Thermochimica Acta, 52 (1982) 255–262
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION REACTIONS OF ALKALI METAL THIOSULPHATOBISMUTHATES(III)

A. CYGANSKI and J KOBYLECKA

Institute of General Chemistry, Technical University, 90-924 Łodz (Poland)

(Received 7 July 1981)

ABSTRACT

The present paper presents a calculation of the kinetic parameters (activation energy, order of reaction) for different stages of the decomposition of alkali metal thiosulphatobismuthates(III) Thermal stabilities and activation energies are compared for the compounds examined The influence of the outer sphere cations is defined as referred to the thermal stability of single ($M_3[Bi(S_2O_3)_3]$, where M = alkali metal ion with the exception of Li) and double ($M_2Na[Bi(S_2O_3)_3]$, where M = K, Cs and $K_5Na[Bi(S_2O_3)_3]_2$) thiosulphatobismuthates(III)

INTRODUCTION

A previous study [1] concerned the investigation of the thermal decomposition of alkali metal thiosulphatobismuthates(III), of general formulae $M_3[Bi(S_2O_3)_3] \cdot H_2O$ where M = Na, K, Rb, Cs, and $M'_2Na[Bi(S_2O_3)_3] \cdot H_2O$ where, M′ = K or Cs. The decomposition products were examined by thermal, chemical, X-ray and IR analyses. The decomposition mechanism was then established. The decomposition is split into three stages for hydrated compounds, or into two stages for non-aqueous compounds. In this paper the calculations of the kinetic parameters (activation energy, order of reaction) are shown for different stages of the thermal decomposition of thiosulphatobismuthates(III) using the methods of Coats and Redfern [2], Horowitz and Metzger [3] and Zsako [4].

METHODS APPLIED TO DETERMINE THE KINETIC PARAMETERS

The kinetic parameters of the thermal decomposition are calculated from the course of TG curves. The decomposition rate can be expressed as

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (1)$$

where α is the ratio of weight loss during time t to total loss of weight at a given decomposition stage

$$\alpha = \frac{W_0 - W}{W_0 - W_t} \tag{2}$$

where W_0, W_t and W are the initial, final and actual sample weights, respectively. $f(\alpha)$ is a function of α and its form depends on the reaction mechanism. It is usually assumed that

$$f(\alpha) = (1 \quad \alpha)^n \tag{3}$$

where n is the order of reaction. k is reaction rate constant, calculated from the Arrhenius equation

$$k = A\ e^{-E/RT} \tag{4}$$

where A is the frequency factor and E is the activation energy.

A sample is heated at a constant heating rate $a = dT/dt$. Using this relationship, and substituting eqn. (4) into eqn. (1), gives

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{a}\ e^{-E/RT}\,dT \tag{5}$$

Equation (5) is used to calculate the kinetic parameters of the thermal decomposition The equation can be solved by integration or differentiation methods [5]. If integration is used expression (5) is considered as a differential equation and the kinetic constants are derived from its integrated form. When using differentiation, the data must be obtained in differential form, and $d\alpha/dT$, α and T are substituted into eqn. (5) in its suitably converted form. Three integral methods were used to determine the kinetic parameters and they need to be discussed in more detail.

Equation (5), after integration, has the form

$$F(\alpha) = \int_0^{\infty} \frac{d\alpha}{f(\alpha)} = \frac{A}{a}\int_{T_0}^{T} e^{-E/RT}\,dt \tag{6}$$

If $u = E/RT$ is introduced such that x has the value of u at the temperature of the sample, eqn. (6), after appropriate conversions, has the form

$$F(\alpha) = \frac{AE}{aR}p(x) \tag{7}$$

where

$$p(x) = -\int_{\infty}^{x} \frac{e^{-u}}{u^2}\,du = \frac{e^{-x}}{x} - \int_{x}^{\infty} \frac{e^{-u}}{u}\,du \tag{8}$$

The main difficulty in the following considerations is that the exponential integral $p(x)$ occurring in eqn. (7) can not be integrated in a final form. Approximated expressions for this integral were used to solve the problem, as well as numerically integrated and tabulated values of the integral, for different activation energies and temperatures.

