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Thermal decomposition of the mixture of antimony(III) oxide and tin(II) chloride

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Abstract

Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) investigations of Sb_2O_3, $SnCl_2$ and their mixture in argon and air atmosphere have been made. In addition, isothermal analyses (ITA) for the mixture of Sb_2O_3 and $SnCl_2$ in atmospheres of argon and air have been performed. The X-ray powder diffraction method (XRD) was used to characterise residues after thermal analyses, and volatile components were identified by mass spectrometry (MS) using the Knudsen cell technique. Scanning electron microscopy (SEM) was used to examine the morphological appearance of crystal particles.

INTRODUCTION

The results presented are from a research project on the thermal stability and flammability of polymers [1–3]. The majority of synthetic polymers are flammable. Flammability is usually reduced by incorporating specific additives into the polymer. Numerous flame retardants from various producers are available on the market. According to the principle of action, flame retardants are divided into several groups. Halogen compounds, known as flame inhibitors in the gas-phase mechanism, represent a group of very efficient, widespread flame retardants. In this mechanism, the flame retardant during heating releases chemical compounds that inhibit the reactions of free radicals in the flame; the flame retardant dissociates into particles that remove free radical intermediates from combustion reactions. Species that are effective in this method of flame retardancy are simple inorganic molecules [4]: HCl, HBr, $SbCl_3$, $SbBr_3$, etc. Owing to their poor hydrolytic and thermal stability, $SbCl_3$ and $SbBr_3$ are not suitable as commercial flame retardant additives.

However, such compounds can be added to polymers that later form SbX_3 in situ in the process of burning. This is usually achieved by adding an organic halogen compound and Sb_2O_3 to the polymer; this has been described in detail elsewhere [5]. In most cases a correctly selected combination of compounds acts synergistically. The synergistic effect of Sb_2O_3 and halogen compounds was first explained in 1947 with respect to the effect of Sb_2O_3 and chlorinated paraffins on burning cellulose fabric [6]. Recently, the synergistically effective system Sb–X is often used with synthetic polymers.

The flame retardant action of antimony trihalide in the gas phase has often been established in a system containing a polymer, Sb_2O_3 and a halogen compound. The best flame retardant action is achieved with the ratio $Sb:X = 1:3$ [7], which confirms the active role of SbX_3. It is well known that the system Sb_2O_3 and HCl causes flame retardance when $SbCl_3$ and SbOCl are formed [8]

$$6HCl + Sb_2O_3 \rightarrow 2SbCl_3 + 3H_2O \tag{1}$$

$$2HCl + Sb_2O_3 \rightarrow 2SbOCl + H_2O \tag{2}$$

From TG and DTG curves, Pitts et al. [9] established that SbOCl decomposes at three different temperature stages, at each of which $SbCl_3$ occurs

$$5SbOCl(s) \xrightarrow{245\text{–}280\,°C} Sb_4O_5Cl_2(s) + SbCl_3(g) \tag{3}$$

$$4Sb_4O_5Cl_2(s) \xrightarrow{410\text{–}475\,°C} 5Sb_3O_4Cl(s) + SbCl_3(g) \tag{4}$$

$$3Sb_3O_4Cl(s) \xrightarrow{475\text{–}565\,°C} 4Sb_2O_3(s) + SbCl_3(g) \tag{5}$$

Although these reactions are often cited in the literature, Belluomini et al. [10] published an extensive study on antimony oxychlorides three years earlier. Quite unlike Pitts et al., he suggested the formation of $Sb_8O_{11}Cl_2$ instead of Sb_3O_4Cl

$$5SbOCl(s) \xrightarrow{190\text{–}240\,°C} Sb_4O_5Cl_2(s) + SbCl_3(g) \tag{6}$$

$$11Sb_4O_5Cl_2(s) \xrightarrow{390\text{–}460\,°C} 5Sb_8O_{11}Cl_2(s) + 4SbCl_3(g) \tag{7}$$

$$3Sb_8O_{11}Cl_2(s) \xrightarrow{470\text{–}540\,°C} 11Sb_2O_3(s) + 2SbCl_3(g) \tag{8}$$

The latest investigation by Costa et al. [11] confirms the occurrence of $Sb_8O_{11}Cl_2$ (by X-ray diffraction and infrared techniques). On heating SbOCl Kellinghaus and Krämer [12] obtained the same products as Costa et al., but found that the transitions took place at different temperatures.

