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STUDIES ON THE THERMAL DECOMPOSITION OF ALKALI METAL THIOSULPHATOBISMUTHATES(III)

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ABSTRACT

The thermal decomposition of thiosulphatobismuthates(III) of alkali metals was investigated. The general formulae of the thiosulphatobismuthates are $M_3[Bi(S_2O_3)_3] \cdot H_2O$ where M = Na, K, Rb or Cs, and $M_2Na[Bi(S_2O_3)_3] \cdot H_2O$ where M = K or Cs.

Typical thermal curves for thiosulphatobismuthates(III) and the results obtained in thermal, X-ray, chemical and spectrophotometrical analyses of the decomposition products are shown. The results were used to determine three stages of the thermal decomposition. At the first stage, at about 200°C, hydrated compounds are dehydrated. At the second stage, above 200°C, there is a rapid decrease in mass which is caused by evolving sulphur dioxide; bismuth sulphide and an intermediate decomposition product are formed. At about 320°C the thermal decomposition products are bismuth sulphide and alkali metal sulphate.

INTRODUCTION

Potassium thiosulphatobismuthate(III), $Bi_2(S_2O_3)_3 \cdot 3\,K_2S_2O_3 \cdot 2\,H_2O$, was obtained for the first time by Carnot [1]. Hauser [2] then synthesized the following compounds: $Na_3[Bi(S_2O_3)_3]$, $K_3[Bi(S_2O_3)_3] \cdot 1/2\,H_2O$, $Rb_3[Bi(S_2O_3)_3] \cdot H_2O$ and $Rb_3[Bi(S_2O_3)_3] \cdot 1/2\,H_2O$, $Cs_3[Bi(S_2O_3)_3]$, $Ba_3[Bi(S_2O_3)_3]_2$. The formation of $K_3[Bi(S_2O_3)_3] \cdot 1/2\,H_2O$ was also described by Dahr [3], Vanino and Mussgnug [4] obtained ammonium, sodium and strontium thiosulphatobismuthates(III). They also tried, but without success, to obtain beryllium, calcium, nickel and cobalt salts. Thallium thiosulphatobismuthate(III) was obtained by Cannneri [5].

The synthesis carried out by us [6] proved that, under the conditions described by Hauser [2], $K_5Na[Bi(S_2O_3)_3]_2 \cdot 2\,H_2O$, $Rb_3[Bi(S_2O_3)_3] \cdot H_2O$ and $Cs_2Na[Bi(S_2O_3)_3]$ occur. To obtain $K_3[Bi(S_2O_3)_3] \cdot H_2O$ and $Cs_3[Bi(S_2O_3)_3]$, calcium, potassium or caesium thiosulphate should be used for the synthesis. $Na_3[Bi(S_2O_3)_3] \cdot H_2O$ and $K_2Na[Bi(S_2O_3)_3] \cdot H_2O$ were obtained by means of a method developed by us [6]. It was not possible to obtain lithium thiosulphatobismuthate(III).

The subject of this paper is the investigation of the thermal decomposition of alkali metal thiosulphatobismuthates(III). The mechanism of thiosulphatobismuthate(III) thermal decomposition was examined in continuation

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of an investigation on the thermal decomposition of inorganic complex bismuth(III) salts [7—9].

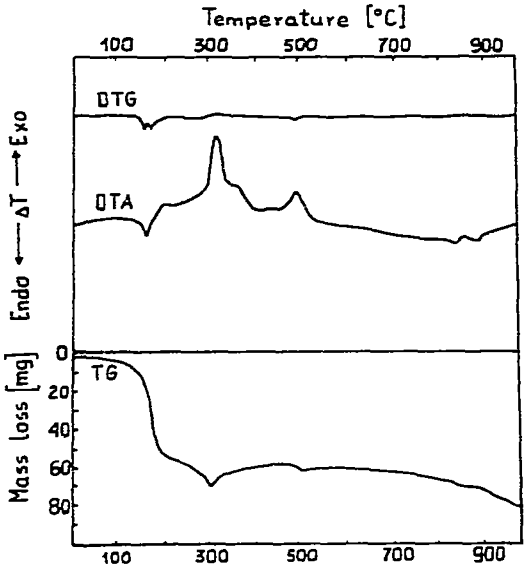
EXPERIMENTAL

Thermal analysis

Thermal analyses were carried out using a thermal analyzer MOM Budapest type OD-102/1500° C. The measurements were made in air, in the temperature range 20—1000° C, at a heating rate of 5° C min^{-1}. The sensitivity of the galvanometer for the DTA curve was 1/5 and for the DTG curve 1/20. TG sensitivity was 200 mg. α-Al_2O_3 was used as reference material. Each sample weighed 250 mg.

