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THERMAL PROPERTIES OF THIOCYANATOTHIOCARBAMIDOBISMUTHATES(III) WITH ALKALINE ELEMENTS

HALINA LADZIŃSKA-KULIŃSKA

Institute of General Chemistry, University of Technology, Łódź (Poland)

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ABSTRACT

The thermal decomposition of complex salts of thiocyanatothiocarbamidobismuthates(III), having the general formula $Me[Bi(SCN)_4(TM)_2]$ where Me = Li, Na, K, Rb, Cs, NH_4 and TM = thiourea, was studied. On the basis of the results of derivatographic studies and chemical analysis, both infrared spectrophotometric and diffractometric, the compositions of the intermediate and final products obtained during the thermal decomposition of those salts were established. On the strength of the experimental data obtained (without analyzing the gaseous products), the most probable overall equation was established of the decomposition reaction of thiocyanatothiocarbamidobismuthates(III) in air at a temperature of 480°C.

INTRODUCTION

Continuing the studies on ternary complexes of bismuth(III) [1], we have examined their thermal properties. The thermal dissociation of complex salts is influenced by the character not only of the central ion and the ligands, but also of the ions in the outer coordination sphere [2]. In the available literature no data can be found on the thermal properties of complex salts of bismuth with thiocyanate and thiourea.

Thermal studies on single thiocyanobismuthates are being conducted by Cygański [3]. The aim of the present work is to examine the thermal stability of complex salts of bismuth having the general formula $Me[Bi(SNC)_4(TM)_2]$ (where Me = Li, Na, K, Rb, Cs, NH_4 and TM = thiourea) and to determine the influence of the outer sphere cations upon the thermal stability of the compounds under study.

EXPERIMENTAL

Thiocyanatothiocarbamidobismuthates(III) with alkaline elements were obtained by the method described previously [1]. The thermal analysis of complex salts was conducted in air using a Hungarian-made OD-102 derivatograph. The measurements were performed within a temperature range 20—1000°C, the heating rate of the samples being 5°C min^{-1}, the sensitivity

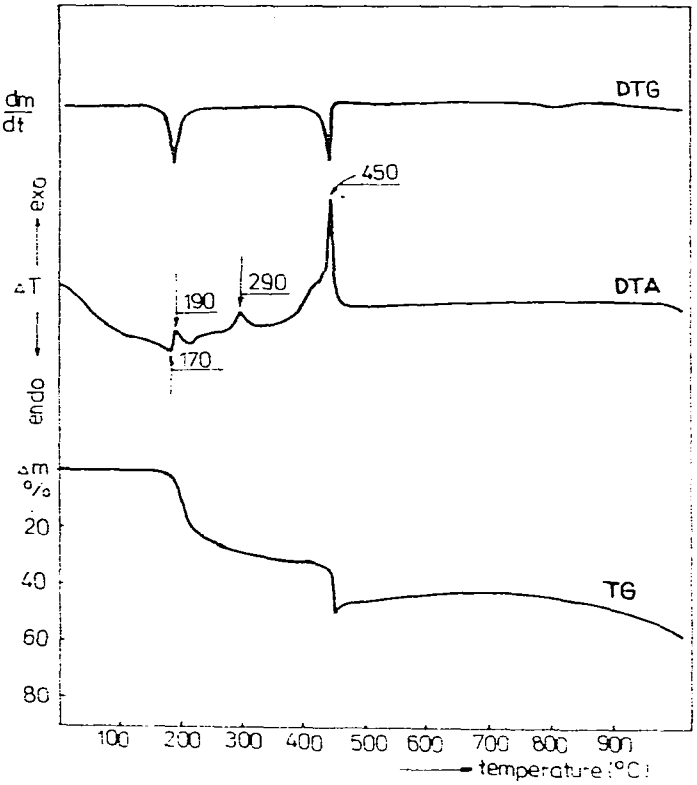

Fig. 1. DTG, DTA and TG curves for Na[Bi(SCN$_4$)(TM)$_2$] in air.