In our investigation into the flammability of polymers [13], $SnCl_2$ was used instead of organic halogen compounds, which in combination with

Sb_2O_3, reduced the flammability of polymers. In this work we studied the processes that take place in the heating of Sb_2O_3, $SnCl_2$ and their mixture in air and in an inert atmosphere of argon. The processes were studied by means of thermogravimetry (TG), derivative thermogravimetry (DTG), difference thermal analysis (DTA) and isothermal analysis (ITA). X-ray powder diffraction (XRD) was used to determine the products of heating, and mass spectrometry (MS) was used to identify the volatile products of heating the Sb_2O_3 and $SnCl_2$ mixtures.

EXPERIMENTAL

Samples

In our investigation, cubic Sb_2O_3 (senarmantite) was obtained from Riedel-de Haën. $SnCl_2$ was prepared from $SnCl_2 \cdot 2H_2O$ (Riedel-de Haën) by gradual addition of $(CH_3CO)_2O$ (Kemika) [14]. The sample that is a mixture of 50 wt.% Sb_2O_3 and 50 wt.% $SnCl_2$ was designated SBSN.

Apparatus

TG, DTG and DTA results were obtained simultaneously by means of a Mettler thermoanalyser with Pt/Pt–Rh thermocouples, Pt crucibles and a TD1 measuring head. Measurements were carried out in a dynamic atmosphere (85 ml min^{-1}) of dry argon and air at the heating rate of 6 °C min^{-1}, and the final temperature of 850 °C. Inert alumina was used as reference material for DTA. The DTG range was 10 mg min^{-1}, and the DTA range was 100 μV.

The starting weights of samples for thermal analysis in dry argon were: Sb_2O_3, 46.8 mg; $SnCl_2$, 70.4 mg; SBSN, 33.5 mg. For thermal analysis in air they were: Sb_2O_3, 46.3 mg; $SnCl_2$, 55.5 mg; and SBSN, 23.2 mg.

The apparatus for isothermal analyses (ITA) was constructed in our laboratory (see Fig. 1).

The analysis of the residues formed after isothermal heating was performed using X-ray powder diffractometry with a Guinier–de Wolff Quadruple Focusing Camera I with a quartz monochromator and Cu Kα radiation (Enraf–Nonius, Delft).

The gaseous products resulting from heating the SBSN sample in a Knudsen effusion cell were analysed by a mass spectrometer MS 8 with Nier's geometry (Institute Jozef Stefan, Ljubljana).

The ultramicro surface structure was examined by scanning electron microscopy JSM-840 (Jeol, Tokyo), the accelerating voltage being 30 kV. The sample was coated with gold that was about 300 Å thick.

RESULTS AND DISCUSSION

Thermal analyses in argon

TG curves for Sb_2O_3, $SnCl_2$ and SBSN samples are presented in Fig. 2. The initial temperatures (T_i) and final temperatures (T_f) of the main decomposition process by TG are given in Table 1. The amounts of mass remaining (MR) after thermal decomposition by TG are given in Table 2.

The DTG curves show that the maximal rate of mass loss for Sb_2O_3 is at 742 ° C, for $SnCl_2$ at 511° C, and for SBSN at 345 and 387 ° C. The melting points (T_m) for Sb_2O_3 (632 ° C) and for $SnCl_2$ (217 ° C) were determined from the DTA curves. $SnCl_2$ has an additional endothermic peak at 513 ° C as a result of volatilisation. The T_m values obtained from our measurements are lower than those cited in the literature [15] ($T_m = 656$ ° C for Sb_2O_3 and $T_m = 246$ ° C for $SnCl_2$). However, Hegedüs et al. [16] obtained $T_m = 635$ ° C for Sb_2O_3 by means of DTA in an atmosphere of N_2, which agrees with our measurements. A polymorphic transition of senarmontite into valentinite was established at 590 ° C. For SBSN, an endothermic peak was observed at 335 ° C.

