EXAMINATION OF THE THERMAL DECOMPOSITION OF CHLOROSTANNATES(IV)

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ABSTRACT

The thermal decomposition of the crystalline Sn(IV) chloride of formula $M_2[SnCl_6]$ (M = Cs, Rb, K) has been investigated. The mechanism of thermal decomposition of these compounds has been established. From the thermogravimetric curves the apparent activation energy and reaction order of the thermal decomposition have been calculated.

INTRODUCTION

The purpose of this work was to determine the thermal resistance of the salts $Cs_2[SnCl_6]$, $Rb_2[SnCl_6]$ and $K_2[SnCl_6]$, to determine the kinetic parameters of the thermal decomposition reaction, and to establish the conditions necessary for obtaining high-purity CsCl by the thermal decomposition of $Cs_2[SnCl_6]$. We chose tin(IV) compounds because caesium chlorostannate has been used for a long time to determine caesium [1,2] and for the liberation of the radiochemical isotope Cs^{138} [3]. Stannic chloride is used for the selective precipitation of caesium as $Cs_2[SnCl_6]$ from a 50% solution of HCl in ethanol. In this case potassium ions are not an obstacle in precipitation of the caesium salt.

EXPERIMENTAL

Preparation of salts

We obtained the Sn(IV) chloride salts with alkaline metals of formulae $Cs_2[SnCl_6]$, $Rb_2[SnCl_6]$ and $K_2[SnCl_6]$ in the following way. The caesium salt was crystallized from a solution containing 1.63 g Cs_2CO_3 dissolved in 10 ml of HCl (2:1) and 1.75 g $SnCl_4 \cdot 5H_2O$ dissolved in 10 ml of water. $Rb_2[SnCl_6]$ was obtained from a solution containing 1.155 g of Rb_2CO_3 dissolved in 10 ml of HCl (2:1) and 1.75 g of $SnCl_4 \cdot 5H_2O$ dissolved in 10 ml of water.

TABLE 1

Results of chlorostannate(IV) analyses

Compound	Ion determined	Content (%)	
		Calc.	Exp.
$Cs_2[SnCl_6]$	Cs	44.49	45.87
	Cl	35.62	35.21
$Rb_2[SnCl_6]$	Rb	34.05	32.90
	Cl	42.37	42.00
$K_2[SnCl_6]$	K	19.32	19.39
	Cl	51.89	51.60
	Sn	28.97	28.17

To obtain the potassium salt we mixed a solution containing 1.49 g of KCl in 10 ml of water with a solution containing 3.5 g of $SnCl_4 \cdot 5H_2O$ in 10 ml of water, and then added 1 ml of concentrated HCl.

All the solutions were left to crystallize in a refrigerator. When the crystals had precipitated, they were filtered through Schot G-4 crucible, washed with HCl (2:1) and dried in a desiccator.

Caesium and rubidium salts crystallized in the form of tiny white crystals which were insoluble in water, and the potassium salt crystallized as large, transparent, regular octahedrons soluble in water.

To establish the constitution of the compounds, caesium, rubidium and potassium were analysed by flame photometry. The chlorides were de-termined by the Volhard method, and tin in the potassium compound was determined by bromometry. Tin(IV) in $Cs_2[SnCl_6]$ and $Rb_2[SnCl_6]$ could not be determined by this method because these compounds are insoluble in water and hydrochloric acid. They dissolve in oxidizing nitric acid $(1 + 1)$ at high temperatures, and for this reason the redoximetric method could not be used. The results of caesium, rubidium, potassium, tin(IV) and chlorides in the analysed salts are presented in Table 1.

THERMAL ANALYSIS

The measurements were carried out in a derivatograph and the products of the compounds decomposition were examined, i.e. quantitative analysis of sinters and determination of trace amounts of crystalline residue. The thermal decomposition reaction was established and the kinetic parameters of the decomposition reaction were calculated. The derivatographic analysis was carried out in air in a MOM derivatograph (Budapest, OD-102). The heating rate was $10°C$ min^{-1}, the temperature range $20–1000°C$, the sample mass 100 mg and α-Al_2O_3 was used as reference material. DTA and DTG sensitivity was 1/10 and TG sensitivity was 100 mg.

