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Studies on thermal decomposition of caesium–sodium fluoro- and iodothiocyanatobismuthates(III)

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Abstract

The thermal decomposition of caesium–sodium fluoro- and iodothiocyanatobismuthates(III) having the formulae $Cs_2Na[Bi(SCN)_3I_3]$, $Cs_2Na[Bi(SCN)_2I_4]$, $Cs_2Na[Bi_2(SCN)_5I_4]$, $Cs_2Na[Bi_2(SCN)_7F_2]$ and $Cs_2Na[Bi_2(SCN)_6F_3]$ has been examined. The thermal analysis curves of the complexes and the results of chemical and X-ray analyses of the solid pyrolysis products are presented. The results have been used to determine the three stages of thermal decomposition. Reactions occurring in each stage are described. The reaction order and activation energy of each stage have been calculated by means of the methods of Coats–Redfern and Zsakó. The mechanisms of decomposition and the thermal stability of all caesium–sodium halidothiocyanatobismuthates(III) so far obtained have been compared.

INTRODUCTION

Among the publications discussing the properties of bismuth(III) complexes there are several referring to compounds containing SCN^- ion in the inner sphere. The thiocyanate ion is a ligand with a strong ability to form complexes, and it can form complex ions with Bi^{3+} ion in acid medium. The anions formed in this way may form simple and double crystal complexes with a number of metals. In such compounds, the coordination number of bismuth is usually 6. A few bismuth(III) compounds containing other ligands along with SCN^- ions in their inner sphere are also known. However, thermal examinations of heteroligand thiocyanatobismuthates(III) have seldom been reported. Reference 1 presented the TG curve and the temperature of decomposition (180–200°C) of $Bi(C_7H_6N_2S)_3(SCN)_3$ but it did not give any data about the reaction of decomposition of the complex. Loginov et al. [2] treated the thermal decomposition as an auxiliary method to examine the properties of $(NH_4)_2Bi(nta)(SCN)_2 \cdot 2H_2O$ (where nta is nitrilotriacetic acid).

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Ladzińska-Kulińska [3,4] described the mechanism of thermal decomposition of thiocyanatothiocarbamidobismuthates(III) of the formula M[Bi-$(SCN)_4(TU)_2$] (where M = Li, Na, K, Rb, Cs or NH_4; TU = thiourea). The pyrolysis proceeds in three stages, and the final products are metallic bismuth, bismuth sulphide and the sulphate of the respective metal. The author calculated the reaction order and activation energy for the first and the third stage of decomposition.

The purpose of this paper, which is a continuation of our previous studies [5,6], was to establish the mechanism of thermal decomposition of caesium–sodium fluoro- and iodothiocyanatobismuthates(III). The reactions of decomposition and the thermal stability of the compounds under examination were compared with the data obtained for the previously discussed chloro- and bromothiocyanate complexes. Reaction order and activation energy were calculated for all the caesium–sodium halidothiocyanatobismuthates(III).

EXPERIMENTAL

Preparation

Caesium–sodium fluoro- and iodothiocyanatobismuthates are obtained as a result of reaction of an aqueous solution of the respective sodium halide (NaX) of a defined concentration with solid caesium tetrathiocyanatobismuthate(III), which is a coordinationally unsaturated compound of bismuth(III) [7]. When $Cs[Bi(SCN)_4]$ is treated with the halide solution, reactions of addition and substitution occur. The following amounts of substrates were used (the volume of NaX solution was 5ml): for $Cs_2Na[Bi(SCN)_3I_3]$ 2 mol l^{-1} NaI and 2.7 g of $Cs[Bi(SCN)_4]$, for $Cs_2Na[Bi(SCN)_2I_4]$ 3 mol l^{-1} NaI and 3.0 g of $Cs[Bi(SCN)_4]$, for $Cs_2Na[Bi_2(SCN)_5I_4]$ 1 mol l^{-1} NaI and 3.3 g of $Cs[Bi(SCN)_4]$, and for $Cs_2Na[Bi_2(SCN)_7F_2]$ and $Cs_2Na[Bi_2(SCN)_6F_3]$ 1 mol l^{-1} NaF and 3.5 g and 2.5 g of $Cs[Bi(SCN)_4]$, respectively. The mixtures of reagents prepared in this way were shaken for 2 h, then filtered, and the precipitates were dried at room temperature.