Coats and Redfern [2] assumed asymptotic development to solve the integral $p(x)$

and f(α) as shown in eqn. (3). They derived the formulae

$$\left.\begin{array}{l} \log F(\alpha) = -\log \dfrac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \\ \quad (\text{for } n \neq 1) \\ \log F(\alpha) = -\log \dfrac{-\log(1-\alpha)}{T^2} \\ \quad (\text{for } n = 1) \end{array}\right\} \cong \log\frac{AR}{aE}\left(1-\frac{2RT}{E}\right) - \frac{E}{2.3RT} \tag{9}$$

and they found that $\log AR/aE\,[1-2RT/(E)]$ is constant for most of the thermal decomposition reactions. The activation energy is found by a graphical method; log F(α) is plotted against $1/T$. For suitably selected values of n the plot is a straight line, the slope being $-E/2.3\,R$.

Horowitz and Metzger [3] derived a simple approximated equation to calculate the activation energy for a reaction, the order of which is $n = 1$.

$$\ln\ln C \cong \frac{E\theta}{RT_s^2} \tag{10}$$

The conversion rate, C, is defined as

$$C = \frac{W_0 - W_t}{W - W_t} \tag{11}$$

whereas $\theta = T - T_s$, T_s being the temperature at which the reaction rate is maximum. The value T_s can be determined as the temperature corresponding to the minimum on the DTG curve [6]. The activation energy is also determined by a graphical method; lnln C is plotted against θ. The plot is a straight line of E/RT_s^2 slope.

The method developed by Zsakó [4] is a modification of the well-known methods of Doyle [7]. The author logged eqn. (7) and obtained an expression

$$\log\frac{AE}{aR} = \log F(\alpha) - \log p(x) = B \tag{12}$$

where B is constant for a given reaction and a defined heating rate a. The value of conversion rate α was determined by Zsakó according to eqn. (2). Expression (3) was assumed for defining the function f(α); then, by solving integral (6) $F(\alpha) = \int_0^\infty d\alpha/f(\alpha)$, formulae allowing for the calculation of the value of the F(α) function, for different orders of reaction, were derived. Zsakó also gave tabulated values of logarithms of integrals p(x) for different temperatures and activation energies. Kinetic parameters are determined by a trial-and-error method. For each assumed order of reaction values of F(α) are calculated, for different decomposition temperatures; the value of B is then calculated for different activation energies. The correlation between experimental data and assumed activation energy is a quantitative measure of the standard deviation δ for a single value B_i from the arithmetic mean $\bar{B}$. The minimum value δ indicates the correct order of reaction and the best assumed activation energy.

RESULTS AND DISCUSSION

The conditions for plotting the thermal curves for thiosulphatobismuthates(III) were described in an earlier paper [1]. In this study, on the basis of the course of TG curves, data required for the determination of the kinetic parameters of individual stages of the thermal decomposition of thiosulphatobismuthates(III) were obtained. The methods discussed above were used for the calculation. Figure 1 shows the thermal curves for potassium-sodium thiosulphatobismuthate(III) $K_2Na[Bi(S_2O_3)_3] \cdot H_2O$. This compound will be used to exemplify the results obtained.

Coats and Redfern's method

Figure 2 shows the course of log $F(\alpha)$ vs $1/T$ for the second stage of the thermal decomposition of potassium-sodium thiosulphatobismuthate(III), with assumed orders of reaction 1/2, 1 and 2. The straight-line relationship was obtained for $n = 1$. A similar procedure proved that the order of dehydration reaction (the first stage of decomposition) is 2 and that for the third stage $n = 1$. Analogical values were obtained for most of the compounds investigated, using the same method. The slopes of the respective curves were used to calculate the activation energies for individual stages of thermal decomposition.

Horowitz and Metzger's method

Figure 3 shows the relationship of $\ln\ln C$ as a function of θ, obtained for the second stage of the thermal decomposition of $K_2Na[Bi(S_2O_3)_3] \cdot H_2O$. The plot is a straight line; its slope was used to determine the activation energy. Similar curves were obtained for the second and third stages of the decomposition of most of the compounds under investigation. Dehydration caused some deviation from the straight line since the order of reaction is 2, as determined by the methods of Coats and Redfern and Zsako.

Zsako's method

The value of $F(\alpha)$ was calculated for individual stages of the decomposition thiosulphatobismuthates(III), with different assumed orders of reaction. The following formulae were used

$n = 1/2 \quad F(\alpha) = 2(1 - \sqrt{1-\alpha})$
$n = 1 \quad F(\alpha) = -\ln(1-\alpha)$
$n = 2 \quad F(\alpha) = \dfrac{\alpha}{1-\alpha}$

The order of reaction and the activation energy were then determined using the procedure described above. The method could be used to determine the kinetic parameters of reactions whose activation energies do not exceed 66 kcal mole^{-1}; because tables quoted by Zsakó [4] contain logarithms $p(x)$ of integrals for activation energies between 10 and 66 kcal mole^{-1}.

