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THERMAL STUDIES OF THE TRIPHENYLTIN CHLORIDE BENZIL SEMICARBAZONE COMPLEX

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ABSTRACT

The thermal decomposition of Ph_3SnCl(BenzSCZ), where Ph = phenyl and BenzSCZ = benzil semicarbazone (i.e. $C_{15}H_{13}N_3O_2$) has been studied in the temperature range 27–715 ° C using TG, DTG and DTA techniques. The decomposition of the complex takes place in four steps in the temperature range 127–550 ° C, giving SnO_2 as an end product. The decomposition products at each stage were analysed chemically and further confirmed by IR studies. The end product was also characterised by X-ray analysis. A scheme for the decomposition of the complex is proposed.

INTRODUCTION

A survey of the existing literature reveals that very little work has been done on the thermal decomposition of organotin(IV) compounds [1–3]. The interpretation of pyrolysis reactions involved in the decomposition of a series of organotin(IV) adducts and carbohydrate derivatives has been shown to be difficult [3] because of the lack of information on the thermal decomposition of simple organotin(IV) compounds. A thermal decomposition scheme involving a reductive elimination reaction has recently been reported for triphenyltin(IV) hydroxide [1]. The adducts of triphenyltin azide with 2-methylimidazole and *N,N'*-diethylacetamide decompose in two steps giving SnO_2 as an end product at higher temperatures [2]. In continuation of our previous thermal studies on copper(II) and cobalt(II) semicarbazones [4], the present communication reports on studies of the thermal decomposition of triphenyltin chloride benzil semicarbazone.

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EXPERIMENTAL

Chemicals

Triphenyltin chloride (Fluka) and benzil (E. Merck) were used without further purification. Absolute methanol and ethanol were prepared by refluxing on magnesium turnings for several hours, and then distilled and stored under nitrogen.

Preparation of triphenyltin chloride benzil semicarbazone

The complex was prepared according to a previously reported method [5]. 1.06 g (0.004 mol) of benzil semicarbazone in a minimum amount of absolute methanol was added to 1.5 g (0.004 mol) of triphenyltin chloride in hot absolute methanol ($\approx$ 20 ml) in a dry atmosphere with constant stirring. The mixture was stirred for 1–2 h and then refluxed for 3–4 h. The excess of solvent was removed by distillation and the product dried under vacuum. It was then recrystallized from the same solvent and finally dried under vacuum.

Analytical procedures

Microanalysis for carbon, hydrogen and nitrogen was performed using an Elementary Analyser, CHN–Rapid, at the Indian Institute of Technology, New Delhi.

Thermal measurements

The thermal measurements were carried out using a Stanton Redcroft thermal analyser, STA-780 Series, which simultaneously records DTA, DTG and TG curves. The sample (15.03 mg) was heated at a rate of 5 °C min^{-1} in a platinum crucible to a temperature of around 715 °C in static air. Alumina was used as a standard reference material. A thermobalance with 0.01 mg sensitivity was used. The chart speed was maintained at 20 cm h^{-1}.

IR spectra

IR spectra of the complex and the decomposition products at different temperatures were recorded in a KBr matrix on a Beckman IR 20 spectrophotometer in the region 4000–200 cm^{-1}.

X-ray diffraction

The X-ray diffraction pattern was taken with a Phillips diffractometer, using Cu $K\alpha$ radiation.

RESULTS AND DISCUSSION

The composition and structure of triphenyltin chloride benzil semicarbazone as given in Fig. 1 was confirmed using the methods reported in our previous studies [5].

The complex decomposes in four steps in the temperature range 127–550 °C to give SnO_2 as the end product. Figure 2 gives TG, DTA and DTG curves for $Ph_3SnCl(BenzSCZ)$. The intermediates formed at each stage were isolated and characterized by elemental analysis and IR spectra (see Tables 1 and 2).

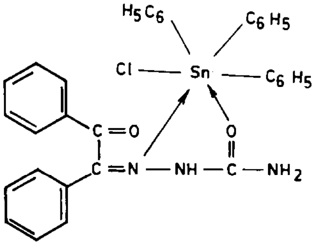

Fig. 1. Octahedral structure of $Ph_3SnCl(BenzSCZ)$.

