PYROLYSIS AND THERMAL DISSOCIATION OF METAL – IBA, IPA AND NAA COMPLEXES

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ABSTRACT

Chauhan, Sawhney and Chandra (1), Koepfliet.al. (2) and Heath and Clark (3-20)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 derivatives of IBA, IPA and NAA (1-napthalone acetic acid) followed by pyrolysis and kinetic studies of the thermal dissociation of Tb(III)-IBA, Tb(III)IPA,Tb(III)- NAA chelates.

INTRODUCTION

Discussions 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 their some other properties, the isolated metal complexes of some of the lanthanides series elements: Tbwith 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 – All the chemical used were of analytical grade.

Chelate Isolation

Theaqueous salt solution of indole-3-butyric acid, indole-3-propionic acid and l-naphthalene acetic acid, was added, in small increment, 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 structure (cf schemes: 1 to 2).
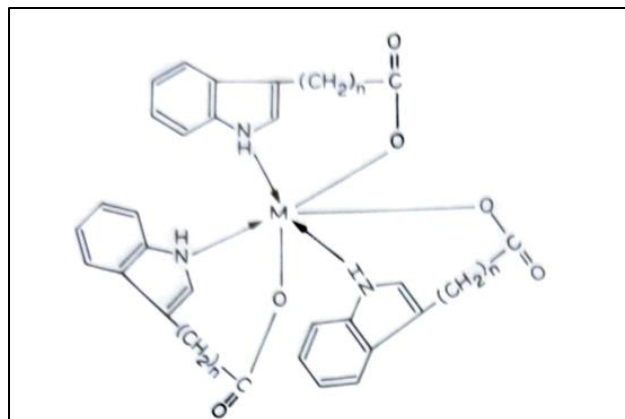
Scheme 1 . M=Tb , n=2 for IBA , IPA Complex
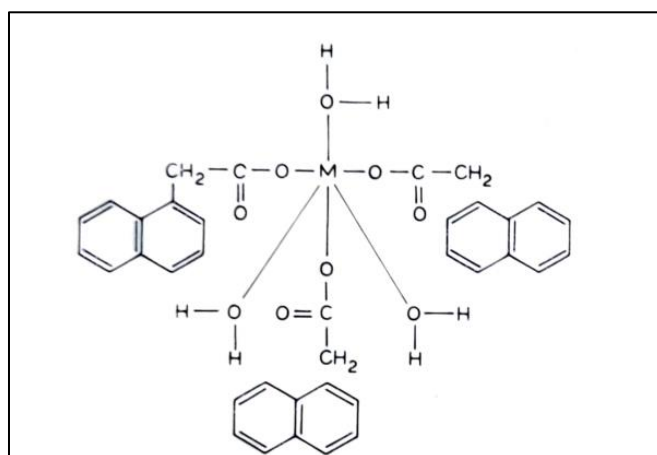
Scheme 2. X=1 , M=Tb for NAA Complex

Reagents

The plant auxins studied were IBA, IPA and NAA and the metal salt used were Tb $(NO_3)_3$.

Apparatus

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

RESULTS AND DISCUSSION

The isolated metal complexes were pyrolysed and resulting pyrolysis curves led us to the following information.

IBA and IPA are bidentate (cf. Scheme 1 and 2) 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.

Thermal stability limits of Tb. R_3, (**I**) Tb, R'_3 (**II**)and Tb.R''_3 $(NO_3)_3$(**III**) are from ambient temperatures to 70°C, 85°C and 100°C respectively. Slightly above the last limits of stability, the organic matter of (I) and (II) began to cleave and upto 195°C and 275°C, the calculated loss i.e.$\frac{29}{16}R'$ and $\frac{3}{4}R'$ agreed to the experimental observations, producing, as indicated by the plateaus on pyrolysis curns, intermediates of stoichiometries: Tb. $\frac{19}{16}$ R(195⁰-275°C) and Tb. $\frac{9}{4}$ R' (275-325°C). Further temperature appreciation resulted in the formation of metal oxides (Tb_2O_3). The isolated complex NAA

i.e. $Tb.R''_3$ $(NO_3)_3$ (ambient to 100°C) lost most probably $\frac{3}{2}$ R'' part of the parent compound from 100°-270°C and reached a stage showing an agreement to a definite composition: $Tb. \frac{3}{2}$ R''.$(NO_3)_3$ (270°-330°C) which became Tb_2O_3, slightly above 550°C.

