Journal of Thermal Analysis, Vol. 7 (1975) 635–641

STUDIES ON ANTIMONY OXIDES: PART I

THERMAL ANALYSIS OF Sb_2O_3 IN AIR, NITROGEN AND ARGON

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(Received December 18, 1973: in revised form May 7, 1974)

Thermogravimetry (TG), differential thermal analysis (DTA) and X-ray diffraction studies of antimony(III) oxide, (Sb_2O_3), in air, nitrogen and argon atmospheres have been made.

In air Sb_2O_3 becomes oxidized to Sb_2O_4 above 510°. The oxidation reaction proceeds in two stages as revealed by the TG and DTA curves.

The behaviour of Sb_2O_3 is similar in both N_2 and Ar. Sb_2O_3 remains unaffected up to 430°, above which there is a slow, and continuous mass loss up to 550°. Above 550° Sb_2O_3 volatilizes resulting in an enormous weight loss. X-ray studies of the sublimate and the residue indicate the former to be the cubic form of Sb_2O_3 (Senarmontite) while the residue is the orthorhombic (Valentinite) structure.

From the DTA curves in air, N_2 and Ar, the transition temperature for the cubic to the orthorhombic modification has been estimated to be around 610°.

A survey of the current literature reveals that studies on the physico-chemical properties of the oxides of antimony are scanty. Remy [1] has given a brief account of some of the physical properties and chemical reactions of the oxides Sb_2O_3, Sb_2O_4 and Sb_2O_5. Sb_2O_3 exists in two crystallographic modifications, namely, senarmontite (cubic) and valentinite (orthorhombic). The cubic form transforms into the rhombic form at temperatures above 570° and the heat of this transition is 3.24 kcals/mole. Recently White *et al.* [2] have followed this transition by high pressure-temperature techniques and found the transition temperature to be at 610°.

On heating in air, Sb_2O_3 becomes oxidized to Sb_2O_4, the crystal structure of which has been determined by Skapski *et al.* [3].

So far no report has yet been made of the thermogravimetric (TG) and differential thermal analysis (DTA) of Sb_2O_3 and the related oxides of Sb. In the present paper, the results obtained from the TG and DTA of cubic Sb_2O_3 in air, nitrogen and argon are discussed.

Experimental

Thermal analyses

The TG and DTA curves of Sb_2O_3, in different atmospheres, were recorded on a Mettler thermal analyser maintaining the following instrumental factors in all the experiments:

TG range – 1 mg full scale sensitivity, DTA range – 50 μV, Heating rate – 8°/minute, Gas flow rate – 100 ml.min^{-1}, Mass of the sample – ~10 mg.

X-ray studies

The products, obtained after the thermal analyser runs as well as those obtained by the isothermal heating of Sb_2O_3 in air and N_2 at various predetermined temperatures (from TG curves), were characterized by X-ray powder diffraction method on a Philips instrument (PW 1050) using Cu–K_α radiation.

Preparation of the samples

Sb_3O_3 used in this study was of 99.999% purity as supplied by M/S. Schuchardt and Co., Germany. The sample was a white crystalline solid and gave sharp peaks in the X-ray diffraction patterns.

For the isothermal studies a known mass of the sample (Sb_2O_3) was heated in a tubular furnace at the desired temperature for about 12 hours and thereafter cooled in the furnace. The products were later characterized by the X-ray method.

Results

Thermal analysis in air

The TG and DTA curves of Sb_2O_3 in air are shown in Fig. 1. Sb_2O_3 is stable in air up to 510° above which temperature it starts absorbing oxygen. Between 510° and 600° a net weight gain of 4.5% is observed and there is no further change in the mass of the sample up to 630°. A subsequent weight gain of ≈1% occurs in the temperature range 630° to 670°. Above this temperature and up to 1000° (the maximum temperature in this study) the mass of the sample remains constant.

The corresponding DTA curve shows two endothermic peaks, the one at 570° is very strong whilst the high temperature peak is fairly weak.

The final product of this oxidation process was Sb_2O_4 as revealed by its X-ray pattern.

Thermal analyses in N_2 and Ar

The thermal characteristics (TG and DTA) of Sb_2O_3 in N_2 and Ar are more or less the same as indicated in Figs 2 and 3.