Thermal analysis

Thermal analyses were carried out using an MOM Budapest OD-102/1500°C thermal analyser. Samples of 200 mg were heated in porcelain crucibles in air over the temperature range 20–1000°C at a heating rate of 5°C min^{-1}. The sensitivity for the DTA curve was 1/15, for the DTG curve 1/20 and for the TG curve. 200 mg α-Al_2O_3 was used as the reference material. Table 1 lists the temperatures and the corresponding DTA peaks

TABLE 1

Temperatures, DTA peaks and temperature ranges of decomposition stages of caesium–sodium fluoro- and iodothiocyanatobismuthates(III)

Compound	Beginning of the first exothermic peak (°C)	DTA peaks (°C)	Ranges of decomposition stages (°C)
$Cs_2Na[Bi(SCN)_3I_3]$	210	210 endo	
		240 exo	210–280
		380 exo	280–400
		440 exo	400–470
		570 endo	
$Cs_2Na[Bi(SCN)_2I_4]$	210	210 endo	
		240 exo	210–280
		350 exo	280–390
		420 exo	390–430
		550 endo	
		580 endo	
$Cs_2Na[Bi_2(SCN)_5I_4]$	150	150 endo	
		230 exo	150–260
		330 exo	260–390
		440 exo	390–490
$Cs_2Na[Bi_2(SCN)_7F_2]$	190	150 endo	
		230 exo	150–260
		310 exo	260–360
		430 exo	360–460
		540 exo	
		840 endo	
$Cs_2Na[Bi_2(SCN)_6F_3]$	200	150 endo	
		240 exo	150–260
		310 exo	260–360
		420 exo	360–460
		540 exo	

of the compounds under study and the temperature ranges of the stages of thermal decomposition.

The thermal analysis curves of $Cs_2Na[Bi(SCN)_3I_3]$ are presented in Fig. 1. The first endothermic peak (210°C) is small; the next three exothermic peaks correspond with the successive stages of thermal decomposition and they are accompanied by continuous mass loss observed in the TG curve. Above 470°C a rapid mass loss occurs, which results from the decomposition of the products of the third stage of pyrolysis.

The thermal analysis curves of $Cs_2Na[Bi(SCN)_2I_4]$ are slightly different from those described above. The exothermic peaks in the DTA curve are less intense and the loss in mass corresponding with the successive stages of

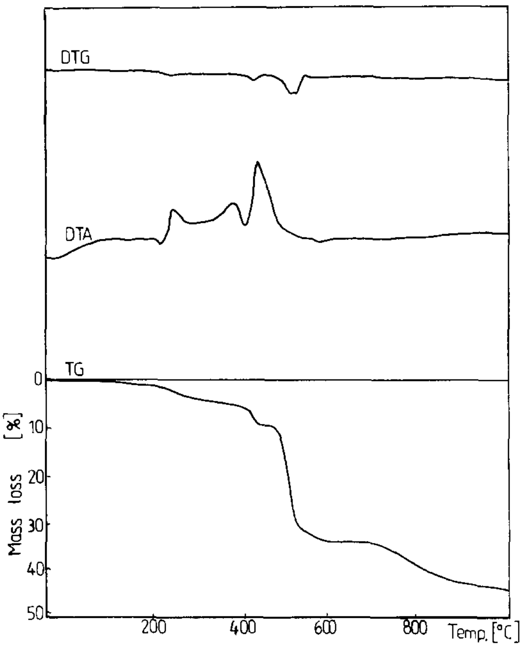

Fig. 1. Thermal analysis curves of $Cs_2Na[Bi(SCN)_3I_3]$.

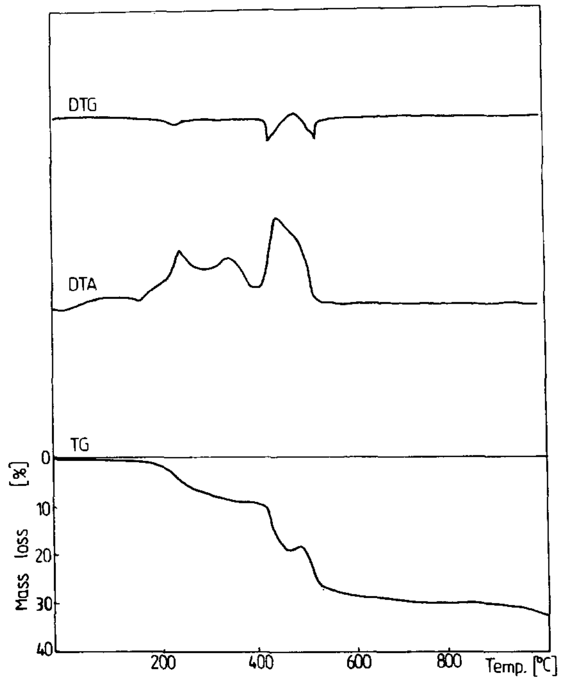

Fig. 2. Thermal analysis curves of $Cs_2Na[Bi_2(SCN)_5I_4]$.