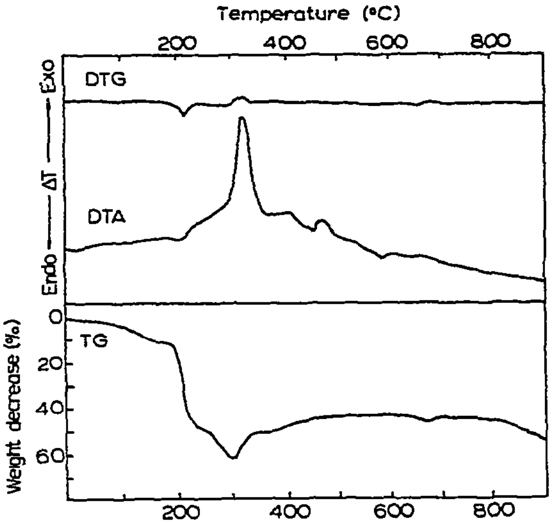

Fig 1 Thermal curves for potassium-sodium thiosulphatobismuthate(III) $K_2Na[Bi(S_2O_3)_3]\cdot H_2O$

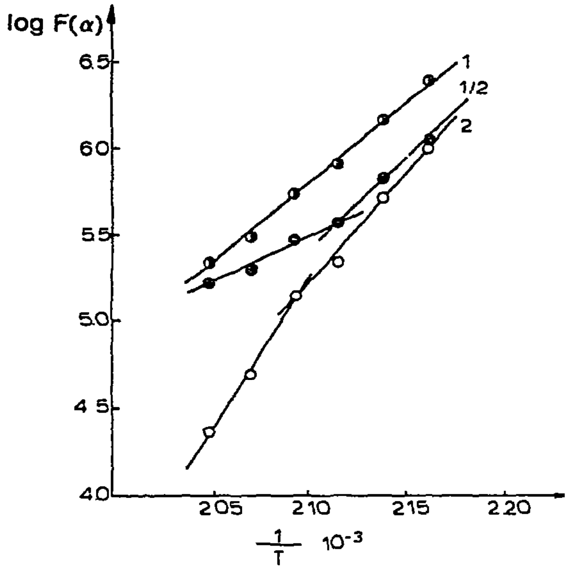

Fig 2 Determination of the order of reaction and activation energy at the second stage of the thermal decomposition of $K_2Na[Bi(S_2O_3)_3]$ H_2O by Coats and Redfern's method

The kinetic parameters for the individual stages of the thermal decomposition of thiosulphatobismuthates(III), as obtained by the three methods, are shown in Table 1. The order of dehydration reaction (first stage) is $n = 2$ for most hydrated compounds; the exception is the dehydration of sodium thiosulphatobismuthate(III) where $n = 1$. The activation energies of dehydration, as determined by the three methods, are about 11 kcal mole^{-1} for all hydrated compounds. These values are relatively low, which indicates the zeolithic nature of the water. This conclusion was confirmed by X-ray analysis.

The order of reaction is $n = 1$ for the second and third stages of the decomposition of hydrated thiosulphatobismuthates(III). The values are 1 for non-aqueous caesium thiosulphatobismuthate(III) and 1/2 for non-aqueous caesium-sodium thiosulphatobismuthate(III).

The activation energies for the basic decomposition stage, involving formation of intermediate products (second stage for hydrated compounds, first stage for non-aqueous salts) differ considerably for individual thiosulphatobismuthates(III). The sodium compound has the lowest activation energy (about 34 kcal mole^{-1}), and the potassium compound has the highest parameter (about 100 kcal mole^{-1}). The activation energies of double potassium-sodium salts are only half the value shown by potassium thiosulphatobismuthate(III). Thus, substituting a sodium atom for potassium causes a considerable decrease of the activation energy. It is quite different in the case of caesium. Substituting a sodium atom for caesium doubles the activation energy.

