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THERMAL DECOMPOSITION OF POTASSIUM, RUBIDIUM AND CAESIUM FLUOROANTIMONATES(III)

B. PTASZYŃSKI

Institute of General Chemistry, Polytechnical University, 90924 Łódź (Poland)

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ABSTRACT

The thermal decomposition of crystalline complexes of the types $M_2[SbF_5]$, $M[SbF_4]$, $M[Sb_2F_7]$ and $M[Sb_4F_{13}]$ (where M = K, Rb, Cs) was studied. Crystals were prepared by slight modifications of the methods described in the literature. On the basis of the results of thermal analyses the mechanisms of thermal decomposition were proposed. From thermogravimetric curves kinetic parameters were calculated using the methods of Coats and Redfern and Zsako. A comparison was made of the thermal stabilities in the light of available structural data.

INTRODUCTION

Antimony(III) fluoride reacts with alkali metal fluorides to form numerous crystalline complexes of general formula $M_2[SbF_5]$, $M[SbF_4]$, $M[Sb_2F_7]$ and $M[Sb_4F_{13}]$ (where M = alkali metal ion with exception of Li^+). A number of X-ray and spectroscopic studies of these compounds have been made, the point of interest being the arrangement of the fluorine atoms around the antimony atom [1—13] as well as the influence of the outer sphere cation on the structure of the complex anion. At higher temperatures alkali metal fluoroantimonates(III) decompose, with the liberation of SbF_3. In earlier papers [14—17], the thermal decomposition of some of these complexes in air was studied and the mechanisms of the decomposition reactions were established. Some conclusions were drawn concerning the effect of outer sphere cations on thermal stability. The thermal decomposition of fluoroantimonates(III) under an atmosphere of oxygen is complicated because of the partial oxidation of SbF_3 at high temperatures.

The subject of the present work is the study of the thermal stability and of the kinetics of thermal decomposition reactions of potassium, rubidium and caesium fluoroantimonates(III) of the types $M_2[SbF_5]$, $M[SbF_4]$, $M[Sb_2F_7]$, and $M[Sb_4F_{13}]$ (M = alkali metal) under dynamic conditions in an inert gas atmosphere. Kinetic parameters of decomposition reactions will be evaluated from TG curves. An attempt will also be made to determine the influence of the outer sphere cation on the thermal stability of complexes and to correlate, whenever possible, their structural properties with thermal parameters.

EXPERIMENTAL

Materials and apparatus

Well-formed crystals of the fluoroantimonates under study were prepared by slight modifications to the methods described in the literature [1—4, 18—20]. The starting materials were analytical grade K_2CO_3, Rb_2CO_3 and Cs_2CO_3, chemically pure Sb_2O_3 and 40% HBr. Antimony, alkali metals and fluorine were determined by means of standard chemical methods. The thermal investigations were carried out using a Derivatograph MOM Budapest OD-102/1500°C. Measurements were made in helium in the temperature range 20—1000°C at a heating rate of 10°C min^{-1}. The sensitivity of the galvanometers for DTG and DTA were 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.

Thermoanalytical studies

Complexes of the type $M_2[SbF_5]$

Typical thermal analysis curves of pentafluoroantimonates(III) are shown in Fig. 1. Thermal measurements indicate that $K_2[SbF_5]$ undergoes a one-step decomposition which takes place between 300 and 700°C. The corresponding endothermic peak on the DTA curve is at 520°C and the flat peak on the DTG curve at 600°C. The decomposition is preceded by melting of the sample (peak on DTA at 295°C). The weight loss determined from TG (12.0%) is in good agreement with that calculated from the following

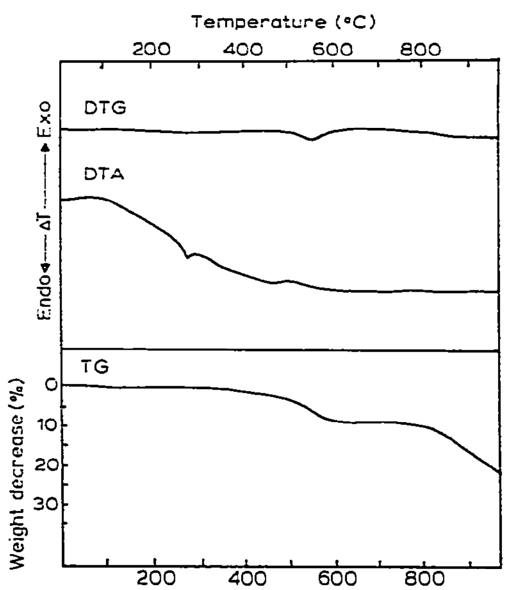


Fig. 1. Thermal analysis curves of $Rb_2[SbF_5]$.