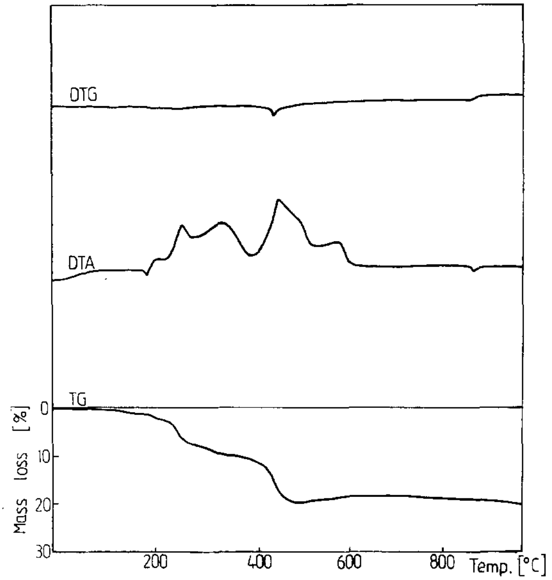

Fig. 3. Thermal analysis curves of $Cs_2Na[Bi_2(SCN)_7F_2]$.

decomposition is smaller, whereas the mass loss resulting from the decomposition of the products of the third stage is greater and the process occurs at 430°C.

Figure 2 presents the thermal analysis curves of $Cs_2Na[Bi_2(SCN)_5I_4]$. The temperature of the first endothermic peak is much lower (150°C) than in the case of the two salts discussed above. The shapes of the TG and DTA curves are also different (the successive decomposition stages are clearly visible; the mass loss above 490°C is considerably lower, and the exothermic peaks corresponding with the stages of pyrolysis are more intense).

The DTA curve for $Cs_2Na[Bi_2(SCN)_7F_2]$ (Fig. 3) has a shape similar to that for $Cs_2Na[Bi_2(SCN)_5I_4]$. The difference consists in the presence of the fourth exothermic peak (540°C), which is probably related to the formation of $(BiO)_2SO_4$, and an endothermic peak at 840°C (corresponding with melting of Na_2SO_4 [8]). The TG curve reaches its minimum in the third stage of decomposition and remains stable up to about 900°C.

The course of the thermal curves of $Cs_2Na[Bi_2(SCN)_6F_3]$ is analogous to the shape of the curves for $Cs_2Na[Bi_2(SCN)_7F_2]$.

The comparison of the thermal curves of the compounds examined suggests that these complexes follow a three-stage course of decomposition. The decomposition is related to the exothermic effects (three clear peaks in the DTA curves) and to the continuous mass loss observed in the TG curves. The differences in the course of the TG curves of fluoro- and iodocomplexes indicate a slightly different mechanism of decomposition of these compounds.

TABLE 2

Results of chemical analyses of caesium–sodium fluoro- and iodothiocyanatobismuthates(III)

Compound	Temp. (°C)	Composition of sinter		Eqn.
		Detected	Calculated	
$Cs_2Na[Bi(SCN)_3I_3]$	380	21.65% Bi 4.51% S 1.18% C 1.91% N mass loss 5.72%	21.04% Bi 4.26% S 1.17% C 1.85% N mass loss 5.63%	(4)
	460	22.70% Bi 3.49% S mass loss 9.20%	21.68% Bi 3.88% S mass loss 8.44%	(7)
	600	31.93% Bi 4.14% S	30.86% Bi 3.94% S	(11)
	800	34.01% Bi 4.38% S	32.97% Bi 4.21% S	(12)
$Cs_2Na[Bi(SCN)_2I_4]$	380	20.86% Bi 2.47% S 0.38% C 0.52% N mass loss 4.23%	19.48% Bi 2.35% S 0.41% C 0.56% N mass loss 4.32%	(5)
$Cs_2Na[Bi_2(SCN)_5I_4]$	260	30.72% Bi 5.83% S 2.52% C 3.20% N mass loss 6.22%	29.42% Bi 5.64% S 2.25% C 3.24% N mass loss 5.60%	(3)
	380	31.97% Bi 5.26% S 1.94% C 2.68% N mass loss 9.20%	30.60% Bi 4.96% S 1.46% C 2.34% N mass loss 9.22%	(6)
	460	35.55% Bi 4.81% S mass loss 18.66%	34.15% Bi 4.58% S mass loss 18.67%	(8)
$Cs_2Na[Bi_2(SCN)_7F_2]$	260	38.51% Bi 13.45% S 5.13% C 7.37% N mass loss 7.71%	39.37% Bi 13.41% S 5.06% C 7.36% N mass loss 7.78%	(1)
	460	44.22% Bi 10.53% S mass loss 19.40%	44.64% Bi 10.61% S mass loss 18.67%	(9)
$Cs_2Na[Bi_2(SCN)_6F_3]$	260	39.51% Bi 12.63% S 4.24% C 6.27% N mass loss 6.47%	40.27% Bi 12.13% S 4.38% C 6.32% N mass loss 6.67%	(2)

