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KINETIC PARAMETERS OF THERMAL DECOMPOSITION OF THIOCYANATOBISMUTHATES(III).
Part II. Double salts

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ABSTRACT

Kinetic parameters of the thermal decomposition of double alkali metal thiocyanatobismuthates of general formula $M_2M'[Bi(SCN)_6]$, where M' = Li, Na, K and M = K, Rb, Cs, and $r_M > r_{M'}$, are determined. The reaction order and activation energy of three stages of the decomposition are determined, and the effect of the outer sphere cations on the thermal stability and activation energy of the first stage of decomposition is defined. The thermal stabilities of double thiocyanatobismuthates and double thiosulphatobismuthates are compared.

INTRODUCTION

Our previous work [1] established the kinetic parameters of thermal decomposition of thiocyanatobismuthates(III) containing one kind of cation in the outer sphere (single salts). The purpose of the present work is to establish the kinetic parameters of thermal decomposition of double thiocyanatobismuthates containing two different cations of alkali metals in the outer sphere (double salts).

The course of the thermal decomposition reactions of double thiocyanatobismuthates(III) [2] and thiosulphatobismuthates(III) [3] were examined previously. However, the kinetic parameters of the decomposition reaction of double thiocyanatobismuthates were not determined at that stage. The present work compares the thermal stability and activation energy of the first stage of decomposition of single and double thiocyanatobismuthates(III) belonging to different groups and of double thiocyanatobismuthates(III) and thiosulphatobismuthates(III) of the sodium groups.

EXPERIMENTAL

Thermal analyses were carried out using a MOM Budapest type OD-102 1500 °C thermal analyzer. The measurements were made in air, in the temperature range 20–1000 °C, at a heating rate of 5 °C min^{-1}.

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The sensitivity of the galvanometer for the DTA curve was 0.2 and that for the DTG curve was 0.05. The TG sensitivity was 200 mg. α-Alumina was used as reference material. Each sample weighed 250 mg.

The X-ray analysis of sinters was carried out with a DRON-1 X-ray analyzer with copper source radiation and a nickel filter. The intensity of the reflections was measured with a scintillation counter. Diffractograms were recorded automatically for 2θ angles from 2 to 70 °.

The infrared spectra were obtained by means of a Zeiss IR-10 infrared spectrophotometer. The KBr disc method and the Nujol mull technique were employed to obtain spectra over the ranges 2300–1900 and 700–400 cm^{-1}.

THERMAL DECOMPOSITION OF DOUBLE THIOCYANATOBISMUTHATES(III) AND THIOSULPHATOBISMUTHATES(III)

The thermal decomposition of double thiocyanatobismuthates proceeds in a way similar to that of the single salts [1,4]. It is considered in this work

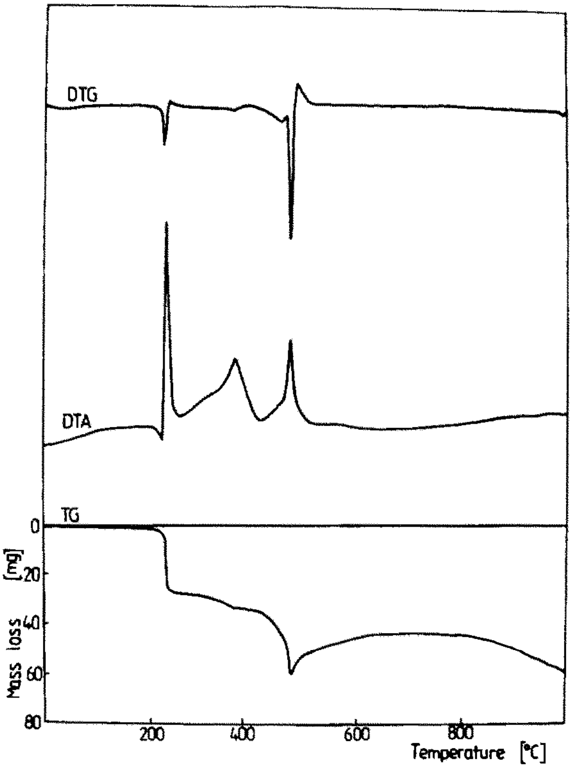

Fig. 1. Thermal analysis curves of potassium–sodium thiocyanatobismuthate(III).