reaction scheme (12.1%)

$$5\ K_2[SbF_5] = 10\ KF \cdot 4\ SbF_3 + SbF_3\uparrow \tag{1}$$

According to the thermal investigations, $Rb_2[SbF_5]$ decomposes within the temperature range 280—620°C. Endothermic peaks occur on the DTA curve sharp at 270°C (melting of the sample) and blurred at about 480°C (decomposition). Only one peak appears on the DTG at 480°C. A mass loss of 8.4% is found, calculated according to eqn. (2) and also from the TG curve.

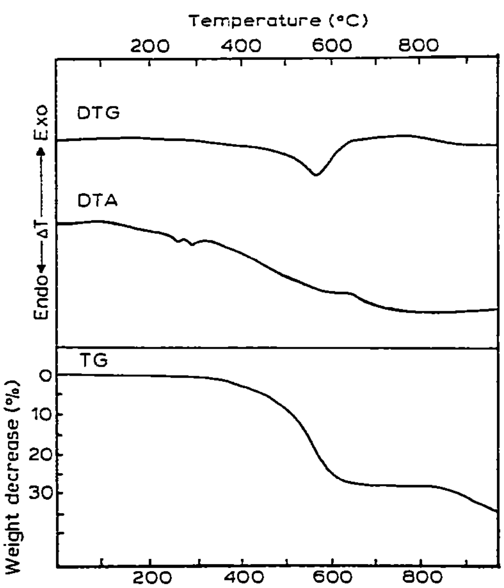
$$5.5\ Rb_2[SbF_5] = 11\ RbF \cdot 4.5\ SbF_3 + SbF_3\uparrow \tag{2}$$

Slow and continuous decomposition of $Cs_2[SbF_5]$ is observed within a large temperature range of 220—640°C. On the DTA curve only one slight endothermic peak at 240°C is visible. On the basis of accessible experimental data it is difficult to write the decomposition scheme of caesium pentafluoroantimonate(III).

Complexes of the general formula $M[SbF_4]$

According to the thermoanalytical curves (as an example thermal analysis curves of $Rb[SbF_4]$ are presented in Fig. 2), the decomposition of potassium, rubidium and caesium tetrafluoroantimonates(III) are single-step processes. On the TG curves of $Rb[SbF_4]$ and $Cs[SbF_4]$ slow decreases in mass are also observed at temperatures above 750°C for caesium and 800°C for rubidium tetrafluoroantimonates(III).

Decomposition of the potassium compound starts at about 240°C and is complete at 590°C. The one sharp endothermic peak on the DTA curve at 252°C is connected with the melting and decomposition of the complex.



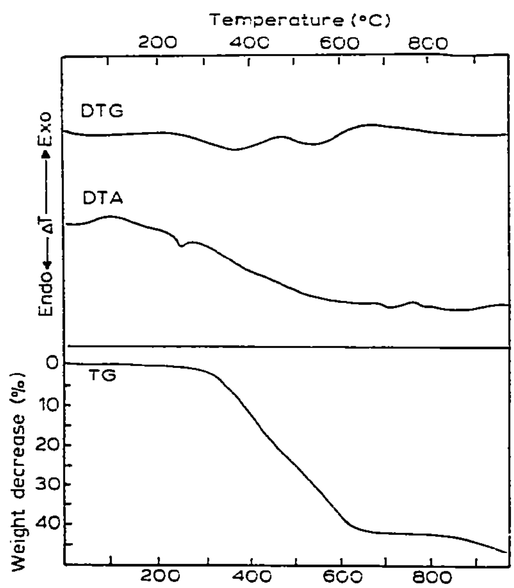


Fig. 2. Thermal analysis curves of $Rb[SbF_4]$.

Fig. 3. Thermal analysis curves of $Rb[Sb_2F_7]$.