TABLE 2 (continued)

Compound	Temp. (°C)	Composition of sinter		Eqn.
		Detected	Calculated	
$Cs_2Na[Bi_2(SCN)_6F_3]$	460	44.54% Bi 9.98% S mass loss 16.91%	45.10% Bi 9.94% S mass loss 16.68%	(10)

The mechanism of thermal decomposition of caesium–sodium fluoro- and iodothiocyanatobismuthates(III) was determined on the basis of chemical and X-ray analyses of the solid pyrolysis products. For this purpose, sinters of the compounds under study were prepared under conditions similar to those for the thermal analysis. Samples of 200 mg were heated in a drier or a silite furnace at a heating rate of about 5°C min^{-1} up to a temperature determined from the thermal curves while the mass loss was compared with the corresponding values on the TG curve.

Chemical analysis

The chemical composition of the solid decomposition products was determined on the basis of the content of bismuth [9], sulphur [10] and nitrogen and carbon (elemental analysis). The sinters were leached with water and the composition of the water-soluble and water-insoluble fractions was analysed. The content of sulphates in the water-soluble fraction was determined by a gravimetric method, the content of thiocyanates by bromatometry, the content of fluorides by argentometry (after precipitation in the form of PbClF [11]) and the sum of iodides and thiocyanates also by argentometry. Table 2 presents the results of the analysis of the sinters.

X-ray analysis

X-ray analysis was carried out on a DRON-1 diffractometer using Cu $K\alpha$ radiation and a nickel filter. The diffraction curves were recorded over the range $2\theta = 2$–60°. Table 3 compares the reflexes occurring in the diffraction pattern of $Cs_2Na[Bi(SCN)_3I_3]$ sinter obtained at 380°C with the literature data.

Methods applied to determine the kinetic parameters

Two integral methods, those of Coats–Redfern [12] and Zsakó [13], were used to determine the reaction order n and activation energy E of each stage of thermal decomposition of the caesium–sodium halidothiocyanato-

TABLE 3

X-ray identification of $Cs_2Na[Bi(SCN)_3I_3]$ sinter (380°C)

Data from X-ray patterns of the sinter		Literature data	
2θ (deg)	d/n (Å)	d/n (Å)	Compound
13.0	6.81	6.86	$Cs_3Bi_2I_9$
21.3	4.17	4.20	$Cs_3Bi_2I_9$
24.3	3.66	3.68	Cs_2SO_4
25.5	3.49	3.51	$Cs_3Bi_2I_9$
26.1	3.41	3.45	$Cs_3Bi_2I_9$
27.7	3.22	3.23	NaI
		3.23	CsI
		3.23	$Cs_3Bi_2I_9$
28.3	3.15	3.18	Na_2SO_4
		3.14	Cs_2SO_4
29.4	3.04	3.07	Na_2SO_4
30.0	2.98	3.00	$Cs_3Bi_2I_9$
32.6	2.74	2.78	Na_2SO_4
33.7	2.66	2.65	Na_2SO_4
		2.65	Cs_2SO_4
43.2	2.09	2.11	Cs_2SO_4
46.2	1.96	1.95	NaI
49.1	1.85	1.87	CsI
		1.87	NaI
		1.86	Na_2SO_4
51.0	1.79	1.80	Cs_2SO_4
		1.80	Na_2SO_4
52.2	1.75	1.75	$Cs_3Bi_2I_9$
56.7	1.62	1.62	NaI
		1.61	CsI

bismuthates(III). A computer programme was used for calculations. The results are presented in Table 4.

DISCUSSION

A comparison of the results of thermal, chemical and X-ray analyses allows us to conclude that the thermal decomposition of caesium–sodium fluoro- and iodothiocyanatobismuthates(III) proceeds in three stages, which are discussed below. The mechanisms of pyrolysis of these compounds are similar, and are associated with the mass loss observed in the TG curves and the presence of exothermic peaks in the DTA curves.