with the compound $K_2Na[Bi(SCN)_6]$ as an example. The thermal curves of this compound are presented in Fig. 1. The endothermic peak at 230 °C is connected with the thermal dissociation of the compound

$$K_2Na[Bi(SCN)_6] \rightarrow 2KSCN + NaSCN + Bi(SCN)_3 \qquad (1)$$

The directly following intense exothermic peak at 240 °C involves a rapid mass loss and corresponds to the decomposition of $Bi(SCN)_3$, in which bismuth sulphide and an intermediate product of decomposition containing bismuth, sulphur, carbon and nitrogen are formed [5]. The equation for the first stage of decomposition is

$$6K_2Na[Bi(SCN)_6] \rightarrow 12KSCN + 6NaSCN + Bi_2S_3 + 4BiS_xC_yN_z + \text{gaseous products} \qquad (2)$$

In the second stage of decomposition, with the corresponding exothermic peak at 380 °C, sodium and potassium thiocyanates are oxidized to form sulphates. In the third stage (the third exothermic peak, at 490 °C) the intermediate product is decomposed and, as a result, bismuth sulphide and bismuth are formed. The general equation illustrating the decomposition at about 500 °C is as follows

$$6K_2Na[Bi(SCN)_6] + 75O_2 \rightarrow 2Bi_2S_3 + 2Bi + 6K_2SO_4 + 3Na_2SO_4 + 36CO_2 + 18N_2 + 21SO_2 \qquad (3)$$

The increase in mass occurring on the TG curve above 500 °C is related to the oxidation of bismuth sulphide and bismuth and the resulting formation of bismuthyl sulphate and bismuth oxide.

The above equation (3) was based on thermal analysis, chemical analysis of solid and gaseous decomposition products and X-ray and IR analysis of the solid decomposition products.

The course of the thermal decomposition of double thiosulphatobismuthates(III) was examined in a similar way. It is analogous to the previously described decomposition of the single salts [1,3]. Figure 2 presents the thermal curves for caesium–sodium thiosulphatobismuthate. In the first stage of decomposition the compound is dissociated into simple caesium, sodium and bismuth thiosulphates; the bismuth thiosulphate is immediately decomposed to form bismuth sulphide and alkali metal thiosulphates are oxidized to form an intermediate product and sulphur

$$2Cs_2Na[Bi(S_2O_3)_3] \rightarrow Bi_2S_3 + S + Cs_4Na_2S_5O_{12} + 3SO_2 \qquad (4)$$

In the second stage the intermediate compound is decomposed and alkali metal sulphates are formed along with more sulphur, which is immediately oxidized

$$2Cs_2Na[Bi(S_2O_3)_3] + 3O_2 \rightarrow Bi_2S_3 + 2Cs_2SO_4 + Na_2SO_4 + 6SO_2 \qquad (5)$$

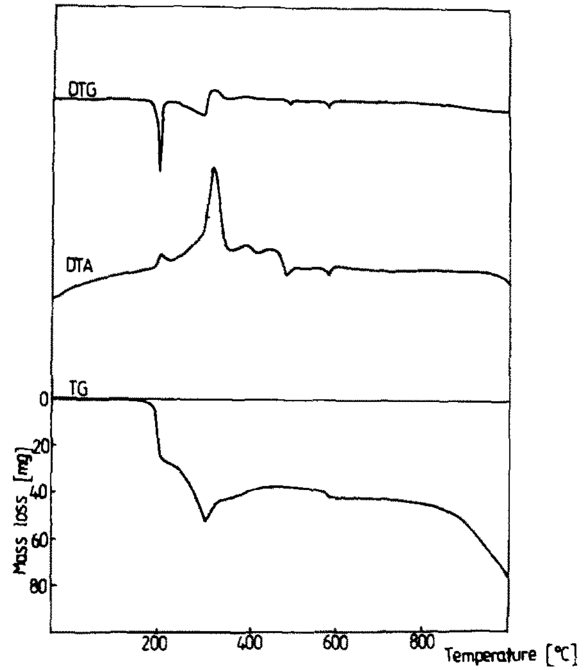

Fig. 2. Thermal analysis curves of caesium–sodium thiosulphatobismuthate(III).