Given below is the decomposition progression of the Tb- Plant auxin complexes.

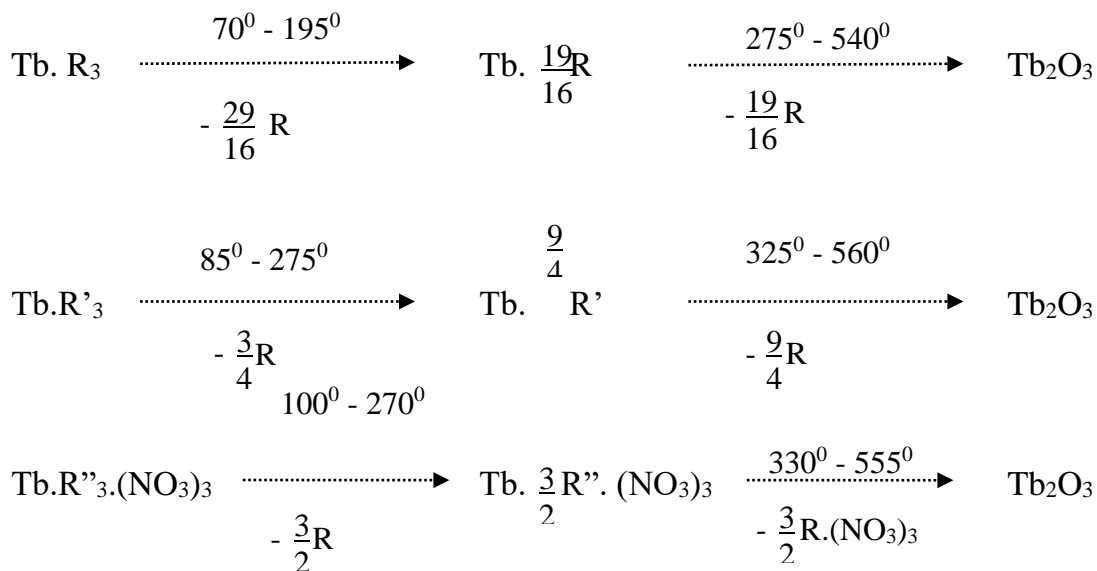$$Tb. R_3 \xrightarrow[- \frac{29}{16} R]{70^0 - 195^0} Tb. \frac{19}{16}R \xrightarrow[- \frac{19}{16} R]{275^0 - 540^0} Tb_2O_3$$

$$Tb.R'_3 \xrightarrow[- \frac{3}{4}R \quad 100^0 - 270^0]{85^0 - 275^0} Tb. \frac{9}{4} R' \xrightarrow[- \frac{9}{4}R]{325^0 - 560^0} Tb_2O_3$$

$$Tb.R''_3.(NO_3)_3 \xrightarrow[- \frac{3}{2}R]{} Tb. \frac{3}{2}R''. (NO_3)_3 \xrightarrow[- \frac{3}{2}R.(NO_3)_3]{330^0 - 555^0} Tb_2O_3$$