The thermal analysis curves of sodium thiosulphatobismuthate(III), $Na_3[Bi(S_2O_3)_3] \cdot H_2O$, and potassium thiosulphatobismuthate(III), $K_3[Bi(S_2O_3)_3] \cdot H_2O$, are shown in Figs. 1 and 2.

The DTA curve of sodium thiosulphatobismuthate(III) (Fig. 1) has three distinct peaks: an endothermic peak at 165° C, a very intense exothermic peak at 325° C and an exothermic peak at 500° C. The curve also has two weak endothermic peaks at 880 and 930° C. The endothermic peak at 165° C involves a rapid mass loss. The courses of the DTA and DTG curves suggest two transformations. First there occurs an endothermic transformation, followed by an exothermic one, involving considerable and rapid mass loss. The intense exothermic peak at 325° C involves rapid mass loss, followed by slow mass growth. The following peaks do not involve distinct mass changes.



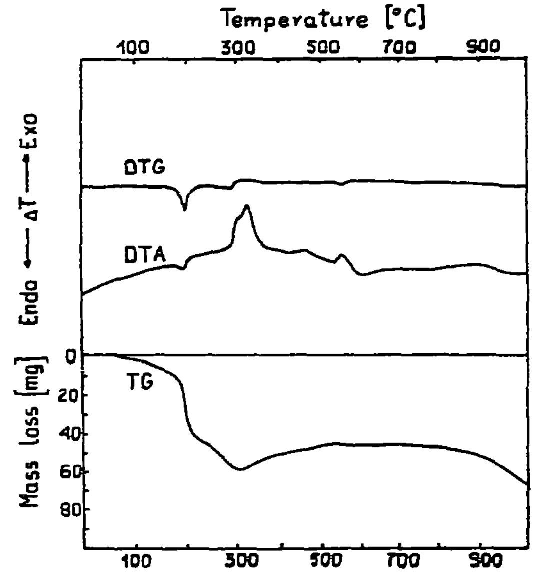


Fig. 1. Thermal analysis curves of sodium thiosulphatobismuthate(III).

Fig. 2. Thermal analysis curves of potassium thiosulphatobismuthate(III).

TABLE 1

DTA peak temperatures of thiosulphatobismuthates(III)

No.	Compound	Temperatures (°C) and characters of DTA peaks				
1	$Na_3[Bi(S_2O_3)_3] \cdot H_2O$	165-endo	325-exo intensive	500-exo	875-endo	930-endo
2	$K_3[Bi(S_2O_3)_3] \cdot H_2O$	190-endo	330-exo intensive	480-exo	560-exo	630-endo
3	$K_5Na[Bi(S_2O_3)_3]_2 \cdot 2\,H_2O$	190-endo	335-exo intensive	470-exo	560-exo	620-endo
4	$K_2Na[Bi(S_2O_3)_3] \cdot H_2O$	195-endo	330-exo intensive	400-exo	450-endo 470-exo	610-endo
5	$Rb_3[Bi(S_2O_3)_3] \cdot H_2O$	195-endo	320-exo intensive	450-exo	520-exo	620-endo
6	$Cs_2Na[Bi(S_2O_3)_3]$	205-exo	325-exo intensive	390-exo 455-exo	480-endo	590-endo
7	$Cs_3[Bi(S_2O_3)_3]$	210-exo	320-exo intensive	490-exo	530-endo	580-endo

The thermal curves of potassium thiosulphatobismuthate(III) (Fig. 2) follow similar courses. The first endothermic peak on the DTA curve, at 190° C, involves considerable mass loss, visible on the TG and DTG curves. At 330° C there occurs an intense exothermic peak on the DTA curve, with corresponding slow mass increase on the TG curve. Two exothermic peaks at 480 and 560° C and an endothermic peak at 630° C do not involve distinct mass changes.