The corresponding mass loss amounts to 39.0% and is in agreement with the weight loss calculated from eqn. (3) (37.7%)

$$2\ K[SbF_4] = 2\ KF \cdot SbF_3 + SbF_3\uparrow \qquad (3)$$

At higher temperatures a slight perturbation in the course of the end part of the TG curve is observed. The DTG curve of $K[SbF_4]$ is flat and cannot be localized exactly.

The thermal decomposition of the rubidium salt takes place between 300 and 580°C. There are two slight peaks on the DTA curve: the first at 230°C corresponds to the melting of the sample, and the second at 260°C is connected with the decomposition. On the DTG curve a distinct peak at 540°C is visible. The theoretical mass loss calculated for reaction (4) amounts

$$5\ Rb[SbF_4] = 5\ RbF \cdot 3\ SbF_3 + 2\ SbF_3\uparrow \qquad (4)$$

to 25.2% and that determined from the TG curve is 26.8%. According to the thermoanalytical curves, decomposition of $Cs[SbF_4]$ begins at 200°C and finishes at 500°C and is accompanied by a slight peak on the DTA curve at 210°C. On the DTG curve a blurred peak at about 365°C is visible. The results of analysis are compatible with the following reaction

$$7\ Cs[SbF_4] = 7\ CsF \cdot 5\ SbF_3 + 2\ SbF_3\uparrow \qquad (5)$$

A mass loss according to this scheme amounts to 15.4%, while that determined from the TG curve is to 15.2%.

Complexes of the type $M[Sb_2F_7]$

The process of thermal decomposition of the heptafluorodiantimonates(III) under study can be divided into two overlapping steps (Fig. 3). The first endothermic peaks on the DTA curves of potassium, rubidium and caesium salts connected with the first reaction step are at 258, 225 and 228°C, respectively. It is difficult to localize peaks on the DTA curve corresponding to the second reaction step. Besides, there is one distinct exothermic peak on the DTA curve of $K[Sb_2F_7]$ at 595°C. On the TG curves of each compound there are two rather blurred peaks at 390 and 555°C (for $K[Sb_2F_7]$), 380°C and 595°C (for $Rb[Sb_2F_7]$) and 400°C and ca. 560°C (for $Cs[Sb_2F_7]$). The experimental results are compatible with the following thermal decomposition reaction of $K[Sb_2F_7]$ (I + II steps between 250 and 600°C)

$$K[Sb_2F_7] = KF \cdot SbF_3 + SbF_3\uparrow \qquad (6)$$

The theoretical mass loss calculated for this reaction is 43.0%, while the experimental result gives 45.0%. The proposed decomposition reactions of rubidium and caesium heptafluorodiantimonates(III) are as follows

$$Rb[Sb_2F_7] = RbF \cdot SbF_3 + SbF_3\uparrow (240\text{—}600°C) \qquad (7)$$

$$2.5\ Cs[Sb_2F_7] = 2.5\ CsF \cdot 3\ SbF_3 + 2\ SbF_3\uparrow (240\text{—}580°C) \qquad (8)$$

The mass losses calculated on the basis of eqns. (7) and (8) are 38.7% and 27.0% and those determined from TG curves are 40.0% and 27.0%, respec-

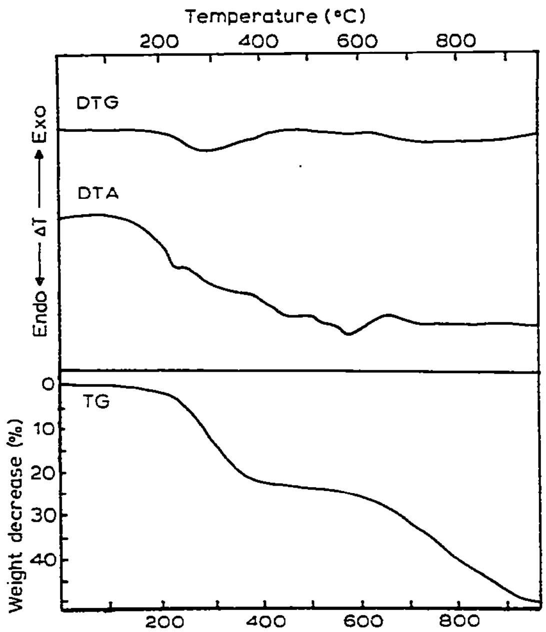


Fig. 4. Thermal analysis curves of Rb[Sb_4F_{13}].

tively. Further slow decomposition of the complexes M[Sb_2F_7] starts at about 800°C for K[Sb_2F_7] and Rb[Sb_2F_7] and at about 680°C for Cs[Sb_2F_7].