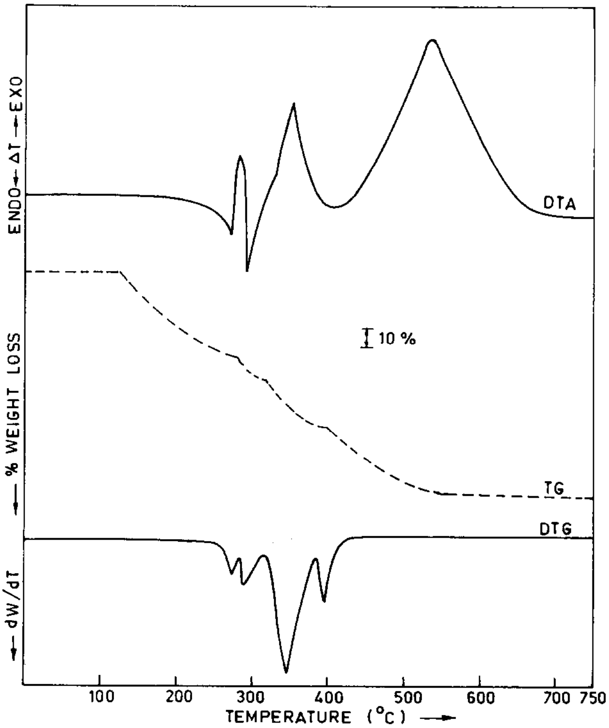

Fig. 2. DTA, TG and DTG of $Ph_3SnCl(BenzSCZ)$.

TABLE 1

Analytical data for $Ph_3SnCl(BenzSCZ)$ and the decomposition products

Empirical formula	Molecular wt. Calc.	Elemental analysis % Exp. [a]		
		C	H	N
$C_{33}H_{28}N_3O_2SnCl$	652.74	60.80 (60.72)	3.85 (4.32)	6.49 (6.44)
$C_{14}H_{10}NOSnCl$ (**I**)	362.38	47.27 (46.40)	2.72 (2.78)	3.37 (3.86)
$C_{13}H_9NOSn$ (**II**)	313.91	49.10 (49.74)	2.36 (2.88)	3.65 (4.46)
C_7H_5NOSn (**III**)	237.81	35.48 (35.35)	2.11 (2.12)	5.91 (5.88)
SnO_2 (end product)	150.68	–	–	–

[a] Calculated values are given in parentheses.

As can be seen from the TG curve, the complex was found to be stable up to 127 ° C. The first stage of the decomposition of the complex continues up to 284 ° C, and corresponds to the loss of the three phenyl groups attached to the tin atom, 1 mol of nitrogen, 1 mol of carbon monoxide and 3/2 mol of hydrogen, to give an intermediate (I) having the tentative composition $C_{14}H_{10}NOSnCl$. The observed weight loss was 44.00%, as against the calculated value of 44.48%. This is represented in the DTA and DTG curves as endothermic peaks at 277 and 280 ° C, respectively. The second stage occurs between 284 and 320 ° C, and involves the loss of one mol of HCl and one carbon atom to give another intermediate (II), with the tentative composition $C_{13}H_9NOSn$. The observed weight loss was 12.97%, as against the calculated value of 13.37%. The DTA and DTG curves show endothermic peaks at 290 and 286 ° C, respectively. In the DTA curve an exothermic

TABLE 2

IR frequencies for $Ph_3SnCl(BenzSCZ)$ and the decomposition products

Complex/ Decomposition products	IR frequencies (cm^{-1}) [a]					
	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu(C{=}O)$	$\nu(C{=}N)$	$\nu(Sn \leftarrow O)$ /(Sn–O)	$\nu(Sn \leftarrow N)$
$C_{33}H_{28}N_3O_2SnCl$ [b]	3455 s (3455 s)	3355 w (3355 w)	1650 s (1695 vs)	1580 s (1555 m)	480 m	435 vs
$C_{14}H_{10}NOSnCl$ (**I**)	–	–	–	1590 m	–	430 m
$C_{13}H_9NOSn$ (**II**)	–	–	–	1600 s	550 w	435 w
C_7H_5NOSn (**III**)	–	–	–	1610 m	550 bm	430 w
SnO_2 (end product)	–	–	–	–	540 m	–

[a] vs, very strong; s, strong; m, medium; w, weak; b, broad.

[b] Values in parentheses are for the ligand.

peak at 284 ° C is also observed, which may be due to the dominant effect of oxidation to carbon dioxide of carbon monoxide formed during the first stage. The third stage occurs between 320 and 399 ° C. The observed weight loss was 23.90%, as compared to the calculated value of 24.24%. This corresponds to the loss of an aromatic phenyl ring attached to the C≡N group to give an intermediate (III) of tentative composition C_7H_5NOSn. An exothermic peak at 349 ° C is observed in the DTA curve, whereas DTG gives an endothermic peak at 347 ° C. The fourth and last stage of the decomposition continues up to 550 ° C and corresponds to the loss of 1/2 mol of nitrogen and the remaining aromatic skeleton to give SnO_2 as the end product (IV). The observed weight loss was 36.51%, as against the calculated value of 36.63%. A broad exothermic peak with peak maxima at 535 ° C is observed in the DTA curve, whereas the DTG curve shows an endothermic peak at 399 ° C. DTA also reveals an exothermic peak between 417 and 645 ° C, which may be due to escape of nitrogen and oxidation of the organic skeleton.

