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THERMAL DECOMPOSITION REACTIONS AND KINETIC PARAMETERS OF NITRITOBISMUTHATES(III)

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ABSTRACT

Thermal studies have been carried out on nitritobismuthates(III) of the silver group having the general formula $M_2Ag[Bi(NO_2)_6]$ where M = Cs, Rb, K, and the sodium group having the formula $M_2Na[Bi(NO_2)_6]$ where M = Cs, Rb.

Typical thermal curves, temperatures of the endothermic peaks and percentage weight loss, calculated from the TG curve, are shown. On the basis of the results of thermal and X-ray analysis the mechanisms of the thermal decomposition reaction were determined for nitritobismuthates(III).

The thermal curves were used to calculate kinetic parameters, activation energy E_a and order of reaction n by Zsako's and Coats and Redfern's methods. A comparison of the thermal stabilities of the salts under study was made. Within the same group of nitritobismuthates(III), the activation energy and the decomposition temperatures of the salts increases when the difference between the radii of outer sphere cations increases.

INTRODUCTION

Ball and Abram[1] described the method for obtaining nitritobismuthates(III) of the general formula $M_2M'[Bi(NO_2)_6]$ where M = Cs, Rb, K and M′ = Ag, Na. Their preparation studies are restricted, however, since they only give methods for obtaining the compounds and determining their composition without describing their properties. The compound $6\ NaNO_2 \cdot 9\ CsNO_2 \cdot 5\ Bi(NO_2)_3$, used by Ball for the determination of sodium or caesium[2], was the only one that had undergone thermal analysis[3]. The compound is stable at 160–670°C. Duval did not investigate the behaviour of the compound or its products at higher temperatures.

This paper presents results of the thermal examination of nitritobismuthates(III) of the sodium group of general formula $M_2Na[Bi(NO_2)_6]$, where M = Cs, Rb, and the silver group $M_2Ag[Bi(NO_2)_6]$, where M = Cs, Rb, K. The subject of this paper is to study the mechanism of the thermal decomposition reactions as well as the thermal stability of examined nitritobismuthates(III) based on thermal curves and calculated kinetic parameters.

EXPERIMENTAL

Apparatus

The thermal studies were made with a derivatograph MOM OD-102 with α-Al_2O_3 as the inert substance. Other operating conditions were heating rate 6°/min, TG sensitivity 100 mg, DTA sensitivity 1/10, DTG sensitivity 1/10.

The X-ray analysis of sinters was carried out on a USSR-made diffractometer, type DRON-1, using Cu-K_α radiation filtered through a nickel filter and recording by a scintillation counter, the counter arm of which rotated at 20 r.p.m. with the automatic recording potentiometer tape moving at a speed of 20 mm/min. The X-ray diffraction patterns were recorded for 2θ angles from 2 to 70°.

Thermal analysis

The thermal curves for potassium–silver nitritobismuthates are illustrated in Fig. 1. The DTA curve exhibits several endothermic peaks. Among them, peaks I (170°C) and III (470°C) and also IV (520°C) and V (770°C) are connected with the immediate weight loss of the sample. Peak II (320°C) is not connected with the weight loss. The TG curve indicates that, after three stages of weight loss, the mass of the sample becomes stable (above 800°C). The thermal curves for rubidium–silver and caesium–silver nitritobismuthates have a similar pattern.

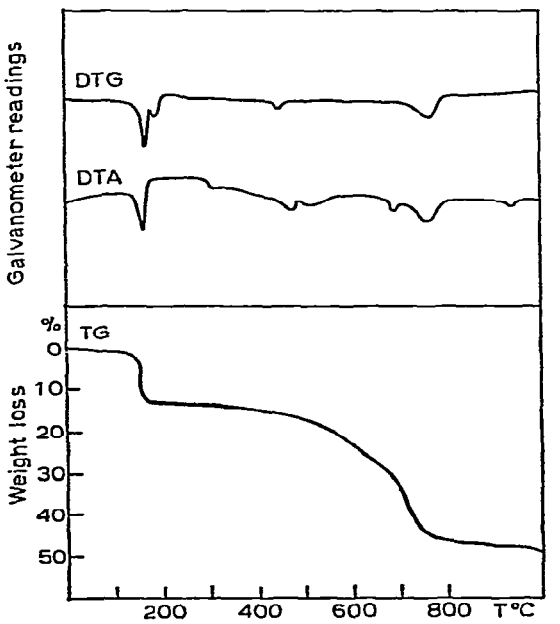

Fig. 1. Thermal analysis curves for $K_2Ag[Bi(NO_2)_6]$.