The TG curves for the two compounds show that during the second stage of thermal decomposition, involving rapid mass loss, $Na_3[Bi(S_2O_3)_3] \cdot H_2O$ loses its mass to a far larger extent than $K_3[Bi(S_2O_3)_3] \cdot H_2O$. This suggests differences in the reactions in the second stage of decomposition. The temperatures and the characteristics of the peaks occurring on the DTA curves for all investigated thiosulphatobismuthates are shown in Table 1.

The reactions taking place during the thermal decomposition of thiosulphatobismuthates(III) were exemplified by investigation of the sinters of a potassium compound. Sinters of a sodium compound were also examined since their thermal curves, as well as analytical results, show slightly different character to the reaction suggested.

The sinters were obtained under conditions similar to those used in thermal analysis — i.e. 250 mg weighed samples of the compound were heated in an electric silite furnace at a heating rate of 5° C min^{-1}. On the basis of the TG curves (Figs. 1 and 2) the temperatures for obtaining the sinters were 200, 320, 700 and 1000° C for the potassium compound, and 200, 300, 550 and 900° C for the sodium compound.

Chemical analysis

The sulphur contained in the sinters was determined by melting the sample with Na_2O_2 and Na_2CO_3. Bismuth was determined by precipitating Bi_2S_3 with thioacetamide [10]. The sinters were then separated into water-soluble and water-insoluble fractions by boiling for a few hours. In the soluble frac-

TABLE 2

Results of the chemical analysis of sinters of potassium thiosulphatobismuthate(III)

No.	Temp. (°C)	Composition of sinter		Amount of evolved SO_2		Eqn.
		Detd.	Calcd.	Detd.	Calcd.	
1	200	25.50% S 37.48% Bi	25.47% S 36.88% Bi	14.61%	14.12%	6
2	320	18.95% S 38.75% Bi	18.55% S 40.31% Bi	26.56%	28.23%	9
3	700	13.72% S 36.85% Bi	13.33% S 37.24% Bi	34.10%	34.50%	10
4	1000	12.16% S 39.27% Bi	11.28% S 40.11% Bi			13

TABLE 3

Results of the chemical analysis of the soluble and insoluble fractions of sinters of potassium thiosulphatobismuthate(III)

No.	Temp. (°C)	Soluble fraction		Insoluble fraction		Eqn.
		Detd.	Calcd.	Detd.	Calcd.	
1	200	26.65% SO_4		23.06% S total	23.48% S total	6
				5.64% S free	5.87% S free	
				79.43% Bi	76.52% Bi	
		m.fr. 51.54%	m.fr. 50.87%	m.fr. 48.46%	m.fr. 49.13%	
2	320	27.35% SO_4	27.79% SO_4	16.77% S	18.71% S	9
				83.22% Bi	81.29% Bi	
		m.fr. 52.48%	m.fr. 50.42%	m.fr. 47.52%	m.fr. 49.58%	
3	700	30.40% SO_4	31.39% SO_4	16.54% SO_4	17.59% SO_4	12
		in this	in this	77.82% Bi	76.55% Bi	
		5.96% H_2SO_4	5.71% H_2SO_4			
		m.fr. 52.55%	m.fr. 51.86%	m.fr. 47.45%	m.fr. 48.14%	
4	1000	29.74% SO_4	27.65% SO_4	12.90% SO_4	12.33% SO_4	13
				78.54% Bi	80.48% Bi	
		m.fr. 49.58%	m.fr. 50.17%	m.fr. 50.42%	m.fr. 49.83%	

m.fr. = mass fraction.

tion the sulphates were determined by a gravimetric method and sulphuric acid was determined by acid—base titration for the soluble fraction of the sinters obtained at 700 or 550° C. In the water-insoluble fraction sulphur was determined as $BaSO_4$ after oxidation with a mixture of HNO_3, HCl, Br_2 (3 : 1 : 1 parts by weight). Bismuth was determined as Bi_2S_3.

Sulphur dioxide, a gaseous product of the thermal decomposition of thio-

TABLE 4

Results of the chemical analysis of the 200°C sinter of sodium thiosulphatobismuthate-(III)

Composition of sinter		Amount of evolved SO_2		Eqn.
Detd.	Calcd.	Detd.	Calcd.	
27.58% S 42.78% Bi	26.89% S 42.06% Bi	19.96%	18.57%	14
Soluble fraction		Insoluble fraction		Eqn.
Detd.	Calcd.	Detd.	Calcd.	
31.14% SO_4		24.78% S	23.48% S	14
		77.73% Bi	76.52% Bi	
m.fr. 46.14%	m.fr. 45.04%	m.fr. 53.86%	m.fr. 54.96%	

m.fr. = mass fraction.