The $Cs_2Na[Bi(S_2O_3)_3]$ is an anhydrous compound. Potassium–sodium thiosulphatobismuthates are hydrated salts and thus their decomposition proceeds in three stages, the first of which is dehydration.

DETERMINATION OF KINETIC PARAMETERS

In line with our earlier work [1] in determining the activation energy and reaction order for each stage of decomposition of double alkali thiocyanatobismuthates, two methods from the group of integral methods, those of Coats and Redfern [6] and Zsakó [7], were employed. Computer programs were based on the mathematical formulae given by the authors.

The results of the calculations are listed in Table 1.

RESULTS AND DISCUSSION

The comparison of thermal stability and activation energy of the first stage of decomposition of double thiocyanatobismuthates (Table 1) and the initial single compounds [1] indicates that the double salts are more stable than the single ones if a cation with larger radius has been substituted for a cation with smaller radius.

TABLE 1

Kinetic parameters and initial decomposition temperatures of double alkali metal thiocyanatobismuthates(III)

Compound	First stage				Second stage				Third stage				Initial decomposition temperature (°C)
	Z		C–R		Z		C–R		Z		C–R		
	n	*E*	*n*	*E*	*n*	*E*	*n*	*E*	*n*	*E*	*n*	*E*	
Sodium group													
$K_2Na[Bi(SCN)_6]$	0.4	38	0.4	38	1.0	20	1.1	20	1.9	57	2.0	58	220
$Rb_2Na[Bi(SCN)_6]$	1.9	68	2.0	70	1.3	20	1.3	20	1.8	88	1.8	86	215
$Cs_2Na[Bi(SCN)_6]$	1.9	67	2.0	70	0.4	14	0.3	13	1.5	89	1.5	89	230
Potassium group													
$Rb_2K[Bi(SCN)_6]$	1.2	22	1.2	21	0.0	13	1.0	13	1.4	90	1.4	96	165
$Cs_2K[Bi(SCN)_6]$	1.9	32	2.0	33	1.8	18	1.9	19	0.4	52	0.4	53	180
Lithium group													
$Rb_2Li[Bi(SCN)_6]$	0.0	22	0.0	22	0.5	13	0.4	12	0.0	43	0.0	43	195
$Cs_2Li[Bi(SCN)_6]$	0.0	16	0.0	16	1.7	23	1.7	24	0.4	30	0.4	29	155

Z = Zsakó method; C–R = Coats and Redfern method; *n* = order of reaction; *E* = activation energy (kcal mol^{-1}).

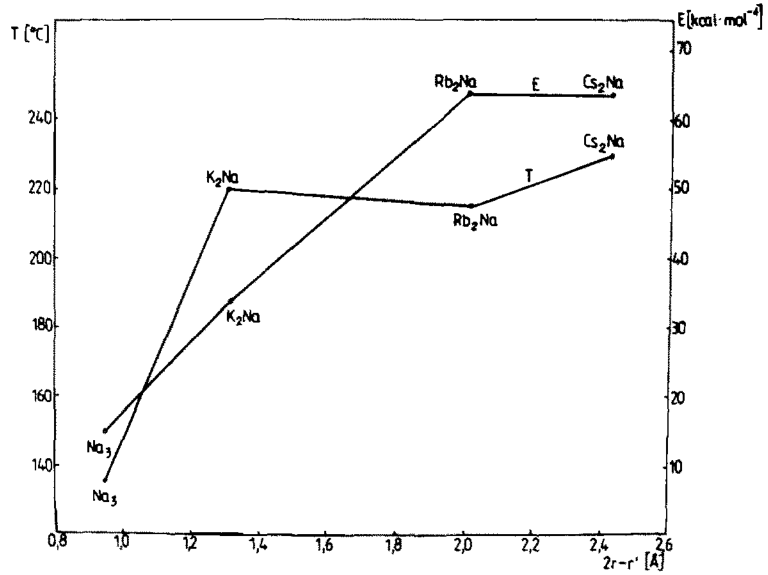

Fig. 3. Effect of the difference between ionic radii of the outer sphere cations on the initial decomposition temperature and activation energy of the sodium group thiocyanatobismuthates(III).