When heating Sb_2O_3 (Fig. 2), the mass remains unchanged up to 500 ° C. Above this temperature, volatilisation begins. The maximal mass loss is

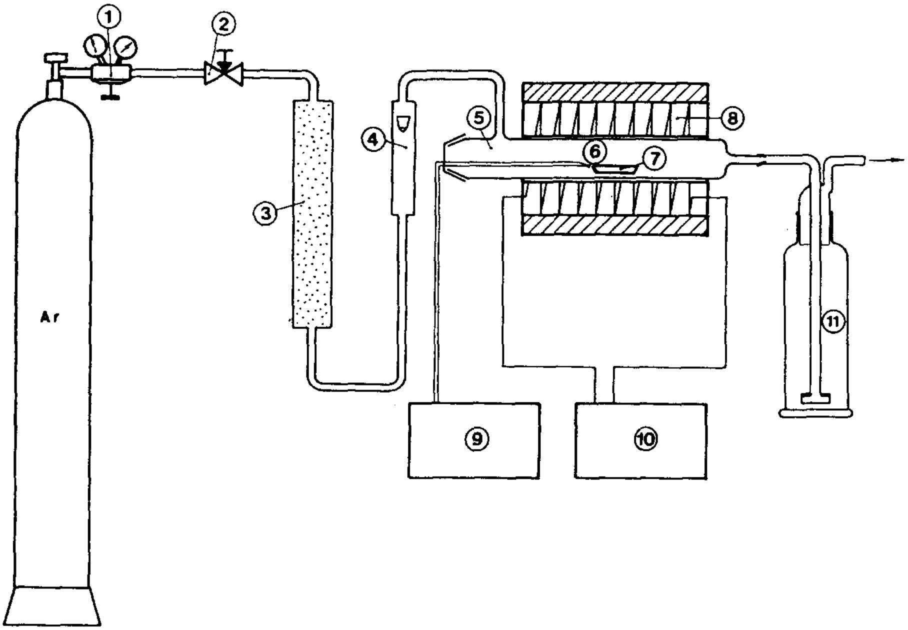

Fig. 1. Schematic diagram of the ITA. 1, pressure regulator; 2, flow-control needle valve; 3, gas dryer; 4, gas flow-meter; 5, quartz tube; 6, thermocuple NiCr/Ni; 7, sample holder; 8, furnace; 9, digital thermometer; 10, furnace temperature regulator; 11, gas washing bottle.

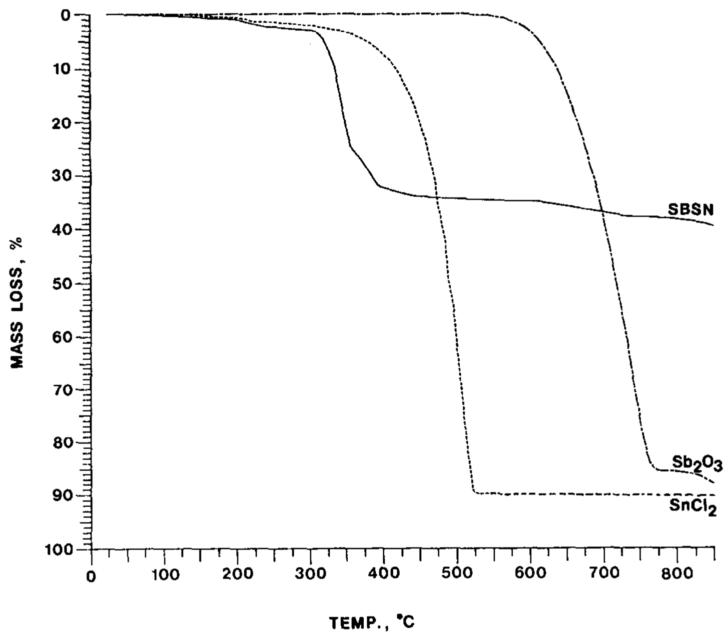

Fig. 2. TG curves for samples in argon: (-----), Sb_2O_3; (------), $SnCl_2$; (———), SBSN.

reached at 742 °C and ends at 780 °C. This agrees with data cited in the literature [17], where the slow mass loss is described as beginning at 430 °C, with the main volatilisation process starting at 510 °C and ending by 600 °C. According to Golunski et al. [18] the first perceptible loss in

TABLE 1

Initial and final temperatures of the main decomposition process in argon

Sample	T_i(°C)	T_f(°C)
Sb_2O_3	501	780
$SnCl_2$	354	530
SBSN	298	418

TABLE 2

The mass remaining after TG in argon

Sample	MR_f [a] (%)	MR_{850} [b] (%)
Sb_2O_3	14.5	12.3
$SnCl_2$	10.2	10.2
SBSN	66.9	60.1

[a] MR_f indicates the MR at the temperature T_f.

