CHAPTER 6

THERMAL STUDIES OF YTTRIUM AND LANTHANIDE COMPLEXES OF SOME SCHIFF BASES
6.1 Introduction

Thermal analysis refers to the group of methods in which some physical property of the sample is progressively and continuously measured as a function of temperature, whilst the sample is subjected to a controlled temperature change. The study of the changes involving solids has three aspects, viz., the phenomenological, the thermodynamic and the kinetic. The phenomenological aspects deals with the qualitative and the semiquantitative observations of the phenomena occurring during the process. The thermodynamic aspect is related to the initial, final and the equilibrium states of the system and the driving force behind the change. The kinetic study is mostly concerned with the rate of transformation of the reactants into products and the mechanism of the transformation.

On heating, a solid may undergo physical or chemical changes which may include solid state phase transformations, sintering, melting and thermal decomposition. The general features of thermal
decomposition and its kinetics have been discussed by Garner, Galway and Tompkins. Wendlandt and coworkers studied the relationship between thermal stability of metal chelates and the structure of the chelating ligands using TG and DTG data.

Thermogravimetry (TG)

Thermogravimetry is an analytical technique whereby the change in mass of a sample is recorded as a function of time or temperature, as it is continuously heated or cooled in a suitable environment at a controlled rate. Mainly two methods are employed in thermogravimetry, (1) isothermal or static thermogravimetry, where the sample mass is recorded as a function of time at constant temperature. (2) Nonisothermal or dynamic thermogravimetry, where the sample is heated in an environment whose temperature is changing in a linear manner.

In derivative thermogravimetry (DTG) the derivative of mass change with respect to time is recorded as a function of time or temperature. The derivative curve may be obtained either from the TG curve by manual differentiation method or by electronic differentiation of the TG signals. The area under the DTG curve is directly proportional to the mass change and the height of the DTG
peak at any temperature gives rate of mass change at that temperature. The DTG curve allows the direct determination of the temperature at which the rate of mass change is maximum (T_s) and the initial temperature (T_i) at which cumulative mass change begins and the final temperature (T_f) at which the cumulative mass change reaches a maximum corresponding to the complete reaction.

Differential Thermal Analysis (DTA)

DTA is a thermal technique in which the temperature of a sample compared with the temperature of a thermally inert material is recorded as a function of the sample or furnace temperature, as the sample is heated or cooled at a programmed rate. The temperature changes in the sample are due to endothermic or exothermic reactions that occur during the temperature programme and the corresponding deviation from the reference temperature is monitored. The difference in temperature from the sample and reference, i.e., \( T = T_{\text{sample}} - T_{\text{ref}} \), is recorded as a function of temperature.

In nonisothermal studies the following aspects are studied:

(a) Phenomenological aspects: This study is used to find the initial temperature (T_i), the final
temperature \((T_f)\) and the maximum mass loss temperature \((T_s)\) from TG peaks. The TG plateau gives the percentage mass loss during each stage of decomposition. The DTA curve identifies the exothermic or endothermic nature of the different changes undergone by the sample.

(b) **Kinetic aspects:** Nonisothermal thermogravimetric analysis has been used in the investigation of the thermal stability of solid state materials. Using this method the kinetic parameters can be calculated over the entire range of temperature in a continuous manner. The kinetic equation for the thermal decomposition is derived based on the following assumptions.

\[
\frac{da}{dt} = Kf(a) \tag{1}
\]

Where \(K\) - specific rate constant, \(a\) - amount of sample undergoing reaction, \(f(a)\) the conversion functions.