Figures 1, 2 and 3 give the thermal curves of caesium, rubidium and potassium chlorostannates, respectively. On the DTA and DTG curves of the caesium compound there are peaks with maxima at 620 and 610°C. The peak on the DTA curve shows that the reaction is endothermic. The mass loss from the TG curve corresponds with this change. At 640°C there is a peak in the DTA curve connected with the melting of CsCl. On the DTG curve there is a peak with a maximum at 680°C, reflecting a reaction with a violent mass loss. This is also shown in the TG curve. The decomposition of rubidium salts takes place at 400–640°C. The mass loss on the TG curve corresponds to the peaks (with maxima at 610°C) on the DTA and DTG curves. The peak on the DTA curve shows that the reaction is endothermic. The next peak on the DTA curve with a maximum at 710°C corresponds to melting of RbCl. Above 740°C evaporation of RbCl begins which is connected with a mass loss on the TG curve.

From the thermal curves of the potassium salt it follows that an endothermic decomposition reaction of the compound occurs at 350–550°C. On the DTA and DTG curves there is a clear, acute peak with a maximum at 530°C, corresponding to a violent mass loss visible on the TG curve. In the temperature range 550–750°C there is a horizontal line on the TG curve; the mass of the sample does not change. Above 750°C loss of sample mass begins again, connected with the evaporation of KCl. The melting temperature of KCl is shown as a clear peak on the DTA curve with a maximum at
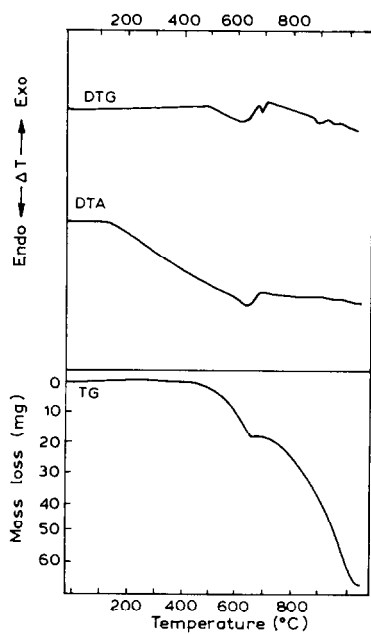

Fig. 1. Thermal analysis curves of $Cs_2[SnCl_6]$.

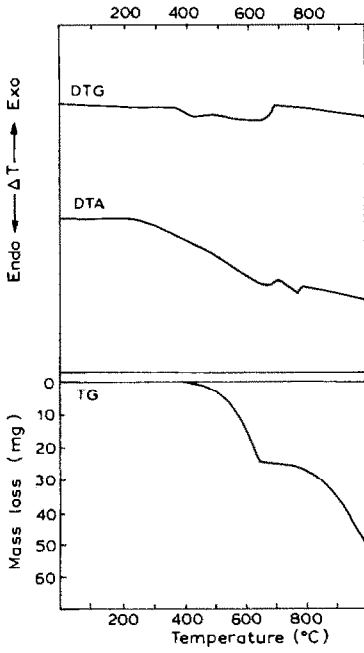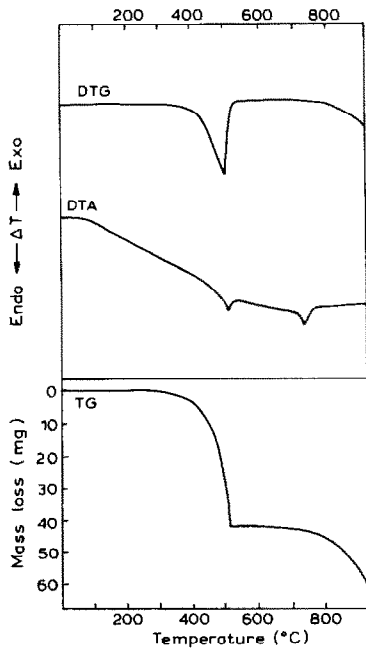Fig. 2. Thermal analysis curves of $Rb_2[SnCl_6]$.

