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Note

THERMOGRAVIMETRIC STUDY OF THE KINETICS OF THE NON-ISOTHERMAL DECOMPOSITION OF METAL DERIVATIVES OF INDOLE-3-ACETIC ACID

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The nature of interaction of plant auxins with metal ions, which baffled botanists for a long time, has been highlighted by Heath and Clark [1] and Cohen et al. [2], who provided evidence for chelation as a possible mode of action for the plant auxins. Recently, Sahai et al. [3] supported the findings of the aforesaid authors by investigating the complexation of some plant auxins with metal ions of biological interest in solution. No attempt has been made so far to synthesize and characterize the metal derivatives of plant auxins, i.e. IAA, IPA, IBA, NAA. This communication concerns the thermogravimetric study of metal complexes of IAA (indole-3-acetic acid) with Cu(II), oxozirconium and Pr(III), with a view to probing kinetically the non-isothermal decomposition of the metal derivatives following the expressions of Dave and Chopra [4] which are applicable, even under conditions where the factors, known to be sensitive to kinetic data [5], remain inconsistent under experimental conditions. Sawhney et al. [6–8] reported comparable and dependable kinetic data, using Dave and Chopra expressions, associated with the non-isothermal decomposition of metal complexes of amino acids, acetophenone derivatives and naphthoquinone derivatives

$$k = \frac{(A/m_0)^{n-1}(-\mathrm{d}x/\mathrm{d}t)}{(A-a)^n} \tag{1}$$

where the terms have their usual meanings. If $n = 1$, eqn. (1) reduces to

$$k = \frac{(-\mathrm{d}x/\mathrm{d}t)}{(A-a)} \tag{2}$$

EXPERIMENTAL

All the reagents were of B.D.H. quality. For the synthesis of the metal complexes, the sodium salt of indole-3-acetic acid was added slowly with constant stirring to the metal solution; the precipitate immediately appeared,

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and was filtered, washed with distilled water and dried at 35–40°C. A tally of found and calculated values of elemental analysis for $Cu(C_{10}H_8O_2N)_2 \cdot 0.25\ H_2O$, $ZrO(C_{10}H_8O_2N) \cdot 4.5\ H_2O$ and $Pr(C_{10}H_8O_2N)_3 \cdot 7.25\ H_2O$, was observed. Samples were pyrolyzed at the rate of 10°C min^{-1} manually using a modern thermogravimetric balance with a Toshniwal furnace in air.

RESULTS AND DISCUSSION

Pyrolysis curves of metal complexes showed only two sigmoidal traces. Having 4.5 H_2O molecules, (indole-3-acetic acetato) oxozirconium displayed its stability up to 40°C, after which departure of the water molecules commenced and was completed at 150°C; a plateau (150–175°C) corresponding to (indole-3-acetic acetato) oxozirconium was observed. Between 175 and 520°C, organic matter was lost. Bis(indole-3-acetic acetato) copper(II) containing 0.25 H_2O lost 0.25 H_2O molecule between 40 and 60°C; the plateau between 60 and 100°C pointed to bis(indole-3-acetic acetato) copper(II), which decomposed quickly up to 200°C after which slow

TABLE 1

Analytical data

Complex	H_2O %		Oxide % [a]	
	Found	Calcd.	Found	Calcd.
$(C_{10}H_8O_2N)_2Cu \cdot 0.25\ H_2O$	1.95	1.08	22.80	18.89
$(C_{10}H_8O_2N)ZrO \cdot 4.5\ H_2O$	12.96	12.46	40.74	34.84
$(C_{10}H_8O_2N)_3Pr \cdot 7.25\ H_2O$	16.67	16.44	18.20	20.07

[a] The larger found values than calculated ones appears to be due to the adsorption of the evolved gases, etc., on the final residue during pyrolysis of the metal complexes.