Stage I

The analysis of the thermal curves allows only an approximate determination of the temperature range limits in this stage. The shape of the TG

TABLE 4

Kinetic parameters and initial decomposition temperatures of halidothiocyanatobismuthates(III)

Compound	First stage				Second stage				Third stage				Initial decomposition temp. (°C)
	Z [a]		C–R [b]		Z		C–R		Z		C–R		
	n [c]	*E* [d]	*n*	*E*	*n*	*E*	*n*	*E*	*n*	*E*	*n*	E	
$Cs_2Na[Bi(SCN)_4Cl_2]$	1.9	89.0	2.0	91.4	1.9	33.0	2.0	34.0	1.1	54.0	1.1	54.7	210
$Cs_2Na[Bi(SCN)_3Cl_3]$	1.9	86.0	2.0	89.3	0.1	12.0	0.0	11.2	1.6	61.0	1.6	60.8	205
$Cs_2Na[Bi(SCN)_2Cl_4]$	1.9	80.0	2.0	82.5	0.0	13.0	0.0	13.1	1.0	51.0	1.0	51.1	200
$Cs_2Na[Bi_2(SCN)_7Cl_2]$	1.8	60.0	2.0	61.1	1.6	37.0	1.6	37.4	1.2	72.0	1.2	71.8	220
$Cs_2Na[Bi_2(SCN)_6Cl_3]$	0.8	67.0	0.8	68.1	1.8	40.0	1.8	40.1	0.6	66.0	0.6	65.7	200
$Cs_2Na[Bi(SCN)_3Br_3]$	1.1	45.0	1.1	44.9	1.5	32.0	1.5	31.3	1.0	51.0	1.0	51.3	210
$Cs_2Na[Bi(SCN)_2Br_4]$	1.1	51.0	1.1	50.3	0.6	22.0	0.6	21.8	1.4	38.0	1.4	38.0	210
$Cs_2Na[Bi_2(SCN)_7Br_2]$	1.1	75.0	1.1	74.8	1.3	36.0	1.3	35.6	1.7	68.0	1.8	69.9	205
$Cs_2Na[Bi_2(SCN)_6Br_3]$	1.9	79.0	2.0	80.8	1.6	26.0	1.6	25.5	1.9	94.0	2.0	97.0	205
$Cs_2Na[Bi(SCN)_3I_3]$	0.4	28.0	0.3	27.7	0.8	25.0	0.8	24.7	1.2	42.0	1.2	42.1	200
$Cs_2Na[Bi(SCN)_2I_4]$	0.6	29.0	0.6	28.7	1.7	27.0	1.7	26.8	1.5	40.0	1.4	39.0	210
$Cs_2Na[Bi_2(SCN)_5I_4]$	0.5	18.0	0.5	17.6	0.0	11.0	0.1	11.1	1.4	84.0	1.4	84.0	155
$Cs_2Na[Bi_2(SCN)_7F_2]$	0.1	19.0	0.1	18.7	1.9	35.0	2.0	35.7	1.0	54.0	1.0	53.5	165
$Cs_2Na[Bi_2(SCN)_6F_3]$	0.0	16.0	0.0	16.3	1.4	32.0	1.4	31.9	1.6	74.0	1.7	75.5	170

[a] Zsako's method

[b] Coats and Redfern's method.

[c] Order of reaction.

[d] Activation energy (kcal mol^{-1}).

curve in this stage did not allow us to prepare sinters of the mononuclear complexes. Equations (1)–(3) represent the reactions at 260°C

$$\begin{aligned}&6Cs_2Na[Bi_2(SCN)_7F_2]\\&\xrightarrow{O_2} 3Bi_2S_3 + 6BiS_{0.86}C_{3.06}N_{4.16}F_{1.75} + 1.5MF + 8.5MNCS + 4M_2SO_4\\&\qquad + \text{gaseous products}\end{aligned}\tag{1}$$

$$\begin{aligned}&6Cs_2Na[Bi_2(SCN)_6F_3]\\&\xrightarrow{O_2} 3Bi_2S_3 + 6BiS_{0.26}C_{2.2}N_{3.1}F_{2.75} + 1.5MF + 9.5MNCS + 3.5M_2SO_4\\&\qquad + \text{gaseous products}\end{aligned}\tag{2}$$

$$\begin{aligned}6Cs_2Na[Bi_2(SCN)_5I_4] \xrightarrow{O_2} {}& Cs_3Bi_2I_9 + 10BiS_{0.45}C_{1.0}N_{1.37}I_{1.5} + 6MNCS\\& + 4M_2SO_4 + \text{gaseous products}\end{aligned}\tag{3}$$

where $M = Cs$ or Na and the sum of caesium and sodium atoms is 18 (the number of caesium atoms is 12, and that of sodium atoms is 6). The equations give the solid products of decomposition; the composition of the gaseous products was not examined.