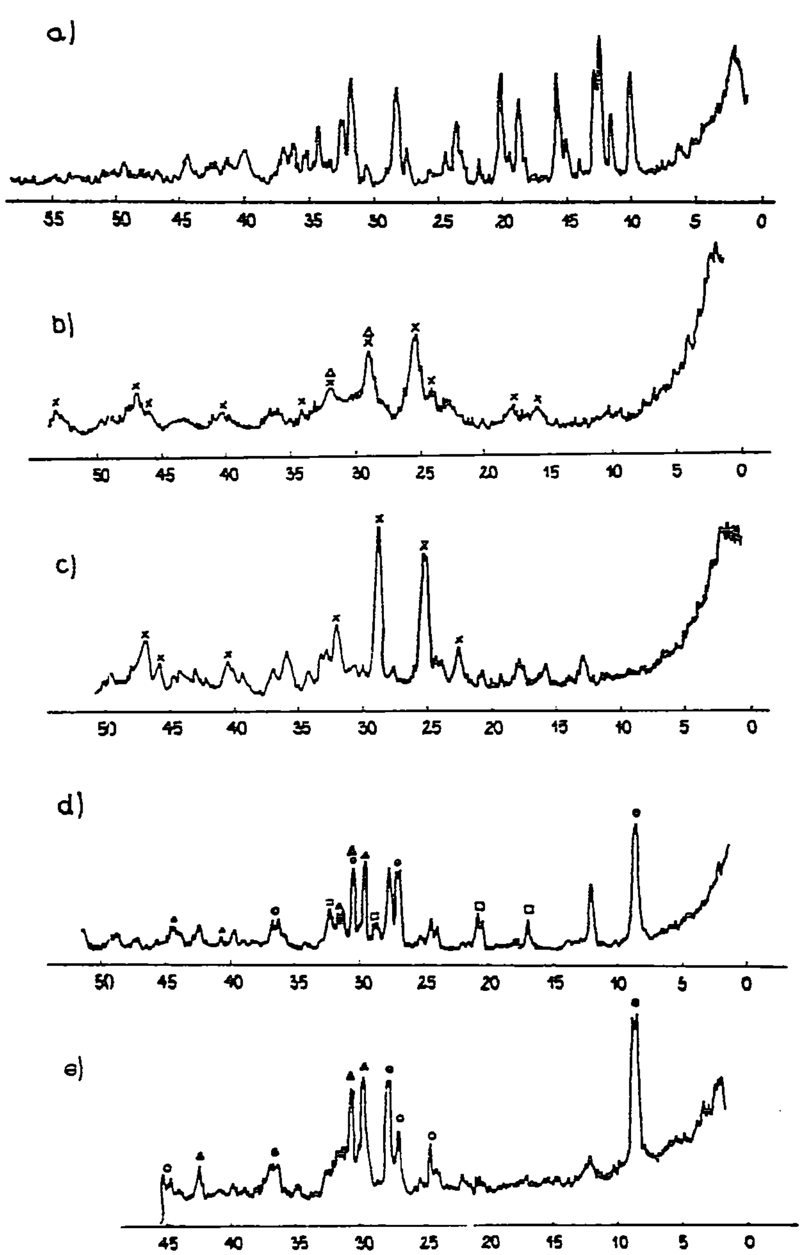


Fig. 3. X-Ray diffraction patterns of potassium thiosulphatobismuthate(III): a, before sintering; b, after sintering to 200°C; c, after sintering to 320°C; d, after sintering to 700°C; e, after sintering to 1000°C. ×, Bi_2S_3; △, S; ▲, K_2SO_4; □, $Bi_2(SO_4)_3$; ●, $(BiO)_2SO_4$; ○, Bi_2O_3.

sulphatobismuthates(III), was also determined. This was done at the temperatures used to obtain the sinters. Evolved SO_2 was absorbed in sodium tetrachloromercurite(II) solution and the formed hydrochloric acid was determined by alkalimetric titration.