Fig. 3. Thermal analysis curves of $K_2[SnCl_6]$.

TABLE 2

Data from thermal curves of caesium, rubidium and potassium chlorostannates

Compound	Initial decomp. temp. (°C)	Maximum peak temp. in DTG	Maximum peak temp. in DTA	Mass loss (%)		Melting temp. (°C)	
				from TG curve	calc. from reaction	from DTA curve	from literature
$Cs_2[SnCl_6]$	450	610, 680	620, 640	18.2		640	646
$Rb_2[SnCl_6]$	400	610	610, 710	25.9	24.9	710	715
$K_2[SnCl_6]$	350	520	530, 760	42.0	42.4	760	776

760°C. Table 2 presents temperature data corresponding to peaks on the DTA and DTG curves and calculated mass losses based on the TG curve.

To establish how the thermal decomposition reaction of chlorostannates proceeds, we carried out quantitative analyses of the stable products of decomposition, the so-called sinters. Weighed samples of caesium, rubidium and potassium chlorostannates were heated in an electric furnace with a regulated heating rate ($10°C$ min^{-1} in accordance with the measurement conditions in the derivatograph). The samples were heated to temperatures determined from the thermal curves corresponding with the first stage of thermal decomposition of the investigated compounds: 660°C for the caesium salt, 650°C for the rubidium salt and 550°C for the potassium salt. In the obtained sinters, caesium, rubidium and potassium were determined by flame photometry and tin(IV) was determined by spectrophotometry. In order to determine caesium, rubidium and potassium, the sinters were dissolved in distilled water. The insoluble part was separated on a Schott G-4 crucible. The solution was used for photometric analysis and then the contents of caesium, rubidium and potassium were read from the appropriate calibration curves. The results of Cs, Rb and K in chlorides are presented in Table 3.

In order to determine the purity of the solutions obtained, we fouled them with tin(IV) compounds. Tin(IV) was determined by two methods: (1) The

TABLE 3

Results of caesium, rubidium and potassium analyses

Sinter	Determined (%)			Calc. in chlorides (%)		
	Cs	Rb	K	Cs	Rb	K
$CsCl \cdot SnCl_4 + 3CsCl$	80			78.97		
$RbCl \cdot SnCl_4 + 3RbCl$		68.25			70.71	
$KCl \cdot SnCl_4 + 5KCl$			50.31			52.48

TABLE 4

Results of Sn(IV) determination

Sinter	Sn(IV) determined at $\lambda = 555$ nm (%)	Sn(IV) determined at $\lambda = 218$ nm (%)
$CsCl \cdot SnCl_4 + CsCl$	0.031	0.0358
$RbCl \cdot SnCl_4 + 3RbCl$	–	–
$KCl \cdot SnCl_4 + 5KCl$	0.177	0.162

colour of an Sn(IV) solution with pyrocatechol violet was measured by absorbance of a series of standard solutions and of the samples at $\lambda = 555$ nm wavelength; (2) using an absorption band in the range of light UV for $SnCl_4$ solution, the absorbance was measured for the series of standard solutions and for the investigated samples with maximum absorption at $\lambda = 218$ nm. The results of both methods are presented in Table 4.

KINETIC PARAMETERS

The reaction order and the apparent activation energy were determined by the Coats–Redfern method [4] (Table 5). The rectilinear dependence of y

TABLE 5

Activation energy and reaction order for the chlorostannates(IV)

