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Kinetic parameters of thermal decomposition of thiocyanatobismuthates(III). Part 3. Ammonium salts

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Abstract

Kinetic parameters of thermal decomposition of thiocyanatobismuthates(III) of formulae $(NH_4)_3[Bi(SCN)_6]$, $(NH_4)_2M[Bi(SCN)_6]$ (where M is Li, Na, K, Rb) and $NH_4Ca[Bi(SCN)_6] \cdot 5H_2O$ have been determined. The thermal stabilities (expressed by initial decomposition temperature and activation energy of the first step of decomposition) of thiocyanatobismuthates(III) containing alkali metal and ammonium group are compared with those of alkali metals in the outer sphere.

INTRODUCTION

In our previous works kinetic parameters of the thermal decomposition reactions of the alkali metal thiocyanatobismuthates(III) containing one or two different alkali metal cations in the outer sphere of complexes were determined [1, 2]. The purpose of the present work is to establish kinetic parameters of thermal decomposition of all thiocyanatobismuthates(III) with the ammonium group in the outer sphere prepared so far and to compare their thermal stabilities with the thermal stabilities of other single and double alkali metal thiocyanatobismuthates(III).

EXPERIMENTAL

Preparation of thiocyanatobismuthates(III)

Ammonium thiocyanatobismuthate(III) was prepared in the same way as alkali metal thiocyanatobismuthates(III) [3] by neutralisation of $H_3[Bi(SCN)_6]$ solution with ammonium carbonate. The hexathiocyanobismuthic acid was prepared by dissolution of $(BiO)_2CO_3$ in the thiocyanic

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acid obtained by vacuum distillation of NH_4NCS and H_2SO_4 in the presence of $(NH_4)_2SO_4$ [4]. The quantity of bismuthyl carbonate was such that the proportion of SCN to bismuth in solution was approximately 6 (5 g $(BiO)_2CO_3$ was dissolved in 40 ml of 18% HCN solution). To the limpid solution of $H_3[Bi(SCN)_6]$, ammonium carbonate was gradually added while mixing until the stable precipitate was formed. The precipitate was dissolved in several millilitres of HNCS solution. This solution was then evaporated under vacuum in the presence of P_2O_5 at room temperature. After some days orange crystals of $(NH_4)_3[Bi(SCN)_6]$ were formed in the solution. In order to prepare $(NH_4)_2Na[Bi(SCN)_6]$ and $(NH_4)_2K[Bi(SCN)_6]$ the solution of $(NH_4)_3[Bi(SCN)_6]$ and $Na_3[Bi(SCN)_6]$ or $(NH_4)_3[Bi(SCN)_6]$ and $K_3[Bi(SCN)_6]$ having the same concentrations were mixed in the proportion 2:1 for the ammonium-sodium salt and 3:1 for the ammonium-potassium salt and evaporated under vacuum in the presence of P_2O_5 [5]. The solutions of $Na_3[Bi(SCN)_6]$ and $K_3[Bi(SCN)_6]$ were prepared by neutralisation of $H_3[Bi(SCN)_6]$ solution with sodium or potassium carbonate. Ammonium-lithium thiocyanatobismuthate(III) was obtained from the solutions of the single salts $(NH_4)_3[Bi(SCN)_6]$ and $Li_3[Bi(SCN)_6]$ mixed in the proportions 1:1 and evaporated under vacuum in the presence of phosphorus pentoxide [6]. Ammonium-rubidium thiocyanatobismuthate(III) was prepared by dissolving $Rb[Bi(SCN)_4]$ in NH_4NCS solution (to 6.5 g of $Rb[Bi(SCN)_4]$ 10 ml of 2.5 M NH_4NCS solution was added). Excess of rubidium tetrathiocyanatobismuthate was filtered off and the saturated solution slowly evaporated at room temperature [5]. Ammonium-calcium thiocyanatobismuthate(III) was prepared by mixing $Ca_3[Bi(SCN)_6]_2$ and $(NH_4)_3[Bi(SCN)_6]$ solutions in molar proportions 2:1 and evaporating at room temperature [7].

Thermal analysis

The apparatus and experimental conditions were similar to those described in our previous paper [1].

