NON-ISOTHERMAL THERMOGRAVIMETRIC INVESTIGATION OF THE THERMAL DISSOCIATION KINETICS OF Eu(III) AND Gd(III) PLANT AUXIN CHELATES

A Thermogravimetric and Kinetic Study Using Coats–Redfern and Dave–Chopra Methods

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ABSTRACT

The thermal decomposition behaviour of lanthanide complexes with plant auxins has attracted significant interest because of its importance in coordination chemistry, thermal analysis and solid-state kinetics. In the present investigation, the non-isothermal thermal dissociation kinetics of europium and gadolinium complexes of plant auxins such as indole-3-butyric acid (IBA), indole-3-propionic acid (IPA) and 1-naphthalene acetic acid (NAA) were studied using thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG). The kinetic parameters were evaluated by employing Coats and Redfern and Dave and Chopra methods. The decomposition processes were found to follow first-order kinetics. The activation energy values obtained from both methods showed satisfactory agreement. The decomposition of hydrated complexes occurred initially through dehydration followed by ligand degradation and finally the formation of stable lanthanide oxides. The present work demonstrates that thermogravimetric techniques are highly useful for understanding the thermal stability and decomposition kinetics of lanthanide-auxin chelates.

Keywords: *Thermogravimetric analysis, europium complexes, gadolinium complexes, auxin chelates, non-isothermal kinetics, Coats and Redfern equation..*

INTRODUCTION

Thermal decomposition kinetics of coordination compounds has become an important field of research in coordination chemistry and materials science. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) are widely employed for studying the thermal stability, decomposition mechanism and kinetic behaviour of metal complexes.

Lanthanide complexes with plant growth regulators such as indole-3-butyric acid (IBA), indole-3-propionic acid (IPA) and 1-naphthalene acetic acid (NAA) are of particular interest because these ligands possess oxygen donor atoms capable of forming stable chelates with rare earth ions. The thermal behaviour of these compounds provides valuable information regarding hydration, ligand coordination and decomposition pathways.

The present study deals with the thermal dissociation kinetics of europium and gadolinium auxin chelates under non-isothermal conditions. The decomposition kinetics were evaluated using thermogravimetric methods and the kinetic parameters such as activation energy (E), order of reaction (n) and frequency factor (Z) were determined.

NON-ISOTHERMAL KINETIC METHODS

Several mathematical approaches are available for evaluating the kinetic parameters of solid-state decomposition reactions. In the present work, the following methods were considered:

1. Freeman and Carroll Method
2. Doyle Method
3. Coats and Redfern Method
4. Horowitz and Metzger Method
5. Van Krevelen Method
6. Dave and Chopra Method

Among these, the Coats and Redfern and Dave and Chopra methods were extensively employed for kinetic analysis.

THEORETICAL BACKGROUND

The thermal decomposition kinetics of solid compounds under non-isothermal conditions are generally described by the Arrhenius equation:

$k = Ze^{(-E/RT)}$

where:

- k = rate constant
- Z = frequency factor
- E = activation energy
- R = gas constant
- T = absolute temperature

The fraction decomposed (α) during decomposition was evaluated from thermogravimetric data using the relationship:

$\alpha = (W - W_t)/(W - W_f)$

where:

- W = initial mass of sample
- Wt = mass at time t
- Wf = final mass after decomposition

Coats and Redfern Method

The Coats and Redfern integral method was employed for evaluating the kinetic parameters of thermal decomposition reactions. For a first-order reaction (n = 1), the integrated equation may be written as:

$\log [-\log (1 - \alpha)/T^2] = \log (ZR/\beta E) - E/2.303RT$

where:

- β = heating rate
- E = activation energy
- Z = frequency factor
- T = absolute temperature

A plot of:

$\log [-\log (1 - \alpha)/T^2]$ versus $1/T$

produced a straight line confirming first-order kinetics for the decomposition reactions.

The slope of the straight line is equal to:

$\text{Slope} = -E/2.303R$

from which the activation energy (E) was calculated, while the intercept yielded the frequency factor (Z).

Dave and Chopra Method

In the Dave and Chopra method, the kinetic parameters were obtained from DTG curves assuming first-order kinetics. The values of α, decomposition rate and rate constants were calculated from the thermogravimetric data.

A straight-line relationship was obtained by plotting:

$\log k$ versus $1/T$

The slope of the plot gave the activation energy whereas the intercept provided the logarithm of the frequency factor.