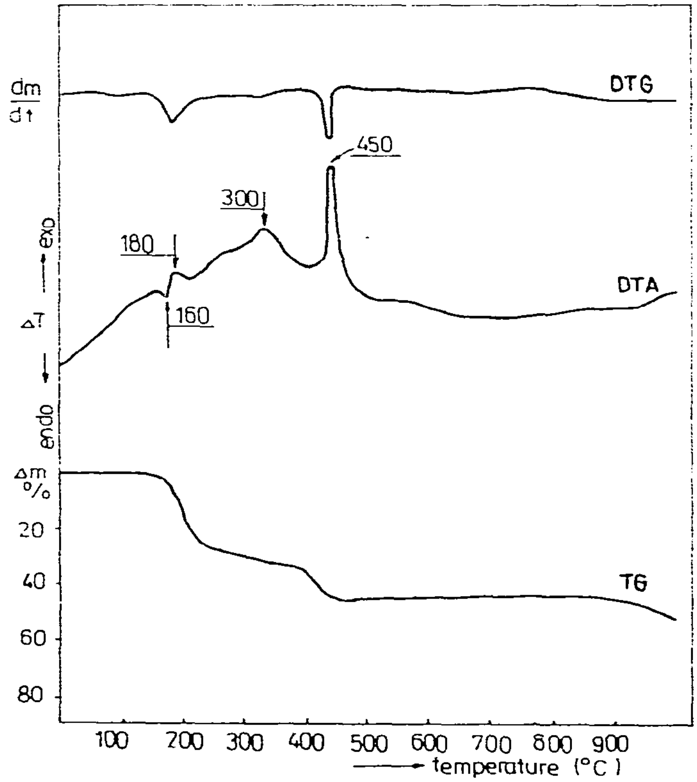

Fig. 2. DTG, DTA and TG curves for K[Bi(SCN)$_4$(TM)$_2$] in air.

TABLE 1

Steps in the thermal decomposition of thiocyanatothiocarbamidobismuthates(III)

Compound *	Temp. of endothermic peak (°C)	Temperatures of exothermic peaks				
		Peak I		Peak II	Peak III	
		Temp. range DTA (°C)	Max. temp. DTA (°C)	Temp. range DTA (°C)	Temp. range DTA (°C)	Max. temp. DTA (°C)
LiR	120	140—200	150	280—320	430—480	450
NaR	170	180—210	190	280—320	420—480	450
KR	160	170—210	180	260—320	420—480	450
RbR	130	160—190	170	220—280	430—470	450
CsR	130	160—200	170	280—320	400—480	450
NH_4R	130	150—200	160	270—310	400—480	440

* R = $[Bi(SCN)_4(TM)_2]$.

TABLE 2

Product of pyrolysis of thiocyanatothiocarbamidobismuthates (III) at 200°C

Compound *	Mass loss (mg)	Pyrolysis residue		Pyrolysis products			
				SCN (%)		Bi (%)	
		Found (%)	Calcd. from eqn. (2) (%)	Found	Calcd. from eqn. (2)	Found	Calcd. from eqn. (2)
LiR	50 — 14.5 = 35.5	71.0	71.7	25.9	27.1	49.0	48.7
NaR	50 — 14.0 = 36.0	72.0	72.4	25.6	26.0	48.1	46.9
KR	50 — 13.0 = 37.0	74.0	73.1	24.5	25.1	45.0	45.2
RbR	50 — 12.0 = 38.0	76.0	74.9	22.1	22.8	42.0	41.1
CsR	50 — 11.0 = 39.0	78.0	77.5	19.4	20.6	37.3	37.1
NH_4R	50 — 15.0 = 35.0	70.0	72.2	25.3	26.0	48.3	47.3

* R = $[Bi(SCN)_4(TM)_2]$.