Complexes of the type M[Sb_4F_{13}]

Typical thermoanalytical curves are shown in Fig. 4. The thermal decomposition reactions of M[Sb_4F_{13}] (where M = K, Rb) are one-step processes which take place within the temperature range 140—400°C for K[Sb_4F_{13}] and 180—400°C for Rb[Sb_4F_{13}]. The corresponding peaks on the DTA curves of potassium and rubidium compounds are at 240 and 228°C and on the DTG curves at 290 and 320°C, respectively. On the basis of the experimental data the following reaction scheme can be supposed

$$M[Sb_4F_{13}] = MF \cdot 3\ SbF_3 + SbF_3\uparrow\ (M = K, Rb) \qquad (9)$$

The mass losses calculated according to eqn. (9) are 23.1% for K[Sb_4F_{13}] and 21.8% for Rb[Sb_4F_{13}]. The weight losses determined from TG curves are ca. 25.0% and 22.0%. The next slow decrease in mass, being a consequence of the second step of decomposition of K[Sb_4F_{13}] as well as the volatilization of the decomposition products, starts at ca. 570°C, and reaches 49.0% at 1000°C. The TG curve of Rb[Sb_4F_{13}] above the temperature of about 500°C drops slowly and the total weight loss at 1000°C amounts to 50.0%. The first step of the decomposition of Cs[Sb_4F_{13}] begins at 220°C and finishes at ca. 460°C. The appropriate peaks on the DTA and DTG curves are at 227 and 330°C, respectively. Within the temperature range 460—600°C a small mass loss (ca. 10%) is observed. The experimental weight loss (34.5%) is in good agreement with the theoretical value calculated from the following reaction (33.0%)

$$2.5\ Cs[Sb_4F_{13}] = 2.5\ CsF \cdot 6\ SbF_3 + 4\ SbF_3\uparrow \qquad (10)$$

Kinetic analysis of thermogravimetric data

Reaction order and apparent activation energy of the first steps of decomposition of the compounds under study were calculated from thermogravimetric data. Using the method of Coats and Redfern [21] the following plots were drawn

$$y = \log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-\alpha)}\right] \text{ vs. } 1/T \text{ for } n = 0, 1/2, 2$$

and

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

where α is the fraction of the substance decomposed at temperature T and n is reaction order. The values of n for which straight lines were obtained were chosen as correct reaction orders. From the slopes of lines activation energies were calculated. In order to determine kinetic parameters the method of Zsako [22] was also employed. 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 order reactions using an analytical form of the function $g(\alpha)$ given in the literature [22]. The values of $-\log p(x)$ for different temperatures and activation energies were taken from ref. 22. For intermediate E_a

TABLE 1

Kinetic parameters of decomposition reactions of fluoroantimonates(III)

Compound	No. of reaction	Range of α	Method of Coats and Redfern [21]		Method of Zsako [22]	
			n	E_a (kcal/mole^{-1})	n	E_a (kcal/mole^{-1})
$K_2[SbF_5]$	1	0.2 —0.9	0	6.1		
$Rb_2[SbF_5]$	2	0.2 —0.8	0	8.8		
$Cs_2[SbF_5]$						
$K[SbF_4]$	3	0.08—0.80	2	15.0	2	15.7
$Rb[SbF_4]$	4	0.1 —0.9	0	15.2		
$Cs[SbF_4]$	5	0.1 —0.9	2	18.9	2	19.4
$K[Sb_2F_7]$	6	0.08—0.9	1	14.1	1	14.3
$Rb[Sb_2F_7]$	7	0.07—0.9	1	14.4	1	15.0
$Cs[Sb_2F_7]$	8	0.08—0.7	1	13.5	1	13.7
$K[Sb_4F_{13}]$	9	0.08—0.9	2	14.7	2	15.0
$Rb[Sb_4F_{13}]$	9	0.1 —0.9	2	17.0	2	17.7
$Cs[Sb_4F_{13}]$	10	0.05—0.6	2	17.4	2	17.9

values the corresponding $-\log p(x)$ values were found by means of linear interpolation. The agreement between experimental data and presumed E_a was characterized by standard deviation δ of individual B values from their arithmetical mean $\bar{B}$. The final results of calculations of kinetic parameters are shown in Table 1.

