn (ppm)
$Bu_2Sn(OCO\cdot C_{11}H_{23})_2$	0.35	−153.2
$Oct_2Sn(OCO\cdot C_{11}H_{23})_2$	Neat	−161.8
$Bu_2Sn(OCO\cdot C_{17}H_{35})_2$	0.42	−153.4
$OctSn(OCO\cdot CH_3)_3$	Neat	−533.3
$OctSn(OCO\cdot C_{11}H_{23})_3$	Neat	−530.5
$OctSn(OCO\cdot C_{17}H_{35})_3$	0.36	−528.1

[a] Samples were either neat liquids or CCl_4 solutions.

EXPERIMENTAL

Organotin compounds

The following compounds were commercial products and were used without further purification:

$$\left.\begin{array}{l}R_2SnO\\ RSn(O)OH\end{array}\right\}[R = \text{butyl(Bu) and octyl(Oct)}]$$

The di- and mono-organotin carboxylates listed below were prepared by azeotropic dehydration in refluxing toluene of the appropriate mole ratios of either a dialkyltin oxide or an alkanestannonic acid with the relevant carboxylic acid. The purity of these compounds was checked by ^{119}Sn NMR, and chemical shifts are consequently reported in Table 1.

$R_2Sn(OCO\cdot C_{11}H_{23})_2$ (R = Bu and Oct)
$Bu_2Sn(OCO\cdot C_{17}H_{35})_2$
$OctSn(OCO\cdot CH_3)_3$
$OctSn(OCO\cdot C_{11}H_{23})_3$
$OctSn(OCO\cdot C_{17}H_{35})_3$

Thermal analysis

Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) of the organotin samples were carried out on a Stanton–Redcroft

STA 780 instrument with a computer enhancement facility (CETA). A rapid heating rate of 50 °C min^{-1} from ambient temperature to 180 °C was employed, followed by 50 °C min^{-1} thereafter, to a maximum temperature of up to 480 °C. The atmosphere was either air or oxygen, with a flow rate of approximately 40 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. Measured temperatures are accurate to ±5 °C. Sample weights were approximately 10 mg.

NMR spectroscopy

^{119}Sn NMR spectra were recorded at ambient temperature on a JEOL FX60Q spectrometer at 22.24 MHz, under nuclear Overhauser suppressed conditions. Field frequency lock was to external D_2O. Chemical shifts (δ^{119} Sn) are relative to Me_4Sn and are accurate to ±0.1 ppm.

Mössbauer spectroscopy

^{119m}Sn Mössbauer spectra were obtained by using a constant-acceleration microprocessor spectrometer (E. S. Technology Ltd, Oxford) with a 512-channel data store. A 10 mCi $Ba^{119m}SnO_3$ source was used at room temperature and the samples were cooled to 80 K by means of a liquid nitrogen cryostat. The spectra were computer-fitted to a sum of Lorentzian curves using a least-squares procedure. The experimental error in the measured values of isomer shift (δ), quadrupole splitting (ΔE_q) and line width (Γ) is ±0.1 mm s^{-1}.

RESULTS

The results of TG and DTA studies of the organotin compounds are shown in Fig. 1, 2 and 3 and are described below. At the commencement of the experiment, the top, middle and bottom traces are due to the TG, DTA and temperature measurements respectively.

The theoretical weight losses reported refer to those calculated on the basis of complete conversion of the appropriate organotin to tin (IV) oxide

