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STUDY OF THE THERMAL DECOMPOSITION OF SOME COMPLEX TRIFLUOROCHLOROANTIMONATES(III) AND TRIFLUOROBROMOANTIMONATES(III)

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ABSTRACT

The thermal decompositions of crystalline complexes of formulae $Na[SbF_3Cl] \cdot H_2O$, $Na[SbF_3Br] \cdot H_2O$, $M[SbF_3Cl]$ (where M = K, Rb) and $M[SbF_3Br]$ (where M = Rb, Cs) were studied. Crystals were prepared by slow evaporation of water solutions of SbF_3 and alkali metal chlorides or bromides. On the basis of the results of thermal and chemical analyses, the mechanisms of thermal decomposition reactions were established. Kinetic parameters were calculated from TG curves using Zsako's and Coats and Redfern's methods. A comparison of the thermal stabilities of the compounds under study was made.

INTRODUCTION

Antimony trihalides SbX_3 (where X = F, Cl, Br, I) form numerous crystalline complexes with alkali metal halides. The following fluoroantimonates(III) are formed: $M[Sb_4F_{13}]$, $M[Sb_2F_7]$, $M[SbF_4]$ and $M_2[SbF_5]$ (where M = Na, K, Rb, Cs]. Less numerous are compounds with other halides and their number decreases in the order: Cl → Br → I. Most characteristic of these are complexes of general formula $M_3[Sb_2X_9]$. Recently, mixed salts, $M[SbF_3Cl]$ and $M[SbF_3Br]$, have been prepared [1—3]. X-ray studies have been made on a number of these compounds, the point of interest being the arrangement of halide atoms around the antimony atom as well as the influence of the alkali metal cation on the crystal structure of complex anions [4—9]. At higher temperatures complex halides of antimony(III) decompose with liberation of SbX_3. The mechanism and kinetics of the thermal decomposition of some of these complexes under dynamic temperature conditions, as well as the effect of the outer sphere cation on the thermal stability of these compounds, have been studied using thermal, chemical and X-ray analyses [10—13]. This paper presents results of the thermal examination of complexes of general formulae $M[SbF_3Cl]$ (where M = Na, K, Rb), $M[SbF_3Br]$ (where M = Na, Rb, Cs), $Na[SbF_3Cl] \cdot H_2O$ and $Na[SbF_3Br] \cdot H_2O$.

EXPERIMENTAL

Materials

The crystalline compounds $Na[SbF_3Cl] \cdot H_2O$ and $M[SbF_3Cl]$ ($M = K$, Rb) were prepared by dissolving SbF_3 and the appropriate alkali metal chloride in the molar proportion 1 : 1 in water and evaporating the solutions under reduced pressure at room temperature. Crystals of $Na[SbF_3Br] \cdot H_2O$ and $M[SbF_3Br]$ ($M = Rb$, Cs) separated after slow evaporation of the solutions of SbF_3 and metal bromide in water at room temperature. The crystals were separated from the mother liquor by filtration and rinsed first with icy water and then methanol. $Na[SbF_3Cl] \cdot H_2O$ and $Na[SbF_3Br] \cdot H_2O$ were dried in air and the other compounds were dried in a vacuum dessicator. Crystals were stored in hermetic polyethylene vials. All the syntheses were carried out with analytical grade reagents. In the prepared salts, as well as in the products of their thermal decomposition, antimony was determined as the sulphide by precipitating it with thioacetamide [14], alkali metals by means of flame photometry, fluorine by colorimetry, and halogen by Volhard's method. $Cs[SbF_3Cl]$ and $K[SbF_3Br]$ did not crystallize under the conditions described above.