In equations (1)–(3) it can be seen that one of the products in all the sinters is an intermediate compound of the formula $BiS_xC_yN_sX_z$. The composition of this compound is different for different initial salts, and moreover it depends on the conditions of decomposition. The compound $Cs_3Bi_2I_9$ is present in the sinter of $Cs_2Na[Bi_2(SCN)_5I_4]$. No analogous fluoride compound was found in the product of pyrolysis of fluorocomplexes, whereas the presence of Bi_2S_3 was observed in this instance. The ratio at which thiocyanates, sulphates and caesium and sodium fluoride occur is not known.

Stage II

Reactions occurring in stages I and II of the pyrolysis partly overlap. The changes are exothermic and the loss in mass observed in the TG curves is slower than in stage I. Equations (4)–(6) illustrate the decomposition reactions of caesium–sodium iodothiocyanatobismuthates(III) at 380°C

$$\begin{aligned}6Cs_2Na[Bi(SCN)_3I_3] \xrightarrow{O_2} {}& Cs_3Bi_2I_9 + 4BiS_{0.98}C_{1.45}N_{1.79}I_{0.5} + 4M_2SO_4\\& + 7MI + \text{gaseous products}\end{aligned}\tag{4}$$

$$\begin{aligned}6Cs_2Na[Bi(SCN)_2I_4] \xrightarrow{O_2} {}& Cs_3Bi_2I_9 + 4BiS_{0.43}C_{0.55}N_{0.65}I_{1.5} + 3M_2SO_4\\& + 9MI + \text{gaseous products}\end{aligned}\tag{5}$$

$$\begin{aligned}6Cs_2Na[Bi_2(SCN)_5I_4] \xrightarrow{O_2} {}& Cs_3Bi_2I_9 + 10BiS_{0.45}C_{1.0}N_{1.37}I_{1.29}\\& + 7.5M_2SO_4 + \text{gaseous products}\end{aligned}\tag{6}$$

The main reaction of the second stage is oxidation of sodium and caesium thiocyanates to the corresponding sulphates. The intermediate compound begins to decompose (eqn. (6)).

Stage III

The last stage of pyrolysis of the complexes under study is the most distinct, except in the case of $Cs_2Na[Bi(SCN)_2I_4]$, where the exothermic peak is very weak and the loss in mass is continuous. Equations (7)–(10) show the reactions of the third stage of thermal decomposition

$$6Cs_2Na[Bi(SCN)_3I_3] \xrightarrow{O_2} Cs_3Bi_2I_9 + Bi_2S_3 + 2BiOI + 4M_2SO_4 + 7MI + \text{gaseous products} \quad (7)$$

$$6Cs_2Na[Bi_2(SCN)_5I_4] \xrightarrow{O_2} Cs_3Bi_2I_9 + Bi_2S_3 + 8BiOI + 7.5M_2SO_4 + \text{gaseous products} \quad (8)$$

$$6Cs_2Na[Bi_2(SCN)_7F_2] \xrightarrow{O_2} 3Bi_2S_3 + (BiO)_2SO_4 + 4BiOF + 1.5MF + 8.25M_2SO_4 + \text{gaseous products} \quad (9)$$

$$6Cs_2Na[Bi_2(SCN)_6F_3] \xrightarrow{O_2} 3Bi_2S_3 + 6BiOF + 8.25M_2SO_4 + 1.5MF + \text{gaseous products} \quad (10)$$

From the equations presented above it is evident that in the third stage the intermediate product is decomposed, which leads to the formation of bismuthyl halide and bismuth sulphide.

The proposed mechanism of thermal decomposition is in accordance with the results of the analysis of solid products of pyrolysis (Table 2), and was confirmed by the analysis of water-soluble and insoluble fractions and by the diffractometric method. As a result of the thermal decomposition of caesium–sodium fluoro- and iodothiocyanatobismuthates(III) the mass of the samples continuously decreases. The more thiocyanate groups in the initial compound, the greater the mass loss; the loss is considerably greater for binuclear complexes. The stages of pyrolysis partly overlap, which makes the interpretation of the thermal curves difficult and sometimes even impossible.

When the third stage of the decomposition of caesium–sodium fluorothiocyanatobismuthates(III) ends (at 460°C) the mass of the sinters grows slightly as a result of oxidation of Bi_2S_3 to $(BiO)_2SO_4$ (exothermic peak in the DTA curve at 540°C) and it then remains stable up to about 900°C.