For a linear heating rate \(\phi\), \(T = T_0 + \phi t\)

where, \(T_0\) - temperature of initiation

\[
\frac{dT}{dt} = \phi \tag{2}
\]
Substituting (2) in (1)

\[
\frac{d\alpha}{dt} = \frac{K.f(\alpha)}{\phi} \quad \ldots \quad (3)
\]

The temperature dependence of the specific rate constant \( K \) is expressed by the Arrhenius equation,

\[
K = A.e^{-E/RT} \quad \ldots \quad (4)
\]

where

- \( A \) - pre-exponential factor
- \( E \) - energy of activation
- \( R \) - gas constant
- \( T \) - temperature in Kelvin scale

Substituting (4) in (3)

\[
\frac{d\alpha}{dT} = \frac{A.e^{-E/RT}}{\phi}.f(\alpha) \quad \ldots \quad (5)
\]

On integration taking initial temperature as zero (this assumption is justifiable as no reaction occurs between \( T = 0 \) and \( T = T_i \)).

\[
\int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} \int_{0}^{T} e^{-E/RT}dT
\]

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where \( g(\alpha) \) is the conversion integral. Coats and Redfern\(^{160,161} \) evaluated the temperature integral with the aid of the Rainville\(^{162} \) function. The temperature integral thus obtained is

\[
g(\alpha) = \frac{A}{\phi} \int_0^T e^{-E/RT} dT \quad \ldots \ldots (6)
\]

This equation is known as the Coats-Redfern equation. A plot of LHS of the equation against \( 1/T \) is a straight line, from the slope and intercept of which one can calculate the energy of activation (\( E \)) and the pre-exponential factor (\( A \)).

The entropy of activation (\( \Delta S \)) can be calculated using the equation,

\[
A = \frac{kT \sigma_s}{h} e^{\Delta S/R}
\]

where

- \( k \) - Boltzmann constant
- \( h \) - Planks constant
- \( \Delta S \) - entropy of activation
c) **Mechanistic studies:** The mechanism of solid state reactions is quite complex and includes several elementary steps such as:

i) **Sorption phenomenon** (adsorption and desorption)

ii) **Reaction on atomic scale** (homogeneous or interphase reactions).

iii) **Nucleation of a new phase and the growth of the nuclei** (in the bulk or at the surface of the reaction solid).

iv) **Transport phenomenon** (particle diffusion through the phase boundary separating the reactant and the product, i.e., a mass transfer process).

Avrani, Tompkins, Mampel, etc. have derived a number of relations to study the kinetics of the reactions based on the above assumptions. The kinetic equations which govern the reaction mechanism are based on the assumption that the form of $g(a)$ depends on the reaction mechanism. For the present study the nine mechanism based equations proposed by Satava have been used (Table 6.1).

In the present study, the experimental data are fed into the nine mechanism based equations proposed by Satava and the correlation coefficients calculated out of the nine forms of $g(a)$ which are given in Tables 6.7 to 6.12.
<table>
<thead>
<tr>
<th>Eq. No.</th>
<th>Form of $g(\alpha)$</th>
<th>Rate controlling process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\alpha^2$</td>
<td>One dimensional diffusion</td>
</tr>
<tr>
<td>2</td>
<td>$\alpha + (1-\alpha)\ln(1-\alpha)$</td>
<td>Two dimensional diffusion</td>
</tr>
<tr>
<td>3</td>
<td>$[1-(1-\alpha)^{1/3}]^2$</td>
<td>Three dimensional diffusion, Spherical symmetry, Jander equation</td>
</tr>
<tr>
<td>4</td>
<td>$(1-2/3\alpha)(1-\alpha)^{2/3}$</td>
<td>Three dimensional diffusion, Spherical symmetry - Ginstling - Brounshtein equation</td>
</tr>
<tr>
<td>5</td>
<td>$-\ln(1-\alpha)$</td>
<td>Random nucleation - one nucleus on each particle - Mampel equation</td>
</tr>
<tr>
<td>6</td>
<td>$[-\ln(1-\alpha)]^{1/2}$</td>
<td>Random nucleation - Avrami equation I</td>
</tr>
<tr>
<td>7</td>
<td>$[-\ln(1-\alpha)]^{1/2}$</td>
<td>Random nucleation - Avrami equation II</td>
</tr>
<tr>
<td>8</td>
<td>$1-(1-\alpha)^{1/2}$</td>
<td>Phase boundary reaction cylindrical symmetry</td>
</tr>
<tr>
<td>9</td>
<td>$1-(1-\alpha)^{1/3}$</td>
<td>Phase boundary reaction spherical symmetry</td>
</tr>
</tbody>
</table>
The form of $g(a)$, the conversion integral, representing the best experimental data is considered as the mechanism of the reaction.