Apparatus

Thermal analyses of the compounds under study were carried out using a MOM Budapest type OD-102/1500° thermal analyzer. The measurements were made in helium in the temperature range 20—1000°C at a heating rate 10°C min^{-1}. The sensitivity of the galvanometer for the DTA and DTG curves was 1/10; TG sensitivity was 100 mg. α-Al_2O_3 was used as reference material. The mass of the sample amounted to 100 mg. In order to follow the course of the thermal decomposition, the samples of ca. 100 mg were heated in a silite furnace at a rate of 10°C min^{-1} up to the appropriate temperature determined from the thermal analysis curves. The decomposition products which showed a mass loss similar to those determined from the TG curves were used for further investigations.

Thermoanalytical studies

Two typical thermal analysis curves are shown in Figs. 1 and 2. Thermal measurements indicate that the $Na[SbF_3Cl] \cdot H_2O$ undergoes decomposition in three steps. The first step appears between 120 and 160°C and is associated with an endothermic peak on the DTA curve at 156°C. The weight loss of 7.2% approximates to 7%, calculated for the following equation

$$Na[SbF_3Cl] \cdot H_2O = Na[SbF_3Cl] + \uparrow H_2O \qquad (1)$$

The second step takes place within the temperature range 160—580°C and is accompanied by an endothermic heat change peak at 205°C on the DTA curve. Chemical analysis results are compatible with the following reaction

$$2\ Na[SbF_3Cl] = Na_2SbF_3Cl_2 + \uparrow SbF_3 \qquad (2)$$

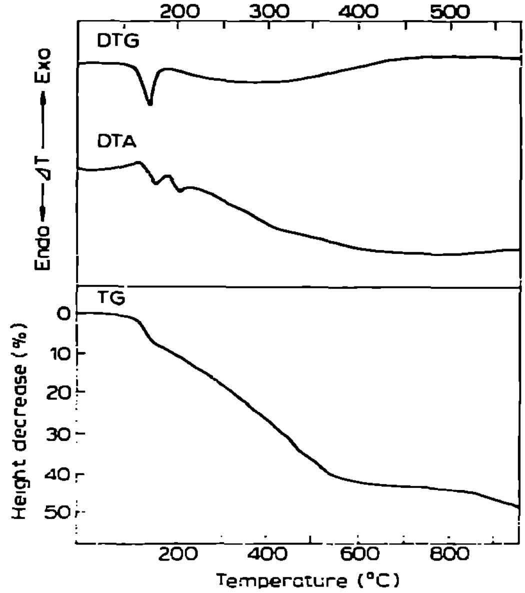

Fig. 1. Thermal analysis curves for $Na[SbF_3Cl] \cdot H_2O$.

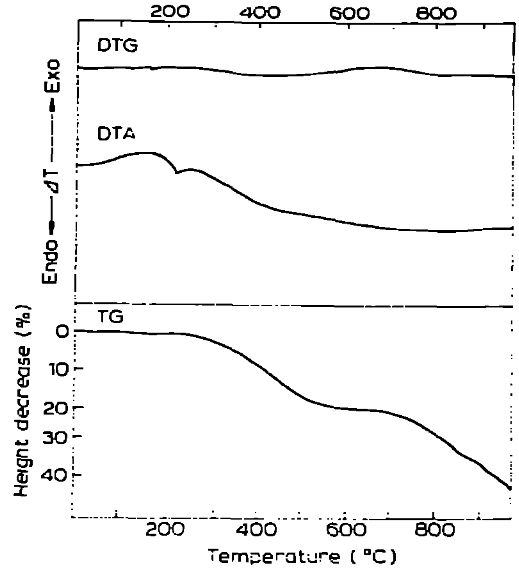

Fig. 2. Thermal analysis curves for $Rb[SbF_3Cl]$.

A mass loss calculated according to this scheme amounts to 35%, while that determined from the TG curve is 34%. The slow decomposition of $Na_2SbF_3Cl_2$ is represented on the DTA curve by a weak endothermic peak at 733° C. The overall weight decrease at 1000° C is 43%.