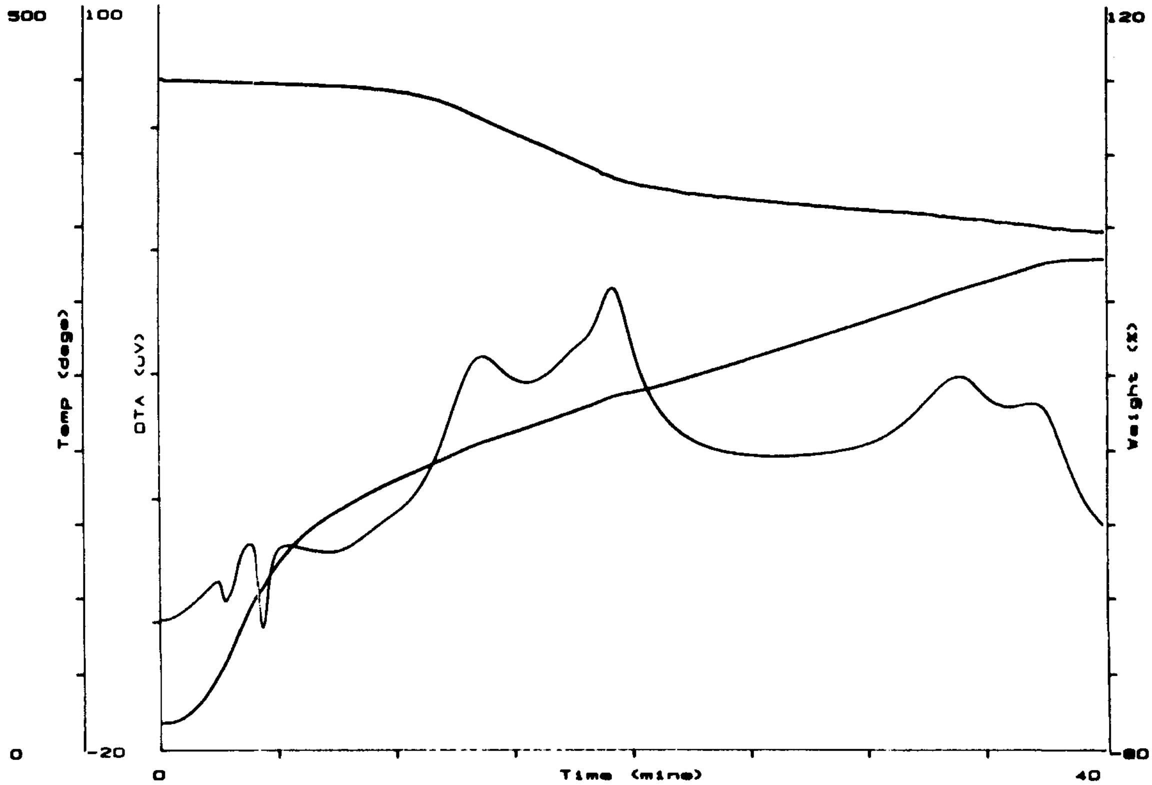

Figure 1 TG/DTA trace for Bu_2SnO/air.