6.2 Experimental

6.2.1 Preparation of the ligand and the complexes

The method of preparation of the ligand FAA and its complexes with yttrium and lanthanides are presented in Chapter 3. The preparation of the ligand TAA and its complexes with yttrium and lanthanides are discussed in Chapter 4. Synthesis of the ligand NTA and its complexes with yttrium and lanthanides are given in Chapter 5. All the above complexes have been characterized by elemental analyses, electrical conductance in nonaqueous solvents, magnetic susceptibility, infrared, proton NMR and electronic spectral studies.

6.2.2 Instrumentation

The thermograms of the present complexes were recorded using the DuPont 2000 and the Shimadzu-DT-40 thermal analysers. The thermal investigations were carried out from room temperature to $900^\circ$C with a heating rate of $10^\circ$C/min. in analar nitrogen atmosphere.
In the present chapter both the phenomenological and kinetic aspects of the thermal decomposition reactions of the complexes were discussed.

6.3 Results and Discussion

We have studied 50 different complexes of yttrium and lanthanides. They are the perchlorate complexes of yttrium and lanthanides with FAA, TAA and NTA, nitrate complexes of yttrium and lanthanides with FAA and iodide complexes of yttrium and lanthanides with FAA. Both phenomenological aspects and kinetic aspects were studied.

6.3.1 Phenomenological aspects

Yttrium and lanthanide perchlorate complexes of FAA

These ten complexes are represented by the general formula \([\text{Ln}(\text{FAA})_3(\text{ClO}_4)_2](\text{ClO}_4)\), where FAA is 4-N-(2'-furfurylidene)aminoantipyrine, and \(\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er}\). A coordination number of eleven is assigned to the metal ion in these complexes.

The complexes are stable up to 180\(^\circ\)C with a mass loss of 2-3\% below 110\(^\circ\)C which may be due to the desorption of adsorbed moisture\(^{164}\) (Table 6.2). The complexes decompose in two stages. The first stage involving a mass loss of about 27\% starts at about 200-220\(^\circ\)C and ends at about 340-
380°C. The DTG peak of this stage is observed at about 305°C. This stage may be due to the loss of one ligand and the decomposition of one perchlorate ion to the chloride ion. The presence of chloride after the first stage is confirmed by the chemical analysis of the intermediate compound. The second stage starts at about 360-380°C and this slow decomposition is complete by about 780-860°C which involves the decomposition of the remaining ligands and the perchlorate groups. The second stage could not be well-characterized because of the volatile nature of the metal chlorides. The lanthanide chlorides sublime in the range 602-855°C. The final residue consists of the respective metal chloride and traces of carbon. The general decomposition pattern is the same for all the complexes pointing to the similarity in their structure.

Yttrium and lanthanide nitrate complexes of FAA

The general formula of the ten nitrate complexes can be represented as [Ln(FAA)(NO$_3$)$_2$]NO$_3$ where FAA is 4-N-(2'-furfurylidene)aminoantipyrine and Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er. A coordination number of seven may be assigned to the metal ion in these complexes.
The complexes are thermally stable up to about 200°C (Table 6.3). A mass loss of nearly 4% below 120°C may be attributed to the desorption of moisture. The first stage of decomposition starts at 220-240°C and ends in the range 340-370°C. This involves a mass loss of about 26% which corresponds to the decomposition of the nitrate to the oxide. This result is supported by the absence of nitrate ion in the intermediate obtained at 360°C on IR spectral analysis. The DTG peak of this stage is observed at about 310°C. The second stage starts around 360°C and ends at about 520°C which involves the decomposition of the ligand moiety. The final residue on analysis after 900°C shows the presence of traces of carbon and the corresponding metal oxide. The fact that the thermograms of all these ten complexes are comparable, points to the similarity in their structure.

