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Note

PYROLYSIS AND KINETIC STUDIES OF THE NON-ISOTHERMAL DECOMPOSITION OF METAL–NAA COMPLEXES

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ABSTRACT

Sawhney and Chandra [1], Koepfli et al. [2] and Heath and Clark [3] have studied the affinity of metals to plant auxins—a subject which even today engages the attention of researchers studying the mode of action of plant auxins. This note describes the preparation of metal derivatives of NAA (1-napthaleneacetic acid) followed by pyrolysis and kinetic studies of the non-isothermal decomposition of Pr(III), Ce(III) and Nd(III) derivatives, following the equations of Dave and Chopra [4].

EXPERIMENTAL

All the chemicals used were of analytical grade. Addition of aqueous solution of metal nitrate to an aqueous solution of the sodium salt of NAA precipitated the metal derivative of NAA, which was filtered, washed and dried at 35–40 °C. Chemical analysis showed that the composition of the metal–NAA products agreed with the formula $(C_{12}H_9O_2)_3 \cdot M(NO_3)_3$, where M ≡ Pr, Nd, Ce).

A thermogravimetric balance equipped with a Towhniwal furnace was used for pyrolysis of the samples, with a continuous temperature increase of 10 °C min^{-1}.

RESULTS AND DISCUSSION

Pr(III)–, Nd(III)– and Ce(III)–NAA derivatives are insoluble in water and soluble in organic solvents. The pyrolysis data gave information on the progress of decomposition with temperature rise, and the structures of the derivatives.

From the TG curve of tris(1-naphthaleneacetato)praseodymium(III) nitrate, which shows two sigmoids, the possible loss of organic matter and anions in two stages was concluded. The parent compound was stable up to

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50 °C. Loss of $3/10(C_{12}H_9O_2)$ commenced at 50 °C and ended at 200 °C. The weight at 200–250 °C was constant; this indicates the appearance of a new species of definite composition, which in all probability agreed with $Pr \cdot 27/10(C_{12}H_9O_2)\ (NO_3)_3$, which further split off the remaining part including all anions up to 775 °C. A plateau (775 °C and above tallied with Pr_2O_3. In the second sigmoid (475–525 °C), decomposition slowed, pointing to the presence of an intermediate compound of indefinite composition.

A single sigmoid appeared in the pyrolysis curve of tris(1-naphthaleneacetato)cerium(III) nitrate, which indicates complete loss of organic matter and anions (60–750 °C); a plateau, which coincides with Ce_2O_3 formation (at 750 °C and above) was observed. A similar situation was present in the pyrolysis curve of tris(1-naphthaleneacetato)neodymium(III) nitrate, except for the appearance of a slow decomposition zone spanning 480–550 °C for which a compound of definite composition could not be identified.

The solid-state reactions (1)–(4) as derived from the pyrolysis data are

$$(C_{12}H_9O_2)_3 \cdot Pr(NO_3)_3 \xrightarrow{50-200\,^\circ C} 3/10(C_{12}H_9O_2)\uparrow + (C_{12}H_9O_2)_{2.7} \cdot Pr(NO_3)_3 \quad (1)$$

$$(C_{12}H_9O_2)_{2.7} \cdot Pr(NO_3)_3 \xrightarrow{250-775\,^\circ C} Pr_2O_2 + \text{decomposition products} \quad (2)$$

$$(C_{12}H_9O_2)_3 \cdot Nd(NO_3)_3 \xrightarrow{50-750\,^\circ C} Nd_2O_3 + \text{decomposition products} \quad (3)$$

$$(C_{12}H_9O_2)_3 \cdot Ce(NO_3)_3 \xrightarrow{60-750\,^\circ C} Ce_2O_3 + \text{decomposition products} \quad (4)$$

These reactions were studied kinetically, using the equations of Dave and Chopra, application of which for inconsistent applied conditions, (i.e. heating rate, crucible geometry, etc.) has been recommended [4] and DTG curves.

$$k = \frac{(dx/dt)}{A - a} \quad (5)$$

$$\frac{-E/2.303R(T^{-1})}{\log(A-a)} = n + \frac{\log(dx/dt)}{\log(A-a)} \quad (6)$$

The above reactions follow first-order kinetics as a plot (log k versus $1/T$, eqn. (5)) gave a straight line ($n = 1$). The value of n, determined by eqn. (6), ranged from 0.81 to 1.07. Log Z values were abnormally low, which indicates that the reactions were slow. Further examination of the data showed close agreement between k values calculated from eqns. (5) and (6).

The kinetic data and the solid-state reactions are given in Table 1.

TABLE 1

Kinetic parameters for the non-isothermal decomposition of NAA–metal complexes

Reactions [a]	Temp. range (°C)	Eqn. (1)			Eqn. (2)	
		n	E (kcal mol^{-1})	log Z	n	E (kcal mol^{-1})
$(C_{12}H_9O_2)_3 \cdot Pr(NO_3)_3 \rightarrow$ $3/10(C_{12}H_9O_2) + (C_{12}H_9O_2)_{2.7} \cdot Pr(NO_3)_3$	50–200	1	7.97	−0.20	0.88	6.90
$(C_{12}H_9O_2)_{2.7} \cdot Pr(NO_3)_3 \rightarrow Pr_2O_3 + dp$	250–775	1	6.39	−1.40	1.07	6.58
$(C_{12}H_9O_2)_3 \cdot Nd(NO_3)_3 \rightarrow Nd_2O_3 + dp$	50–750	1	2.88	−1.80	0.81	3.32
$(C_{12}H_9O_2)_3 \cdot Ce(NO_3)_3 \rightarrow Ce_2O_3 + dp$	60–750	1	4.24	−1.25	0.94	4.19

[a] dp, Decomposition products.

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