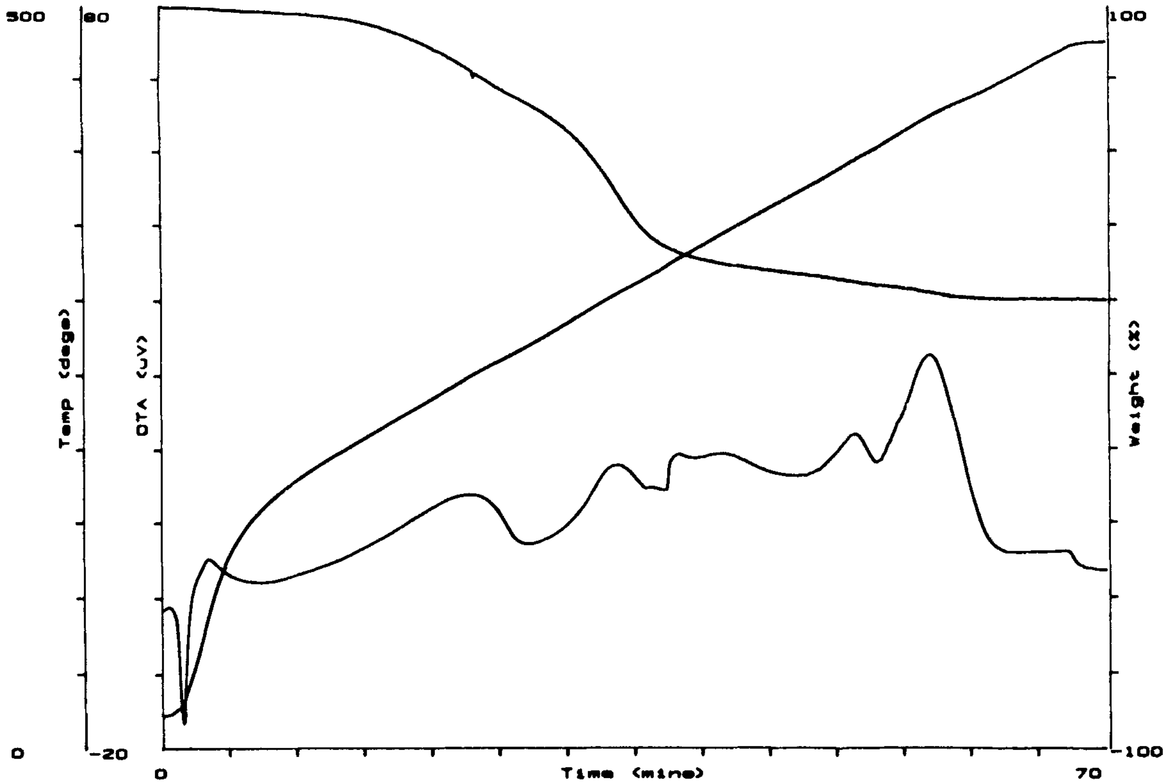

Figure 2 TG/DTA trace for $Bu_2Sn(OCO \cdot C_{11}H_{23})_2$/air.

(SnO_2). Equation [1] gives the example for Bu_2SnO.

$$Bu_2SnO \xrightarrow{\Delta} SnO_2 \text{ (Theoretical wt loss: 39.4\%)} \quad [1]$$

Bu_2SnO (Theoretical weight loss: 39.4%)

Atmosphere	Air (Fig. 1)
Actual weight loss	42.7%

Endotherms occurred between 50 and 130 °C with minima at 55 and 110 °C. Exotherms took place beginning at approximately 160, 220, 280 and 315 °C. Weight loss had ceased by approximately 335 °C.

Atmosphere	Oxygen
Weight loss	42.3%

Endotherms occurred between 45 and 120 °C with minima at 55 and 105 °C. An exotherm occurred at 165 °C followed by a larger exotherm at 219 °C, after which weight loss ceased.

Oct_2SnO (Theoretical weight loss: 58.2%)

Atmosphere	Air
Actual weight loss	52.6%

An endotherm occurred between 60 and 120 °C with a minimum at 90 °C. A series of exotherms then took place beginning at 160 °C, with maxima at 205, 225, 250, 280 and 290 °C. Weight loss ceased at approximately 325 °C.

Atmosphere	Oxygen
Actual weight loss	60.9%

An endotherm occurred between 60 and 120 °C with a minimum at 85 °C. A small exotherm took place at 180 °C, followed by a larger exotherm at 225 °C, after which weight loss ceased.

$Bu_2(OCO \cdot C_{11}H_{23})_2$ (Theoretical weight loss: 76.0%)

Atmosphere	Air (Fig. 2)
Actual weight loss	80.0%

An endotherm took place at 25 °C due to melting. A series of exotherms occurred, beginning at 160 °C, with obvious maxima at 245, 300, 390 and