Yttrium and lanthanide iodide complexes of FAA

The general formula of the iodide complexes of FAA can be represented as [Ln(FAA)₃I₂]I where FAA is 4-N-(2'-furfurylidene)aminoantipyrine and Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er. A coordination number of eleven may be assigned to the metal ion in these complexes.
The thermogram of the iodide complexes indicate that they are stable up to about 170°C (Table 6.4). A mass loss of about 3-4% below 100°C is due to the desorption of moisture. The decomposition pattern of the iodide complexes is characterized by an initial mass loss of about 20% which starts at about 170-180°C and ends at about 360-390°C. This is due to the decomposition of one ligand. After the first stage the thermogram do not give a distinct stage, but give only a spurious mass loss. It may be assumed that this mass loss amounting to about 45% may be a combined effect of the decomposition of the first intermediate compound formed and the volatilization of final residue, the corresponding metal iodide. The metal iodides volatilize in the range 740-994°C and hence the second stage could not be well-characterized. The DTG peaks of the first and second stages are observed at 250 and 450°C, respectively. The close similarity among the TG curves of the complexes in this series indicates the similarity in their structure.

**Yttrium and lanthanide perchlorate complexes of TAA**

The perchlorate complexes of TAA are represented by \([\text{Ln(TAA)}_3\text{ClO}_4](\text{ClO}_4)_2\), where \(\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er}\) and \(\text{TAA} = 4-N-(2'\text{'-thienylidene})\text{amino-antipyrine}.\)
The thermal analysis of the complexes in analar nitrogen atmosphere indicate that the complexes are stable up to about 220-240°C. The initial mass loss of about 4% below 120°C may be attributed to the desorption of moisture. The complexes decompose in two stages (Table 6.5). The first stage starts at about 210-240°C and ends at about 330-360°C and corresponds to a mass loss of 26-27% which may be attributed to the loss of one ligand and the decomposition of one perchlorate to chloride. This result has been confirmed by IR spectra and chemical analysis. The DTG peak corresponding to this change is observed at 285°C. The second stage starts at 360-370°C and ends around 500°C. This may be due to the loss of the remaining two ligands and the decomposition of two perchlorates to chloride. The metal chlorides sublime in the range 602-855°C and hence a steady mass loss is observed. The final residue obtained is the corresponding metal chloride with a slight amount of carbon. The thermogram of all the ten complexes are similar pointing to their structural similarity.

**Yttrium and lanthanide perchlorate complexes of NTA**

The perchlorate complexes of NTA are represented by the formula \([\text{Ln(NTA)}_2(\text{ClO}_4)_2](\text{ClO}_4)\), where \(\text{Ln} = \text{Y, La, Pr,}\)
Nd, Sm, Eu, Gd, Dy, Ho or Er and NTA = 4-N-(5'-nitro-2'-thienylidene)aminoantipyrine.

The complexes are thermally stable up to about 170°C and the mass loss of 4% below 110°C may be due to the desorption of adsorbed moisture. The first stage of decomposition commences at about 170-180°C and ends at about 410°C (Table 6.6). This stage accounts for a mass loss of about 30%, which may be attributed to the loss of one ligand. The DTG peak of the first stage is observed at about 370°C. The second stage starts at 410°C and it could not be well characterized because the metal chloride formed starts volatilization in the range of temperature 602-855°C depending upon the individual metal ion.165 The residue obtained after 700°C on analysis indicates the presence of metal chloride associated with little carbon. This stage may be due to the conversion of the perchlorate groups to the chloride and the loss of the remaining ligand. The close similarity among the thermograms of the complexes in the series points to their structural similarity.