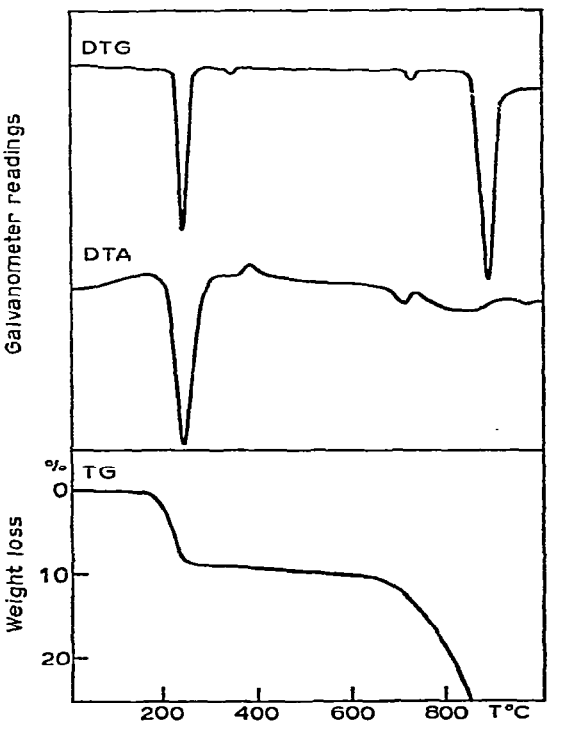

Fig. 2. Thermal analysis curves for $Cs_2Na[Bi(NO_2)_6]$.

TABLE 1

THERMAL ANALYSIS DATA ON THE DECOMPOSITION OF NITRITOBISMUTHATES (III) WITH RESPECT TO SETS OF DECOMPOSITION REACTIONS

Compound	*Temperatures of endothermic maxima on DTA curves*				*Weight loss corresponding to the maxima (%)*			
					I		*III*	
	I	*II*	*III*	*IV*	*Calcd. from reaction*	*Calcd. from TG*	*Calcd. from reaction*	*Calcd. from TG*
$Cs_2Ag[Bi(NO_2)_6]$	210	358	475	540	10.71	10.82	4.71	4.70
$Rb_2Ag[Bi(NO_2)_6]$	195	270	440	490	12.05	12.32	5.36	5.37
$K_2Ag[Bi(NO_2)_6]$	170	320	470	520	13.71	13.20	6.22	4.78
$Cs_2Na[Bi(NO_2)_6]$	240	340			8.37	8.75		
$Rb_2Na[Bi(NO_2)_6]$	190	340			9.72	9.60		

Thermal curves for the $Cs_2Na[Bi(NO_2)_6]$ and $Rb_2Na[Bi(NO_2)_6]$ compounds differ from those of the silver group nitritobismuthates(III). Up to 600 °C, there occur only two endothermic peaks connected with a weight loss. The first one, at about 200 °C, is very intense and involves a rapid weight loss. The second one, at 340 °C, is weakly marked on both the DTA and TG curves. Starting from 705 °C, there is a distinct peak on the DTG curve reaching the maximum at 890 °C. It is connected with a continuous weight loss marked on the TG curve. Thermal curves of $Cs_2Na[Bi(NO_2)_6]$ salts are shown in Fig. 2.

In Table 1, the temperatures of the endothermic maxima on the DTA curves and the percentages of weight loss for the nitritobismuthates(III) are given up to 600 °C, two main stages of decomposition taking place within that temperature range.

X-ray analysis

In order to examine the course of the reactions, sinters were prepared of the compounds under study under conditions similar to those of the derivatographic examination. Sinters of the following compounds were examined diffractometrically:

$Cs_2Na[Bi(NO_2)_6]$ heated to 300°, 400 °C
$Rb_2Na[Bi(NO_2)_6]$ heated to 250°, 400 °C
$Cs_2Ag[Bi(NO_2)_6]$ heated to 250°, 400°, 560°, 900 °C
$Rb_2Ag[Bi(NO_2)_6]$ heated to 200°, 300°, 500 °C
$K_2Ag[Bi(NO_2)_6]$ heated to 200°, 350°, 550 °C

and Bi_2O_3, Ag.

