February, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***55****, 615—616 (1982)*

The Thermal Decomposition of Crystalline Antimonic(V) Acid

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(Received December 8, 1980)

Synopsis. The thermal decomposition of crystalline antimonic(V) acid (C-SbA) was studied by means of DTA, DSC, and DTG. The amount of water evolved from the heated C-SbA was determined by the Karl Fischer method. The material heated in the range of 600—1000 °C is Sb_6O_{13}, neither $Sb_3O_6(OH)$ nor $H_2Sb_{12}O_{26}$. The thermal decomposition of C-SbA consists of four dehydration and two reduction steps up to 1000 °C.

The thermal analysis of antimonic(V) acid or hydrous antimony(V) oxide has been studied by various authors.[1-9] The existence of the two forms, valentinite and senarmontite of Sb_2O_3, is unquestionable, and both the Sb_2O_4 dimorphs (α- and β-) have been well characterized by single-crystal X-ray studies. However, much confusion can be found in the literature regarding the higher oxides and their hydrous oxides. Especially, the material heated at 600—800 °C gave an X-ray pattern with a pyrochlore structure (Fd3m) rather than that of Sb_2O_4, which prompted Dihlstöm and Westgren to reassign the Sb_3O_6OH composition.[4] This compound is accepted on the basis of many present texts.

Moreover, the X-ray powder data of material heated at 780 °C is erroneously listed in the ASTM X-ray powder data card file (No. 11-690 in the 1966 edition) as having the composition of Sb_2O_5.[5,7]

Extensive studies of the materials obtained by heating the different antimonic(V) acids (amorphous, glassy, and crystalline) have been carried out by Abe and Ito using X-ray, DTA, TG, IR, and chemical analysis.[5,6] The thermal decomposition of crystalline antimonic(V) acid (C-SbA) up to 1300 °C follows the scheme:

$$(H_3O)_2Sb_2O_5(OH)_2 \xrightarrow{200°C} H_2Sb_2O_5(OH)_2 \xrightarrow{350°C}$$

$$Sb_2O_5 \xrightarrow{550°C} Sb_6O_{13} \xrightarrow{800°C} Sb_2O_4(\alpha\text{- and }\beta\text{-}) \xrightarrow{1200°C}$$

$$Sb_2O_3 \xrightarrow{1250°C} \text{sublimation.}$$

A similar conclusion was recently observed by Stewart *et al.*[7] Kleshchev *et al.* have suggested that the product of the antimonic acid heated at 600—800 °C is $H_2Sb^{III}_5Sb^{V}_7O_{26}$ or $H_2Sb^{III}_{10}Sb^{V}_{16}O_{56}$,[8,9] from structural studies of its pyrochlore phase, and that it is not possible to determine such a hydrogen content by means of gravimetric analysis. Another scheme of the thermal decomposition of crystalline antimonic acid, leading to the stepwise formation of H_3OSbO_3 (148 °C at DTA temp.), Sb_3O_6OH(348 °C), Sb_6O_{13}(620 °C), and Sb_2O_4 (940 °C), has been reported by Novikov *et al.*[10] However, no direct evidence has been obtained for the existence of Sb_3O_6OH or $H_2Sb^{III}_{10}Sb^{V}_{16}O_{56}$.

In the present work, the thermal decomposition of the C-SbA has been reexamined by means of DTA, DTG, and DSC, and the water content has been determined by using the modified Karl Fischer method.[11]

Experimental

The C-SbA was prepared as has been described previously.[5] The C-SbA air dried for over 1 year was humidified on a desiccator over saturated NaCl solution (with a relative humidity of 75% at 20 °C) and was then used in the following experiments.

The inside of the systems of the heating and titration apparatus was free from moisture by passing through dried air at a flow rate of 70 cm^3 min^{-1}. The dried air was obtained by passing through (in the order), silica gel, anhydrated $Mg(ClO_4)_2$, and finally diphosphorus pentoxide. The titration apparatus was set at 20 ± 0.3 °C in order to prevent volumetric error caused by the thermal expansion of the Karl Fischer reagent. The C-SbA of 240 mg was heated in dried air by using a Rigaku Denki Thermoflex 8002 with a thermogravimetric analyser at a heating rate of 10 °C min^{-1} up to the desired temperature, it was then kept for 12 h at that temperature. The water evolved from the heated C-SbA was absorbed into an anhydrous solvent "Mitsubishi ME" (a mixture of methanol and ethylene glycol)supplied by the Mitsubishi Kasei Co.; it was then titrated by using Karl Fischer reagent of SS "Mitsubishi." The strength of the Karl Fischer reagent was standardized with appropriate amounts of deionized water.

For the thermal analysis, about a 40-mg portion of the C-SbA was packed in a platinum crucible. The DTG curve of the C-SbA was determined by differentiating the TG curve obtained with the temperature. The DSC and DTG curves thus obtained were separated into individual peaks by means of non-linear least-squares fit, assuming that each peak of the DSC and DTG curves can be approximated by the following equation:

$$\text{Peak} = A\cdot\exp\{-B\cdot(C-T)^2\}.$$

Where A, B, and C are parameters, and T is the temperature from thermal analysis (°C).

The X-ray diffraction data for the heated C-SbA were determined by using a JEOL X-ray diffractometer, Model JDX-7E, with Ni-filtered Cu $K\alpha$ radiation.