The thermal analysis curves of $(NH_4)_2Rb[Bi(SCN)_6]$ are presented in Fig. 1 while those of $(NH_4)_3[Bi(SCN)_6]$ and $(NH_4)_2Na[Bi(SCN)_6]$ are given in a previous publication [8]. The course of thermoanalytical curves of $(NH_4)_2Rb[Bi(SCN_6)]$ is similar to those of alkali metal thiocyanatobismuthates(III). The DTA curve of this compound exhibits three exothermic peaks corresponding to the three decomposition stages. The endothermic peak at 120°C is probably connected with the thermal dissociation of the complex compound to simple thiocyanate salts

$$(NH_4)_2Rb[Bi(SCN)_6] \rightarrow 2NH_4NCS + RbNCS + Bi(SCN)_3$$

Bismuth thiocyanate [9] and ammonium thiocyanate [10] are characterised by relatively low thermal stability and decompose at about 160°C. The

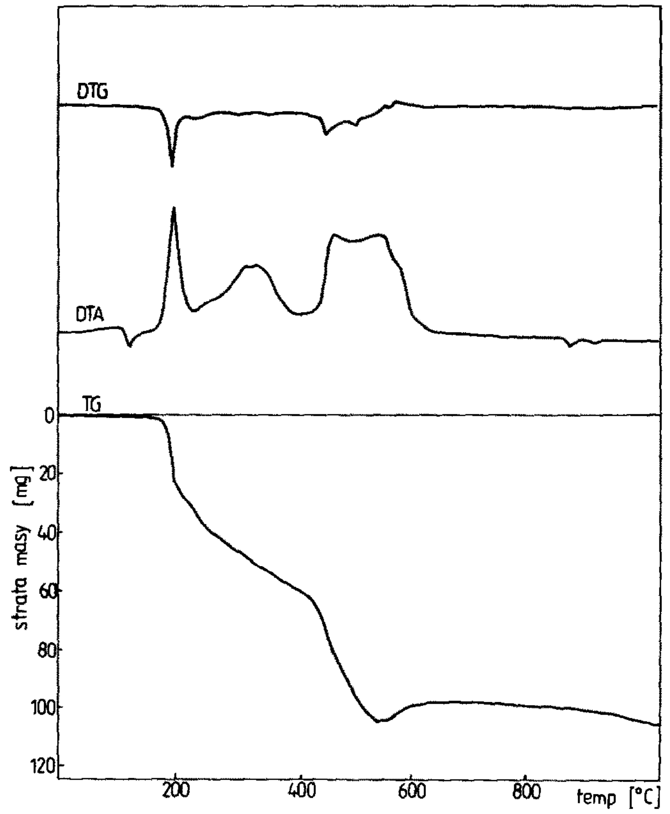

Fig. 1. Thermal analysis curves of ammonium-rubidium thiocyanatobismuthate(III).

decomposition of bismuth thiocyanate results in the formation of bismuth sulphide and of the intermediate product of general formula $BiS_xC_yN_z$, which at higher temperature decomposes to form bismuth sulphide and bismuth [9]. Ammonium thiocyanate transforms partially into thiourea and decomposes forming gaseous (ammonia, carbon disulphide and hydrogen sulphide) and solid (guanidine and melamine) products [10]. Besides, NH_4NCS and $Bi(SCN)_3$ may react forming complex intermediate products.

In the second stage of the decomposition rubidium thiocyanate oxidises forming rubidium sulphate. At 550°C solid decomposition products are formed in agreement with the equation

$$6(NH_4)_2Rb[Bi(SCN)_6] \rightarrow 2Bi_2S_3 + 2Bi + 3Rb_2SO_4$$

The increase in mass visible on the TG curve above 550°C is related to the oxidation of bismuth sulphide to bismuthyl sulphate and of bismuth to bismuth oxide.

