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Note

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

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In our earlier work [1] on the thermal decomposition of thiocyanatothiocarbamidobismuthates(III) with alkaline elements, having the general formula $Me[Bi(SCN)_4(TM)_2]$ where Me = Li, Na, K, Rb, Cs, NH_4 and TM = thiourea, using thermal, chemical infrared spectrophotometric and X-ray analysis, the compositions of the intermediate and final products obtained were established. In the present paper, kinetic parameters (energy of activation and reaction order) were calculated for some of the decomposition steps of thiocyanatothiocarbamidobismuthates(III) with alkaline elements using the Coats—Redfern [2] and Horowitz—Metzger [3,4] methods.

RESULTS AND DISCUSSION

The thermal decomposition reaction of thiocyanatothiocarbamidobismuthates(III) may be examined based on the equation

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

where $A_{(s)}$, $B_{(s)}$ and $C_{(g)}$ are solid and gaseous components of the reaction.

The decomposition rate of the compounds under study may be expressed by

$$\frac{d\alpha}{dt} = -k(1-\alpha)^n \tag{1}$$

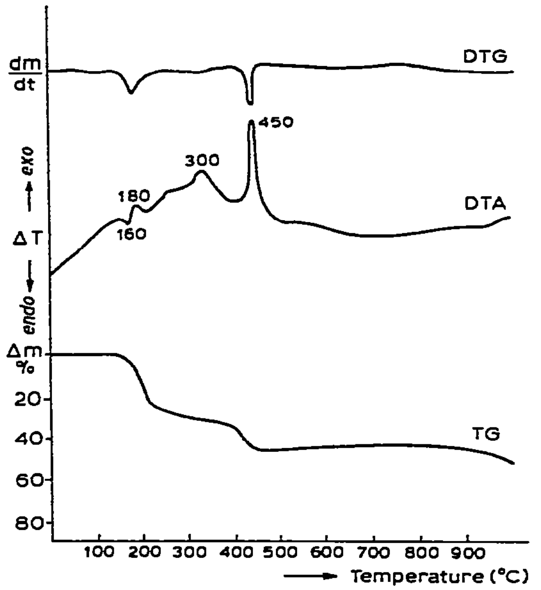
where k is the rate constant, n the reaction order, and α the ratio of the actual weight loss to the total weight loss during the step considered, i.e.

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

Here, W_0, W_t and W are the initial,final and current weights of the sample, respectively.

The rate constant, k, is connected with the activation energy through the expression

$$k = A\exp(-E/RT) \tag{2}$$



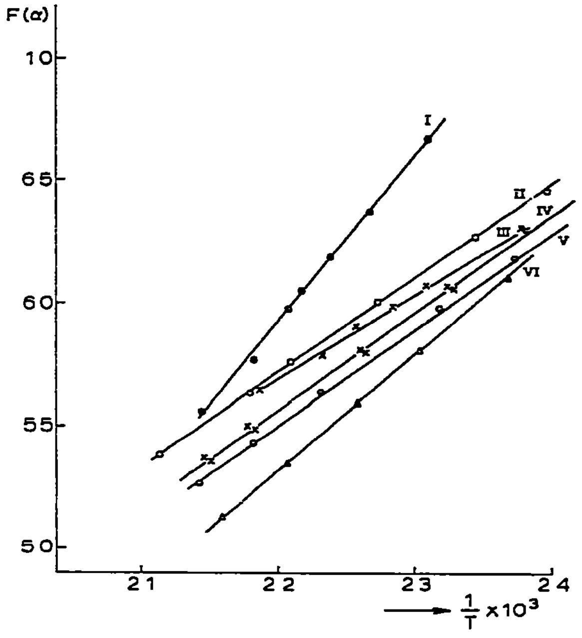


Fig. 1. DTG, DTA and TG curves for $K[Bi(SCN)_4(TM)_2]$ in air.

Fig. 2. Plots of F(α) vs. $1/T$ for $n = 1$. I, NaR; II, NH_4R; III, LiR; IV, RbR; V, CsR; VI, KR. $R = [Bi(SCN)_4(N_2H_4CS)_2]$.

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

For a linear heating rate $a = dT/dt$, Coats and Redfern used the following relationships.

$$\log F(\alpha) = \log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.3RT} \qquad (3)$$

when $n \neq 1$ and

$$\log F(\alpha) = \log\left[-\log\frac{(1-\alpha)}{T^2}\right] = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.3RT} \qquad (4)$$

when $n = 1$.