DISCUSSION

The thermal decomposition of the crystalline complexes of the types $M_2[SbF_5]$, $M[SbF_4]$, and $M[Sb_4F_{13}]$ (where M = K, Rb, Cs) are single-staged processes while the compounds of the general formula $M[Sb_2F_7]$ decompose in two steps. In the course of decomposition gaseous SbF_3 is liberated. The thermal stability of the compounds under study defined by the temperature of the first endothermic peak on the DTA curve corresponding to the decomposition decreases in the order: potassium salts > rubidium salts > caesium salts. It is inconsistent with the results of most of the publications [23—30] that the thermal stability of complexes increases with increasing radius of the monovalent cation, although there are a number of works leading to the reverse conclusions [31—34]. On the other hand, the ratio of the number of moles of SbF_3 liberated to those bonded in the compound heated decreases, with the exception of $Cs[Sb_4F_{13}]$, in the same order, suggesting an increase of resistance against the thermal decomposition. Compounds of the type $M_2[SbF_5]$ are distinctly more stable than the other complexes whose thermal stabilities differ slightly. Also, the difference in stability between rubidium and caesium salts is always smaller than between potassium and rubidium salts. At higher temperatures the decreases in mass connected with further slow decomposition and evaporation of alkali metal fluorides are observed but they were not studied in detail. Using the Coats—Redfern and Zsako's methods, the kinetic parameters of the decomposition reactions were calculated from the thermogravimetric data. The results are presented in Table 1. In all kinds of complexes under study, the apparent activation energy increases in the order K → Cs.

The E_a values calculated by the method of Zsako are always a little higher (1—4%) than those calculated by the Coats—Redfern method. Some of the conclusions drawn above become clearer in the light of the structural informations available for the investigated fluoroantimonates. X-Ray studies have been made of a number of these complexes [1—13] the point of interest being the arrangement of fluorine atoms about the antimony atom. Complexes of the type $M_2[SbF_5]$ are isomorphous [3]. The F atoms around the Sb atom occupy five corners of an octahedron, the sixth corner being occupied by the stereochemically active pair of electrons. The discrete mononuclear anions SbF_5^{2-} are formed (Fig. 5a). The mean distance of Sb—5 F is 2.03 Å. The complexes $M[SbF_4]$ all have different structures. In $K[SbF_4]$ [4] the five fluorine atoms occupy, five of the six corners of an octahedron, as in $M_2[SbF_5]$. Two F atoms are shared between two Sb atoms and thus large tetranuclear complexes of formula $Sb_4F_{16}^{4-}$ are formed (Fig. 5b), these being cemented together by the potassium atoms. The mean

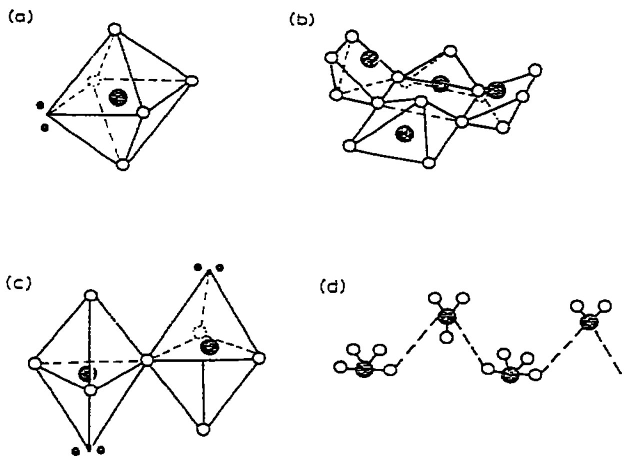


Fig. 5. (a) Mononuclear anion SbF_5^{2-}; (b) tetranuclear anion $Sb_4F_{16}^{4-}$; (c) binuclear anion $Sb_2F_7^{2-}$ in $Cs[Sb_2F_7]$; (d) chain $(—SbF_3—SbF_4^-)_x^{x-}$ in $K[Sb_2F_7]$.

distance Sb—F for the fluorine atoms linked to only one Sb atom is 2.01 Å and the mean distance in Sb—F—Sb bridges is 2.24 Å.