The course of the thermal analysis curves of $NH_4Ca[Bi(SCN)_6] \cdot 5H_2O$ differs from that of $(NH_4)_2Rb[(SCN)_6]$ (Fig. 2). The continuous mass loss

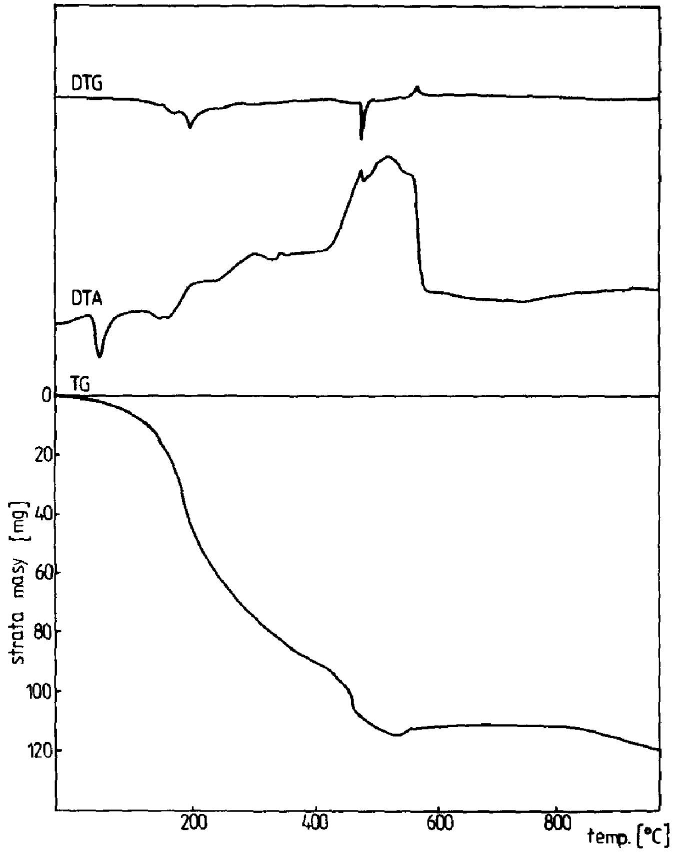

Fig. 2. Thermal analysis curves of ammonium–calcium thiocyanatobismuthate(III).

on the TG curve is connected with the loss of water of crystallisation followed by the thermal decomposition of ammonium and bismuth thiocyanates. The exothermic peaks on DTA are indistinct and blurred except for a broad peak at 500°C. The thermal decomposition of $NH_4Ca[Bi(SCN)_6]$ at 500°C proceeds in a manner similar to that of $(NH_4)_2Rb[Bi(SCN)_6]$. Instead of rubidium sulphate, calcium sulphate is then formed.

DETERMINATION OF KINETIC PARAMETERS

Kinetic parameters (activation energy, reaction order) of the first stages of thermal decomposition reactions of the thiocyanatobismuthates under study were calculated from thermogravimetric curves using the Coats and Redfern [11] and Zsakó [12] methods. Computer programs were based on the mathematical formulae given by the authors.

RESULTS AND DISCUSSION

Kinetic parameters of the thermal decomposition of double ammonium–alkali metal thiocyanatobismuthates(III) as well as the initial decomposition temperatures defined from TG curves (temperatures at which the first distinct loss of mass is observed) are presented in Table 1.

The comparison of the initial decomposition temperatures and activation energies of the first stage of decomposition of ammonium–alkali metal thiocyanatobismuthates (Table 1) and the double alkali metal thiocyanatobismuthates [2] indicates that the complex salts containing ammonium group are of the lowest thermal stability among the compounds in each particular group of double salts. Thus, in the sodium group $(NH_4)_2Na[Bi(SCN)_6]$ is less stable (lower initial decomposition temperature and activation energy value of the first stage of reaction) than the compounds of general formula $M_2Na[Bi(SCN)_6]$ (where $M = K$, Rb, Cs). In the potassium group $(NH_4)_2K[Bi(SCN)_6]$ is less stable than $Rb_2K[Bi(SCN)_6]$ and $Cs_2K[Bi(SCN)_6]$. By analogy, $(NH_4)_2Li[Bi(SCN)_6]$ is characterised by low thermal stability as compared to $Rb_2Li[Bi(SCN)_6]$ and $Cs_2Li[Bi(SCN)_6]$. Thus, the replacement of two outer sphere cations in double alkali metal thiocyanatobismuthates by the ammonium groups results in a distinct decrease of thermal stability and activation energy.