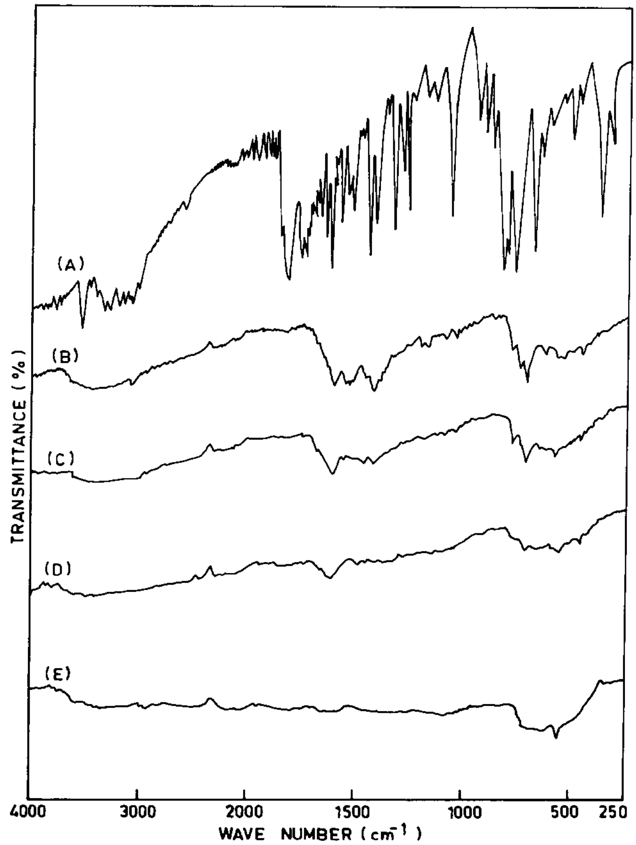

Fig. 3. IR spectra of $Ph_3SnCl(BenzSCZ)$ (A) and $Ph_3SnCl(BenzSCZ)$ heated to 285 ° C (B), 320 ° C (C), 400 ° C (D) and 550 ° C (E).

The compositions assigned to the intermediates are well supported by the results of elemental analysis (Table 1) and by the IR spectra of samples obtained by heating $Ph_3SnCl(BenzSCZ)$ isothermally at 285, 320, 400 and 550 °C (Fig. 3). The observed values of CHN for the samples at each stage correspond to the values calculated for the tentative intermediates. Intermediate **I** does not show the asymmetric and symmetric stretchings of an NH_2 group at 3455 and 3355 cm^{-1}, respectively, or $\nu_{C=O}$ at 1650 cm^{-1} [5–7]. $\nu_{C=N}$ is observed at 1590, 1600 and 1610 cm^{-1} for the intermediates **I**, **II** and **III**, respectively, indicating that coordination occurs through the nitrogen of the azomethine group [5,8,9]. $\nu_{Sn \leftarrow N}$ has been assigned at ≈ 430 cm^{-1} for the complex and for all the intermediates [10]. ν_{Sn-Cl} at ≈ 260 cm^{-1} has not been assigned for the complex or for intermediate **I**, owing to the limits of the IR spectra. A very weak band at 550 cm^{-1} has been assigned to ν_{Sn-O} [6] in the IR spectrum of intermediate **II**, and this is in accordance with the proposed structure. No major differences are observed between the spectra of the intermediates **II** and **III** except that the intensities of the aromatic CH stretching and bending vibrations are greatly reduced. They are virtually absent in the end product **IV**. The end product shows a well defined characteristic ν_{Sn-O} at ≈ 540 cm^{-1} [6]. The end product has also been characterized by X-ray analysis. All *d* values together with their intensities (measured by peak height) were in accordance with the reported values [11].

On the basis of these results, the scheme shown in Fig. 4 is proposed for the thermal decomposition of $Ph_3SnCl(BenzSCZ)$.

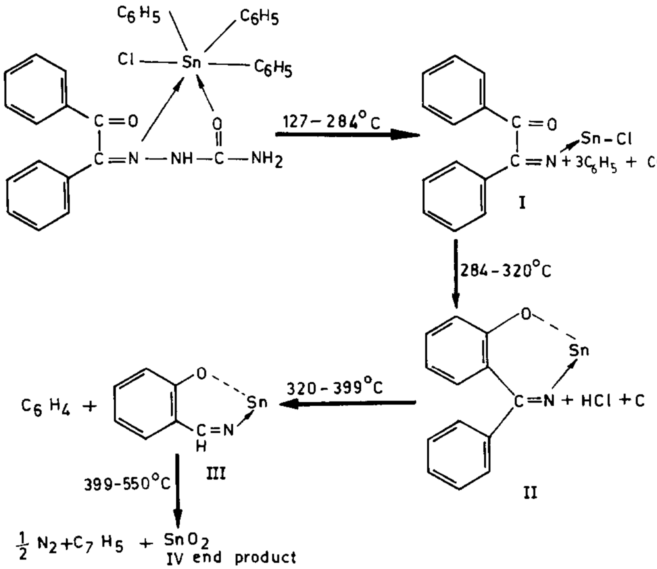

Fig. 4. Proposed scheme for decomposition of $Ph_3SnCl(BenzSCZ)$.

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