TABLE 3

Products of pyrolysis of thiocyanatothiocarbamidobismuthates (III) at 480°C

Compound *	Mass loss (mg)	Pyrolysis residue		Pyrolysis residue composition		
		Found (%)	Calcd. from eqn. (3) (%)	Me_2SO_4 (%)	Bi (%)	S (%)
LiR	50 — 26.5 = 23.5	47.1	47.8	19.3	72.3	8.1
NaR	50 — 25.0 = 25.0	50.0	49.3	23.0	67.8	7.9
KR	50 — 24.5 = 25.5	51.0	50.6	27.5	65.0	7.2
RbR	50 — 23.0 = 27.0	54.1	54.0	36.2	57.1	6.2
CsR	50 — 22.0 = 28.0	56.0	57.0	43.7	50.2	5.7
NH_4R	50 — 31.0 = 19.0	37.9	38.1		88.7	10.9

* R = $[Bi(SCN)_4(TM)_2]$.

TABLE 4

Fundamental valence vibration frequencies (cm^{-1}) (nujol diluted samples)

Thiourea	NaR *	KR *	Sinter NaR *		Sinter KR *		NaNCS	KNCS	Type of vibration	Group
			200°C	480°C	200°C	480°C				
3320	3400	3350							$\nu(NH)$	Thiourea
3250	3300	3250								
3120	3200	3150								
	2100	2090	2080		2070		2080	2057	$\nu(CN)$	SCN
1620	1630	1630							$\delta(NH_2)$	Thiourea
1470	1505	1500							$\nu(NCN)$	Thiourea
1412	1422	1412							$\nu(CS)$	
	1395	1385							$\delta(NH_2)$	
1080	1105	1100							$\nu(CS)$	Thiourea
									$\nu(NCN)$	
728	700	700	730		725				$\nu(CS)$	Thiourea
	720	720	760		750		758	749	$\nu(NCN)$	SCN

* R = $[Bi(SCN)_4(TM)_2]$.

TABLE 5

Diffractometric identification of sinter $K[Bi(SCN)_4(TM)_2]$ at 200°C

Data from X-ray pattern of the sinter		Literature data	
2θ	d/n (Å)	d/n (Å)	Formula and relative intensity of lines
15.90	5.57		Not identified
17.80	4.98		Not identified
21.50	4.13		Not identified
22.60	3.94	3.97	Bi_2S_3 (38)
23.90	3.72	3.75	Bi_2S_3 (20)
25.40	3.51	3.53	Bi_2S_3 (60)
27.70	3.22		
28.80	3.10	3.12	Bi_2S_3 (100)
30.30	2.95	2.94	KNCS (100)
32.10	2.79	2.79	KNCS (80)
33.10	2.71	2.72	Bi_2S_3 (34)
34.00	2.64	2.64	Bi_2S_3 (24)
35.90	2.50	2.51	KNCS (40)
39.20	2.30	2.30	Bi_2S_3 (24)
40.20	2.24	2.23	KNCS (2)
42.80	2.11	2.12	Bi_2S_3 (15)
45.80	1.98	1.99	Bi_2S_3 (33)
46.80	1.94	1.94; 1.95	KNCS (25); Bi_2S_3 (55)
49.20	1.85	1.85	Bi_2S_3 (17)
51.50	1.77	1.77	Bi_2S_3 (5)
52.80	1.73	1.73	Bi_2S_3 (35)

of the galvanometers 1/10 for the DTA curve, 1/15 for the DTG curve, and 100 or 200 mg for the TG curve. The size of the samples was 50 and 250 mg. The DTA and DTG curves in the derivatograms of the complex salts under study are of a similar character. This is indicated by the same decomposition mechanism of the respective salts in the group of compounds in question. The thermal characteristics of the compounds under study are given in Table 1 and Figs. 1 and 2.