[b] MR_{850} indicates the MR at 850 °C.

mass became apparent at about 640 ° C and ended at 860 ° C, both temperatures being much higher than in our experiment. The differences in the data are due to various factors affecting TG curves, such as the heating rate, the geometry of the sample holder and furnace, the amount of sample etc. [19]. Cody et al. [20] also obtained a TG curve that matched ours, the only difference being that, in their case, volatilisation was about 99%, and in all other cases, including ours, it was about 80%.

For $SnCl_2$, volatilisation begins at 354 ° C and ends abruptly at 530 ° C. The final residue of 10.2% is rather high and is probably due to the partial disproportionation of $SnCl_2$ into Sn and $SnCl_4$. We found no confirmation of this in the literature. Abate et al. [21] established that $SnCl_2$ exhibited the melting process at 260 ° C and that it remained stable up to 295 ° C.

However, the TG curve of the sample SBSN, which is a mixture of Sb_2O_3 and $SnCl_2$, is quite different. The main decomposition has already begun at 298 ° C and ends at 418 ° C. It is evident from both the TG and DTG curves that at least two different reactions take place because the slope of the TG curve changes at about 360 ° C. For the TG curves of Sb_2O_3 and $SnCl_2$, there is a surprisingly small mass loss at 850 ° C (39.9%). We expected the mass loss to be higher because of the presence of $SbCl_3$. From a comparison of the mass losses, we anticipated one of the following reactions during the heating of SBSN

$$2Sb_2O_3 + 2SnCl_2 \rightarrow SbCl_3 + SbOCl + 2SnO + Sb_2O_3 \tag{9}$$

$$2Sb_2O_3 + 3SnCl_2 \rightarrow 2SbCl_3 + 3SnO + Sb_2O_3 \tag{10}$$

The theoretically calculated mass losses are 41.7% for reaction (9) and 39.6% for reaction (10). Reaction (9) does not correspond to the molar ratio of our SBSN because $Sb_2O_3 : SnCl_2 = 1 : 1.54$ (weight ratio 1 : 1). Reaction (10) is not possible despite the excellent agreement of the mass loss because the X-ray diffraction pattern confirms that in addition to SnO_2, Sb also occurs. Consequently, the following reaction takes place during the heating

$$2Sb_2O_3 + 3SnCl_2 \rightarrow 2SbCl_3 + 3SnO_2 + 2Sb \tag{11}$$

The theoretical mass loss of this reaction is 39.6%, which agrees well with the mass loss of 39.9% obtained experimentally by means of TG. The occurrence of $SbCl_3$ during the heating of SBSN in a vacuum at 150 ° C was confirmed by MS.

Thermal analyses in air

The TG curves of samples Sb_2O_3, $SnCl_2$ and SBSN are shown in Fig. 3. Initial (T_i) and final (T_f) temperatures of the main decomposition are given in Table 3 and the mass remaining (MR) after thermal decomposition by TG is shown in Table 4.