Elementary sulphur, present in the water-insoluble fraction of the sinters at 200° C, was determined by extraction with carbon disulphide, followed by solvent evaporation.

Tables 2 and 3 give the results for potassium thiosulphatobismuthate(III) sinters. Table 4 gives the results for sinters of sodium thiosulphatobismuthate(III) obtained at 200° C.

X-Ray analysis

X-Ray analyses of the sinters were carried out on a DRON-1 diffractometer using CuK_α radiation with a nickel filter. The diffraction curves were recorded over the range 2θ angles 3—50°. The diffractograms of potassium thiosulphatobismuthate(III) and its sinters are given in Fig. 3.

Analysis of the diffractograms of the sinters proved that in the sinters of potassium thiosulphatobismuthate(III), obtained at 200° C, there is bismuth sulphide, and the presence of sulphur is possible. In the sinters obtained at 320° C X-ray analysis proved the presence of bismuth sulphide, while potassium sulphate was not present, which may be explained by its formation in the amorphous form. In the sinters obtained at 700° C the following compounds were found by diffractometric analysis: $Bi_2(SO_4)_3$, $(BiO)_2SO_4$, K_2SO_4; and in the sinters prepared at 1000° C; $(BiO)_2SO_4$, Bi_2O_3 and K_2SO_4.

Comparison of the reflexes occurring in the diffractogram of the sinter of sodium thiosulphatobismuthate(III) prepared at 300° C with the reference

TABLE 5

X-ray identification of the sodium thiosulphatobismuthate(III) sinter (prepared at 200°C)

Date from X-ray pattern of the sinter		Literature data		
2θ (°)	d/n (Å)	d/n (Å)	Compound	Intensity of lines (%)
15.5	5.72		Unidentified	
22.5	4.40		Unidentified	
23.5	3.79		Unidentified	
24.8	3.59	3.56	Bi_2S_3	94
		3.59	Bi_2S_3	60
28.5	3.13	3.11	Bi_2S_3	100
		3.08	Na_2SO_4	27
31.7	2.82	2.81	Bi_2S_3	63
32.9	2.72	2.78	Na_2SO_4	100
		2.72	Bi_2S_3	34
33.8	2.65	2.64	Na_2SO_4	40
		2.64	Bi_2S_3	24
35.6	2.52	2.52	Bi_2S_3	35
39.8	2.26	2.26	Bi_2S_3	36
45.5	1.99		Unidentified	
46.5	1.95	1.95	Bi_2S_3	55
52.7	1.74	1.73	Bi_2S_3	35

TABLE 6

Infrared spectra absorption bands and types of vibrations

No.	Compound	Frequencies of vibration (cm^{-1})						
		ν(SO); E	ν(SO); F	ν(SO); A	ν(SO), A	δ(OSO); A	δ(OSO); F	δ(OSO), E
1	$K_3[Bi(S_2O_3)_3] \cdot H_2O$	1185		1020		645		535
2	80°C sinter	1185		1020		645		535
3	180°C sinter	1185		1020		640		540
4	200°C sinter		1115	1022	990	645	618	540
5	320°C sinter		1115		990		620	
6	$Na_2S_2O_3 \cdot 5\,H_2O$	1135		1000		670		555
7	K_2SO_4		1115		983		618	

literature data is given in Table 5. The data prove that sodium sulphate may be present in the sinter.

Infrared analysis

Infrared spectra were recorded on a UR-10 Zeiss spectrophotometer. The spectra were obtained in the 1700—400 cm^{-1} range using the KBr pellet technique. Infrared spectra absorption bands and the corresponding vibrations of potassium thiosulphatobismuthate(III) and its sinters prepared at 80, 180, 200 and 320°C, as well as of standard substances sodium thiosulphate and potassium sulphate, are given in Table 6. The data proved that there are bands characteristic of the thiosulphate anion (shifted by coordination [6]) in the spectrum of the unheated compound, as well as in the sinters prepared at 80 and 180°C. In the sinters obtained at 200 and 320°C these bands do not appear, but new bands, corresponding to vibrations of the sulphate anion, are formed.

DISCUSSION

The mechanism of the thermal decomposition of thiosulphatobismuthates(III)

The thermal curves of thiosulphatobismuthates(III) show that their thermal decomposition occurs in three stages (in the case of non-aqueous caesium thiosulphatobismuthate(III) two stages occur).

