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Note

KINETIC PARAMETERS OF THE DECOMPOSITION OF HYDRATED TRIS(INDOLE-3-BUTYRATO)Ho(III)

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The affinity of metals for plant auxins has been little explored. Sawhney and Chandra [1] added to the existing knowledge of the chelating nature of auxins. This note highlights the thermal stability and kinetics of the non-isothermal decomposition of tris(indole-3-butyrato) Ho(III) · $1\frac{3}{4}H_2O$, using techniques by Dave and Chopra [2] and Borchardt and Daniels [3].

EXPERIMENTAL

All the chemicals were of analytical grade. The holmium(III)-3-indolebutyric acid complex was isolated by adding the metal to sodium salt of the plant auxin, slowly and with constant stirring. The white precipitate was immediately filtered, washed with distilled water and dried at 35–40 °C. Chemical analysis indicated the following structure: $(C_{12}H_{12}O_2N)_3Ho \cdot 1\frac{3}{4}H_2O$.

Elemental analysis

The results of the elemental analysis are presented in Table 1.

A differential thermal analyser (Mettler Instrument) with reference material Al_2O_3, chart speed 10 cm h^{-1}, heating rate 5, 10, or 15 °C min^{-1}, instrument sensitivity 40 mV, and applied voltage 220 V was employed for the thermal studies.

TABLE 1
Elemental analysis

	Element			
	C	H	N	Ho
Found (%)	55.00	5.32	5.70	23.44
Calculated (%)	53.83	4.48	5.23	20.56

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RESULTS AND DISCUSSION

Three sigmoids corresponding to the loss of $1\frac{3}{4}$ lattice water molecules $\frac{7}{4}$ ($C_{12}H_{12}O_2N$) and $\frac{5}{4}$ ($C_{12}H_{12}O_2N$) were indicated on the TG curve. Tris(indole-3-butyrato)Ho(III) · $1\frac{3}{4}H_2O$ was thermally stable up to 70.92 °C, after which 100% lattice water ($1\frac{3}{4}H_2O$) was lost up to 85.56 °C. The anhydrous metal complex tris(indole-3-butyrato)Ho(III) did not undergo any change in weight until 173.4 °C, after which decomposition began and the appearance of a new species having composition $\frac{5}{4}$($C_{12}H_{12}O_2N$)Ho was recorded. Further organic loss between 378.36 and 472.17 °C was observed. On the DTG curve the dips at 70.92–92.88 °C, 173.40–345.42 °C and 378.36–472.17 °C agree to the sigmoids on the TG curve. On the DTA curve, an endotherm at

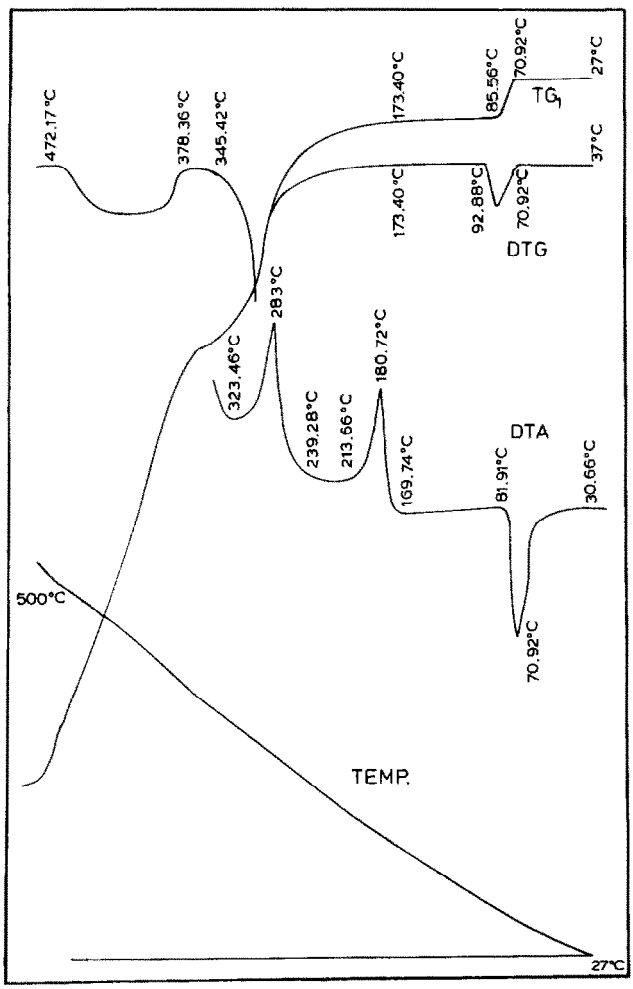

Fig. 1. TG, DTG and DTA of hydrated tris(indole-3-butyrato)Ho(III).

TABLE 2

Kinetic data

	Method					
	Dave and Chopra [2]			Borchardt and Daniels [3]		
Reaction	n	E (Kcal)	Z [a] (min^{-1})	n	E (Kcal)	Z (min^{-1})
$HoR_3 \cdot 1\frac{3}{4}H_2O \xrightarrow{70-93°C} HoR_3 + 1\frac{3}{4}H_2O$	1	63.93	−0.29	1	27.40	−1.43
$HoR_3 \xrightarrow{173-346°C} Ho\frac{5}{4}R + \frac{7}{4}R$	1	18.26	−1.45	–		–
$Ho\frac{5}{4}R \xrightarrow{378-473°C} Ho_2O_3 + dp$ [b]	1	18.26	−1.07	–		–

[a] Z, collision number. [b] dp, dissociation product.

The kinetics of water loss were studied using the Borchardt and Daniels [3] equation for $n = 1$, $k = \Delta T/(A - a)$ where A and a are areas under the DTA curve and ΔT is deviation from the base line. From a plot of log k against $1/T$, which was a straight line in reaction (1), the values of E and Z were calculated (Table 2), and were found to be nearly in agreement with those calculated using the Dave and Chopra method.

70.92° C, corresponding to dehydration of the complex, and two exotherms at 180.72 and 283° C, showing loss of organic material, were observed. These tallied to the features exhibited by the TG and DTG curves.

The Dave and Chopra [2] equation for $n = 1$ (n = order of reaction) was used to represent kinetics of non-isothermal decomposition of a metal complex of the type

$$A(s) \rightarrow B(s) + C(g)$$

as chosen by Freeman and Carroll [4] for kinetic study. Plots of log k ($k = (dx/dt)/(A - a)$ where A and a are the total area and the area at time t, respectively, under the DTG curve; dx/dt is deviation from the base line) plotted against $1/T$ gave straight lines, supporting the assumption that the reactions (1–3) follow first-order kinetics:

$$HoR_3 \cdot 1\tfrac{3}{4}H_2O \xrightarrow{70-93°C} HoR_3 + 1\tfrac{3}{4}H_2O \quad (1)$$

$$HoR_3 \xrightarrow{173-346°C} Ho\tfrac{5}{4}R + \tfrac{7}{4}R \quad (2)$$

$$Ho\tfrac{5}{4}R \xrightarrow{378-473°C} Ho_2O_3 + dp \quad (3)$$

The slopes and intercepts give activation energy E and the collision number for reactions (1)–(3). Table 2 contains the kinetic data.

In Fig. 1, TG, DTG and DTA of tris(indole-3-butyrato)Ho(III) $\cdot 1\frac{3}{4}H_2O$ are shown.

REFERENCES

1 S.S. Sawhney and N. Chandra, Thermochim. Acta, 61 (1983) 357.
2 N.G. Dave and S.K. Chopra, Z. Phys. Chem. NF., 48 (1966) 257.
3 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
4 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.