Figure 3 shows the X-ray pattern of $Cs_2Ag[Bi(NO_2)_6]$ and its sinters. The results of X-ray analysis for $K_2Ag[Bi(NO_2)_6]$ are collected in Table 2.

Determination of kinetic parameters

In this paper, the kinetic parameters of thermal decomposition of examined compounds were determined from thermogravimetric curves obtained on the derivato-

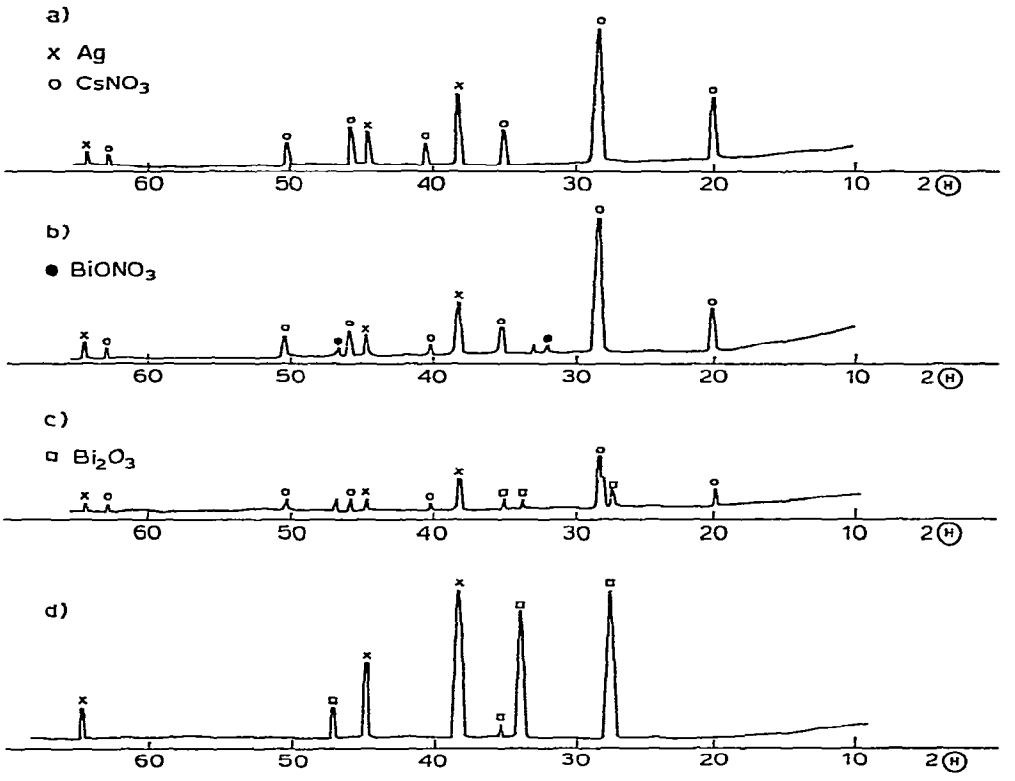

Fig. 3. X-Ray diffraction patterns of $Cs_2Ag[Bi(NO_2)_6]$ heated to (a) 250°C; (b) 400°C; (c) 560°C; (d) 900°C.

TABLE 2

X-RAY DIFFRACTION DATA FOR $K_2Ag[Bi(NO_2)_6]$

200°C *Data from patterns*		*Compounds*	*500°C* *Data from patterns*		*Compound*
2 θ	$\frac{d}{n}$		*2 θ*	$\frac{d}{n}$	
23.5	3.77	KNO_3	26.0	3.43	Bi_2O_3
27.5	3.25		27.1	3.29	
29.5	3.05	KNO_3	27.6	3.23	Bi_2O_3
31.8	2.81		28.2	3.17	
32.4	2.763	KNO_3	33.5	2.71	Bi_2O_3
34.0	2.636	KNO_3	38.2	2.356	Ag
38.2	2.356	Ag	44.4	2.04	Ag
44.4	2.04	Ag	44.6	2.03	Bi_2O_3
64.6	1.443	Ag	46.4	1.958	Bi_2O_3
			55.8	1.648	
			64.4	1.448	Ag

graph. The order of reaction and activation energy were determined using Coats and Redfern's method[4] and Zsako's method[5], which is a modification of the widely used Doyle method[6].