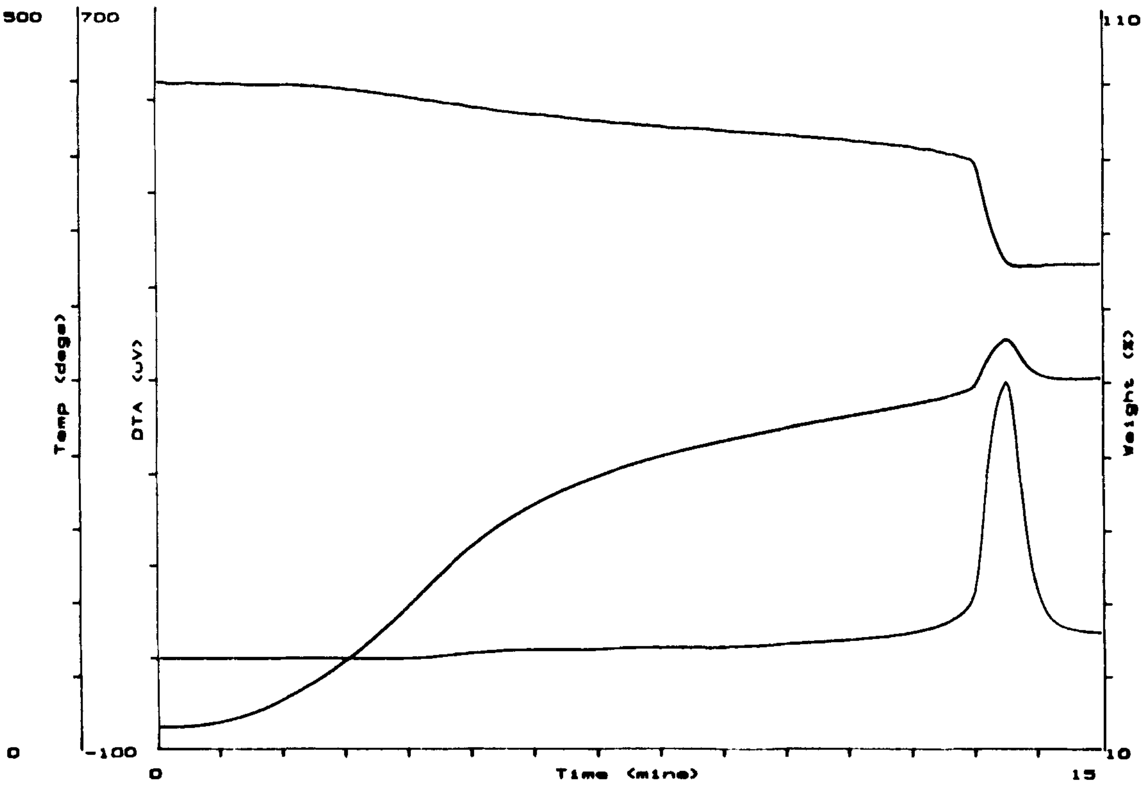

Figure 3 TG/DTA trace for BuSn(O)OH/air.

425 °C. Weight loss ceased at approximately 430 °C.

Atmosphere	Oxygen
Actual weight loss	78.3%

An endotherm occurred at 25 °C due to melting. A series of exotherms took place, beginning at 160 °C, with maxima at 235, 290, 320, 360 and 375 °C. Weight loss ceased at approximately 420 °C.

Oct$_2$Sn(OCO·C$_{11}$H$_{23}$)$_2$

(Theoretical weight loss: 79.8%)

Atmosphere	Air
Actual weight loss	80.8%

A series of exotherms occurred, beginning at 150 °C, with obvious maxima at 250, 320, 350, 395 and 420 °C. Weight loss ceased at approximately 450 °C.

Atmosphere	Oxygen
Actual weight loss	81.9%

A series of exotherms occurred, beginning at 160 °C, with maxima at 235, 290, 315, 360 and 380 °C. Weight loss ceased at approximately 450 °C.

Bu$_2$Sn(OCO·C$_{17}$H$_{35}$)$_2$

(Theoretical weight loss: 81.1%)

Atmosphere	Air
Actual weight loss	89.4%

An endotherm, probably due to melting, occurred at 48 °C. Weight loss accompanied by a series of exotherms began at approximately 100 °C. Stronger exotherms occurred at 321 and 353 °C. The thermal breakdown had not been completed by the time the maximum temperature of 475 °C had been reached.

Atmosphere	Oxygen
Actual weight loss	84.7%

An endotherm, probably due to melting, occurred at 46 °C. Weight loss accompanied by a series of exotherms began to occur at approximately 100 °C. A strong exotherm took place at 436 °C, after which weight loss ceased.