In the structures of $Rb[SbF_4]$ and $Cs[SbF_4]$ the distorted tetranuclear complexes are formed, the distortion being stronger in the caesium salt [12]. The compounds $M[Sb_2F_7]$ have different structures [2,7,13]. In $Cs[Sb_2F_7]$ the Sb atoms are surrounded by four fluorine atoms situated at four of the five corners of a trigonal bipyramid. The fifth corner in the axial position is occupied by the stereochemically active pair of electrons. Two bipyramids share one fluorine atom so that discrete anions $Sb_2F_7^-$ are formed (Fig. 5c). The Sb—F distance in the Sb—F—Sb bridge is 2.22 Å. Mastin and Ryan [6] show that the structure of $K[Sb_2F_7]$ is quite different. It is built up of SbF_4^- ions and SbF_3 molecules joined together by the Sb—F—Sb bridges to infinite chains $(—SbF_3—SbF_4^-)_x^{x-}$ (Fig. 5d). In the complexes $M[Sb_2F_7]$ the Sb—F distances in the Sb—F—Sb bridges are

$$\mathrm{Sb} \overset{2.24\ \text{Å}}{} \mathrm{F} \overset{2.24\ \text{Å}}{} \mathrm{Sb} \text{ in } Cs[Sb_2F_7]$$

$$\cdots \mathrm{Sb} \overset{2.05 \times 2.24\ \text{Å}}{} \mathrm{F} \overset{2.24\ \text{Å} \times 2.55\ \text{Å}}{} \mathrm{Sb} \cdots \text{ in } Rb[Sb_2F_7]$$

$$\mathrm{Sb} \overset{2.05\ \text{Å}}{} \mathrm{F} \overset{2.55\ \text{Å}}{} \mathrm{Sb} \overset{2.55\ \text{Å}}{} \mathrm{F} \overset{2.05\ \text{Å}}{} \mathrm{Sb} \text{ in } K[Sb_2F_7]$$

The compounds $M[Sb_4F_{13}]$ form an isomorphous series with tetragonal symmetry [1]. In these structures four SbF_3 molecules are arranged around the 13th F atom. The Sb—F distances within the SbF_3 molecule are about 2.0 Å and the distances to the central 13th fluorine atom are about 3 Å. The individuality of SbF_3 molecules in $Sb_4F_{13}^-$ groups is preserved. The results of the structural investigations indicate that the trivalent antimony atoms has no fixed coordination number, but has instead an ability to change its coordination number (CN) after the ratio SbF_3: MF and the radius of the outer sphere cation. In the complexes under study the CN decreases with increase in the ratio SbF_3 : MF and with increasing radius of the cation. Thus we find CN = 5 in $M_2[SbF_5]$ and $M[SbF_4]$, Cn = 4 and 5 in $K[Sb_2F_7]$, CN = 4 in $Cs[Sb_2F_7]$ and CN = 3 in $M[Sb_4F_{13}]$. The compounds with small SbF_3 : MF ratio forming discrete mononuclear complexes are distinctly more stable than the complexes forming polymeric anions with Sb—F—Sb bridges. The $Cs[Sb_2F_7]$, built up of discrete, binuclear anions, is a little more stable than $Rb[Sb_2F_7]$. The decrease in the thermal stability of the complexes $M[SbF_4]$ with increasing radius of M is probably caused by the increasing deformation of the large tetranuclear anions $Sb_4F_{16}^{4-}$. It seems that the thermal stability of the complexes $M[Sb_4F_{13}]$ built up of independent SbF_3 groups loosely joined to the 13th F atom and the $K[Sb_2F_7]$ built up of polymeric anions $(Sb_4^-...SbF_3)_x^{x-}$ should be distinctly smaller than the stability of the other compounds with polymeric anions, but it is not observed. Perhaps the loss of one molecule of SbF_3 leads to another more stable crystalline phase. In the series of isomorphous compounds the reaction order is the same.

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