TABLE 2

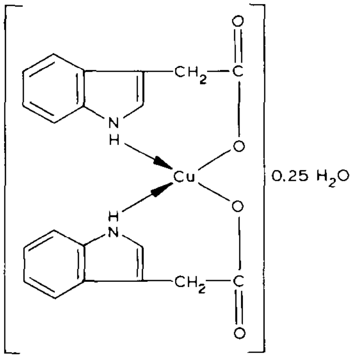
Kinetic data

	E (kcal $mole^{-1}$)	log *Z*
$(C_{10}H_8O_2N)_2Cu \rightarrow CuO + v.p.$	2.29	0.40
$(C_{10}H_8O_2N)ZrO\ 4.5\ H_2O \rightarrow (C_{10}H_8O_2N)ZrO + 4.5\ H_2O$	10.07	4.90
$(C_{10}H_8O_2N)ZrO \rightarrow ZrO_2 + v.p.$	5.49	0.15
$(C_{10}H_8O_2N)_3Pr \rightarrow Pr_2O_3 + v.p.$	4.93	0.12

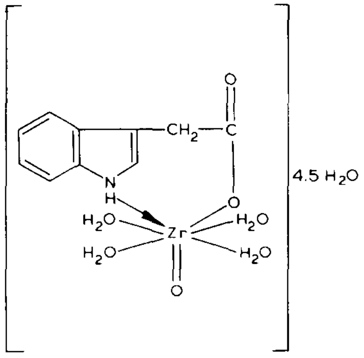
v.p. = Volatile products.

decomposition up to 505°C was observed. From 505°C onwards a plateau for CuO was observed. Hydrated tris(indole-3-acetic acetato) Pr(III), being stable up to 80°C, lost 7.25 H_2O molecules up to 100°C, after which a constant weight corresponding to tris(indole-3-acetic acetato) Pr(III) was observed up to 140°C. Organic matter was delinked between 140 and 400°C, after which a plateau showing Pr_2O_3 appeared.

Analytical data are shown in Table 1. Tentative structures of the metal complexes may be shown as



Central metal ligandcy 4



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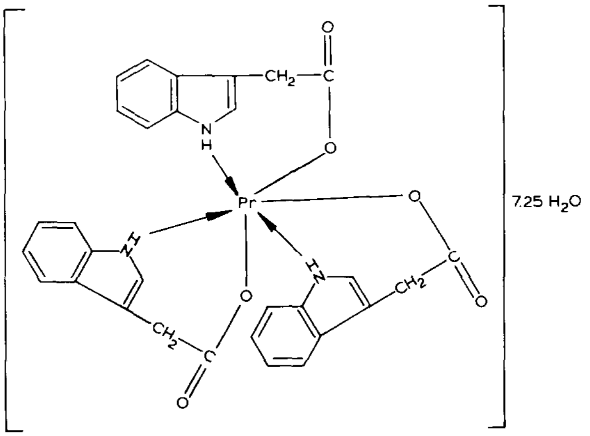

Central metal ligandcy 6

For kinetic study, each sigmoidal trace was analyzed. Non-isothermal decomposition of the metal complexes under study resembles the reaction

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

which can be kinetically studied.

A, a, and dx/dt were calculated from DTG curves; k values corrosponding to different temperatures were computed, using eqn. (1) for first order kinetics. A straight-line relationship on plotting log k vs. T^{-1} indicates that the non-isothermal decomposition/desolvation follows first order kinetics. The slope and intercept gave the values of E and Z (collision number). Desolvation of hydrated bis(indole-3-acetic acetato) Cu(II) and hydrated tris(indole-3-acetic acetato) Pr(III) was too fast to be probed kinetically. The reactions under study appear to be slow processes, as the log Z value is abnormally low. Kinetic data are given in Table 2.

With a manually operated assembly, as used in the present study, kinetic data computed using the Dave and Chopra method are quite dependable, even if such factors as heating rate, temperature variance, etc., which contribute significantly if the slope-dependent procedures [9,10] are employed, could not be kept reasonably constant.

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