BuSn(O)OH (Theoretical weight loss: 27.7%)

Atmosphere	Air	(Fig. 3)
Actual weight loss	23.8%	

On heating to 245 °C a weight loss of 10% took place. This was followed by a large exotherm, which resulted in an additional weight loss of 14%.

Atmosphere	Oxygen
Actual weight loss	29.3%

On heating to 230 °C a weight loss of 9.5% took place. This was then followed by a large exotherm which resulted in an additional weight loss of 20%.

OctSn(O)OH (Theoretical weight loss: 43.0%)

Atmosphere	Air
Actual weight loss	36.0

On heating to 250 °C a weight loss of 12% took place. At this point a two-stage exotherm occurred, resulting in a further weight loss of 22%.

Atmosphere	Oxygen
Actual weight loss	45.3%

On heating to 225 °C a weight loss of 11% occurred. At this point a two-stage exotherm took place resulting in a further weight loss of 34%.

$OctSn(OCO \cdot CH_3)_3$
(Theoretical weight loss: 63.0%)

Atmosphere	Air
Actual weight loss	67.0%

A series of exotherms, with maxima at 220, 299 and 354 °C, commenced at 170 °C. Weight loss ceased at 450 °C.

Atmosphere	Oxygen
Actual weight loss	66.7%

A series of exotherms, with maxima at 220, 282 and 338 °C, commenced at 160 °C. Weight loss ceased at 450 °C.

$OctSn(OCO \cdot C_{11}H_{23})_3$
(Theoretical weight loss: 81.7%)

Atmosphere	Air
Actual weight loss	86.5%

A series of exotherms occurred, commencing at approximately 170 °C, with obvious maxima at 225, 315, 360 and 420 °C. Weight loss ceased at approximately 460 °C.

Atmosphere	Oxygen
Actual weight loss	85.2%

A series of exotherms occurred, commencing at approximately 165 °C, with maxima at 217, 295, 317, 345 and 375 °C. Weight loss ceased at approximately 460 °C.

$OctSn(OCO \cdot C_{17}H_{35})_3$
(Theoretical weight loss: 86.0%)

Atmosphere	Air
Actual weight loss	86.5%

An endotherm occurred between 30 and 90 °C, with a minimum at 49 °C. A series of exotherms took place commencing at 165 °C, with maxima at 243, 329 and 475 °C. Weight loss ceased at approximately 480 °C.

Atmosphere	Oxygen
Actual weight loss	92.8%

An endotherm took place between 30 and 95 °C, with a minimum at 49 °C. A series of exotherms occurred, commencing at 165 °C with maxima at 234, 312 and 455 °C. Weight loss ceased at approximately 470 °C.

TG and DTA traces of *all* of the above compounds can be obtained from the authors.

DISCUSSION

From the results reported, it may be seen that the actual weight losses were found to be within approximately 10% of the theoretical values, suggesting that, in each case, complete conversion to SnO_2 had occurred.

Further evidence for the pyrolytic conversion of the organotin compounds to SnO_2 was obtained from the Mössbauer spectra (Table 2) of 2 g samples of BuSn(O)OH and OctSn(O)OH which had been heated to 270 °C for 3 h in air in an oven. A further 2 g sample of BuSn(O)OH

Table 2 ^{119m}Sn Mössbauer data

Sample	δ (mm s^{-1})	ΔE_q (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})
SnO_2	0.08	—	2.7	—
BuSn(O)OH	0.71	1.91	1.2	1.6
BuSn(O)OH (300 °C for 2 min)	−0.02	—	2.9	—
BuSn(O)OH (270 °C for 3 h)	0.09	—	3.8	—
BuSn(O)OH (170 °C for 96 h)	0.07	—	3.7	—
OctSn(O)OH	0.65	1.81	1.4	1.5
OctSn(O)OH (270 °C for 3 h)	0.04	—	3.0	—
Bu_2SnO	0.99	2.11	1.25	1.27
Bu_2SnO (160 °C for 84 h)	0.82	1.67	2.20	1.58
Bu_2SnO (170 °C for 96 h)	0.02	—	4.20	—
Bu_2SnO (160 °C for 84 h/N_2)	0.99	2.09	1.14	1.18
Bu_2SnO (200 °C for 1 h/N_2)	0.99	2.08	1.16	1.16
Bu_2SnO (280 °C for 1 h/N_2)	0.97	2.01	1.40	1.29

heated to 300 °C for just 2 min also gave a Mössbauer spectrum consistent with SnO_2 (Table 2).

