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# KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION OF THIOCYANATOBISMUTHATES(III). PART 1. SINGLE SALTS OF ALKALI METALS

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## ABSTRACT

Kinetic parameters of the thermal decomposition of alkali metal thiocyanatobismuthates, of general formula $M_3[Bi(SCN)_6]$, where $M \equiv$ Li, Na, K, Rb, and $M[Bi(SCN)_4]$, where $M \equiv$ Rb and Cs, and bismuth thiocyanate $Bi(SCN)_3$ have been determined. The reaction order and activation energy of several stages of the decomposition have been determined and the effect of the outer-sphere cations on the thermal stability and activation energy has been defined. The thermal stabilities of thiocyanatobismuthates and thiosulphatobismuthates have been compared.

## INTRODUCTION

The course of the thermal decomposition of thiocyanatobismuthates(III) of alkali metals was previously defined on the basis of thermal, chemical, X-ray and IR analyses of the decomposition products obtained at the temperatures of the characteristic conversions [1,2]. However, the kinetic parameters of the decomposition of thiocyanatobismuthates, the most numerous group of thiocyanate complex salts, were never determined. The present paper presents a comparison of the thermal stabilities and activation energies of thiocyanatobismuthates of alkali metals with respect to the outer-sphere cation. In addition, the thermal stabilities of thiocyanatobismuthates and thiosulphatobismuthates whose thermal decomposition [3] and kinetic parameters of decomposition [4] had been previously reported, were compared.

## THERMAL DECOMPOSITION OF ALKALI METAL THIOCYANATOBISMUTHATES(III)

The general course of the thermal decomposition reactions of alkali metal thiocyanatobismuthates is as follows. First, the thiocyanatobismuthates ther-

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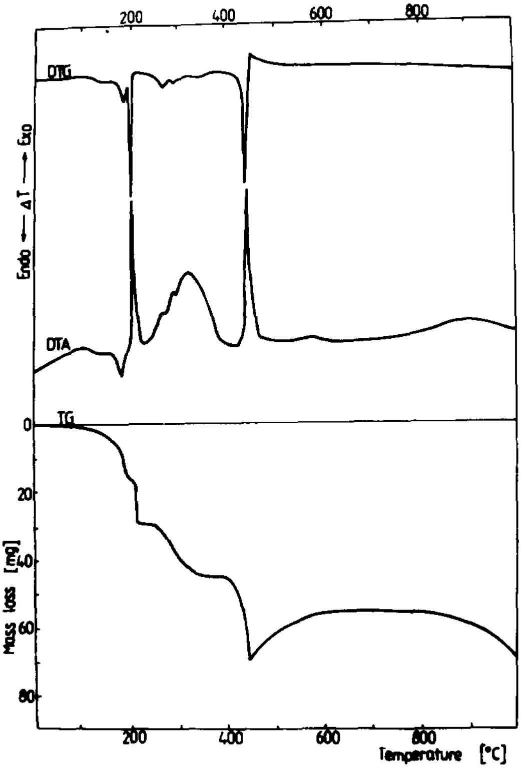

Fig. 1. Thermal analysis curves of sodium thiocyanatobismuthate(III).

mally dissociate into bismuth thiocyanate and alkali metal thiocyanate

$$M_3[Bi(SCN)_6] \rightarrow 3MNCS + Bi(SCN)_3 \qquad (1)$$

In contrast to the alkali metal thiocyanate, bismuth thiocyanate is unstable at the temperature at which the dissociation occurs, and immediately decomposes

$$6Bi(SCN)_3 \rightarrow Bi_2S_3 + 4BiS_xC_yN_z + \text{gaseous products} \qquad (2)$$

As a result of the decomposition at about 200 °C, bismuth sulphide and an intermediate product of decomposition containing bismuth, sulphur, carbon and nitrogen are formed. The composition of the intermediate product depends on the initial compound and the conditions of the decomposition.

By adding eqns. (1) and (2), an equation is obtained describing the solid products of the first stage of decomposition, corresponding to the first exothermic peak on the DTA curve, Fig. 1

$$6M_3[Bi(SCN)_6] \rightarrow 18MNCS + Bi_2S_3 + 4BiS_xC_yN_z + \text{gaseous products} \qquad (3)$$

In the second stage of the decomposition, alkali metal thiocyanate is oxidised to sulphate. The second wide exothermic peak on the DTA curve corresponds with this stage

$$2MNCS \rightarrow M_2SO_4 + \text{gaseous products} \tag{4}$$

In the third decomposition stage, the third exothermic peak on the DTA curve, the decomposition of the intermediate compound into bismuth sulphide and bismuth takes place

$$4BiS_xC_yN_z \rightarrow Bi_2S_3 + 2Bi + \text{gaseous products} \tag{5}$$

The general equation of decomposition at about 450 ° C reads as follows

$$6M_3[Bi(SCN)_6] + 81O_2 \rightarrow 2Bi_2S_3 + 2Bi + 9M_2SO_4 + 18N_2 + 36CO_2 + 27SO_2 \tag{6}$$

The gaseous products shown in eqn. (6) were determined at this temperature.