In order to determine the kinetic parameters of the thermal decomposition of thiocyanatothiocarbamidobismuthates(III), the value of the function F(α) was calculated for the assumed reaction orders $n = 1/2$, 1, and 2. Experimental data needed for the calculations were taken from the thermogravimetric curve for $Me[Bi(SCN)_4(TM)_2)]$ (Fig. 1) discussed in detail in ref. 1. Plots of log F(α) versus $1/T$, eqn. (4), for all the complex salts gave straight lines for $n = 1$, for the first and third decomposition steps (temperature ranges 140—200°C and 400—480°C, respectively). The slopes of the straight lines (Fig. 2) correspond to $E/2.3R$. Activation energies and reaction orders calculated from the thermogravimetric data for the first and third decomposition steps of the complex salts $Me[Bi(SCN)_4(TM)_2]$ are presented in Table 1.

In order to verify the determined activation energies, the Horowitz—

TABLE 1

Calculated kinetic parameters

Compound	Horowitz–Metzger method				Coats–Redfern method			
	Step I		Step III		Step I		Step III	
	n	*E* (kcal mole^{-1})	*n*	*E* (kcal mole^{-1})	*n*	*E* (kcal mole^{-1})	*n*	*E* (kcal mole^{-1})
$Na[Bi(SCN)_4(N_2H_4CS)_2]$	1	32.0	1	69.2	1	32.4	1	69.6
$K[Bi(SCN)_4(N_2H_4CS)_2]$	1	22.3	1	65.1	1	22.5	1	65.3
$Rb[Bi(SCN)_4(N_2H_4CS)_2]$	1	18.2	1	60.2	1	18.9	1	58.9
$Cs[Bi(SCN)_4(N_2H_4CS)_2]$	1	18.5	1	56.2	1	18.8	1	56.4
$NH_4[Bi(SCN)_4(N_2H_4CS)_2]$	1	17.9	1	48.1	1	17.6	1	46.2
$Li[Bi(SCN)_4(N_2H_4CS)_2]$	1	15.9	1	44.6	1	14.8	1	44.2

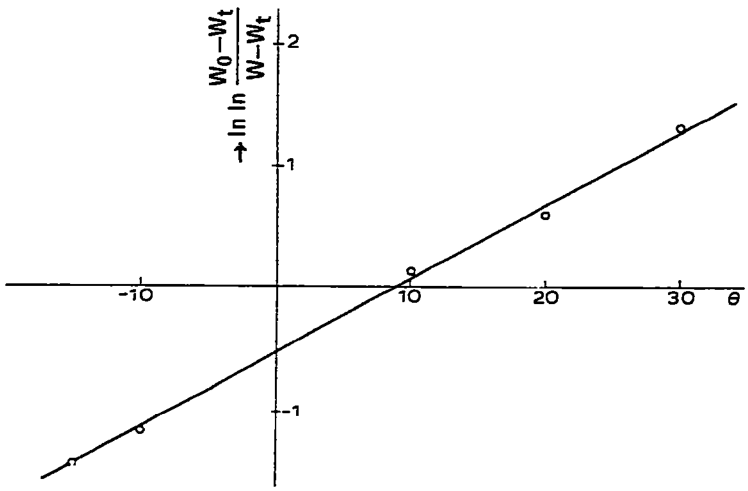


Fig. 3. Plot of lnln$[(W_0 - W_t)/(W - W_t)]$ vs. θ for step I of the decomposition of K[Bi(SCN)$_4$(TM)$_2$].

Metzger method was employed. The following relation for the first-order process was applied for the calculations.

$$\ln\ln\frac{W_0 - W_t}{W - W_t} = \frac{E\theta}{RT_s^2} \tag{5}$$

where W_0 and W_t are the initial and final weights of the sample, W is the weight at temperature T, and $\theta = T - T_s$. T_s is the temperature at which $(W - W_t)/(W_0 - W_t) = 1/e$ and the maximum decomposition rate is reached.

Using a graphic method, it is possible to determine the activation energies of the first-order reactions from eqn. (5). The linear dependence lnln$[(W_0 - W_t)/(W - W_t)]$ vs. θ (Fig. 3) allows the activation energies of the decomposition processes to be determined from the slopes, $\tan\alpha = E/RT_s^2$. The results are presented in Table 1. The temperature, T_s, for steps I and III of the decomposition was determined as that corresponding to the minimum on the DTG curves [4].

Activation energies and reaction orders of the first and third decomposition steps calculated from the thermogravimetric curves using the Coats—Redfern and Horowitz—Metzger methods show satisfactory agreement. The activation energies of the first decomposition step confirm the conclusion that the thermal stabilities in this group of complex compounds depends upon the ionic radius of the outer sphere cation. The thermal stabilities for complexes containing p-electronic cations increases in the order Na > K > Rb ≃ Cs.

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