The identification of the solid products, both intermediate and final, of a thermolysis of thiocyanatothiocarbamidobismuthates(III) was made on the basis of indications of the TG curves, chemical and elementary analysis, infrared spectrophotometry and diffractometry, this identification being needed for establishing the decomposition diagrams. In order to study the thermal decomposition reaction of the salts, sinters were prepared under conditions similar to those in the derivatograph. The salts were heated at a rate of 5°C min^{-1} up to the temperature determined from the derivatogram, the mass decrements being controlled simultaneously. Up to a temperature of 200°C, the samples of mass 0.5 and 1 g were heated in a drier. The samples subjected to thermolysis at a higher temperature were prepared in an electrical resistance furnace with SiC heating elements. The chemical composition of solid sinters was established on the basis of the determination of bismuth [4], thiocyanate, and total sulphur [5] as well as carbon and nitrogen. The infrared spectrophotometric identification was conducted on the basis of the spectra obtained on the Spectronom 2000 spectrophotometer. The samples were studied diluted with paraffin oil and KBr within the range 700—5000 cm^{-1}. The diffractometric analysis of sinters was carried out on the Dron diffractometer and by using CuK_{α} radiation. The diffraction curves were recorded within the range of 2θ angles from 3 to 70°. The results obtained are tabulated in Tables 2—5.

DISCUSSION

The DTA curves in the derivatogram of complex salts $Me[Bi(SCN)_4(TM)_2]$ show the presence of one endothermic and three exothermic transformations. The endothermic process attains a maximum at a temperature of 120—170°C (Table 1), the TG curves showing no mass decrement. The endothermic effect results from the melting of the substance. The melting points of the complex salts under study were determined in capillary tubes and were in agreement with those determined from derivatograms. Thermal decomposition of the substances under investigation begins at 140—180°C, the mass of the samples decreasing with increase of temperature. The absence on the TG curves of the characteristic horizontal sections which would separate the first two exothermic transformations indicates that there is a decomposition reaction taking place. The third exothermic transformation with a sharp maximum begins at a temperature of 400—430°C and terminates at a temperature of 480°C; it corresponds to the steep section of the TG curves. From Figs. 1 and 2, it follows that the greatest mass decrements occur at 200 and 480°C. At these temperatures, the DTG curves show the maximum decomposition rate. In order to establish the diagrams of the thermal decomposition reaction, the samples of complex salts heated to temperatures of 200 and 480°C were subjected to chemical, infrared absorptiometric and diffractometric analyses. The processes occurring during heating at these temperatures can be represented as

$$Me[Bi(SCN)_4(TM)_2] \xrightarrow{Q} MeNCS + Bi(SCN)_3 + 2\,TM \qquad (1)$$

$$4\,Me[Bi(SCN)_4(TM)_2] \xrightarrow{200^{\circ}C} 4\,MeNCS + 4\,NH_4NCS + Bi_2S_3 + 2\,BiSC_2N_4 \qquad (2)$$

$$4\,Me[Bi(SCN)_4(TM)_2] \xrightarrow{480^{\circ}C} 2\,Me_2SO_4 + Bi_2S_3 + 2\,Bi \qquad (3)$$