The dependence of the thermal stability of the three groups of complex salts mentioned above upon the difference between the radii of the outer sphere cations is presented in Figs. 3–5. All these diagrams exhibit minima for compounds containing ammonium groups. However, the replacement of alkali metal cation by ammonium does not always result in the decrease of thermal stability. This is the case for double salts, but the comparison of the thermal stabilities of single alkali metal thiocyanatobismuthates [1], and the double salts obtained from single salts by the substitution of two alkali metal by ammonium groups indicates that the thermal stability of these ammonium–alkali metal thiocyanatobismuthates depends on the difference between the ionic radii of the outer sphere cations. When the difference between the radii of ammonium and substituted alkali metal atom is large the double ammonium salt is more stable than the initial single salt, so $(NH_4)_2Na[Bi(SCN)_6]$ is thermally more stable than $Na_3[Bi(SCN)_6]$, and $(NH_4)_2Li[Bi(SCN)_6]$ is characterised by higher thermal stability than $Li_3[Bi(SCN)_6] \cdot 3H_2O$. However, if the difference in magnitude of the radii of the outer sphere cations of the double salts is sufficiently small, e.g. NH_4^+ and K^+ or NH_4^+ and Rb^+, the double salts containing ammonia groups are thermally less stable than the appropriate initial single salts. Thus the initial decomposition temperature and activation energy value of the first stage of decomposition of $(NH_4)_2K[Bi(SCN)_6]$ are lower than $K_3[Bi(SCN)_6]$ and the thermal stability of $(NH_4)_2Rb[Bi(SCN)_6]$ is lower than that of $Rb_3[Bi(SCN)_6]$.

TABLE 1

Kinetic parameters and initial decomposition temperatures of thiocyanatobismuthates(III)

Compound	First stage				Second stage				Third stage				Initial decomposition temperature (°C)
	Z[a]		C-R[b]		Z[a]		C-R[b]		Z[a]		C-R[b]		
	n[c]	*E*[d]	*n*[c]	E[d]	*n*[c]	E[d]	*n*[c]	E[d]	*n*[c]	E[d]	*n*[c]	E[d]	
$(NH_4)_3[Bi(SCN)_6]$	0.6	20	0.6	19.9	1.0	10	1.0	9.6	1.8	78	1.8	78.4	130
$(NH_4)_2Li[Bi(SCN)_6]$	0.0	14	0.0	13.4	2.0	19	1.9	18.7	0.5	45	0.5	45.3	110
$(NH_4)_2Na[Bi(SCN)_6]$	0.0	22	0.0	21.9	1.9	18	1.9	19.2	1.8	76	1.8	75.8	140
$(NH_4)_2K[Bi(SCN)_6]$	0.7	16	0.6	15.7	1.9	16	1.9	16.9	0.8	46	0.8	46.2	100
$(NH_4)_2Rb[Bi(SCN)_6]$	1.9	15	1.9	15.2	1.1	27	1.1	26.4	1.9	63	1.9	65.2	180
$NH_4Ca[Bi(SCN)_6] \cdot 5H_2O$	1.3	11	1.3	10.6	0.9	49	0.9	48.6	0.4	13	0.4	13.9	200

[a] Z, Zsakó method [12]. [b] C-R, Coats and Redfern method [11]. [c] *n*, order of reaction. [d] *E*, activation energy (kcal mol^{-1}).