EXPERIMENTAL METHOD

The europium and gadolinium complexes of IBA, IPA and NAA were synthesized and isolated in solid state. The complexes were subjected to thermogravimetric analysis under controlled conditions.

Experimental Conditions

- Heating rate: 10 °C min^{-1}
- Atmosphere: Static air
- Technique used: Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG)
- Temperature range: Ambient temperature to approximately 650 °C

The decomposition products were identified from the percentage mass loss and the final residue obtained after decomposition.

THERMAL DECOMPOSITION BEHAVIOUR

Europium Auxin Chelates

Eu-IBA Chelate

The europium-IBA chelate exhibited a two-step decomposition pattern. The first stage corresponded to ligand degradation while the second stage resulted in the formation of europium oxide.

Decomposition Scheme

$Eu\cdot R_3 \rightarrow Eu\cdot 13/8R + 11/8R$ (270–535 °C)

$Eu\cdot 13/8R \rightarrow Eu_2O_3$ + decomposition products (400–475 °C)

The decomposition process showed first-order kinetics.

Eu-IPA Chelate

The europium-IPA chelate also decomposed in two distinct stages.

$Eu\cdot R'_3 \rightarrow Eu\cdot 19/8R' + 5/8R'$ (250–350 °C)

$Eu\cdot 19/8R' \rightarrow Eu_2O_3$ + decomposition products (400–475 °C)

Eu-NAA Chelate

The europium-NAA complex was hydrated and decomposed through dehydration followed by ligand decomposition.

$[Eu\cdot R''_3\cdot 4H_2O]H_2O \rightarrow Eu\cdot R''_3\cdot 4H_2O + H_2O$ (75–100 °C)

$Eu\cdot R''_3\cdot 4H_2O \rightarrow Eu\cdot R''_3 + 4H_2O$ (150–195 °C)

$Eu\cdot R''_3 \rightarrow Eu\cdot 27/14R'' + 15/14R''$ (250–350 °C)

$Eu\cdot 27/14R'' \rightarrow Eu_2O_3$ + decomposition products (400–475 °C)

The dehydration stage occurred at relatively low temperature indicating the presence of loosely bound water molecules.

Gadolinium Auxin Chelates

Gd-IBA Chelate

The gadolinium-IBA complex initially lost coordinated water molecules followed by ligand degradation.

$Gd\cdot R_3\cdot 2\frac{1}{2}H_2O \rightarrow Gd\cdot R_3 + 2\frac{1}{2}H_2O$ (90–125 °C)

$Gd\cdot R_3 \rightarrow Gd\cdot 3/2R + 3/2R$ (165–320 °C)

$Gd\cdot 3/2R \rightarrow Gd_2O_3$ + decomposition products (365–615 °C)

Gd-IPA Chelate

The Gd-IPA chelate also showed a multistep decomposition process.

$Gd\cdot R'_3\cdot \frac{3}{4}H_2O \rightarrow Gd\cdot R'_3 + \frac{3}{4}H_2O$ (70–105 °C)

$Gd\cdot R'_3 \rightarrow Gd\cdot 3/2R' + 3/2R'$ (150–420 °C)

$Gd\cdot 3/2R' \rightarrow Gd_2O_3$ + decomposition products (470–650 °C)

Gd-NAA Chelate

The Gd-NAA complex underwent dehydration followed by decomposition of the coordinated ligand.

$[Gd\cdot R''_3\cdot 3H_2O]\frac{1}{4}H_2O \rightarrow Gd\cdot R''_3\cdot 3H_2O + \frac{1}{4}H_2O$ (85–115 °C)

$Gd\cdot R''_3\cdot 3H_2O \rightarrow Gd\cdot R''_3 + 3H_2O$ (135–200 °C)

$Gd\cdot R''_3 \rightarrow Gd\cdot 5/8R'' + 19/8R''$ (240–445 °C)

Gd·5/8R'' → Gd_2O_3 + decomposition products (480–600 °C)

KINETIC ANALYSIS

The kinetic parameters obtained from Dave and Chopra (DC) and Coats and Redfern (CR) methods are summarized below.