The TG curve shows that it is stable under these inert atmospheres up to 430° above which a slow, and continuous, weight loss occurs. At 550°, however, an enormous weight loss is observed. The weight of the sample remains constant in

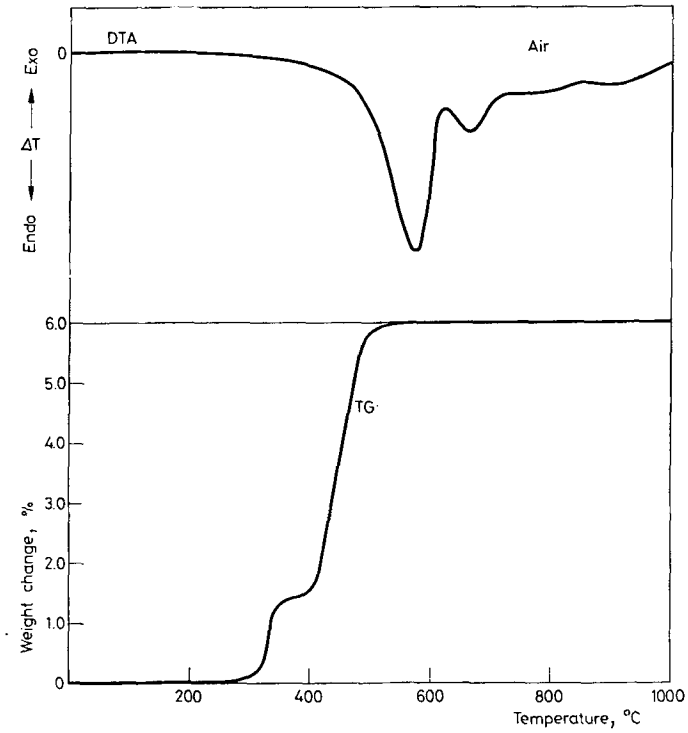

Fig. 1. TG and DTA curves for Sb_2O_3 in Air

Table 1

	Atmosphere	Temp. °C	Time hr	X-ray analysis
1	Air	400	12	Sb_2O_3 (cubic)
2	Air	600	12	Sb_2O_3 (rhombic) Sb_2O_4
3	Air	800	12	Sb_2O_4
4	N_2	400	12	Sb_2O_3 (cubic)
5	N_2	550	12	Sb_2O_3, cubic (sublimate) Sb_2O_3, rhombic (residue)
6	N_2	700	12	—do—