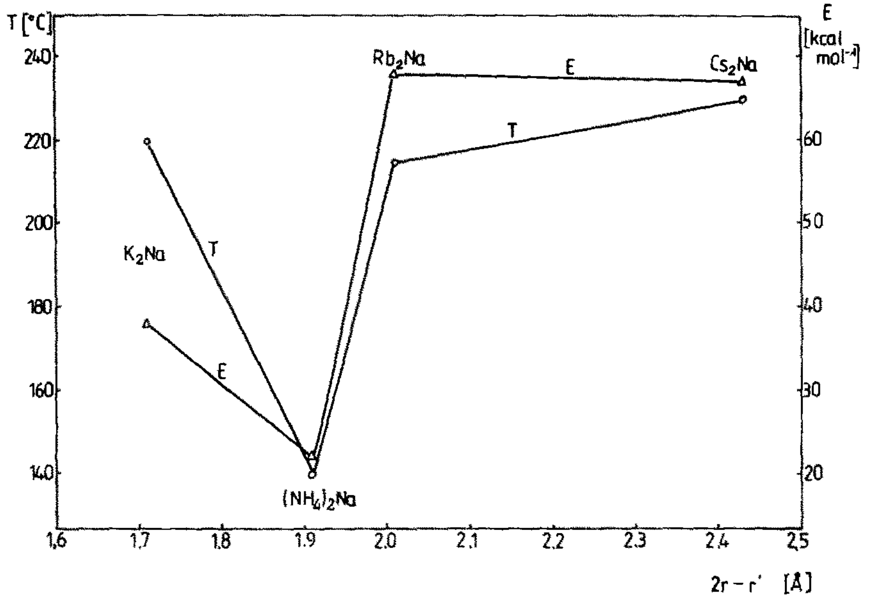

Fig. 3. Effect of the difference between ionic radii of the outer sphere cations on the initial decomposition temperature and activation energy of the sodium group thiocyanatobismuthates(III).

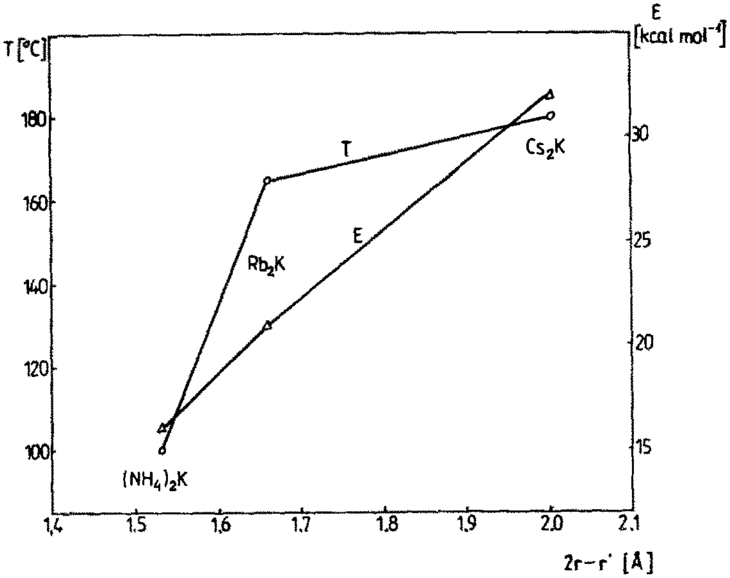

Fig. 4. Effect of the difference between ionic radii of the outer sphere cations on the initial decomposition temperature and activation energy of the potassium group thiocyanatobismuthates(III).

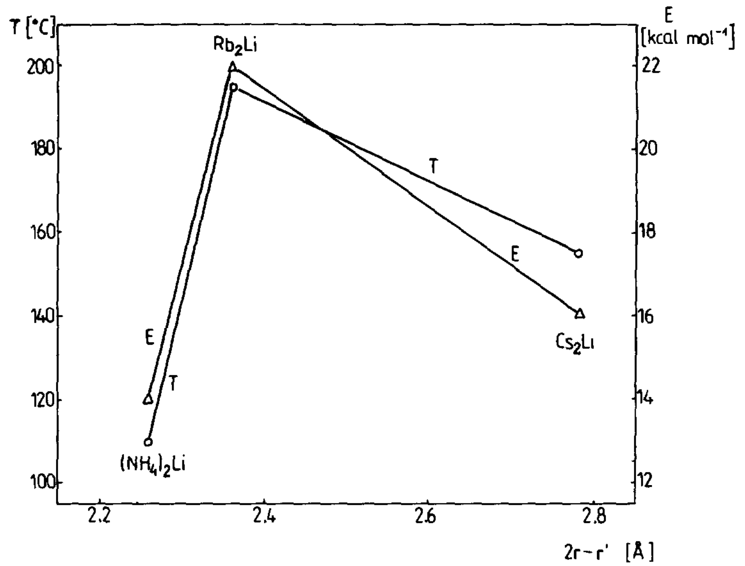

Fig. 5. Effect of the difference between ionic radii of the outer sphere cations on the initial decomposition temperature and activation energy of the lithium group thiocyanatobismuthates(III).

Thus, the replacement of two alkali metal atoms by ammonium group may result in either increase or decrease of thermal stability. When the divalent cation, e.g. calcium, is replaced by two ammonium groups, the resulting ammonium–calcium thiocyanatobismuthate is thermally less stable than the initial calcium thiocyanatobismuthate.

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