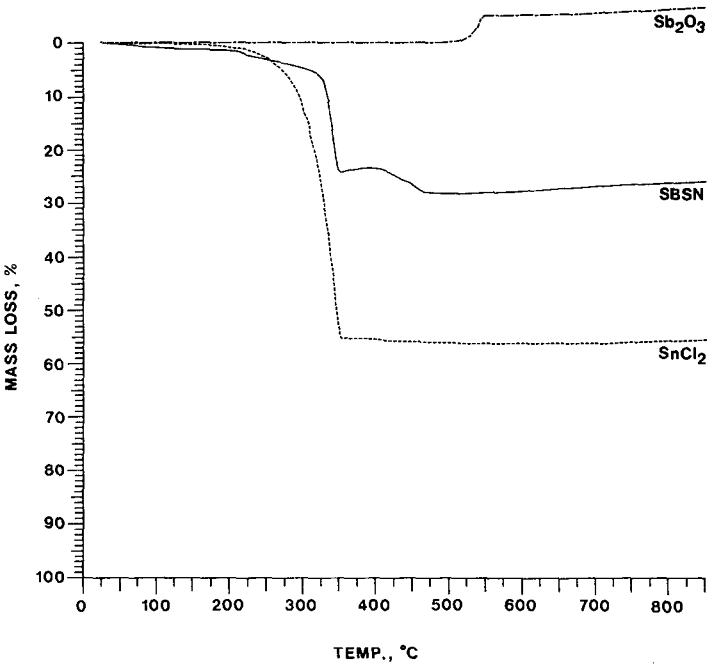

Fig. 3. TG curves for samples in air: (-----), Sb_2O_3; (------), $SnCl_2$; (———), SBSN.

From the DTG curves, it is evident that the maximal mass loss rate for Sb_2O_3 takes place at 543 ° C, for $SnCl_2$ at 345 ° C, and for SBSN at 344 and 445 ° C.

TABLE 3

Initial and final temperatures of the main decomposition process in air

Sample	T_i (° C)	T_f (° C)
Sb_2O_3	493	549
$SnCl_2$	202	352
SBSN	313	350

TABLE 4

The mass remaining after TG in air

Sample	MR_f [a] (%)	MR_{850} [b] (%)
Sb_2O_3	105.0	106.3
$SnCl_2$	45.2	44.5
SBSN	76.2	74.0

[a] MR_f indicates the MR at the temperature T_f.
[b] MR_{850} indicates the MR at 850 ° C.

An exothermic peak appears in the DTA curve of SB_2O_3 which is due to oxidation of Sb_2O_3 to Sb_2O_4 at 543 °C. This temperature is cited in the literature as 570 °C [17] and 630 °C [18]. The T_m of $SnCl_2$ is at 232 °C, and a distinct exothermic peak occurs at 349 °C, whereas the exothermic peak of SBSN occurs at 350 °C.

Of all our TG curves, only the heating of Sb_2O_3 gave a mass gain (6.3%) due to the oxidation of Sb_2O_3 as shown in the reaction

$$Sb_2O_3 + 0.5O_2 \rightarrow Sb_2O_4 \qquad (12)$$

The theoretical mass gain of this reaction is 5.5%, 0.8% less than in our case. Agrawal et al. [17] obtained a mass gain of only 4.5%, but confirmed the occurrence of Sb_2O_4 in the residue after isothermal heating at 800 °C by X-ray studies. Quite differently, Golunski et al. [18] established a mass loss of 32% as a result of volatilisation of the unoxidised Sb_2O_3. Based on TG, Cody et al. [20] established that volatilisation of Sb_2O_3 and oxidation to Sb_2O_4 occurred simultaneously with a 21% mass loss when Sb_2O_3 (senarmontite) was heated in air. Also Costa et al. [11] obtained Sb_2O_4 as a final product on heating Sb_2O_3 in air.

When heating $SnCl_2$ in air, volatilisation and oxidation occur simultaneously. Oxidation takes place according to the equation

$$SnCl_2 + O_2 \rightarrow SnO_2 + Cl_2 \qquad (13)$$

The occurrence of SnO_2 was confirmed by XRD. The theoretical loss of reaction (13) is 20.5%, which is far below our experimental loss (55.5%) because some of the $SnCl_2$ volatilises before oxidation.

At least three reactions occur during TG of the SBSN sample. Volatilisation takes place from 200 to 300 °C. Although the isothermal analysis of SBSN was performed at 260 °C, we could not identify the residue with the XRD method. The main reaction occurs in the temperature range from 313 to 350 °C. The formation of SnO_2 and $Sb_4O_5Cl_2$ was established from the XRD analysis of the residue after isothermal heating at 350 °C. In the final part of the reaction from 350 to 500 °C, first oxidation takes place, which is evident from the mass gain, and then again mass losses are recorded. The final product of decomposition is SnO_2 (see XRD for ITA 6).