TABLE I

Kinetic parameters for individual stages of the thermal decomposition of alkali metal thiosulphatobismuthates(III)

Compound	First stage (dehydration)					Second stage					Third stage				
	C-R		Z		H-M	C-R		Z		H-M	C-R		Z		H-M
	n	*E*	*n*	*E*	*E*	*n*	*E*	*n*	*E*	*E*	*n*	*E*	*n*	*E*	*E*
$Na_3[Bi(S_2O_3)_3]\ H_2O$	1	10.5	1	10	12.5	1	34	1	34	38.5	1	27.5	1	26	28
$K_3[Bi(S_2O_3)_3]\cdot H_2O$	2	11	2	10.5	11	1	106.5			101	1	25	1	24.5	25
$K_5Na[Bi(S_2O_3)_3]_2\ 2\,H_2O$	2	10.5	2	11	10	1	67			69.5	1	27.5	1	27.5	30.5
$K_2Na[Bi(S_2O_3)_3]\cdot H_2O$	2	11	2	11	11	1	43	1	44	48.5	1	26	1	25	30.5
$Rb_3[Bi(S_2O_3)_3]\ H_2O$	2	11.5	2	12	11	1	75.5			78.5	1	25	1	25.5	26.5
						First stage					Second stage				
$Cs_3[Bi(S_2O_3)_3]$						1	50	1	49	55	1	27	1	27.5	27
$Cs_2Na[Bi(S_2O_3)_3]$						1/2	90.5			92.5	1/2	28.5	1/2	29	40.5

C-R = Coats and Redfern's method; Z = Zsakó's method, H-M = Horowitz and Metzger's method. *n* = order of reaction, *E* = activation energy (kcal mole^{-1}).

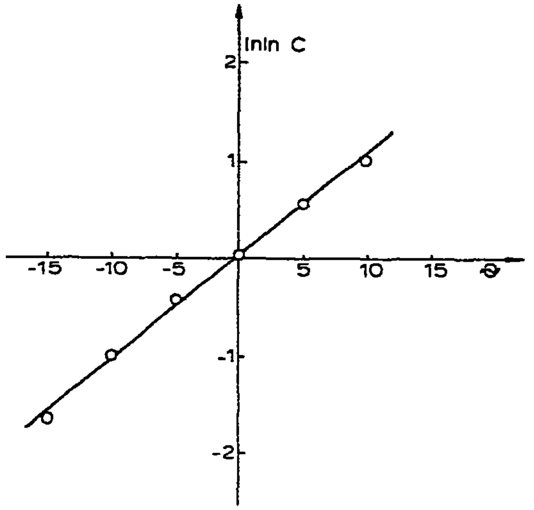

Fig 3 Determination of the activation energy at the second stage of the thermal decomposition of $K_2Na[Bi(S_2O_3)_3]$ H_2O by Horowitz and Metzger's method

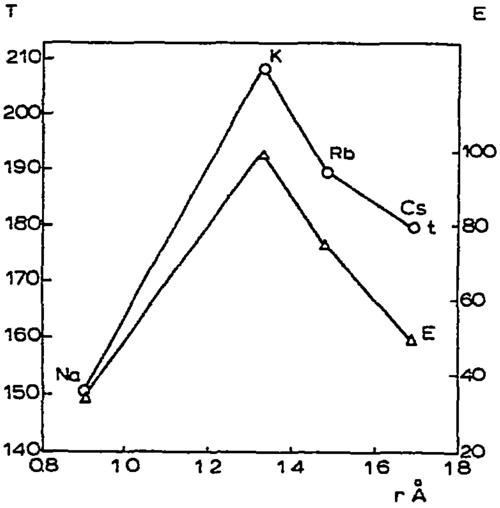

Fig 4 Effect of the outer sphere cations on the initial decomposition temperature, and the activation energy determined by Coats and Redfern's method

The activation energies for the third stage (or second stage for non-aqueous compounds) of decomposition are similar for all investigated thiosulphatobismuthates and range between 25 and 29 kcal mole^{-1}.

The data shown in Table 1 indicate that calculations carried out according to the methods of Coats and Redfern [2] and Zsakó [4] give similar results. When Horowitz and Metzger's [3] method was applied the results were generally higher, and for the second stage of $Cs_2Na[Bi(S_2O_3)_3]$ decomposition much higher results were obtained than by the two methods mentioned above.

The thermal stabilities of the investigated thiosulphatobismuthates(III) were compared. The criterion was the initial decomposition temperature. In the case of the hydrated salts it was the temperature used at the beginning of second stage, as dehydration occurs during the first stage. Dehydration does not involve a change of the compound structure since water is of zeolithic character (as proven by X-ray analysis and the low activation energies of dehydration). In the case of non-aqueous thiosulphatobismuthates(III) the temperature used at the beginning of the first stage was considered.