Stage I

At the first stage of the thermal decomposition of sodium, potassium and rubidium thiosulphatobismuthates(III) water is evaporated, with a corresponding mass loss on the TG curve occurring between 60 and 200°C. While the water is evaporated, gradual, very slow decomposition of thiosulphatobismuthate begins, which is proved by some evolving sulphur dioxide. This decomposition is so slight that there are no changes in the IR spectrum of the compounds. Infrared tests proved that spectra of potassium thiosulphatobismuthate(III) and its sinters obtained at 80 and 180°C are identical (Table 6). Distinct changes in the spectra (the bands corresponding to thiosulphatobismuthates disappear and new bands appear) occur for the sinter prepared at 200°C.

Stage II

The second stage is the most important for the decomposition of thiosulphatobismuthates(III). It begins at about 200°C with the thermal dissociation of thiosulphatobismuthate(III), resulting in the formation of simple thiosulphates of alkali metals and bismuth, according to the equation

$$6\ M_3[Bi(S_2O_3)_3] = 3\ Bi_2(S_2O_3)_3 + 9\ M_2S_2O_3 \qquad (1)$$

where M = cation of alkali metal; values of the coefficients in the equation result from the following reactions.

Heavy metal thiosulphates are much less stable than alkali metal thiosulphates, so the bismuth thiosulphate formed in the reaction decomposes immediately. This is indicated by a rapid mass loss on the TG curve and an endothermic peak on the DTA curve. Bismuth thiosulphate is assumed to decompose according to eqn. (2)

$$3\ Bi_2(S_2O_3)_3 = 3\ Bi_2S_3 + 9\ SO_2 + 4.5\ O_2 \tag{2}$$

The oxygen evolved in the reaction reacts with alkali metal thiosulphate and the sulphate, sulphur and intermediate decomposition product are formed. The formation of the intermediate decomposition product on heating sodium thiosulphate in air was found by Erdey et al. [11]. The authors did not define the product, but simply stated that the residue consisted of sulphite, sulphide and polysulphide.

This complicated process can be presented in the case of potassium thiosulphatobismuthate(III) in the following way

$$9\ K_2S_2O_3 + 4.5\ O_2 = x\ K_2SO_4 + 3\ S + K_{(18-2x)}S_{(15-x)}O_{(36-4x)} \tag{3}$$

while

$$x\ K_2SO_4 + K_{(18-2x)}S_{(15-x)}O_{(36-4x)} = K_{18}S_{15}O_{36} \tag{4}$$

where x = number of moles of formed potassium sulphate.

The coefficient x was used with K_2SO_4 because potassium sulphate could not be determined in the sinter, since, on leaching the sinter in boiling water to separate water-soluble and water-insoluble fractions, the transient product is decomposed and potassium sulphate and gaseous products containing sulphur are formed

$$K_{18}S_{15}O_{36} \rightarrow 9\ K_2SO_4 + \text{gaseous products} \tag{5}$$

In the water-soluble fraction sinter at 200° C an amount of sulphates equal to 9 K_2SO_4 was obtained.

Thiosulphatobismuthate(III) decomposition at 200° C is described by eqn. (6)

$$6\ K_3[Bi(S_2O_3)_3] = 3\ Bi_2S_3 + x\ K_2SO_4 + 3\ S + 9\ SO_2 + K_{(18-2x)}S_{(15-x)}O_{(36-4x)} \tag{6}$$

Stage III

Further heating results in the third stage of decomposition. More potassium sulphate and sulphur are obtained from the intermediate product

$$3\ Bi_2S_3 + x\ K_2SO_4 + 3\ S + K_{(18-2x)}S_{(15-x)}O_{(36-4x)} = 3\ Bi_2S_3 + 9\ K_2SO_4 + 9\ S \tag{7}$$

Sulphur is oxidized immediately, which is illustrated by an exothermic peak on the DTA curve (Figs. 1 and 2)

$$9\ S + 9\ O_2 = 9\ SO_2 \tag{8}$$

Equation (9) summarizes the decomposition of potassium thiosulphatobismuthate(III) at about 320° C

$$6\ K_3[Bi(S_2O_3)_3] + 9\ O_2 = 3\ Bi_2S_3 + 9\ K_2SO_4 + 18\ SO_2 \qquad (9)$$