Typical thermal curves of alkali metal thiocyanatobismuthates are presented in Fig. 1. They are curves for sodium thiocyanatobismuthate. The endothermic peak at 180 ° C and, directly following it, the first exothermic peak at 215 ° C, correspond with the first stage of decomposition, whereas the second exothermic peak at 320 ° C and the third exothermic peak at 450 ° C correspond with the second and third stages, respectively. The increase in mass observed on the TG curve above 450 ° C is associated with the oxidation of bismuth sulphide and bismuth into bismuthyl sulphate and bismuth oxide.

## THERMAL DECOMPOSITION REACTIONS OF ALKALI METAL THIOSULPHATOBISMUTHATES(III)

Thiosulphatobismuthates(III) of alkali metals are hydrated salts; therefore the first stage of their decomposition involves dehydration

$$M_3[Bi(S_2O_3)_3] \cdot H_2O \rightarrow M_3[Bi(S_2O_3)_3] + H_2O \qquad M \equiv Na, K, Rb \tag{7}$$

In the second stage, the basic decomposition of the complex compound into simple thiosulphates of alkali metals and bismuth occurs

$$2M_3[Bi(S_2O_3)_3] \rightarrow Bi_2(S_2O_3)_3 + 3M_2S_2O_3 \tag{8}$$

Thiosulphates of heavy metals, like their thiocyanates, are considerably less stable then those of alkali metals, thus bismuth thiosulphate immediately decomposes at the temperature of dissociation

$$Bi_2(S_2O_3)_3 \rightarrow Bi_2S_3 + 3SO_2 + 1.5O_2 \tag{9}$$

The thiosulphates of alkali metals react gradually with oxygen, forming sulphur and an intermediate compound containing an alkali metal cation, sulphur and oxygen

$$3M_2S_2O_3 + 1.5O_2 \rightarrow S + M_6S_5O_{12} \tag{10}$$

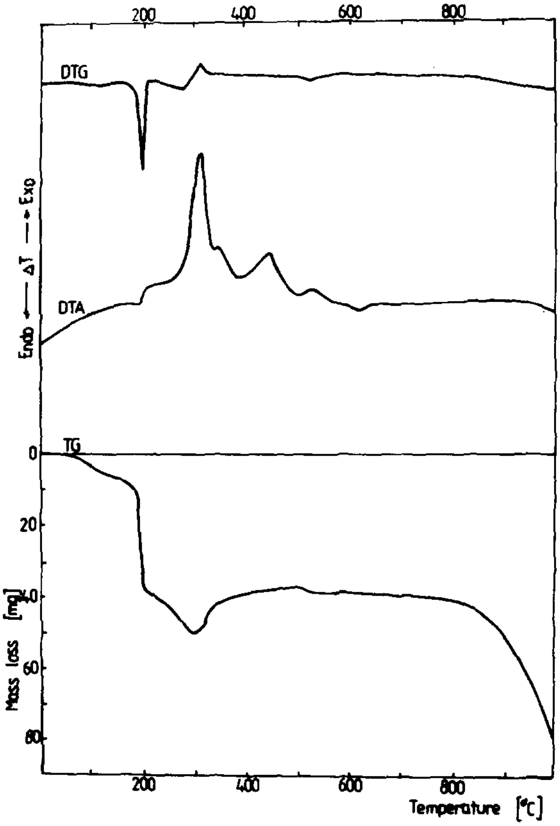

Fig. 2. Thermal analysis curves of rubidium thiosulphatobismuthate(III).

The general reaction of the second decomposition stage of thiosulphatobismuthates is as follows

$$2M_3[Bi(S_2O_3)_3] \rightarrow Bi_2S_3 + S + M_6S_5O_{12} + 3SO_2 \qquad (11)$$