According to the thermal analysis curves of $K[SbF_3Cl]$, the first step of decomposition begins at 200° C and continues up to 580—600° C. The endothermic peak on the DTA curve at 208° C represents melting of the sample. The weight loss amounts to 32% and corresponds to the reaction

$$2\,K[SbF_3Cl] = K_2SbF_3Cl_2 + \uparrow SbF_3 \qquad (3)$$

The theoretical mass loss for this reaction is 35.3%. The weight loss of the second step of decomposition (endothermic peak on the DTA curve at 612° C) begins immediately. There is also a small endothermic peak on the DTA curve at 513° C which is probably the result of a modification change.

The only sharp endothermic peak on the DTA curve of $Rb[SbF_3Cl]$ is at 217° C. The initial weight loss on the TG curve is very slow. Faster decomposition begins at 260° C and continues up to 580° C. The mass loss determined from the TG curve (19%) as well as the results of chemical analyses of the decomposition products correspond to the reaction

$$3\,Rb[SbF_3Cl] = Rb_3Sb_2F_6Cl_3 + \uparrow SbF_3 \qquad (4)$$

The theoretical weight loss for this reaction is 19.9%. The decomposition of $Rb_3Sb_2F_6Cl_3$ begins at 620° C, and the total weight loss at 1000° C amounts to 38%.

According to the thermoanalytical curves, the decomposition of

$Na[SbF_3Br] \cdot H_2O$ can be divided into three steps. The first takes place within the temperature range 110—155° C and corresponds to the splitting-off of water of crystallization. It is represented on the DTA curve by an endothermic peak at 153° C. Experimental results are in agreement with the following scheme

$$Na[SbF_3Br] \cdot H_2O = Na[SbF_3Br] + \uparrow H_2O \qquad (5)$$

A mass loss of 6% is calculated according to this scheme while a value of 5.8% is obtained from the TG curve. The second step of decomposition (160—320° C; endothermic peak on the DTA at 178°C) follows the equation

$$5\ Na[SbF_3Br] = Na_5Sb_3F_9Br_5 + \uparrow 2\ SbF_3 \qquad (6)$$

The calculated weight loss is 29.9% while the TG curve gives a value of 30%. The third step occurs within the temperature range 340—560° C. It is represented on the DTA curve by the endothermic peak at 347° C and can be supposed to run according to the following scheme.

$$2\ Na_5Sb_3F_9Br_5 = Na_{10}Sb_5F_{15}Br_{10} + \uparrow SbF_3 \qquad (7)$$

The weight loss for this reaction is 10.3%, compared to 11.2% determined from the TG curve. The next slow weight decrease begins at 730° C, and at 1000° C total weight loss amounts to 49%.

There is only one distinct endothermic peak at 195° C on the DTA curve of $Rb[SbF_3Br]$ (melting of the sample). The first step of decomposition of this compound begins at 180° C and continues up to 580° C. The experimental results are compatible with the following reaction

$$3\ Rb[SbF_3Br] = Rb_3Sb_2F_6Br_3 + \uparrow SbF_3 \qquad (8)$$

The theoretical mass loss (17.3%) is in good agreement with that observed on the TG curve (17%). The slow decomposition of $Rb_3Sb_2F_6Br_3$ starts almost immediately and at 1000° C the mass loss amounts to 29%. The thermal decomposition of $Cs[SbF_3Br]$ follows a different pattern. The initial decomposition step starts at 180° C and finishes at 520° C. The endothermic peak on the DTA curve corresponding to the melting of the sample has its maximum value at 186° C. The mass loss calculated from the reaction

$$3\ Cs[SbF_3Br] = Cs_3Sb_2F_6Br_3 + \uparrow SbF_3 \qquad (9)$$

amounts to 15.2%, while the TG curve gives a value of 15.0%. In the second step (540—960° C) CsBr is liberated from the heated sample. The broad endothermic peak at 630—670° C is probably the sum of two peaks: one connected with the decomposition and the other corresponding to melting of CsBr. Slow evaporation of CsBr is also observed at higher temperatures.

The DTG curves of the compounds under study are broad and indistinct and were not used for interpretation of the thermal decomposition processes.

