

PRYOLYSIS AND KINETIC STUDIES OF THE NON-ISOTHERMAL DECOMPOSITION OF DY(III) – IBA, IPA AND NAA COMPLEXES

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Abstract

Sawhney, Chauhan and Coworkers (1-9) worked on the affinity of some of the plant auxins: IBA, IPA and NAA to Dy(III) metal ion: in solution as well as in solid state, highlighting their Stoichiometries, stability and thermodynamics. In addition, decomposition progression, on Subjecting the metal complexes to pyrolysis studies, ascertaining the intermediates formed and assigning their compositions, was followed, and the solid-state reactions marked were studied Kinetically. Koepfli et.al. [10] and Heath and Clark [11] have studied the affinity of metals to plant auxins a subject which even today engages the attrition of researchers studying the mode of action of plant auxins. This note describes the preparation derivatives of IBA, IPA and NAA (1-naphthalene acetic acid) followed by pyrolysis and kinetic studies of the thermal dissociation of Dy(III)-IBA, Dy(III)- IPA, Dy(III)-NAA systems.

INTRODUCTION

In preceding chapter embrace the solution chemistry covering the stoichiometries of the resultant complex species, their stability and its variation at higher temperature and lack some of conformational aspects which need attention for the emergence of complete structural picture of the complex: for this purpose it is necessary to know the types of bound water viz. coordination water which is associated in stoichiometric quantities with cations and held by coordinate linkage, and lattice water showing its presence in stoichiometric proportion and occupies definite lattice position, but it is not associated directly with any particularly anion or cation; such condition (presence of might result if neither cation or lattice water) or anion exhibits a strong tendency to attract water molecules or if water molecules in excess of those with which the ions could associate are present.

To gain more on structural aspects of the complexes in reference together with some other

properties, the isolated metal complexes of the lanthanide's series element: Dy with plant auxin; IBA (indole-3- butyric acid), IPA (indole-3-propionic acid) and NAA (1- naphthalene acetic acid) were subjected to pyrolysis studies in air.

EXPERIMENTAL

The aqueous salt solution of indole-3-butyric acid, indole-3-propionic acid and 1-naphthalene acetic acid, was added, in small increment to the metal salt solution (aq.) with constant stirring. The precipitate so appeared was filtered, washed with distilled water, and dried at 40°-50°C. Chemical analysis conformed to the cubic structure of Dy(III) -IBA, Dy(III) -IPA and Dy(III) -NAA complexes.

Metal complexes were pyrolysed on Stanton Redcraft Thermal Analyser STA model 781, at the rate of 10°C/min in air.

RESULTS AND DISCUSSION

The cubic structures, could on the information gathered from the safely be based pyrolysis data.

Tripositive lanthanides series element, Dy(III) which react with these plant auxins to obtained Dy-plant auxin complexes. The isolated metal complexes were pyrolysed and resulting pyrolysis curves led us to the following information.

IBA and IPA are bidentate, whereas NAA is a monodentate complexing agent. The metal complexes of bidentate complexing agent consisted of a molecule of metal and three molecules of ligand satisfying the metal ligancy and oxidation number.

Anions of plant auxins; Indole-3-butyric acid (IBA), Indole-3-Propionic acid (IPA), and 1-Naphthalene acetic acid (NAA), are hereinafter marked as R, R' and R''.

Dy³⁺ - Plant auxin complexes are Dy.R₃ (I), Dy.R'₃ (II) and Dy.R''₃.3H₂O (III).(I), (II) are anhydrous

complexes which began to lose organic matter slightly above 75°C and 95°C respectively. In the weight change curve of (I) , a break was obtained in it at 425°C at the stoichiometry corresponding to Dy₂O₃; whereas from (II) with heating R'' molecule was lost giving definite weight plateau (295⁰-350⁰) i.e. Dy.R'₂ and finally the oxide (Dy₂O₃) above 615°C. (III) had three coordinate water from which these molecules were evolved beginning slightly above 125°C. At about 210°C a break in the curve at composition agreeing to Dy.R''₃ was noticed (plateau 210⁰-265⁰). R'' molecules left the anhydrous complex from 265⁰-375⁰ signalling another constant weight plateau having a tally with Dy.R'' (375⁰-415⁰) which became Dy₂O₃ as the heating was continued.