Thus, the replacement of two atoms of sodium in $Na_3[Bi(SCN)_6]$ by atoms of potassium, rubidium or caesium results in a considerable increase in thermal stability and activation energy of the double salt as compared with the initial single salt (Table 1, Fig. 3).

Similarly, the substitution of atoms of rubidium or caesium for two atoms of lithium in $Li_3[Bi(SCN)_6]$ causes a considerable increase in stability. However, if the difference in magnitude of the radii of the outer sphere cations is significantly smaller than in the above examples, no increase in the stability of the double salt is observed, e.g. $K_3[Bi(SCN)_6]$ and $Rb_2K[Bi(SCN)_6]$. The replacement of two potassium atoms in $K_3[Bi(SCN)_6]$ by caesium atoms results in a distinct increase in thermal stability and activation energy of the first stage of decomposition.

A similar correlation is observed for thiosulphatobismuthates [8]. The substitution of potassium or caesium atoms for two sodium atoms in $Na_3[Bi(S_2O_3)_3]$ results in an increase of thermal stability, which is highest in the case of $Cs_2Na[Bi(S_2O_3)_3]$.

It is possible to divide double thiocyanatobismuthates of the general formula $M_2M'[Bi(SCN)_6]$, where $r_M > r_{M'}$, into two groups, depending on the identity of cation M′ or M. If cation M′ is the basis of this division, the groups are the following: the sodium group $M' = Na$, the lithium group $M' = Li$, and the potassium group $M' = K$. The lithium and potassium groups are represented by two compounds each, and the sodium group comprises three compounds.

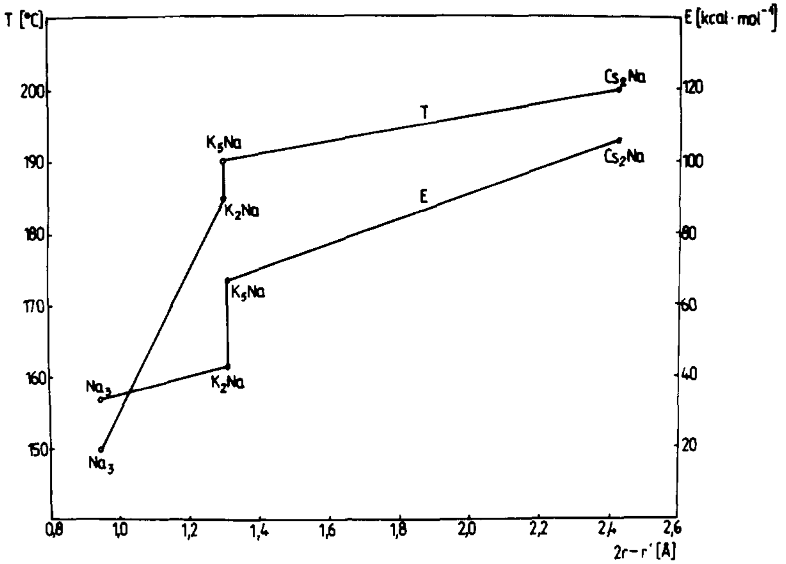

Fig. 4. Effect of the difference between ionic radii of the outer sphere cations on the initial decomposition temperature and activation energy of the sodium group thiosulphatobismuthates(III).

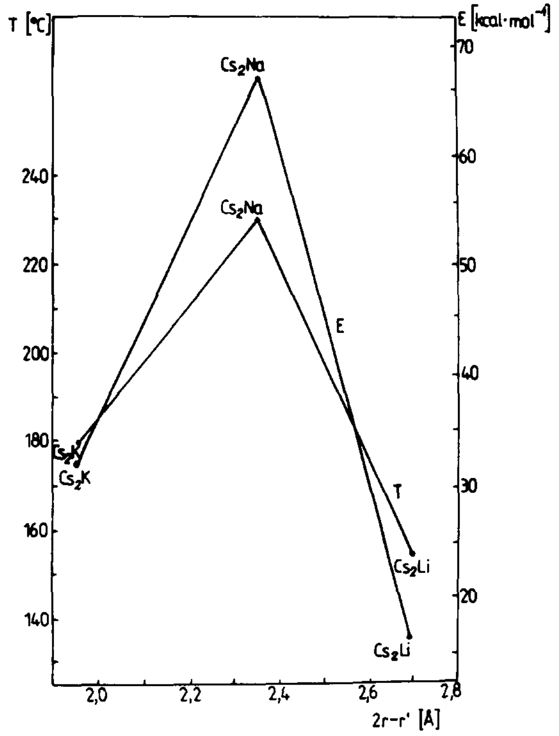

Fig. 5. Effect of the difference between ionic radii of the outer sphere cations on the initial decomposition temperature and activation energy of the caesium group thiocyanatobismuthates(III).