In the third stage, the intermediate product decomposes to form alkali metal sulphate and more sulphur which is immediately oxidised. This is illustrated by a large exothermic peak on the DTA curve, Fig. 2. The reactions are

$$Bi_2S_3 + S + M_6S_5O_{12} \rightarrow Bi_2S_3 + 3M_2SO_4 + 3S \qquad (12)$$

$$3S + 3O_2 \rightarrow 3SO_2 \qquad (13)$$

The final reaction in the thermal decomposition of thiosulphatobismuthates occurs at about 320 ° C, with a corresponding maximum loss in mass on the TG curve

$$2M_3[Bi(S_2O_3)_3] + 3O_2 \rightarrow Bi_2S_3 + 3M_2SO_4 + 6SO_2 \qquad (14)$$

## METHODS OF DETERMINATION OF KINETIC PARAMETERS

The determination of the kinetic parameters describing the process of thermal dissociation of solid bodies (activation energy and order of reaction) by experiments carried out under non-isothermal conditions is based on the equation describing the thermogravimetric curve

$$F(\alpha) = \int_{\alpha_0}^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{a} \int_{T_0}^{T} \mathrm{e}^{-E/RT} \mathrm{d}T \tag{15}$$

where $\alpha$ is the thermal decomposition rate, $A$ is the frequency factor, $a$ is the constant heating rate, $E$ is the activation energy, $R$ is the gas constant and $T$ is the temperature (K). The thermal decomposition rate is calculated in the following manner

$$\alpha = \frac{W_0 - W}{W_0 - W_t} \tag{16}$$

where $W_0$, $W$ and $W_t$ are the initial, actual and final sample weights. It is usually assumed that

$$f(\alpha) = (1 - \alpha)^n \tag{17}$$

where $n$ is the order of reaction.

The exponential integral of the right-hand side of eqn. (15) cannot be mathematically solved in a finite way. Therefore $u = E/RT$ was introduced, assuming that $x$ is the value of $u$ at the sample temperature and the right-hand side of eqn. (15) was transformed to obtain the following equation describing the TG curve

$$F(\alpha) = \frac{AE}{aR} p(x) \tag{18}$$

$$p(x) = -\int_{\infty}^{x} \frac{\mathrm{e}^{-u}}{u^2} \mathrm{d}u = \frac{\mathrm{e}^{-x}}{x} - \int_{x}^{\infty} \frac{\mathrm{e}^{-u}}{u} \mathrm{d}u \tag{19}$$

In order to calculate the activation energy, the two well-known methods of Coats and Redfern [5] and Zsakó [6], based on eqn. (18), were used in the present work. Computer programs were written for these methods which make use of three first fragments of asymptotic expansion to solve the integral $p(x)$. In both methods, the values of reaction order from 0 to 2 were taken into account at every 0, 1.

With Zsakó's method, the assumed range of possible activation energies was 3–100 kcal mol$^{-1}$.

## RESULTS AND DISCUSSION

Table 1 lists the kinetic parameters (reaction order and activation energy) for the reactions of the thermal decomposition of hexa- and tetrathio-

TABLE 1

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

| Compound | First stage | | | | Second stage | | | | Third stage | | | | Initial decomposition temperature (°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* | |
| $Li_3[Bi(SCN)_6]$ | 0.6 | 11 | 0.5 | 11 | 1.5 | 13 | 1.5 | 13 | 1.8 | 80 | 1.8 | 81 | 120 |
| $Na_3[Bi(SCN)_6]$ | 1.2 | 15 | 1.1 | 14 | 1.9 | 18 | 2.0 | 19 | 0 | 96 | 0 | 96 | 135 |
| $K_3[Bi(SCN)_6]$ | 1.4 | 22 | 1.4 | 22 | 1.6 | 20 | 1.7 | 20 | 0.9 | 73 | 0.8 | 71 | 170 |
| $Rb_3[Bi(SCN)_6]$ | 1.3 | 20 | 1.3 | 20 | 1.4 | 15 | 1.3 | 14 | 1.1 | 82 | 1.1 | 81 | 160 |
| $Rb[Bi(SCN)_4]$ | 0 | 35 | 0 | 35 | 0.8 | 12 | 0.8 | 11 | 1.9 | 157 | 2.0 | 160 | 180 |
| $Cs[Bi(SCN)_4]$ | 0 | 17 | 0 | 17 | 1.1 | 15 | 1.1 | 14 | 0 | 53 | 0 | 53 | 155 |
| $Bi(SCN)_3$ | 1.9 | 20 | 2.0 | 21 | 0 | 37 | 0 | 36 | 0 | 30 | 0 | 30 | 145 |

[a] Z, Zsakó's method.

[b] C–R, Coats and Redfern's method.

[c] *n*, order of reaction.

[d] *E*, activation energy (kcal $mol^{-1}$).