Table 1. Kinetic Data on Europium-Plant Auxin Chelates

Reaction	n (DC)	n (CR)	E (DC) kcal mol^{-1}	E (CR) kcal mol^{-1}	Log Z
Eu-IBA: Eu·R_3 → Eu·13/8R + 11/8R	1	1	4.09	6.37	−1.4
Eu·13/8R → Eu_2O_3 + dp	1	1	7.17	28.65	−1.4
Eu-IPA: Eu·R'_3 → Eu·19/8R' + 5/8R'	1	1	5.73	12.06	−0.1
Eu·19/8R' → Eu_2O_3 + dp	1	1	5.54	11.46	−1.4
Eu-NAA: [Eu·R''_3·$4H_2O$]H_2O → Eu·R''_3·$4H_2O$ + H_2O	1	1	33.96	—	−0.6
Eu·R''_3·$4H_2O$ → Eu·R''_3 + $4H_2O$	1	1	24.78	25.75	−0.6
Eu·R''_3 → Eu·27/14R'' + 15/14R''	1	1	9.17	14.06	−1.1
Eu·27/14R'' → Eu_2O_3 + dp	1	1	5.73	41.67	−0.7

Where:

- R = anion of IBA
- R' = anion of IPA
- R'' = anion of NAA
- dp = decomposition products

Table 2. Kinetic Data on Gadolinium-Plant Auxin Chelates

Reaction	n (DC)	n (CR)	E (DC) kcal mol^{-1}	E (CR) kcal mol^{-1}	Log Z
$Gd\cdot R_3\cdot 2\tfrac{1}{2}H_2O \rightarrow Gd\cdot R_3 + 2\tfrac{1}{2}H_2O$	1	1	38.20	19.93	+0.3
$Gd\cdot R_3 \rightarrow Gd\cdot 3/2R + 3/2R$	1	1	17.98	10.92	−0.4
$Gd\cdot 3/2R \rightarrow Gd_2O_3 + dp$	1	1	24.78	25.47	−1.2
$Gd\cdot R'_3\cdot \tfrac{3}{4}H_2O \rightarrow Gd\cdot R'_3 + \tfrac{3}{4}H_2O$	1	1	30.44	22.92	+1.6
$Gd\cdot R'_3 \rightarrow Gd\cdot 1\tfrac{1}{2}R' + 1\tfrac{1}{2}R'$	1	1	13.37	11.76	−1.3
$Gd\cdot 1\tfrac{1}{2}R' \rightarrow Gd_2O_3 + dp$	1	1	43.29	25.47	−1.2
$[Gd\cdot R''_3\cdot 3H_2O]\tfrac{1}{4}H_2O \rightarrow Gd\cdot R''_3\cdot 3H_2O + \tfrac{1}{4}H_2O$	1	1	25.47	—	−0.1
$Gd\cdot R''_3\cdot 3H_2O \rightarrow Gd\cdot R''_3 + 3H_2O$	1	1	8.04	10.92	−0.2

RESULTS AND DISCUSSION

The thermogravimetric curves of europium and gadolinium auxin chelates exhibited sigmoid-type decomposition behaviour characteristic of solid-state reactions. The decomposition generally occurred in multiple stages involving dehydration, partial ligand degradation and final oxide formation.

The hydrated NAA complexes decomposed initially through the loss of lattice and coordinated water molecules. These dehydration steps occurred at relatively low temperatures, indicating weakly bound water molecules.

The decomposition of ligand moieties occurred over a broader temperature range and resulted in intermediate species before conversion into stable lanthanide oxides such as Eu_2O_3 and Gd_2O_3.

The kinetic analysis confirmed first-order decomposition kinetics for all complexes since the value of reaction order, n, was approximately unity in both Dave and Chopra and Coats and Redfern methods.

The activation energy values varied depending on the nature of the ligand and the decomposition stage. Hydrated complexes generally showed higher activation energies for dehydration processes. The low values of log Z suggest that the decomposition reactions proceed through comparatively slow processes.

The activation energy values obtained from the Coats and Redfern method were generally in good agreement with those obtained from the Dave and Chopra method, thereby validating the reliability of the kinetic evaluation.

CONCLUSION

The present investigation demonstrates that thermogravimetric techniques are highly effective for studying the thermal dissociation kinetics of europium and gadolinium plant auxin chelates.

The decomposition of the complexes proceeds through multistep pathways involving dehydration, ligand degradation and oxide formation. The kinetic studies using Coats and

Redfern and Dave and Chopra methods confirmed first-order decomposition kinetics for all complexes.

The activation energy values and thermal decomposition behaviour indicate that the thermal stability of the complexes depends upon the nature of the coordinated auxin ligand and the extent of hydration. The final decomposition products were identified as stable lanthanide oxides.

The study provides useful insight into the solid-state thermal behaviour and kinetic characteristics of lanthanide-auxin complexes.

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