Coats and Redfern, assuming a linear heating rate, obtained the following relationships.

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{aE}\left[1-\frac{2RT}{E}\right]\exp(-E/RT)$$

After logging

$$\log\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303\,RT}$$

where $a = \mathrm{d}T/\mathrm{d}t$, α is the fraction of the substance undecomposed after time t and n is the order of reaction.

The authors determined the value of n for which they obtained a straight line of slope $-E/2.3\,R$ from the plot of $\log\{[1-(1-\alpha)^{1-n}]/[T^2(1-n)]\}$ against $1/T$ or $\log\{[-\log(1-\alpha)]/T^2\}$ against $1/T$ for $n = 1$. They determined the value of E from the slope.

Figure 4 shows a plot of the relationship between $y = -\log\{[1-(1-\alpha)^{1-n}]/[T^2(1-n)]\}$ and $1/T$ for nitritobismuthates where it forms a straight line, i.e. when $n = 2/3$. Values of the activation energy, calculated from the slopes of individual straight lines, are collected in Table 3. Values for the activation energy as calculated by Zsako's method are also given in Table 3.

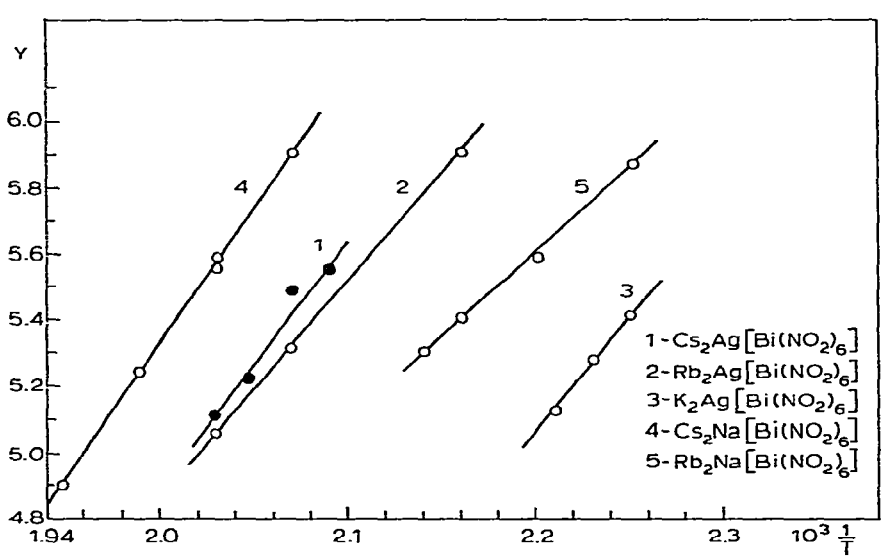

Fig. 4. Plot of $y = -\log\{[1-(1-\alpha)^{1-n}]/[T^2(1-n)]\}$ against $(1/T) \times 10^3$ for $n = 2/3$ nitritobismuthates(III).

TABLE 3

ACTIVATION ENERGIES FOR NITRITOBISMUTHATES(III) OF THE SILVER AND SODIUM GROUPS

Compound	*Order of reaction*	*Activation energy, E_a (kcal/mole)*	
		Coats–Redfern method	*Zsako method*
$Cs_2Ag[Bi(NO_2)_6]$	2/3	32.2	32.1
$Rb_2Ag[Bi(NO_2)_6]$	2/3	30.0	29.8
$K_2Ag[Bi(NO_2)_6]$	2/3	26.5	24.8
$Cs_2Na[Bi(NO_2)_6]$	2/3	34.1	34.0
$Rb_2Na[Bi(NO_2)_6]$	2/3	19.9	20

By using Zsako's method, the value for B was calculated according to the relationship

$$\log \frac{AE}{Rq} = \log g(\alpha) - \log p(x) = B$$

selecting values for $n = 0, 1/3, 1/2, 2/3$, according to the relationship

$$f(\alpha) = (1 - \alpha)^n$$

where α is the weight at the moment of its measurement divided by the total weight loss at the given stage of decomposition.