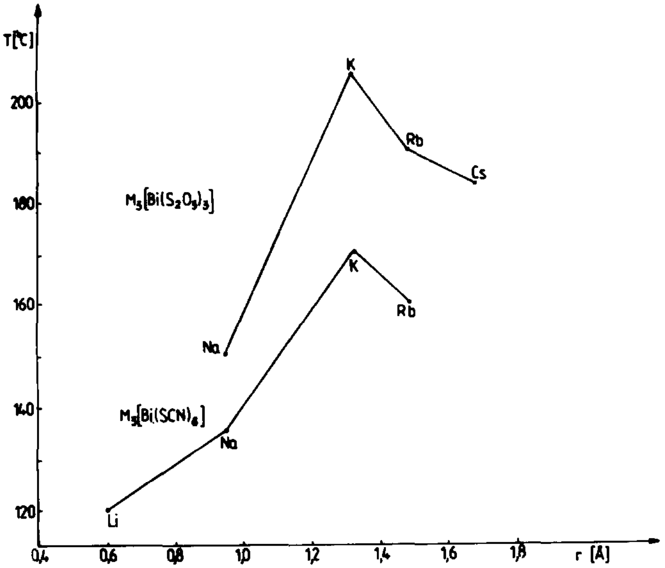

Fig. 3. Effect of the outer-sphere cations on the initial decomposition temperature of thiocyanatobismuthates(III) and thiosulphatobismuthates(III).

cyanatobismuthates(III) of alkali metals and bismuth thiocyanate, along with the temperatures at which their decomposition begins. The kinetic parameters were calculated by two methods and the results obtained were consistent. The initial decomposition temperature was determined from the TG curve.

The decomposition of all the thiocyanatobismuthates under study, except $Li[Bi(SCN)_6] \cdot 3H_2O$, proceeds in three stages. In the case of the lithium salt which crystallises with the addition of three water molecules, the first stage is dehydration, and thus the data presented in the table refer to the second, third and fourth stages of its decomposition.

From a comparison of the initial decomposition temperatures (Fig. 3), it follows that the potassium compound exhibits the highest and the lithium compound the lowest thermal stability among the hexathiocyanatobismuthates. A similar trend is observed for the activation energy of the first decomposition stage (Fig. 4) of sodium, potassium and rubidium salts, and for the second stage of decomposition of the lithium salt. As the direction of the changes in initial decomposition temperatures and in activation energy of the first decomposition stage is the same, it was assumed that they characterise the thermal stability of the compounds.

While comparing the consecutive stages of decomposition of the individual hexathiocyanatobismuthates(III) of alkali metals, it was found that for the first and second stages, the activation energies change over similar ranges: first stage, 11–22 kcal mol$^{-1}$; and second stage, 13–20 kcal mol$^{-1}$; whereas for the third stage they are much higher: 71–96 kcal mol$^{-1}$.

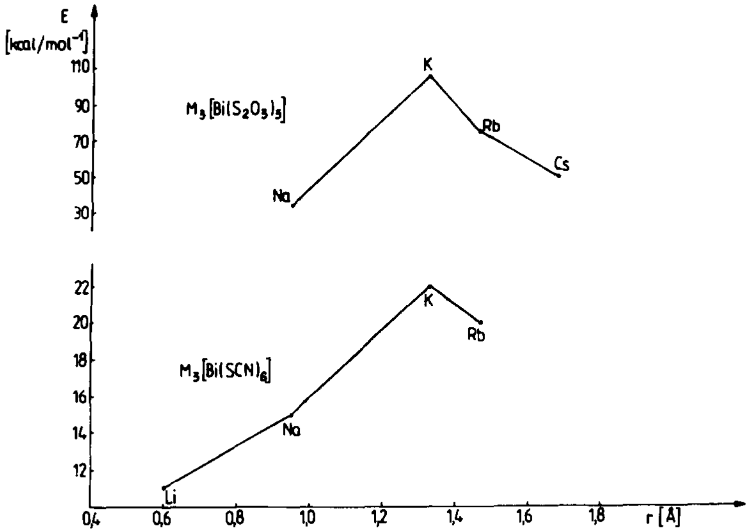

Fig. 4. Effect of the outer-sphere cations on the activation energy of thiocyanatobismuthates (III) and thiosulphatobismuthates(III).

The direction of changes in thermal stability is similar for the thiosulphatobismuthates(III). The potassium salt is the most stable, while the sodium salt is the least stable (the lithium salt was not obtained). The initial decomposition temperatures are higher than those of the thiocyanatobismuthates (Fig. 3). The activation energies are much higher (Fig. 4) but the direction of changes in activation energy is also the same as in the case of the initial decomposition temperatures.

As potassium, rubidium and caesium salts are isostructural, the highest stability of the potassium salt may be accounted for by the principle of the most close packing: in the case of potassium, the structural void reaches optimal filling, the cations of larger radius causing expansion of the void and a decrease is the stability of the compound. This supposition may be confirmed after the structure of these compounds has been determined.

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