Results and Discussion

The X-ray analysis of the C-SbA heated at 900 °C indicated a mixture of a large amount of α-Sb_2O_4 and a small amount of β-Sb_2O_4, as was observed by Abe.[5] Table 1 showed the weight loss and the evolved water from the C-SbA heated at a different temperature for 12 h. The weight loss of C-SbA was obtained as 20.7% at 600—800 °C and as 22.2% at 900 °C. The evolved water contents, as determined by the modified Karl Fischer method showed an almost constant value of 18.0—18.1%, regardless of the heating temperature in the range of 500—900 °C. The calculated composition of the C-SbA is $Sb_2O_5\cdot3.9H_2O$; this agree well with earlier results.[5]

The observed weight loss of 1.8 ± 0.1%, obtained by heating the material from 750 °C to 900 °C for 30 min,

Table 1. Dependence of the weight loss and the evolved water of the C-SbA at the heating temperature for 12 h

Temp °C	Weight loss %	Water evolution %	Water composition$^{a)}$ (n)
100	7.5	7.5	
200	13.6	13.6	
300	16.6	16.1	
400	18.3	17.3	
500	20.6	18.0	3.95
600	20.8	18.1	3.97
700	20.7	18.1	3.97
800	20.7	18.0	3.96
900	22.2	18.0	3.96
1000	40.3	18.0	3.96

a) Water composition: $Sb_2O_5 \cdot nH_2O$.

agree well with the theoretical value of 1.70% from Sb_6O_{13} to Sb_2O_4 within the limits of experimental error. If the change from 700 °C to 900 °C corresponds to that of the hydrated material of the antimony oxide, the weight loss should be obtained as 1.8% from $2Sb_3O_6$-OH to Sb_6O_{13}, as 0.97% from $H_2Sb_{12}O_{26}$ to $Sb_{12}O_{25}$, and as 0.45% from $H_2Sb_{26}O_{56}$ to $Sb_{26}O_{55}$. The value of the evolved water from the heated C-SbA is almost constant in the range of 500—900 °C. The evolved water was less than the blank value of 0.1% and/or the same heating conditions of 750—900 °C. Thus, we conclude that the change in the C-SbA heated at 750 to 900 °C is from Sb_6O_{13} to Sb_2O_4. This conclusion agree well with those of Abe[5] and Stewart *et al.*[7]

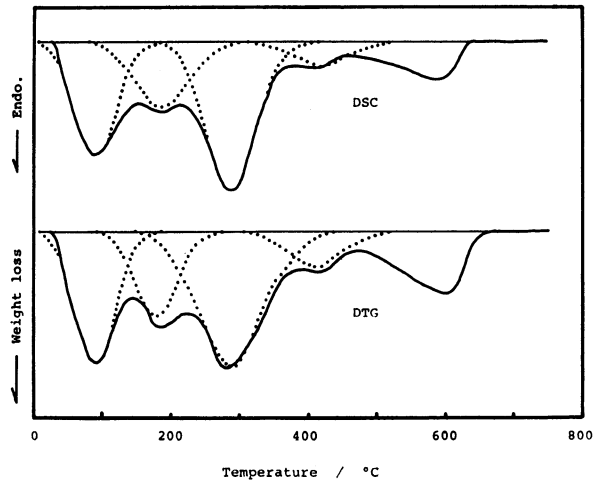

Fig. 1. DSC and DTG curves of C-SbA in H^+ form. Heating rate: 10 °C min^{-1}, sample size: 100—200 mesh, atmosphere: air.
——: Observed, ····: calculated.

The observed DSC and DTG curves are shown in Fig. 1. The maximum temperatures were observed at about 100, 190, 300, 420, and 600 °C up to 700 °C in five curves. This result is in good agreement with that reported earlier, except for the endothermic peak of 190 °C. Such a small peak as that at 190 °C was detectable because the apparatus of thermal analysis used here is more sensitive than that used earlier. The shape of the last peak at 600 °C was different from the other four peaks and would correspond to the deoxidation of Sb_2O_5. We attempted to separate the first four peaks into four individual peaks by means of a non-linear least-square fit. The sum of the four separated peaks was successfully reproducible on the original DTG curve by means of computer curve-fitting. The weight loss of the C-SbA calculated by means of the total area of the four separated peaks at 90, 180, 290, and 420 °C was 17.9%, almost the same as the water content of the C-SbA in Table 1. Thus, thermal decomposition of the C-SbA in the H^+form follows four dehydration and two deoxidation steps up to 1000 °C:

$$Sb_2O_5 \cdot 4H_2O \xrightarrow{90^\circ C} Sb_2O_5 \cdot 2.9H_2O \xrightarrow{180^\circ C}$$
$$Sb_2O_5 \cdot 2.15H_2O \xrightarrow{290^\circ C} Sb_2O_5 \cdot 0.45H_2O \xrightarrow{420^\circ C}$$
$$Sb_2O_5 \xrightarrow{600^\circ C} Sb_6O_{13} \xrightarrow{940^\circ C} Sb_2O_4.$$

The authors wish to express their thanks to Dr. Takumi Hikida and Dr. Hiroshi Hiratsuka of the Tokyo Institute of Technology for their helpful advices regarding the computer curve fitting.

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