Table 1 : Thermal Results on Tb-Plan-Auxin Chelates

Chelate[a]	Sample Size (mg)	T_i (Pdt)[b] (°C)	T_f (°C)	T_f-T_i (°C)	Sigmoid (TG) or dips (DTG) (instability limits)
$Tb.R_3$	119	70	540	471	2 (70-195°C) (275-540°C)
$Tb.R'_3$	110	85	560	475	2 (85-275°C) (325-560°C)
$Tb.R''_3$	74	100	555	455	2 (100-270°C) (330-555°C)

a R, R', R'' are anion of IBA, IPA and NAA respectively

b Pdt, Procedural decomposition

Table 2 : Pyrolysis Data on Tb-Plant Auxin Chelate

Stable phase and Temp. range (^{O}C)	Loss	% Loss		% Eu$_2$O$_3$	
	Temp. ^{0}C	Found	Calc.	Found	Calc.
Tb-IBA Chelate					
Tb.R$_3$ (Upto 70^{0}C)	-	-	-	-	-
Tb.$\frac{19}{16}$ R (195-275^{0}C)	$\frac{29}{16}$ R (70-195^{0}C)	47.95	47.94	-	-
Tb$_2$O$_3$ (540 onwards)	$\frac{19}{16}$ R (275-540^{0}C)	79.20	76.65	27.92	23.36
Tb- IPA Chelate					
Tb. R'$_3$ (Upto 85^{0}C)	-	-	-	-	-
Tb.$\frac{9}{4}$ R' (275-325^{0}C)	$\frac{3}{4}$ R' (85-275^{0}C)	18.75	19.25	--	--
Tb$_2$O$_3$ (560 onwards)	$\frac{9}{4}$ R' (325-560^{0}C)	76.88	78.09	23.13	25.20
Tb-NAA Chelate					
Tb. R"$_3$. (NO$_3$)$_3$ (Upto 100^{0}C)	-	-	-	-	-
Tb. $\frac{3}{2}$ R'. (NO$_3$)$_3$ (270-330^{0}C)	$\frac{3}{2}$ R" (100-270^{0}C)	32.94	30.89	-	-
Tb$_2$O$_3$ (550 onwards)	$\frac{3}{2}$ R" (NO$_3$)$_3$ (330-550^{0}C)	75.88	82.39	24.12	20.04

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

Table 1 contains the thermal data; the stability limits of the various forms of the chelates, together with the analytical data, are given in Table 2.

The overall solid state reaction, which resembles a reaction of the type A(s) → B(s) + C (g),

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

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

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 (21) and the Coats and Redfern method (22)., eqn. (1) &(2)

baseline of the DTG curve and n the order of the reaction. If n = 1, eqn. (1) reduces to

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

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

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

Table 3 : Kinetic Data on Tb-Plant Auxin Chelates

Reaction	n		E (KCal.mol^{-1})		Log z
	DC	CR	DC	CR	DC
Tb-IBA Chelate					
Tb.R$_3$ --------------→	1	1	3.250	7.903	-1.2
Tb. $\frac{9}{4}$ R' + $\frac{3}{4}$ R'					
Tb. $\frac{9}{4}$ R'--------------→	1	1	6.520	11.46	-1.7
Tb$_2$O$_3$ + dp					
Tb-IPA Chelate					

Tb.R$_3$ --------------$\rightarrow$	1	1	5.210	5.209	-1.3
Tb. $\frac{9}{4}$ R' + $\frac{3}{4}$ R'					
Tb. $\frac{9}{4}$ R'--------------$\rightarrow$	1	1	5.230	20.840	-1.3
Tb$_2$O$_3$ + dp					
Tb-NAA Chelate					
Tb.R''$_3$.(NO$_3$)$_3$ --------------$\rightarrow$	1	1	7.540	7.162	-1.2
Tb. $\frac{3}{2}$ R'' (NO$_3$)$_3$ + $\frac{3}{4}$ R''					
Tb. $\frac{3}{2}$ R' (NO$_3$)$_3$ --------------$\rightarrow$	1	1	5.590	12.63	-1.5
Tb$_2$O$_3$ + dp					

a. R, anion of IBA, R', anion of IPA, R'' = anion of NAA,
b. DC, Dave and Chopra method,
c. CR, Coats and Redfern method,
d. Dp, decomposition product
e. Z*, Collision number per unit volume and unit time.

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