Isothermal analyses, XRD and SEM

The SBSN sample was heated isothermally in atmospheres of argon and air at a flow rate of 15 l h^{-1}. The basic parameters for ITA are given in Table 5.

In addition, $SnCl_2$ was heated in the same apparatus from 20 to 850 °C at a heating rate of about 4 °C min^{-1} and with an air flow rate of 15 l h^{-1}. The sample mass was 267.7 mg. A residue of 18.6%, designated TA7, was obtained as a result of heating to 850 °C.

TABLE 5

Conditions of isothermal analyses for sample SBSN

ITA[a]	T (°C)	Time (min)	Sample mass (mg)	MR[b] (%)
ITA 1-Ar	260	420	155.7	86.0
ITA 2-Ar	315	300	285.1	60.9
ITA 3-Ar	405	120	197.9	58.9
ITA 4-Z	260	420	312.5	93.1
ITA 5-Z	315	300	346.1	70.0
ITA 6-Z	405	120	384.0	64.5

[a] Ar denotes heating in Ar; Z denotes heating in air.

[b] MR after heating.

We tried to characterise all the residues of ITA by XRD. Only the three strongest diffraction lines for each compound are given in Table 6. In addition, XRD patterns were recorded for Sb_2O_3 and $SnCl_2$, which correspond to cubic Sb_2O_3 (senarmontite) (ASTM index 5-0534) and $SnCl_2$ (ASTM index 18-1265) [22], respectively.

ITA 1 remains unidentified, although the data have been checked against the latest powder diffraction file. As we can see from the scanning electron micrograph for ITA 1 (Fig. 4), at least two types of crystal particles are present, which are neither Sb_2O_3 nor $SnCl_2$, as is clearly seen from Figs. 5 and 6.

The XRD patterns of ITA 2 and ITA 3 correspond to those reported in the ASTM index for Sb and SnO_2. The reaction is the same as in reaction (11) where volatile $SbCl_3$ is formed (identified by MS). Isothermal heating of SBSN in air at 260 °C (ITA 4) yields compounds that have no lines in

TABLE 6

Interplanar spacings for different residues after ITA of SBSN

Sample	d_1 (Å)	d_2 (Å)	d_3 (Å)	Identical with	ASTM[a]
ITA 1	2.83	3.68	1.924	Unknown	
ITA 2	3.11	2.24	1.363	Sb	5-0562
	3.35	2.64	1.753	SnO_2	21-1250
ITA 3	3.11	2.24	1.364	Sb	5-0562
	3.35	2.645	1.765	SnO_2	21-1250
ITA 4	-	–	–		
ITA 5	3.35	2.65	1.758	SnO_2	21-1250
	3.285	3.11	6.2	$Sb_4O_5Cl_2$	30-0091
ITA 6	3.35	2.64	1.76	SnO_2	21-1250

[a] X-ray Powder Data File.

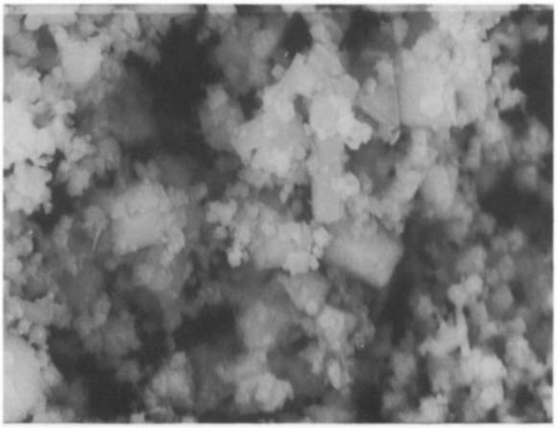

Fig. 4. Micrograph of ITA 1. Original magnification ×550.

the XRD photograph. XRD patterns of ITA 5 showed the presence of SnO_2 and $Sb_4O_5Cl_2$; this can be described by the equation

$$2Sb_2O_3 + 3SnCl_2 + 0.5O_2 \rightarrow SnO_2 + Sb_4O_5Cl_2 + 2SnCl_2 \qquad (14)$$

This reaction has a theoretical mass loss of 31.5%, which is close to the 30% obtained for our ITA. Different authors [9–12] have studied the thermal decomposition of SbOCl leading to $Sn_4O_5Cl_2$ over various temperature ranges, but all these temperatures were lower than our isothermal heating which was carried out at 315 °C. Therefore, according to this mechanism SbOCl should be formed first during the heating of SBSN, but this has not yet been identified in our investigations.