The thermal decomposition of thiocyanatothiocarbamidobismuthates(III) with alkaline elements begins immediately after melting, most likely from the thermal dissociation which proceeds in accordance with eqn. (1). A similar behaviour of complex salts was observed by Tananajew et al. [6] in hexacyanoferrates(II) and by Cygański [3] in thiocyanatobismuthates(III). The products of the thermal dissociation, eqn. (1), show a diversified stability during heating at temperatures of 140—210°C. Suitable thiocyanates, MeNCS (Me = Li, Na, K, Rb, Cs, NH_4), do not undergo decomposition at these temperatures, whereas $Bi(SCN)_3$ and thiourea proceed immediately to further secondary reactions with the production of Bi_2S_3, an intermediate decomposition product containing bismuth, sulphur, carbon and nitrogen as well as NH_4NCS. The isomerisation of thiourea in ammonium thiocyanate above 150°C was also observed by Borisowa [7] when studying the thermal decomposition product of ternary complexes of propionatothiocarbamidolanthanons. The occurrence of the intermediate decomposition product $Bi(SCN)_3$, which contains bismuth, sulphur, carbon and nitrogen, was found by Cygański [3] when studying the thermal decomposition of thiocyanatobismuthates(III). In complex salt samples heated to a temperature of 200°C (the first exothermic transformation), it is possible to determine thiocyanates, bismuth and sulphur analytically in amounts corresponding to eqn. (2). Sinters obtained at this temperature are grey in colour. Extraction by water permits the water soluble products, MeCNS, to be separated from the insoluble ones (Bi_2S_3 and $BiS_xC_yN_z$). The determined masses of the soluble fractions and the amounts of thiocyanates estimated in them are in agreement with eqn. (2). In the samples of sinters free of water soluble substances, the presence of Bi_2S_3 was found diffractometrically. The content of bismuth, sulphur, carbon and nitrogen determined in those samples permits the approximate generalized formula of the intermediate compound $BiSC_2N_4$ (calculated atomic ratio S : C : N 1 : 2 : 4) to be established. In the IR spectra of solid sinters (Table 4), the 3350, 3270 and 3150 cm^{-1} bands, ascribed to tensile vibration $\nu(NH_2)$, fade as do the bands of about 1600 cm^{-1} corresponding to bending vibration $\delta(NH_2)$ of thiourea in the complexes [8]. The bands, characteristic of the bonding of the SCN group by the sulphur atom, also undergo a shift. The bands $\nu(CS)$ of the SCN group, which occur in the initial compounds at 700—705 cm^{-1}, undergo a shift up to 740 cm^{-1}. The frequency of vibration $\nu(CN)$ of the SCN group also decreases from 2100 cm^{-1} in the initial compounds to 2080—2070 in the samples of sinters obtained at a temperature of 200°C. The frequency variations of the vibration $\nu(CS)$ and $\nu(CN)$ observed in sinters in comparison with the vibration frequencies of the appropriate alkaline thiocyanate indicate the destruction of the Bi—SCN bond in the complexes with the formation of the thiocyanate of the alkaline metal which occupies the outer coordination sphere in the complexes. The presence of the thiocyanates of alkaline metals is also corroborated by the diffractometric studies (Table 5). The amount of thiocyanates determined in the water extract of sinters is in approximate agreement with the amount of SCN^- calculated according to eqn. (2) (Table 2); there is also agreement between the determined and the calculated mass decrements. The second exothermic transformation at a temperature of 220—320°C is associated with an insignificant mass decrement. The main reaction occurring at this temperature is the decomposition of alkaline thiocyanates to the corresponding sulphates. In the water extracts of sinter samples obtained at a temperature of 300°C, small amounts of thiocyanates (about 3.5%) were determined analytically in addition to sulphates. A strong exo-effect with the maximum at a temperature of 440—450°C is linked with the decomposition of the intermediate product $BiSC_2N_4$ to free bismuth. Analysis of the sinter samples obtained at a temperature of 480°C for sulphate (water extract), bismuth and sulphur (insoluble fraction) as well as comparison of mass decrements (Table 3) indicate that the course of decomposition is in accord with eqn. (3). Such a course of the reaction is corroborated by both spectrophotometric and diffractometric studies. In the IR spectra, the 750—760 cm^{-1} and 2080—2070 cm^{-1} bands fade. The presence was found diffractometrically, in sinters, of intensities characteristic of proper sulphates, Bi_2S_3 and free bismuth. On the strength of the experimental data presented above, the most likely overall equation for the thermolysis reaction of thiocyanatothiocarbamidobismuthates(III) in the air at a temperature of 480°C can be presented in the form

$$4\,Me[Bi(SCN)_4(N_2H_4CS)_2] + 55\,O_2 = 2\,Me_2SO_4 + Bi_2S_3 + 2\,Bi + 16\,N_2 + 16\,H_2O + 19\,SO_2 + 24\,CO_2 \qquad (4)$$

The studies reported here indicate that the thermal stability in the group of complex compounds in question depends upon the electron structure and the ionic radius of the outer sphere cation. By comparing the initial temperatures of the decomposition, a thermal stability series may be drawn up, viz.

$$Na[Bi(SCN)_4(TM)_2] > K[Bi(SCN)_4(TM)_2] > Rb[Bi(SCN)_4(TM)_2] = Cs[Bi(SCN)_4(TM)_2] > NH_4[Bi(SCN)_4(TM)_2] > Li[Bi(SCN)_4(TM)_2]$$

Earlier studies on the solubility and resistance to the hydrolytic action of water [1] yielded results which are in accord with the above stability series obtained in thermal investigations.

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