The least stable compound is sodium thiosulphatobismuthate(III) $Na_3[Bi(S_2O_3)_3] \cdot H_2O$; potassium thiosulphatobismuthate(III) $K_3[Bi(S_2O_3)_3] \cdot H_2O$ is the most stable. Starting with the potassium salt, the thermal stability (initial decomposition temperature, activation energy) of thiosulphatobismuthates(III) decreases along with the increase of ionic radius of an element belonging to the potassium group. This relationship is shown in Fig. 4. The stability of the isostructural thiocyanatobismuthates(III) of the potassium group [8] decreases as the radius of the outer sphere cation increases [as in the case of thiosulphatobismuthates(III)]. However, the sodium salt was the most stable of the thiocyanatobismuthates(III) of alkali metals, while the lithium salt was the least stable. A similar relationship was observed in the case of thiocyanatothiocarbamidobismuthates(III) of alkali metals [9] $M[Bi(SCN)_4(TM)_2]$. Lithium thiosulphatobismuthate(III) was not obtained by us [10]. When sodium is substituted for potassium in $K_3[Bi(S_2O_3)_3] \cdot H_2O$ the compound becomes less stable. The thermal stability for three isostructural compounds containing potassium decreases as shown by the formulae: $K_3[Bi(S_2O_3)_3] \cdot H_2O > K_5Na[Bi(S_2O_3)_3]_2 \cdot 2\ H_2O > K_2Na[Bi(S_2O_3)_3] \cdot H_2O$.

The decrease in thermal stability, caused by substituting sodium, rubidium or caesium for potassium, can be explained in the following way. In the case of $K_3[Bi(S_2O_3)_3] \cdot H_2O$, the most stable compound, there is the greatest density of atoms in a cell. If potassium is substituted by a cation of a shorter radius (sodium) or of a longer radius (rubidium, caesium) the stability of the structure is destroyed because the greatest density in the ionic crystalline network is not maintained. Therefore, potassium, sodium, rubidium, and caesium thiosulphatobismuthates(III) are less stable.

If caesium ions are substituted by sodium the relationship is different: $Cs_2Na[Bi(S_2O_3)_3] > Cs_3[Bi(S_2O_3)_3]$.

The higher stability of the caesium-sodium salt is also evidenced by the fact that it is far more difficult to obtain $Cs_3[Bi(S_2O_3)_3]$ than $Cs_2Na[Bi(S_2O_3)_3]$. The double salt is precipitated even if only a little sodium is present [10]. This is analogical to thiocyanatobismuthate(III) in the case of which $Cs_3[Bi(SCN)_6]$ was not obtained [8], and the sodium-caesium salt $Cs_2Na[Bi(SCN)_6]$ has the greatest thermal stability and is the most resistant to hydrolytic decomposition of all the hexathiocyanatobismuthates(III) [11]. As in the case of caesium thiosulphatobismuthates, substituting sodium for potassium in $K_3[Bi(SCN)_6]$ increases the stability of the compound [11] A different relationship for potassium-sodium thiosulphatobismuthates can be explained by the lowest thermal stabilities of $Na_3[Bi(S_2O_3)_3]$ and $K_3[Bi(SCN)_6]$ in the given group of complex salts, unlike $K_3[Bi(S_2O_3)_3] \cdot H_2O$.

REFERENCES

1 A Cyganski and J Kobyłecka, Thermochim Acta 45 (1981) 65

2 A W Coats and J P Redfern, Nature (London), 201 (1964) 68

3 H H Horowitz and G Metzger, Anal Chem, 35 (1963) 1464

4 J Zsako, J Phys Chem, 72 (1968) 2406

5 J H Flynn and L A Wall, J Res Natl Bur Stand, Sect A, 70 (1966) 427

6 A Szkarın, N Topor and C Zabrowa, Zh Fiz Khim, 42 (1968) 2832

7 C D Doyle, J Appl Polym Sci, 5 (1961) 285

8 A Cyganski, Rocz Chem, 39 (1965) 193

9 H Laczinska-Kulinska, Thermochim Acta, 42 (1980) 99.

10 A Cyganski and J Kobyłecka, Zesz Nauk Politech Lodz Chem, in press

11 A Cyganski, Rocz Chem, 39 (1965) 1735