Thermochimica Acta, 85 (1985) 31–34
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THE THERMAL AND HYDROLYTIC INTER-RELATIONSHIP BETWEEN THE PRODUCTS OF THE ANTIMONY(III) CHLORIDE/WATER SYSTEM

J. FENERTY, J. PEARCE AND S.A. JONES
Department of Chemistry and Biochemistry, Liverpool Polytechnic,
Byrom Street, Liverpool L3 3AF, (England).

ABSTRACT

Controlled hydrolysis of $SbCl_3$ resulted in two well defined intermediate oxychlorides; SbOCl and $Sb_4O_5Cl_2$. TG indicated that SbOCl decomposed rapidly at 530K to $Sb_4O_5Cl_2$. Chemical analysis and XRD showed that the decomposition product was identical to $Sb_4O_5Cl_2$ produced by the hydrolysis of $SbCl_3$. Complete hydrolysis of $SbCl_3$ and the thermal decomposition of intermediate oxychlorides both gave Sb_2O_3; the product of hydrolysis was shown by XRD to be valentite, whilst that obtained by thermal decomposition was senarmontite. Our findings have been related to the synergistic effect of Sb_2O_3, a flame retardant additive, in conjunction with chlorinated hydrocarbons.

INTRODUCTION

A pronounced synergistic effect occurs when Sb_2O_3, a flame retardancy additive, is incorporated with organo-halide type polymers (ref.1). The effect appears to be dependent upon the transport of volatile antimony compounds to the flame. One proposed mechanism (ref.2) is the reaction of hydrogen chloride, evolved from the substrate polymer, with Sb_2O_3, resulting in the in-situ formation of the intermediate compound SbOCl. Subsequent thermal decomposition of the oxychloride yields the actual flame retardant species, $SbCl_3$, which is itself too hydrolytically unstable to be incorporated with a flammable substrate. In order to test the validity of the above mechanism, a study of the thermal and hydrolytic inter-relationships between antimony(III) oxychlorides was made.

EXPERIMENTAL METHODS

Materials

Antimony(III) chloride (99.5%) ex Aldrich Chemical Company, was used as the starting material of all antimony(III) compounds in this study.

Techniques

Thermogravimetry was carried out using the Du Pont 990 Thermal Analyzer in conjunction with a 951 Thermogravimetric Analyzer. DSC was carried out using the Du Pont R90 Thermal Analyzer in conjunction with the 910 Differential Scanning Calorimeter. A heating rate of 5K min^{-1} was used throughout.

0040-6031/85/$03.30

XRD was performed using a Phillips PW1700 X-ray powder diffraction system.

The antimony(III) content of samples was determined by titration with standard potassium bromate(V) solution. Chloride was determined gravimetrically as silver chloride.

RESULTS AND DISCUSSION

The complete hydrolysis of antimony(III) chloride yielded antimony(III) oxide according to the overall equation:

$$2SbCl_3 + 3H_2O = Sb_2O_3 + 6HCl \qquad (1)$$

The composition of the product was confirmed by chemical analysis. By controlling the amount of water present in the reaction, two intermediate oxychloride compounds were isolated, SbOCl (ref.3) and $Sb_4O_5Cl_2$(ref.4). The composition of these intermediates was confirmed by chemical analysis for antimony(III) and for chloride.

TABLE 1

Preparation and analysis of antimony(III) compounds.

Reaction stoichiometry	antimony(III) content		chloride content	
	theoretical	experimental	theoretical	experimental
	(/%)	(/%)	(/%)	(/%)
$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$	70.29	70.59	20.47	20.74
$4SbCl_3 + 5H_2O \rightarrow Sb_4O_5Cl_2 + 10HCl$	76.34	76.16	11.11	11.08
$2SbCl_3 + 3H_2O \rightarrow Sb_2O_3 + 6HCl$	83.53	82.71	-	<0.1%

Thermal analysis revealed that the decomposition of SbOCl occurred rapidly, in a single stage, at 530K (see fig.1). TG indicated a mass loss of 25.8% for decomposition in air, and 25.9% in argon. These results were consistent with the formation of $Sb_4O_5Cl_2$.

$$5SbOCl = Sb_4O_5Cl_2 + SbCl_3 \qquad \text{(26.34\% mass loss)} \qquad (2)$$

XRD confirmed the oxychloride product to be identical to that produced by the controlled hydrolysis of $SbCl_3$ (ref.4). The reaction was also characterised by a single sharp thermal event in the DSC at 530K, corresponding to an enthalpy absorption to 10.6 kJ mol^{-1}. The rapid endothermic evolution of $SbCl_3$ recorded here is possibly implicated in the flame retardancy process.