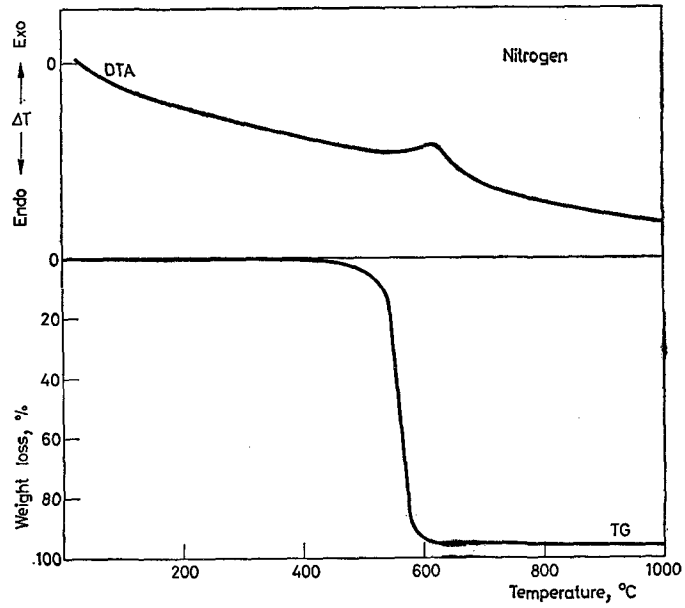

Fig. 2. TG and DTA curves for Sb_2O_3 in Nitrogen

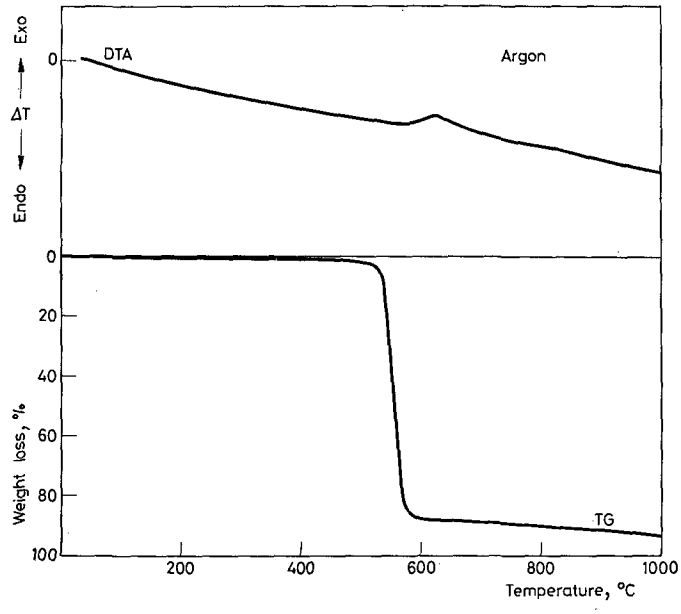

Fig. 3. TG and DTA curves for Sb_2O_3 in Argon

the range 600° to 630° and again above 630° and up to 900° a slow and continuous weight loss is observed.

The corresponding DTA curves in N_2 and Ar do not show any peaks. As a matter of fact, the base line is shifted continuously in the endothermic direction.

Isothermal studies in air and N_2

The results of the isothermal heating of Sb_2O_3 at various known temperatures (for 12 hours in each case) in air and N_2 are listed in Table 1.

The products obtained on heating Sb_2O_3 in air at 400°, 600° and 800° have been identified by X-ray diffraction as Sb_2O_3 (cubic), Sb_2O_4 + Sb_2O_3 (rhombic), and Sb_2O_4 respectively.

In N_2, samples of Sb_2O_3 were heated for 12 hours at 400°, 550° and 700°. Samples heated at 400° do not undergo any change and the X-ray data confirm the compound to be cubic Sb_2O_3. At 550° and 700° partial volatilization of Sb_2O_3 takes place and it is interesting to find that the sublimate collected at the cooler parts of the sample tube corresponds to cubic Sb_2O_3 while the residue left behind corresponds to the rhombic form.

Discussion

The above results indicate that cubic Sb_2O_3 becomes oxidized to Sb_2O_4 in air at temperatures above 510°. This reaction seems to proceed in two stages. In the temperature range 510° to 600° a weight gain of 4.5% is observed (TG) and the corresponding peak in DTA is quite strong. However the reaction,

$$2Sb_2O_3 + O_2 \rightarrow 2Sb_2O_4$$

should in theory produce a weight gain 5.49%. This suggests that the oxidation of Sb_2O_3 is incomplete, perhaps due to the fact that, as pointed out by Remy [1], at temperatures above 570°, the cubic form of Sb_2O_3 transforms itself to a stable orthorhombic form. Therefore, only a part of the sample becomes transformed into this stable Sb_2O_3 form while the remaining is oxidized to Sb_2O_4. The second weight gain step can thus be attributed to the oxidation of the rhombic Sb_2O_3 to Sb_2O_4 at a higher temperature. A further evidence to this conclusion comes from the fact that in the isothermal studies of Sb_2O_3 in air, it was observed that samples heated at an intermediate temperature (600°) consisted of both Sb_2O_4 and Sb_2O_3 (rhombic) and the final product is Sb_2O_4 only.

The rhombic form of Sb_2O_3 appears to be the stabler phase among the two modifications in N_2 and Ar atmospheres also. This conclusion comes out from the fact that on heating in N_2 or Ar, the cubic form volatilizes at 550° while the rhombic form remains stable up to 630°. Here also the partial volatilization of Sb_2O_3 occurs due to the simultaneous transformation to the orthorhombic form at around 600°.

From the above discussion, therefore, it appears that the transition from the cubic senarmontite to the orthorhombic valentinite occurs at 600 ± 10°. This is in good agreement with the results of White *et al.* [2].