Progressive losses in these complexes are depicted below:

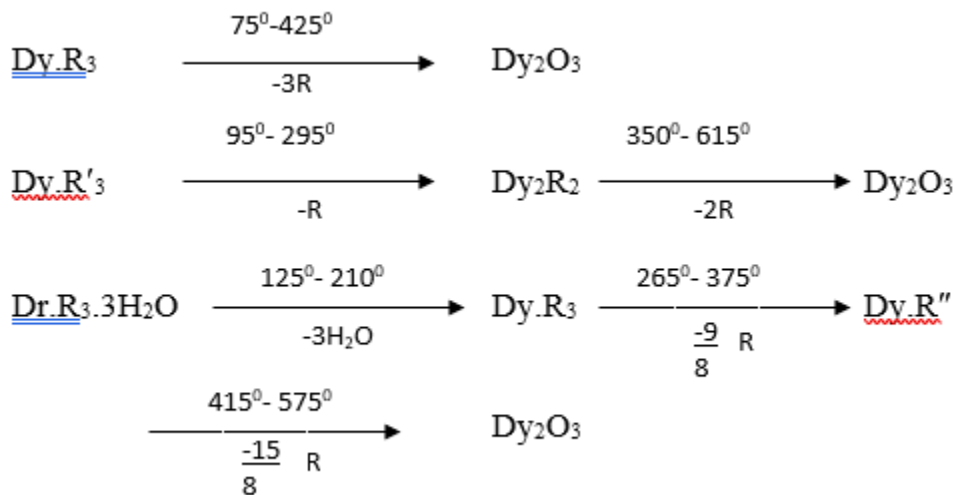


Table 1 : Pyrolysis Data on Dy-Plant Auxin_Chelates

Stable phase and Temp. range (°C)	Loss	% Loss		% Eu ₂ O ₃	
	Temp. °C	Found	Calc.	Found	Calc.
Dy-IBA Chelate					
Dy.R ₃ (Upto 75°C)	-	-	-	-	-
Dy ₂ O ₃ (425 onwards)	3R (75-425°C)	76.00	75.83	24.00	24.17
Dy- IPA Chelate					
Dy. R' ₃ (Upto 95°C)	-	-	-	-	-
Dy. 2R' (295-350°C)	R' (95-295°C)	25.19	25.91	--	--
Dy ₂ O ₃ (615 onwards)	2R' (350-615°C)	74.04	73.06	25.93	26.94
Dy-NAA Chelate					
Dy. R'' ₃ . 3H ₂ O (Upto 125°C)	-	-	-	-	-
Dy. R'' (210-265°C)	3H ₂ O (125-210°C)	7.50	6.97	-	-
Dy ₇ ¹⁵ / ₁₈ R'' (375-415°C)	⁹ / ₈ R'' (265-375°C)	33.33	33.96	-	-
Dy ₂ O ₃ (575 onwards)	¹⁵ / ₈ R'' (415-575°C)	75.88	82.39	24.12	20.04

[Where R = Anion of IBA, R' = anion of IPA and R'' = anion of NAA].

Table2 : Kinetic Data on Dy-Plant Auxin Chellates

Reaction	n		E (KCal.mol ⁻¹)		Log z
	DC	CR	DC	CR	DC
Dy-IBA Chelate					
Dy.R ₃ ----->	1	1	4.650	4.500	-1.8
Dy ₂ O ₃ + dp					
DY-IPA Chelate					
Dy. R' ₃ ----->	1	1	4.990	7.64	-1.4
Dy.2R' + 2R'					
Dy. 2R'----->	1	1	18.72	9.55	-1.5
Dy ₂ O ₃ + dp					
Dy-NAA Chelate					
Dy.R'' ₃ . 3H ₂ O ----->	1	1	21.230	12.741	-1.2
Dy.R'' ₃ + 3H ₂ O					
Dy.R'' ----->	1	1	21.820	22.420	-1.1
Dy. $\frac{15}{18}$ R'' + R'' $\frac{9}{8}$					
Dy. $\frac{15}{18}$ R''					
Dy ₂ O ₃					

Where R – anion of IBA, R' = anion of IPA, R'' = anion of NAA, DC = Dave and Chopra method, CR = Coats and Redfern method, dp = decomposition products

The stability limits of the various forms of the chelates, together with the analytical data, are given in Table 1.

The overall solid-state reaction, which resembles a reaction of the type $A(s) \rightarrow B(s) + C(g)$, the kinetics of which could be studied thermally by the Freeman and Carroll methods, follows first order kinetics which can be demonstrated, following the Dave and Chopra method (eqns. (1) and (2) (12) and the Coats and Redfern method (13) (see eqn. (3))

$$k = \frac{(A/m_0)^{n-1} (dx/dt)}{(A-a)^n} \quad (1)$$

Where A is the total area under the DTG curve, m_0 is the mole fraction of the reactant, a is the area at time t under the DTG curve, dx/dt the deviation from baseline of the DTG curve and n the order of the reaction. If $n = 1$, eqn. (1) reduces to

$$k = \frac{(dx/dt)}{(A-a)^n} \quad (2)$$

$$\log \left(\frac{(1 - (1 - \alpha)^{1-n})}{T^2(1-n)} \right) = \log \frac{AR}{aE} \left(1 - \frac{2RT}{E} \right) - \frac{E}{213RT} \quad (3)$$

In eqn. (3), α is the fraction of the sample decomposed at time t, a the heating rate, A the pre-exponential factor, E the activation energy, R the gas constant and n the order of reaction.

Table 2 gives the kinetic data for the different solid-state reactions, with low values of Z, the reactions could be said to slow processes.

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