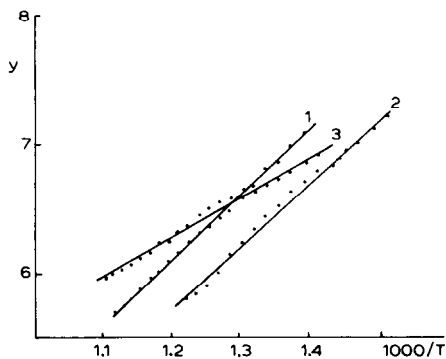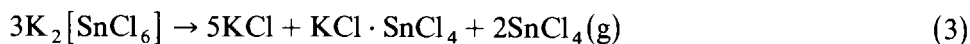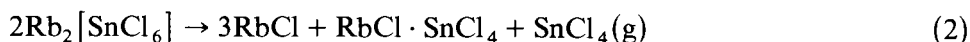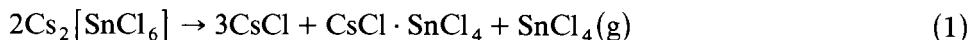| Compound	Reaction order, n	Activation energy, E_a (J mol^{-1})
$K_2[SnCl_6]$	0.00	56.73
$Rb_2[SnCl_6]$	0.00	90.96
$Cs_2[SnCl_6]$	0.56	92.47

Fig. 4. Plots of $y = -\log[1-(1-\alpha)^{1-n}]/T^2(1-n)$ versus $1/T$: (1) for $Cs_2[SnCl_6]$, (2) for $Rb_2[SnCl_6]$, (3) for $K_2[SnCl_6]$.

on $1/T$ (where $y = -\log[1 - (1 - \alpha)^{1-n}]/T^2(1 - n)$, T is the temperature (K), n is the reaction order and α is the mass loss at temperature T) was obtained for the potassium and rubidium salts when $n = 0$, and for the caesium salt when $n = 0.56$ (Fig. 4).

DISCUSSION

Based on the quantitative analysis of sinters and the data from the thermal curves, the following equations for thermal decomposition of caesium, rubidium and potassium chlorostannates were established:

$$2Cs_2[SnCl_6] \rightarrow 3CsCl + CsCl \cdot SnCl_4 + SnCl_4(g) \tag{1}$$

$$2Rb_2[SnCl_6] \rightarrow 3RbCl + RbCl \cdot SnCl_4 + SnCl_4(g) \tag{2}$$

$$3K_2[SnCl_6] \rightarrow 5KCl + KCl \cdot SnCl_4 + 2SnCl_4(g) \tag{3}$$

The mass loss calculated from eqn. (1) corresponds to the loss of $SnCl_4$ and is in accordance with the mass loss from the TG curve. Evaporation of $SnCl_4$ occurs in the temperature range 450–640°C. The mass loss from the TG curve for the rubidium salt is 24.9% which corresponds to the evaporation of $SnCl_4$. From eqn. (2) the mass loss connected with the evaporation of $SnCl_4$ is 25.9%. On the basis of eqn. (3) we calculated the mass loss corresponding to the evaporation of $SnCl_4$ (42.4%). The same mass loss calculated from the TG curve is 42%.

On thermal decomposition of complex crystalline chloride salts of Sn(IV) with caesium, rubidium and potassium, $SnCl_4$ is liberated in gaseous form and the other products of the decomposition reaction (eqns. 1–3) are crystalline and partly soluble in water.

The melting temperatures of alkaline metals chlorides calculated from the position of peaks on the DTA curve are slightly lower than those given in the literature (Table 2).

The thermal effects occurring during heating are endothermic processes. The thermal decomposition of caesium salt takes place at a higher temperature than that of the rubidium salt, and the latter decomposes at a higher temperature than the potassium salt. The thermal resistance decreases as the radius of the cation outer sphere decreases: Cs > Rb > K. On comparing the TG curves of the chlorostannates, a horizontal line is clear: for the caesium salt at 640–680°C, for the rubidium salt at 640–710°C and for the potassium salt at 530–755°C. The caesium salt can therefore be used to obtain pure CsCl (Table 4) by decomposition of $Cs_2[SnCl_6]$ in the temperature range 640–690°C.

When we compare caesium and rubidium chlorostannates with the halide compounds of As(III) and Bi(III) containing caesium and rubidium [5], it is clear that the chlorostannates are thermally more durable. Analytical utiliza-

tion of the thermal decomposition reactions of potassium, rubidium and caesium chlorostannates(IV) for determining potassium, rubidium and caesium will be the topic of further investigations.

ACKNOWLEDGEMENTS

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