Conclusions

The results of the present study on Sb_2O_3 lead us to the following conclusions:

(i) Sb_2O_3 is stable in air up to 510° beyond which it oxidizes to Sb_2O_4. This transformation is irreversible.

(ii) The cubic form of Sb_2O_3 undergoes a structural transformation to a rhombic variety at 600 ± 10°.

(iii) In oxidizing as well as inert atmosphere the rhombic form is stabler than the cubic one.

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We should like to express our grateful thanks to D. M. Chakarvarti and Dr. S. Sampath of B. A. R. C. for the thermal analyser experiments. The award of a SRF to YKA by the CSIR and a JRF to ALS by the IIT (Bombay) is gratefully acknowledged.

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RÉSUMÉ — On a étudié l'oxyde d'antimoine trivalent (Sb_2O_3) par TG, ATD et diffraction des rayons X, dans l'air, l'azote et l'argon.

Dans l'air, l'oxydation de Sb_2O_3 en Sb_2O_4 se produit au-dessus de 510°. La réaction d'oxydation se déroule en deux étapes, comme le montrent les courbes TG et ATD.

Le comportement de Sb_2O_3 est similaire dans l'azote et l'argon. Sb_2O_3 reste stable jusqu'à 430°; au-dessus de cette température, il se produit cependant une perte de poids lente et continue, jusqu'à 550°. Au-delà, Sb_2O_3 se volatilise, ce qui entraîne une perte de poids considérable. L'étude par rayons X indique que la partie sublimée consiste en la forme cubique de Sb_2O_3 (Sénarmontite) et que le résidu possède une structure orthorhombique (Valentinite).

On a estimé à 610° environ la température de la transition cubique-orthorhombique, d'après les courbes ATD obtenues dans l'air, l'azote et l'argon.

ZUSAMMENFASSUNG — Untersuchungen zur Thermogravimetrie (TG), Differential-Thermoanalyse (DTA), sowie Röntgendiffraktion von Antimon(III)-oxid (Sb_2O_3) wurden in Luft, Stickstoff- und Argon-Atmosphäre durchgeführt.

In Gegenwart von Luft wird Sb_2O_3 oberhalb 510° zu Sb_2O_4 oxidiert. Die Oxidationsreaktion vollzieht sich in zwei Stufen, wie aus den TG- und DTA-Kurven hervorgeht.

Das Verhalten von Sb_2O_3 ist ähnlich in N_2 und Ar. Bis zu 430° bleibt es unverändert, bei höheren Temperaturen macht sich bis 550° ein langsamer, kontinuierlicher Gewichtsverlust bemerkbar. Über 550° verflüchtigt sich Sb_2O_3 was in einem überaus großen Gewichtsverlust deutlich wird. Die Röntgenuntersuchungen des Sublimats und des Rückstandes zeigen, daß Ersteres der kubischen Form von Sb_2O_3 (Senarmontit) und Letzterer der rhombischen Form (Valentinit) entspricht.

Aus den in Luft, N_2 und Ar erhaltenen DTA-Kurven wurde die Übergangstemperatur von der kubischen in die orthorhombische Modifikation bei etwa 610° geschätzt.

Резюме — С помощью термогравиметрического (TG), дифференциального термического анализа (*DTA*) и дифракции рентгеновых лучей проведено изучение трехокиси сурьмы на воздухе ,в атмосфере азота и аргона. На воздухе Sb_2O_3 при температуре выше 510° окисляется до Sb_2O_4. Кривые *TG* и *DTA* показывают, что реакция окисления протекает в две стадии. В атмосфере азота и аргона поведение трехокиси сурьмы одинаково. До температуры 430° Sb_2O_3 остается без изменений. В интервале температур 430°—550° происходит медленное и непрерывное уменьшение веса. Выше 550° трехокись сурьмы возгоняется, что приводит к значительной потере веса. Рентгеноструктурные исследования сублимата и остатка показали, что первый представляет собой кубическую форму Sb_2O_3 (сенармантит), в то время как остаток обладает ромбической структурой (валентинит). Из кривых *DTA*, полученных на воздухе, в атмосфере азота и аргона, было установлено, что температура перехода кубической формы в орторомбическую находится около 610°.