Kinetic studies

Kinetic parameters of some steps of decomposition of the compounds under study were calculated from the thermogravimetric (TG) curves. Using the Coast—Redfern method [15] plots of

$$y = \log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-\alpha)}\right] \text{ vs. } 1/T \text{ for } n = \tfrac{1}{3}, \tfrac{1}{2}, \tfrac{2}{3}$$

and

$$y = \left[\frac{-\log(1-\alpha)}{T^2}\right] \text{ vs. } 1/T \text{ for } n = 1$$

(where α is the fraction of the substance decomposed at temperature T and n is reaction order) were drawn. These values of n were chosen as correct for obtaining straight lines. Activation energies were calculated from the slopes of the lines. Values of E_a are presented in Table 1. Kinetic parameters were also calculated by Zsako's method [16]. By means of trial and error, the activation energy was estimated which ensures the maximum constancy of B at different temperatures

$$B = \log g(\alpha) - \log p(x) = \log \frac{ZE_a}{Rq}$$

The values of $g(\alpha)$ at different temperatures were calculated for zero-, half-, first- and second-orders of reaction using an analytical form of the function given in the literature [16]. Values of $-\log p(x)$ for different temperatures and activation energies were taken from the table in ref. 16. For intermediate E_a values the corresponding $-\log p(x)$ values were determined by means of linear interpolation. The agreement between experimental data and presumed E_a values was characterized by the standard deviation, δ, of individual B values from their arithmetical mean B. The final results of the calculated kinetic parameters are shown in Table 1.

TABLE 1

Kinetic parameters of trifluorochloroantimonates(III) and trifluorobromoantimonates (III)

Compound	No. of reaction	Coats and Redfern's [15] method		Zsakó's [16] method	
		n	E_a	n	E_a
$Na[SbF_3Cl] \cdot H_2O$	1	1	38.3	1	38.7
$Na[SbF_3Cl]$	2	2	7.2	—	—
$K[SbF_3Cl]$	3	2	12.4	2	12.7
$Rb[SbF_3Cl]$	4	2	14.4	2	14.7
$Na[SbF_3Br] \cdot H_2O$	5	1	30.4	1	31.1
$Na[SbF_3Br]$	6	2	20.2	2	21.2
$Rb[SbF_3Br]$	8	2	12.3	2	12.5
$Cs[SbF_3Br]$	9	1	8.5	1	9.0

DISCUSSION

Taking into account the thermal and chemical analyses results, it may be stated that the thermal decomposition of trifluorochloro- and trifluorobromoantimonates(III) of alkali metals are multi-step processes represented by the reactions schemas [1—9]. Gaseous SbF_3 is liberated during decomposition. All thermal effects shown on the DTA curves are endothermic. The first peaks on the DTA curve of $Na[SbF_3Cl] \cdot H_2O$ and $Na[SbF_3Br] \cdot H_2O$ are connected with the loss of water of crystallization. The thermal decomposition of complexes under study is preceded by melting of the compounds. The appropriate peak temperatures differ slightly (1—2° C) from the melting points determined from DTA given in the literature [3]. The thermal stability of $M[SbF_3Cl]$ (M = Na, K, Rb), defined by the temperature of the start of the decomposition, as well as the activation energy values increase in the order: $Na[SbF_3Cl] < K[SbF_3Cl] < Rb[SbF_3Cl]$. This is in agreement with results reported previously [17—20], and is consistent with the statement that the thermal stability of the complexes increases with increasing radius of the monovalent cation. The temperatures at which the thermal decomposition of $M[SbF_3Br]$ (where M = Na, Rb, Cs) starts differ slightly, but the activation energy values distinctly decrease in the order $Na[SbF_3Br] > Rb[SbF_3Br] > Cs[SbF_3Br]$. The initial thermal decomposition temperatures of trifluorobromoantimonates(III) are also lower than analogous trifluorochloroantimonates(III).

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