Thermochimica Acta, 126 (1988) 393–395
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

KINETIC AND X-RAY POWDER DIFFRACTION STUDIES ON HYDRATED TRIS(INDOLE-3-ACETATO)M(III) (M = Ce, Pr, Nd)

S.S. SAWHNEY, N.C. SHARMA and N.K. ARORA
Chemistry Department, D.A.V. (P.G.) College Dehra Dun-248 001 (India)

(Received 4 June 1987)

Affinity of metals to plant auxins is still open for discussion. Sawhney et al. [1] have expressed their opinion on the subject through solution study on metal–plant auxin interaction. This note highlights structural aspects of tris(indole-3-acetato)M(III) $\cdot x H_2O$ (M = Ce, $x = 7.25$; M = Pr, $x = 0$; and M = Nd, $x = 0$), the pyrolysis-based reaction mechanism and the kinetics of nonisothermal decomposition of the forementioned metal–plant auxin complexes, employing the Dave and Chopra method [2].

EXPERIMENTAL

All the chemicals used were of analytical grade. Slow addition of metal salt to the sodium salt of IAA precipitated the metal complex; the chemical analysis data agreed with the composition of the complex shown above.

A modern thermogravimetric balance equipped with a Toshniwal furnace, duly standardized with calcium oxalate (10 °C min^{-1}), was used. The diffractograms of recrystallized complexes were recorded on a Phillips (Holland) P.M. 8203 single pan recorder X-ray generator (Model PW-1730) (radiation, Cu K_α 1; goniometer speed, 2° 2θ min^{-1}; recorder speed, 1 cm min^{-1}; current and voltage to tube, 30 mA, 40 kV.

RESULTS AND DISCUSSION

Pyrolysis and X-ray data provided access to the progress of thermal decomposition of metal complexes of IAA with Ce(III), Pr(III) and Nd(III) and their structural features, respectively.

Pyrolysis traces showed the sigmoids (Pr–IAA), and (Ce and Nd–IAA). The Pr–IAA complex was thermally stable up to 80 °C, and by 100% the lattice water molecules ($7.25 H_2O$) had become dissociated, after which a

0040-6031/88/$03.50

TABLE 1

Pyrolysis data on metal complexes of plant auxins

Stable phase and temp. range (°C)	Loss temp. range (°C)	Percentage loss		Percentage metal oxide	
		Exptl.	Calcd.	Exptl.	Calcd.
Metal–IAA complexes (IAA = $C_{10}H_9O_2N$)					
$Pr(C_{10}H_8O_2N_3 \cdot 7.25H_2O$ ($\leqslant 80$)					
$Pr(C_{10}H_8O_2N)_3$ (100–140)	7.25 H_2O (80–100)	16.67	16.44		
Pr_2O_3 ($\geqslant 400$)	$3(C_{10}H_8O_2N)$ (140–400)	65.13	63.49	18.20	20.07
$Nd(C_{10}H_8O_2N)_3$ ($\leqslant 60$)					
Nd_2O_3 ($\geqslant 750$)	$3(C_{10}H_8O_2N)$ (60–750)	71.43	74.77	28.57	25.23
$Ce(C_{10}H_8O_2N)_3$ ($\leqslant 60$)					
Ce_2O_3 ($\geqslant 775$)	$3(C_{10}H_8O_2N)$ (60–775)	73.74	75.23	26.26	24.77

plateau (100–400 °C), due to the formation of metal oxide, was seen. Nd–IAA and Ce–IAA complexes did not show any change up to 60 °C, but, by 750 and 775 °C, respectively, all organic matter had been lost. Pyrolysis and analytical data are shown in Table 1

The solid state reactions (1)–(3) display similarity to the reaction

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

and follow first order kinetics

$$(C_{10}H_8O_2N)_3Pr \xrightarrow{140\text{–}400\,^\circ C} Pr_2O_3 + dp\uparrow \qquad (1)$$

$$(C_{10}H_8O_2N)_3Nd \xrightarrow{60\text{–}750\,^\circ C} Na_2O_3 + dp\uparrow \qquad (2)$$

$$(C_{10}H_8O_2N)_3Ce \xrightarrow{60\text{–}775\,^\circ C} Ce_2O_3 + dp\uparrow \qquad (3)$$

A plot of log k against $10^3/T$ resulted in a straight line; its slope and intercept gave the activation energy of the reaction (E) and the frequency factor (Z) (cf. eqn. (1)). Kinetic parameters obtained from eqn. (2) of Dave and Chopra [2] nearly tallied. The reactions under study are slow processes as the Z values were very low. The kinetic data are shown in Table 2.

X-ray study

The metal complexes in question are crystalline in nature. The factors computed by dividing $\sin^2\theta$ by the common factor (CF), worked out from

TABLE 2

Kinetic parameters for the nonisothermal decomposition of metal complexes of IAA

Reaction	Temp. range (° C)	Equation (1)		*log Z	Equation (2) *	
		n	E (kcal mol^{-1})		n	E (kcal mol^{-1})
$(C_{10}H_8O_2N)_3Pr \rightarrow Pr_2O_3 + dp\uparrow$	140–400	1	4.99	−0.90	0.97	5.53
$(C_{10}H_8O_2N)_3Nd \rightarrow Nd_2O_3 + dp\uparrow$	60–750	1	4.15	−1.40	0.97	4.97
$(C_{10}H_8O_2N)_3Ce \rightarrow Ce_2O_3 + dp\uparrow$	60–775	1	5.58	−1.20	0.94	4.88

* From reference 2.

TABLE 3

X-ray powder diffraction data on tris(indole-3-acetato)Ce(III), Nd(III) and Pr(III) complexes

hkl			d (Å)			I/I_0		
Ce	Nd	Pr	Ce	Nd	Pr	Ce	Nd	Pr
111	111	110	31.56	31.56	31.56	100	100	100
332	332	320	11.63	11.63	12.28	18.69	30	22.78
531	531	332	9.21	9.21	9.41	12.15	22	13.92
611	532	430	8.85	8.85	8.85	14.95	14	18.99
642	722	600	7.33	7.26	7.38	93.46	78	94.93
651	732	621	6.92	6.92	6.92	31.76	36	29.11
811	554	533	6.70	6.71	6.71	7.48	16	7.59
940	665	800	5.54	5.54	5.51	8.41	28	12.66
–	–	653	–	–	5.28	–	–	7.59

Radiation, Cu K_α; λ 1.5405; filter, Ni.

the first two peaks on the diffractograms, were close to the N values (corresponding to the *hkl* values which were obtained from the literature [3]). Further inspection showed the absence of forbidden numbers (7, 15, 23, 28, 31, 39, 47, 55, 60, 63, 71, 79, 87, 92 and 95), suggesting that the crystals have a cubic lattice. Furthermore, *hkl* values are both odd and even, leading us to believe that the crystals are of primitive types. The calculated and experimental d values agreed with the above. The X-ray diffraction data are given in Table 3.

REFERENCES

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