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Note

THERMAL AND STRUCTURAL ASPECTS OF TRIS(INDOLE-3-BUTYRATO)Ce(III)

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There is an upsurge of interest towards the study of the interaction of plant auxins with metals present in the soil: varying views on the subject have been expressed [1–3]. Sawhney and Chandra [4] carried out solution and solid state studies on the complexing behaviour of the plant auxins. This note presents the results on the thermal, including the kinetics of the nonisothermal decomposition, and structural aspects, of tris(indole-3-butyrato)Ce(III).

EXPERIMENTAL

All the chemicals were of analytical grade. Slow addition with constant stirring of the metal salt to an aqueous solution of the sodium salt of indole-3-butyric acid resulted in a water-insoluble precipitate which was filtered, washed and dried at 40 °C; the analysis corresponded with the compound $(C_{12}H_9O_2N)_3Ce$.

The metal complex was pyrolysed on a modern thermogravimetric balance equipped with a Toshniwal furnace, duly standardised with calcium oxalate (10 °C min^{-1}). The X-ray study was carried out on a Phillips P.M. 8203 single pan recorder X-ray generator Model PW-1730 with the parameters: radiation, Cu K_α; goniometer speed, 2° $(20\ min)^{-1}$; recorder speed, 1 cm min^{-1} and current and voltage, 30 mA and 40 kV.

RESULTS AND DISCUSSION

The pyrolysis curve of tris(indole-3-butyrato)Ce(III) showed a sigmoid indicative of a step decomposition. It did not lose any weight up to 60 °C, after which the organic part (three molecules of plant auxin) started decomposing. The rate of weight loss slowed down near 425 °C indicating the possibility of a new compound which could not be assigned definite composition in the absence of a plateau. The loss was complete at 775 °C and

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TABLE 1

Pyrolysis data

Stable phase and temp. range (°C)	Loss temp. range (°C)	Loss %		Metal oxide (%)	
		Found	Calcd.	Found	Calcd.
$Ce(C_{12}H_{12}O_2N)_3$ (up to 60 °C)					
Ce_2O_3 (775 °C and onwards)	$3(C_{12}H_{12}O_2N)$ (60–775 °C)	76.24	78.02	23.76	21.98

onwards, signalling the appearance of Ce_2O_3. The pyrolysis data are given in Table 1.

The use of a manually operated assembly for pyrolysis data prompted the authors to apply the Dave and Chopra method [5] for working out kinetic data under the prevailing conditions (see refs. 6 and 7). The differentially drawn DTG curve from the TG curve was used for the kinetics of the nonisothermal decomposition of tris(indole-3-butyrato)Ce(III); this follows the reaction of the following type: A(s) → B(s) + C(g). DTG dip corresponding to the TG sigmoid was used for estimating values of A, a and dx/dt in eqn. (1) below. A series of log k values corresponding to varying temperatures following eqn. (1) [5]

$$k = (dx/dt)/(A - a) \tag{1}$$

for $n = 1$

was worked out and plotted vs. T^{-1}. The ensuing straight line justifying the said equation gave values of E and Z. Another straight line relationship obtained on plotting $(dx/dt)/\log(A - a)$ vs. $(T^{-1})/\log(A - a)$ justified eqn. (2) according to the same authors

$$\frac{-E/2.303R(T^{-1})}{\log(A - a)} = -n + \log(dx/dt)/\log(A - a) \tag{2}$$

The data suggest that the reaction follows first-order kinetics. Low Z values indicated that the reaction was a slow process. The kinetic data are given in Table 2.

TABLE 2

Kinetic parameters for nonisothermal decomposition of tris(indole-3-butyrato)Ce(III)

Reaction	Temp. range (°C)	Eqn. (1)		Eqn. (2)		
		n	E	log Z	n	E
$(C_{12}H_9O_2N)_3Ce \rightarrow Ce_2O_3 + dp\uparrow$	60–775	1	4.46	−0.25	0.47	3.73

dp, Decomposition product; E in kcal mol^{-1}.

Structurally tris(indole-3-butyrato)Ce(III) assumed a cubic lattice of primitive type. The data showed a near tally between the calculated d values and those found experimentally. Furthermore the absence of the forbidden numbers: 7, 15, 23, 28, 31, 39, 47, 55 and 60 was observed, claiming support for the conclusion drawn concerning the crystal lattice.

REFERENCES

1 R. Sahai, S.S.S. Kushwaha and A.K. Chaudhary, J. Indian Chem. Soc., 57 (1980) 844.
2 D. Cohen, B.Z. Ginzburg and C. Heitner-Werguin, Nature (London), 181 (1958) 688.
3 O.V.S. Heath and J.E. Clark, Nature (London), 117 (1956) 1118; 178 (1956) 600; 183 (1959) 1177.
4 S.S. Sawhney and N. Chandra, Thermochim. Acta, 61 (1983) 357.
5 N.G. Dave and S.K. Chopra, Z. Phys. Chem., 48 (1966) 257.
6 S.S. Sawhney, R.M. Sati and S.D. Matta, Thermochim. Acta, 47 (1982) 95.
7 S.S. Sawhney and B.M.L. Bhatia, Thermochim. Acta, 43 (1981) 243.