Reaction of the decomposition products

Reaction (9) causes the maximum mass loss of the system at about 320° C. The TG curve indicates a distinct mass increase at higher temperatures, involving further reactions of the decomposition products. Analytical results, as well as X-ray diffraction patterns, indicate that in the sinters obtained at 700° C there are products of the following reaction

$$3\ Bi_2S_3 + 9\ K_2SO_4 + 14\ O_2 = Bi_2(SO_4)_3 + 2\ (BiO)_2SO_4 + 9\ K_2SO_4 + 4\ SO_2 \qquad (10)$$

When the sinter is leached with boiling water bismuth sulphate is hydrolized

$$Bi_2(SO_4)_3 + 2\ H_2O = (BiO)_2SO_4 + H_2SO_4 \qquad (11)$$

and, therefore, the composition of the soluble fraction was calculated according to eqn. (12)

$$3\ Bi_2S_3 + 9\ K_2SO_4 + 2\ H_2O = 3\ (BiO)_2SO_4 + \underbrace{9\ K_2SO_4 + 2\ H_2SO_4}_{\text{soluble fraction}} \qquad (12)$$

When heated up to 1000° C, bismuth sulphate is transformed into bismuthyl sulphate. Part of the resultant compound is transformed into bismuth oxide.

$$Bi_2(SO_4)_3 + 2\ (BiO)_2SO_4 + 9\ K_2SO_4 = Bi_2O_3 + 2\ (BiO)_2SO_4 + 9\ K_2SO_4 + 3/2\ O_2 + 3\ SO_2 \qquad (13)$$

The thermal decomposition of rubidium, caesium, potassium-sodium and caesium-sodium thiosulphatobismuthates(III) proceeds in a similar way. This is proved by the thermal curves and corresponding mass losses and mass growths, as determined and calculated from the appropriate equations (Table 7). The data show that the greatest differences between determined and calculated results occur in the case of sodium thiosulphatobismuthate(III). The differences are most evident at the second stage of decomposition. The investigation of sodium thiosulphatobismuthate(III) sinters, as well as determination of evolved SO_2 (Table 4), proved that the decomposition of this compound at 200° C proceeds in a way slightly different from other thiosulphatobismuthates(III)

$$6\ Na_3[Bi(S_2O_3)_3] = 3\ Bi_2S_3 + 3\ S + Na_{18}S_{13}O_{32} + 11\ SO_2 \qquad (14)$$

The investigation gives rise to the conclusion that the thermal decomposition of thiosulphatobismuthates(III) is characterized by a low decomposition temperature. Thiosulphatobismuthates(III) decompose at 320° C with the formation of the alkali metal sulphate and bismuth sulphide. The alkali metal sulphate can be separated from bismuth sulphide easily by leaching the

TABLE 7

Mass changes in the thermal decomposition of thiosulphatobismuthates(III)

No.	Compound	Mass losses (%)						Mass growth (%)	
		Stage I		Stage II		Stage III		Detd.	Calcd.
		Detd.	Calcd.	Detd.	Calcd.	Detd.	Calcd.		
1	$Na_3[Bi(S_2O_3)_3] \cdot H_2O$	3.00	2.83	18.20	15.19	6.40	7.61	5.20	6.74
2	$K_3[Bi(S_2O_3)_3] \cdot H_2O$	2.80	2.64	14.00	14.12	6.80	7.07	6.00	6.26
3	$Rb_3[Bi(S_2O_3)_3] \cdot H_2O$	2.80	2.20	12.00	11.72	5.00	5.81	4.80	5.20
4	$Cs_3[Bi(S_2O_3)_3]$	—	—	10.00	10.18	5.60	5.09	4.00	4.51
5	$K_5Na[Bi(S_2O_3)_3]_2 \cdot 2\,H_2O$	3.20	2.68	14.40	14.29	6.80	7.15	6.00	6.34
6	$K_2Na[Bi(S_2O_3)_3] \cdot H_2O$	3.20	2.73	14.80	14.46	6.40	7.21	7.20	6.41
7	$Cs_2Na[Bi(S_2O_3)_3]$	—	—	11.20	11.52	5.60	5.76	4.88	5.11

sinter with boiling water. It may be used in developing new methods to obtain high purity alkali metal sulphates.

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