XRD confirms that by ITA 6, only SnO_2 is present. This is quite unusual because according to stoichiometry some antimony compound was expected, or even elemental Sb.

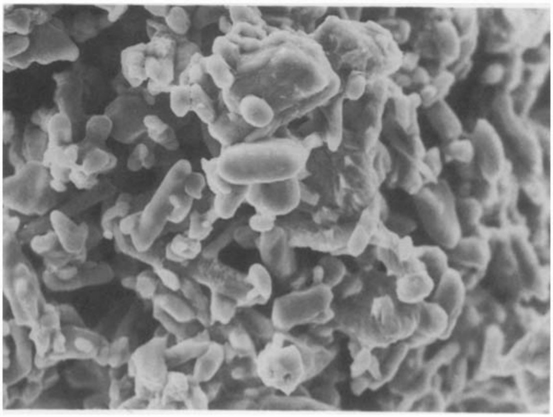

Fig. 5. Micrograph of Sb_2O_3. Original magnification ×7000.

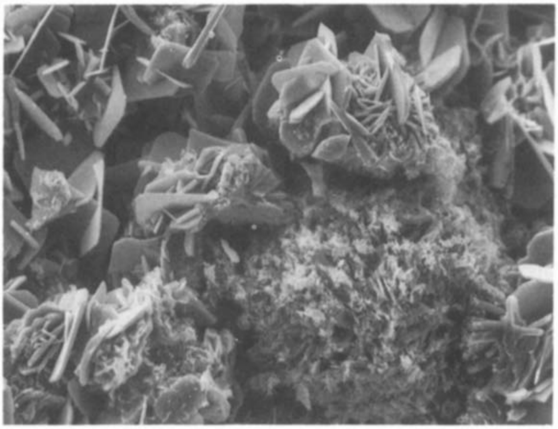

Fig. 6. Micrograph of $SnCl_2$. Original magnification ×650.

The residue after heating $SnCl_2$ in air (TA 7) was SnO_2, as revealed by the XRD pattern (ASTM index 21-1250). This oxidation reaction is the same as in eqn. (13).

CONCLUSIONS

The results of the thermal analyses of Sb_2O_3 and $SnCl_2$ in argon mostly agree with those cited in the literature. Cubic Sb_2O_3 (senarmontite) undergoes a solid phase transition at 590 °C [16], 610 °C [17] or 629 °C [18] to give orthorhombic Sb_2O_3, valentinite, which was not detected by our DTA. $SnCl_2$ also yields a substantial residue which is possible only through disproportionation. The heating of the mixture of Sb_2O_3 and $SnCl_2$ (SBSN) in argon gives the overall reaction

$$2Sb_2O_3 + 3SnCl_2 \rightarrow 2SbCl_3 + 3SnO_2 + 2Sb$$

which was confirmed by thermal analyses and with the XRD pattern for the residue after ITA. The formation of volatile $SbCl_3$ was identified using MS with the Knudsen cell technique. The identification of products resulting from isothermal heating at 260 °C (ITA 1) was not possible by XRD. As we can see from the scanning electron micrograph, at least two types of crystal particles are present, which are totally different from Sb_2O_3 and $SnCl_2$.

In the heating of Sb_2O_3 in air, oxidation occurs at 493 °C to form Sb_2O_4, which does not undergo any change with heating up to 850 °C. When heated in air, $SnCl_2$ simultaneously volatilises and oxidises to SnO_2, which has been identified by the XRD analysis. When SBSN is heated in air, several reactions take place simultaneously. Due to their complexity, these reactions were only partly identified. SnO_2 and $Sb_2O_4Cl_2$ are formed in the intermediate stage, and SnO_2 is the final residue, as confirmed by XRD.

ACKNOWLEDGEMENT

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