$$n = \frac{1}{2} \qquad g(\alpha) = 2\,[1 - \sqrt{1 - \alpha}]$$

$$B = \log 2 + \log\,[1 - \sqrt{1 - \alpha}] - \log p\,(x)$$

$$n = \frac{2}{3} \qquad g(\alpha) = 3\,[1 - \sqrt[3]{1 - \alpha}]$$

$$B = \log 3 + \log\,[1 - \sqrt[3]{1 - \alpha}] - \log p(x)$$

$$n = 1 \qquad g(\alpha) = -\ln (1 - \alpha)$$

$$B = \log \left[\ln \frac{1}{1 - \alpha}\right] - \log p(x)$$

Then, after standard deviations of individual B values from their arithmetic mean $\bar{B}$ had been calculated, an appropriate value of E_a was established for a given order of reaction.

Values of α and those of log $g(\alpha)$ at different temperatures, for orders of reaction 1/2, 2/3 and 1 for caesium–sodium nitritobismuthate are collected in Table 4. The values of the activation energy and the standard deviation are given in Table 5.

As shown in Table 5, in case of caesium–sodium nitritobismuthate the most appropriate parameters are order of reaction $n = 2/3$ and activation energy $E_a =$ 34 kcal/mole. The standard deviations have the lowest values, in case of other nitrito-

TABLE 4

LOG g(α) DATA FOR $Cs_2Na[Bi(NO_2)_6]$ AT DIFFERENT TEMPERATURES FOR $n = 1/2$, 2/3 AND 1

Temp. (°C)	α	*log* g(α)		
		$n = \frac{1}{2}$	$n = \frac{2}{3}$	$n = 1$
210	0.286	−0.5083	−0.4976	0.4725
220	0.514	−0.2173	−0.1925	0.1414
230	0.857	0.0945	0.1556	−0.2889
240	0.971	0.2198	0.4652	−0.5492

TABLE 5

INTERMEDIATE RESULTS OF THE CALCULATION OF KINETIC PARAMETERS FOR $Cs_2Na[Bi(NO_2)_6]$

$n = \frac{1}{2}$		$n = \frac{2}{3}$		$n = 1$	
E_a *(kcal/mole)*	δ	E_a *(kcal/mole)*	δ	E_a *(kcal/mole)*	δ
26	0.8038				
28	0.0634	28	0.0689	28	0.6224
30	0.1215	30	0.0423	30	0.2111
32	0.1844	32	0.02915	32	0.0655
34	0.5514	34	0.00346	34	0.04868
		36	0.0204	36	0.7757
		40	0.0536		

TABLE 6

ACTIVATION ENERGY, E_a, AND STANDARD DEVIATION, δ, FOR NITRITOBISMUTHATES(III) OF THE SILVER AND SODIUM GROUPS

Compound	*Order of reaction n = 2/3*			
	E_a *(kcal/mole)*	δ	E_a *(kcal/mole)*	δ
$Cs_2Ag[Bi(NO_2)_6]$	30	0.0570	32.0	0.0570
	32	0.0298	32.1	0.0092
	34	0.0561	32.2	0.0214
$Rb_2Ag[Bi(NO_2)_6]$	26	0.0194	29.7	0.0160
	28	0.0118	29.8	0.0012
	30	0.0685	29.9	0.0085
$K_2Ag[Bi(NO_2)_6]$	22	0.0556	24.7	0.0490
	24	0.05074	24.8	0.0058
	26	0.05477	24.9	0.0092
$Cs_2Na[Bi(NO_2)_6]$	32	0.02915	33.9	0.01015
	34	0.00346	34.0	0.00346
	36	0.0204	34.1	0.0091
$Rb_2Na[Bi(NO_2)_6]$	18	0.3739	19.9	0.0819
	20	0.0458	20.0	0.0458
	22	0.10099	20.1	0.0620

bismuthate salts, when the assumed order of reaction is $n = 2/3$. The data are collected in Table 6.