Probably the single most important observation from these studies is that, contrary to the belief that the Sn–C bond is stable at temperatures up to 200 °C[3], evidence for decomposition was seen in many cases by the appearance of an exothermic process at temperatures much below this. In the compounds studied there are a number of different bonds that could be cleaved at elevated temperatures e.g. Sn–C, Sn–O, C–C, C–O and C–H. However, from typical thermochemical data[5,6,7] the Sn–C bond must be considered to be the least thermally stable. In order to check that organotin degradation can occur at temperatures below 200 °C, 1 g samples of Bu_2SnO and BuSn(O)OH were placed on a watchglass in an atmosphere of air in an oven at 170 °C for four days. Mössbauer spectra, recorded subsequently, indicated that essentially complete conversion to SnO_2 had taken place in both cases (Table 2). From the thermal analytical data, it appeared that the onset of degradation occurred at approximately 160 °C. This was verified by only small changes in Mössbauer parameters of Bu_2SnO after heating for 84 h at this temperature and by the fact that complete conversion to SnO_2 occurred at 170 °C.

In addition, samples of Bu_2SnO were heated under nitrogen for 1 h at temperatures up to 280 °C and subsequent Mössbauer analyses were performed (Table 2). In contrast to the results in air, very little change in Mössbauer parameters was observed, implying that little or no breakdown of the organotin had taken place. This, together with the fact that reaction temperatures in oxygen were significantly lower, suggests that oygen has an influence on the thermal stability of the organotin derivatives.

The thermal analysis of the organotin carboxylates indicated that relatively high temperatures were required before the samples cease to lose weight. This would imply either that breakdown was not complete until these high temperatures had been achieved or that SnO_2 formation had occurred but organic residues remained. It was also noted that, as the carboxylate chain became longer, so the temperature at which weight loss ceased became higher. This may suggest that the latter explanation is correct, but further work would be required to verify this.

The diorganotin oxides and mono-organotin stannonic acids show much simpler TG and DTA traces. In oxygen the former class of compound exhibits a large exotherm associated with a dramatic rise in sample temperature and weight loss consistent with SnO_2 formation. This event had an onset temperature of approximately 220 °C for both Bu_2SnO and Oct_2SnO. In air, more complex traces are observed for these compounds, suggesting that the local sample temperature rise associated with the more reactive oxygen atmosphere is sufficient to cause all the breakdown steps to occur simultaneously, and thus the DTA trace is simplified. It should be noted that initial *endothermic* reactions observed for the diorganotin oxides are accompanied by weight losses of <5%. These are believed to be due to the presence of an impurity in each sample which is thought to be the appropriate diorganotin dichloride. However, since the level of impurity is low, the TG/DTA traces are considered to be representative of the respective diorganotin oxide.

The mono-organotin alkanestannonic acids, BuSn(O)OH and OctSn(O)OH, initially show small weight losses which could be partially attributed to dehydration, leading to the formation of $(RSnO_{1.5})_n$. Following this, large exotherms took place in both oxygen and air. The onset temperatures of these reactions were 230 and 244 °C for the former compound and 223 and 251 °C for the latter. These data are in line with the general observation that reaction temperatures are lower in oxygen than in air.

CONCLUSIONS

From the studies performed it may be concluded that the organotin carboxylates and oxides thermally degrade to SnO_2 in either air or oxygen. The oxygen atmosphere has the effect of generally reducing reaction temperature by approximately 10–20 °C. At higher temperatures both oxidative and thermal degradative processes are occurring. At lower temperatures only oxidative processes probably occur.

The organotins are less stable than previously believed since evidence for degradation was obtained in many cases at approximatley 160–170 °C.

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