The dependence of the thermal stability of the compounds of the sodium group upon the difference between the radii of the outer sphere cations is presented in Fig. 3. From the figure it follows that the increase in thermal stability is connected with the difference between the radii, although the dependence is not regular.

The substitution of potassium for sodium causes a considerable increase in the thermal stability, while the replacement of sodium by rubidium, the ionic radius of which is similar to that of potassium, does not result in a higher stability of $Rb_2Na[Bi(SCN)_6]$ compared with $K_2Na[Bi(SCN)_6]$, although the activation energy does increase.

The substitution of caesium for sodium results in an increased thermal stability of $Cs_2Na[Bi(SCN)_6]$ compared with $Rb_2Na[Bi(SCN)_6]$. The initial temperature of decomposition of caesium–sodium thiocyanatobismuthate (III) is the highest among all the compounds tested, which indicates that this compound exhibits the highest thermal stability among all the thiocyanatobismuthates. This compound also shows the highest chemical stability and resistance to hydrolytic decomposition. The activation energies of the first stage of decomposition of rubidium–sodium and caesium–sodium salts are, however, similar; thus there is no conformity between the direction of

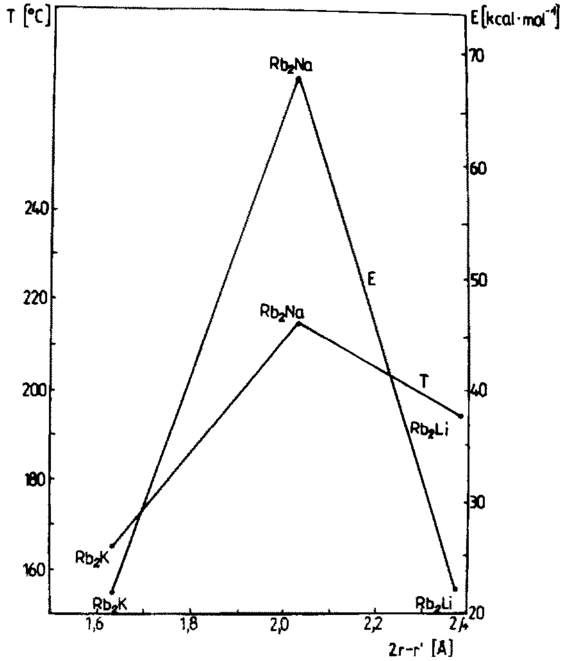

Fig. 6. Effect of the difference between ionic radii of the outer sphere cations on the initial decomposition temperature and activation energy of the rubidium group thiocyanatobismuthates(III).

changes in the initial temperature of decomposition and the activation energy.

Among the sodium thiosulphatobismuthates(III), increased thermal stability related to the increase of differences between ionic radii of the outer sphere cations is also observed (Fig. 4): $K_5Na[Bi(S_2O_3)_3]_2$ being considerably more stable than $K_2Na[Bi(S_2O_3)_3]$.

Depending on the identity of cation M, double thiocyanatobismuthates (III) $[M_2M'Bi(SCN)_6]$ are divided into two groups: the caesium group, $Cs_2M'[Bi(SCN)_6]$, and the rubidium group, $Rb_2M'[Bi(SCN)_6]$.

Figures 5 and 6 illustrate the dependence of the temperature of onset of decomposition and the activation energy upon the difference between the radii of the outer sphere cations. It is evident that the salts containing sodium exhibit the highest stability. Their higher stability may be accounted for by the larger difference between ionic radii (as compared with the potassium-containing compounds) or by the counter-polarizing properties of the lithium cation (in the case of lithium-containing compounds).

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