DISCUSSION

On the basis of the weight losses determined from the TG curves, and of X-ray analysis, the following scheme for the thermal decomposition of nitritobismuthates can be suggested.

$$6\ M_2Ag[Bi(NO_2)_6] \rightarrow 6\ Ag + 12\ MNO_3 + 4\ BiONO_3 \cdot Bi_2O_3 + N_{20}O_{17}{}^{*} \quad (1)$$

where M = Cs, Rb, K. The reaction corresponds to the first, very intense, endothermic peak at about 200°. The weight losses calculated according to this equation and from the TG curve are presented in Table 1. The peaks at about 500 °C correspond to the composition of 4 $BiONO_3 \cdot Bi_2O_3$, which gradually changes to bismuth oxide

$$4\ BiONO_3 \cdot Bi_2O_3 \rightarrow 3\ Bi_2O_3 + N_4O_{10} \quad (2)$$

The weight loss for this stage of the decomposition was calculated from reaction (3) (Table 1).

$$6\,Ag + 12\,MNO_3 + 4\,BiONO_3 \cdot Bi_2O_3 \rightarrow 6\,Ag + 12\,MNO_3 + 3\,Bi_2O_3 + N_4O_{10} \quad (3)$$

where M = Cs, Rb, K.

Nitritolanthanonates of the silver group are decomposed in an analogous way, e.g. 4 $LaONO_3 \cdot La_2O_3$ is gradually formed as a result of $Cs_2Ag[La(NO_2)_6]$ decomposition, and later it transforms into lanthanum oxide[7]. Compounds such as $LaONO_3$ (ref. 8) and $LaONO_3 \cdot n\ La_2O_3$ (ref. 9) are described by other authors.

In the third stage, the thermal dissociation of the alkali metal nitrate takes place. The decomposition results in the formation of metallic silver and bismuth oxide.

$$6\ Ag + 12\ MNO_3 + 3\ Bi_2O_3 \rightarrow 6\ Ag + 3\ Bi_2O_3 \quad (4)$$

The weight loss calculated according to this equation (Fig. 1) and from the TG curve amounts to 37.2% and 38%, respectively. Thermal decomposition of the sodium group is simpler. Nitrites of alkali metals and bismuth oxide are formed as a result of the decomposition at about 200°.

$$2\ Cs_2Na[Bi(NO_2)_6 = 4\ CsNO_3 + 2\ NaNO_3 + Bi_2O_3 + N_6O_5 \quad (5)$$

Comparison of initial thermal decomposition temperatures (first endothermic peaks) and activation energies proves that the thermal stability of the examined compounds, both in the silver group and in the sodium, depends on the magnitude of the M cation radius ($M_2Ag[Bi(NO_2)_6$ or $M_2Na[Bi(NO_2)_6]$. The caesium salt is the most stable, then follow the rubidium and the potassium salts. In the case of the sodium group

* The volatile products were not analyzed. In the reaction equations, the general composition of gaseous products is calculated from the weight loss.

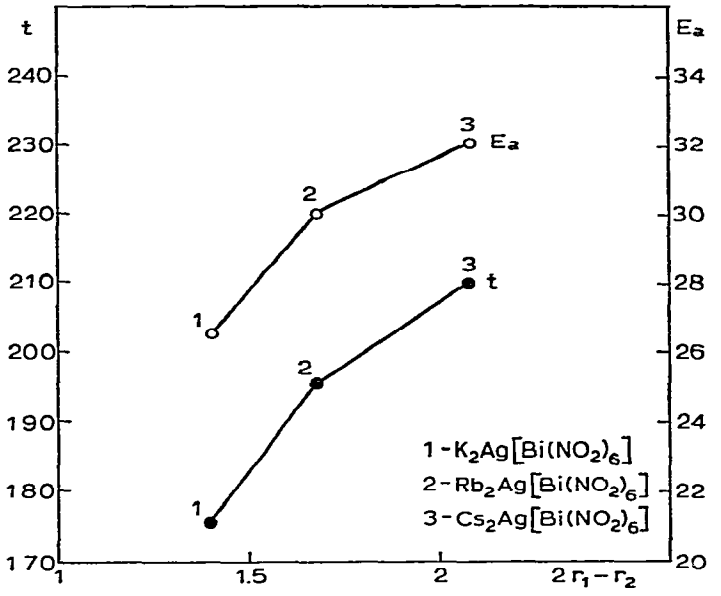

Fig. 5. Decomposition temperatures of nitritobismuthates(III) as a function of the radii of the central ions.

salts, the caesium–sodium salt (the most stable) is far more stable than the rubidium–sodium salt. The relationship between the initial thermal decomposition temperature and the activation energy determined by the Coats–Redfern and Zsako methods, and the differences in ionic radi of outer sphere cations of the silver group compounds, is shown in Fig. 5.

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