The thermal curves of caesium–sodium iodothiocyanatobismuthates(III) differ considerably from those of fluorocomplexes. Following the end of the third stage of decomposition (470°C: $Cs_2Na[Bi(SCN)_3I_3]$, 430°C: $Cs_2Na[Bi(SCN)_2I_4]$ and 490°C: $Cs_2Na[Bi_2(SCN)_5I_4]$) a process occurs that is associated with a considerable loss in mass and weak endothermic peaks in the DTA curves in the temperature range of 550–580°C. The decomposition proceeds in two stages and the loss in mass is greater if the initial salt contains more iodide groups. Equations (11) and (12) represent the pyrolysis reactions of $Cs_2Na[Bi(SCN)_3I_3]$ at 600 and 800°C

$$6Cs_2Na[Bi(SCN)_3I_3] \xrightarrow{O_2} Bi_2O_3 + 2BiOI + (BiO)_2SO_4 + 4M_2SO_4 + 6MI + \text{gaseous products} \quad (11)$$

$$6Cs_2Na[Bi(SCN)_3I_3] \xrightarrow{O_2} Bi_2O_3 + 2BiOI + (BiO)_2SO_4 + 4M_2SO_4 + 5MI + \text{gaseous products} \quad (12)$$

The considerable loss in mass is caused by the decomposition of $Cs_3Bi_2I_9$ and formation of Bi_2O_3, CsI and I_2. Caesium iodide and iodine gradually evaporate from the sinter. This is in agreement with previous examinations of $Cs_3Bi_2I_9$ decomposition [14]. The decomposition of caesium iodobismuthate(III) begins at the lowest temperature (430°C: stage I, 600°C: stage II) in the case of $Cs_2Na[Bi(SCN)_2I_4]$, which is in agreement with the literature data. The decomposition begins at the highest temperature (490°C) for $Cs_2Na[Bi_2(SCN)_5I_4]$. The fact that the second stage of decomposition of $Cs_3Bi_2I_9$ in the sinter of the binuclear complex is not distinct may be due to the relatively low content of CsI in the sinter.

The comparison of the results of the thermal analyses of caesium–sodium halidothiocyanatobismuthates(III) leads to the conclusion that the mechanisms of thermal decomposition of these salts are similar. The pyrolysis of the salts proceeds in three stages associated with the loss in mass and the occurrence of exothermic peaks in the DTA curves. In the first stage an intermediate compound of the formula $BiS_xC_yN_sX_z$, Bi_2S_3 or $Cs_3Bi_2X_9$ and caesium and sodium thiocyanates, sulphates and halides are formed. In the second stage, thiocyanates oxidize to form sulphates, and in the third stage the intermediate compound decomposes and bismuthyl halide, bismuth sulphide or bismuthyl sulphate is formed. The equations representing the reactions of thermal decomposition of salts having the same general formula differ in the proportions of the particular compounds making up the sinters. Certain differences result from different oxidation rates of bismuth sulphide, and, hence, the possibility of forming bismuth sulphide, bismuth sulphate or bismuthyl sulphate in the third stage. More marked differences occur when the products of the third stage of pyrolysis are further decomposed. This is due to the presence of some compounds of caesium halidobismuthate(III) in the sinter. The decomposition of $Cs_3Bi_2I_9$ is observed in all iodide–thiocyanate complexes, and it occurs at the temperature determined for pure $Cs_3Bi_2I_9$ [14,15]. The TG curves are slightly different from those for the other compounds because of a different mechanism of $Cs_3Bi_2I_9$ decomposition [14]. The temperature at which

$Cs_3Bi_2Br_9$ decomposes is a little higher in mononuclear compounds as compared with the literature data [15], and for chlorothiocyanatobismuthates(III) and binuclear bromothiocyanatobismuthates(III) the temperature of pyrolysis of $Cs_3Bi_2X_9$ is considerably higher than for pure caesium halidobismuthates(III). The presence of $Cs_3Bi_2F_9$ was not observed in the sinters of fluorocomplexes, and thus the TG curve at higher temperatures is different from the thermal curves of the other compounds.

The thermal stability of the complex salts determined on the basis of the beginning of the first exothermic peak changes in the order $Cs_2Na[Bi(SCN)_xCl_{6-x}] = Cs_2Na[Bi_2(SCN)_yCl_{9-y}] = Cs_2Na[Bi_2(SCN)_yBr_{9-y}]$ (240°C) > $Cs_2Na[Bi(SCN)_xBr_{6-x}] = Cs_2Na[Bi(SCN)_xI_{6-x}]$ (210°C) > $Cs_2Na[Bi_2(SCN)_6F_3]$ (200°C) > $Cs_2Na[Bi_2(SCN)_7F_2]$ (190°C) > $Cs_2Na[Bi_2(SCN)_5I_4]$ (150°C). These dependences change slightly when the value of activation energy in the first stage of pyrolysis is taken into consideration as the criterion (Table 4), no dependence being observed between activation energy and the temperature at which decomposition begins. However, in both cases it was found that the complexes $Cs_2Na[Bi_2(SCN)_5I_4]$, $Cs_2Na[Bi_2(SCN)_7F_2]$ and $Cs_2Na[Bi_2(SCN)_6F_3]$ ex-