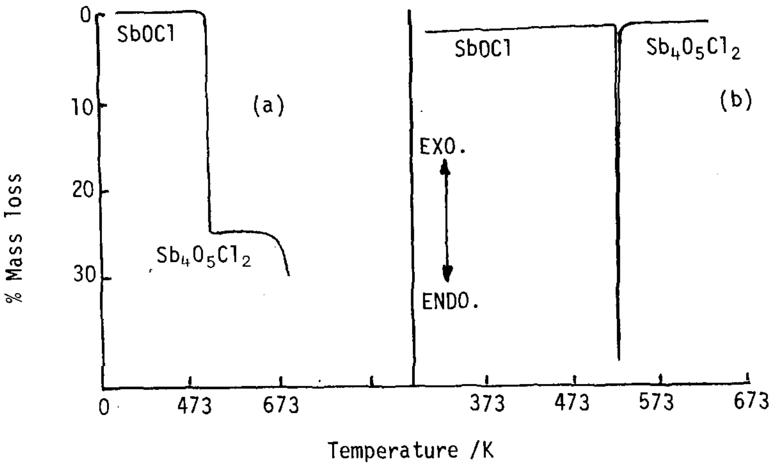

Fig.1. Thermal decomposition of SbOCl in air
(a) TG at 5K min^{-1} (b) DSC at 5K min^{-1}

TG and XRD indicated that thermal decomposition of $Sb_4O_5Cl_2$ in air produced α-Sb_2O_4, cervantite. In argon, $Sb_4O_5Cl_2$ decomposed to Sb_2O_3. XRD indicated this to be the cubic modification, senarmontite, regardless of the method of preparation. Conversely, Sb_2O_3 produced from the complete hydrolysis of $SbCl_3$ was found, by XRD, to be essentially the orthorhombic modification, valentite. Reported intermediates Sb_3O_4Cl (ref.2) and $Sb_8O_{11}Cl_2$ (ref.4) could not be confirmed. One mechanism for the so called synergistic effect has been outlined in the introduction, but an alternative explanation has recently found favour. Whilst in 1969 Pitts (ref.2) stated that the in-situ formation and subsequent decomposition of SbOCl was certainly involved in the flame retardancy process, Simon et al (ref.5) using Sb_2O_3 in conjunction with an organohalide substrate, reported that decomposition according to the Pitts scheme must be excluded as the source of $SbCl_3$, on the basis that atomic adsorption detection of evolved species showed that $SbCl_3$ was formed in one step at 560-580 K. Thus the alternative explanation for the synergistic effect, resulting from a combination of Sb_2O_3 and organohalide based compounds, was that $SbCl_3$, indisputably the active agent in flame retardancy, was formed by direct action of Sb_2O_3 with HCl gas evolved from the substrate, and that antimony oxychloride was not involved. The same authors provided the thermodynamic data given in Table 2.

Whilst the data appears to favour the direct formation of $SbCl_3$, the oxychloride route cannot be excluded on this basis, especially at elevated temperatures. Lum (ref.6) recognised the alternative mechanisms by which $SbCl_3$ may be produced and stated that the relative importance of the two pathways will depend upon the values of the rate constants, k_1 and k_2, at the relevant temperatures corresponding to polymer decomposition. It would also depend critically upon the value of the change in free energy content ΔG, from reactants to products, at elevated temperatures.

TABLE 2

Free energy changes for the Sb_2O_3/HCl system

Reaction pathway	ΔG/kJ mol^{-1}	
	298K	500K
$Sb_2O_3(s) + 2HCl \xrightarrow{k_1} 2SbOCl + H_2O(\ell)$	-19.43	-12.59
$Sb_2O_3(s) + 6HCl \xrightarrow{k_2} 2SbCl_3 + 3H_2O\ (\ell)$	-36.48	-18.89

From the available data, using the Gibbs reaction isotherm equation:

$$\Delta G = -RT\ \ell nK \qquad (3)$$

the value of K, the equilibrium constant, for each of the reactions given in Table 2 was calculated. Using the K values for each reaction at two different temperatures, and the integrated form of the van't Hoff isobar:

$$\ell nK = \frac{-\Delta H}{RT} + \text{constant} \qquad (4)$$

the temperature at which the equilibrium constant, K, for both reactions was equal, was determined graphically. This was found to be 613K. At this temperature, ΔG for the two reactions was equal, indicating an equal thermodynamic probability for their occurrence.

The sharp endothermic decomposition of SbOCl and the accompanying rapid evolution of $SbCl_3$, at typical polymer decomposition temperatures, are observations consistent with the involvement of SbOCl in the flame retardancy process.

REFERENCES

1 R.W. Little, Flameproofing Textile Fabrics (ACS Monograph Series No.104)1947.
2 J.J. Pitts, P.H. Scott and D.G. Powell, Journal of Cellular Plastics, 1970, 35-37.
3 G. Brauer, Handbook of Preparative Inorganic Chemistry, 1965, 1, 615.
4 R. Matsuzaki, A. Sofue and Y. Saeki, Chemistry Letters, 1973, 1311-1314.
5 J. Simon, T. Kantor, T. Kozma and E. Pungor, Journal of Thermal Analysis 25 (1982) 55-77
6 R.M. Lum, Journal of Polymer Science, 15 (1977) 1572-1576.

ACKNOWLEDGEMENT

One of us (SAJ) wishes to thank the SERC for provision of a grant.