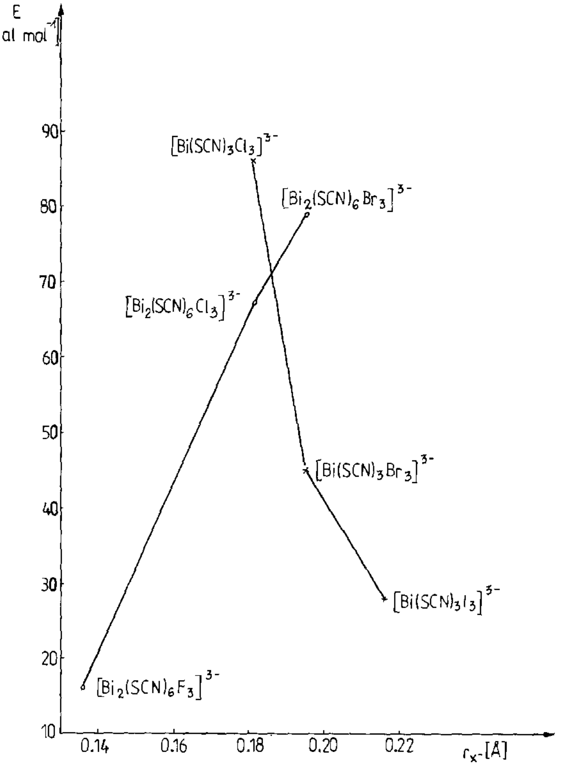

Fig. 4. Effect of the ionic radius of the halide on the activation energy of caesium–sodium halidothiocyanatobismuthates(III).

hibit the lowest stability. This fact may follow from the spatial factor (long radius of I^- ion and short radius of F^- ion). The most stable of the mononuclear complexes are those containing chloride ligands. The complexes with bromide ligands exhibit lower stability and those with iodide ligands are the least stable (the ratio of energy for these three groups of salts is approximately 3:1.7:1). Activation energies of binuclear chloro- and bromocomplexes do not exhibit such great differences. Figure 4 presents the dependence of activation energy upon the radius of the halide ligand. Complexes of analogous composition have been compared. From the dependences presented it follows that the compounds examined can be divided into two groups. The first group includes mononuclear complexes, the stability of which decreases in the order $Cl > Br > I$ (whereas the stability of chlorocomplexes in aqueous solutions is lower than the stability of bromocomplexes [16]) and the second group includes binuclear complexes, which have the reverse order of stability $F < Cl < Br$. It could be helpful to determine the structure of the salts under study in order to find an explanation of these dependences for mono- and binuclear chloro- and bromothiocyanatobismuthates.

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REFERENCES

1 B. Jeżowska-Trzebiatowska and T. Czagier, Rocz. Chem., 51 (1977) 21.
2 A.A. Loginov, M.A. Medkov, W.J. Karasev and R.L. Davidovich, Ukr. Khim. Zh., 55 (1989) 795.
3 H. Ladzińska-Kulińska, Thermochim. Acta, 33 (1979) 293.
4 H. Ladzińska-Kulińska, Thermochim. Acta, 42 (1980) 99.
5 A. Cygański and A. Turek, Thermochim. Acta, 137 (1989) 337.
6 A. Cygański and A. Turek, Thermochim. Acta, 164 (1990) 269.
7 A. Cygański, Rocz. Chem., 39 (1965) 193.
8 L. Erdey, J. Simon, S. Gál and G. Liptay, Talanta, 13 (1966) 67.
9 H. Flaschka and H. Jakoblevich, Anal. Chim. Acta, 4 (1950) 247.
10 W.D. Treadwell, Kurzes Lehrbuch der Analytischen Chemie, Franz Deuticke, Vienna, 1946.
11 M. Struszyński, Analiza ilościowa i techniczna, Warsaw, 1948.
12 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
13 J. Zsakó, J. Phys. Chem., 72 (1968) 2406.
14 K. Bogusławska, A. Cygański and J. Krystek, J. Therm. Anal., 31 (1986) 605.
15 M. Zalewicz and B. Ptaszyński, Pol. J. Chem., 53 (1979) 1437.
16 E. Józefowicz and H. Ladzińska-Kulińska, Symposium, The School of Coordination Chemistry, Karpacz, 1965. Unpublished work.