Comparison of the thermal behaviour of the three series of complexes of FAA

From the thermal analysis data of the perchlorate, nitrate and iodide complexes of FAA it is observed that
the nitrate complexes are stabler than the perchlorate and iodide complexes. The nitrate complexes starts decomposition at about 200-210°C, while the perchlorate complexes at about 180°C and the iodide complexes at about 170°C. The higher thermal stability of the complexes indicates that there are no small molecules like water or solvents present in the complexes. So the stability of the complexes may be represented in the order nitrate > perchlorate > iodide. Even though the decomposition temperatures of these three series are somewhat comparable, their gradation can be accounted. There is only one FAA coordinated to the metal ion in the nitrate complexes while there are three molecules of FAA in both the perchlorate and iodide series. So the nitrate series is sterically less strained. Also, two of the nitrate ions are bidentately coordinated to the metal ion rendering the complex more stable. The smallest size of nitrate ion among the three anions may be one factor for the greater stability of the nitrate complexes.

Comparison of the perchlorate complexes of FAA, TAA and NTA

The stability of the perchlorate complexes decreases in the order:

\[ [\text{Ln(TAA)}_3(\text{ClO}_4)](\text{ClO}_4)_2 > [\text{Ln(FAA)}_3(\text{ClO}_4)_2]\text{ClO}_4 > [\text{Ln(NTA)}_2(\text{ClO}_4)_2]\text{ClO}_4 \]

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The thermal stability of the complexes (170-240°C) indicates that there are no small molecules like water or solvents present in the complexes. Here the complexes contain same anion but different ligands. But the percentage of perchlorate content in the coordination sphere decreases in the order: $[\text{Ln(NTA)}_2(\text{ClO}_4)_2](\text{ClO}_4) > [\text{Ln(FAA)}_3(\text{ClO}_4)_2]\text{ClO}_4 > [\text{Ln(TAA)}_3(\text{ClO}_4)](\text{ClO}_4)_2$ which is the same order of increasing stability of the complexes. Hence the stability of the complexes decreases with increasing percentage of perchlorate ion in the coordination sphere. Also, the presence of nitrogroup in NTA may be an added reason for the least thermal stability of the NTA complex.

6.3.2 Kinetic studies

In the present investigations we have computed the kinetic parameters of the thermal decomposition of the yttrium and lanthanide perchlorate complexes of FAA, TAA and NTA and yttrium and lanthanide nitrate and iodide complexes of FAA in nitrogen atmosphere. Only one distinct stage, viz., the first stage is kinetically analysed for FAA and NTA because the other stages could not be well characterized. However, in the perchlorate complexes of TAA two stages are well defined and hence the kinetic studies could be carried out.
The correlation coefficients calculated using the nine forms of \( g(\alpha) \) are given in Tables 6.7 to 6.12. The kinetic parameters like activation energy (E) and the pre-exponential factor (A) were calculated using the Coats-Redfern equation.

\[
\log[\frac{g(\alpha)}{T^2}] = \log(AR/\phi E) \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.303 RT}
\]

Yttrium and lanthanide perchlorate complexes of FAA

The activation energy calculated (Table 6.13) for the thermal decomposition of the yttrium and lanthanide perchlorate complexes of FAA is in the range 66-139 kJ/mol. This value is very low and is comparable with the activation energy of the dehydration of the hydrated salts.\(^{166,167}\) This indicates that the ligands are loosely bound to the central metal ion and this result is in conformity with the weak covalency in the metal ligand bond due to the non-participation of 4f-electrons in bonding. The pre-exponential factor (A) obtained is from 2.43 to \( 8.35 \times 10^2 \) S\(^{-1}\). The entropy of activation of the decomposition reaction is negative and it varies from -195.5 to -243.29 J/mol. The negative values indicate that the activated complex has a more ordered structure than the reactants and that the reactions are slower than normal.\(^{168,169}\) The activation energy, entropy of
activation and the pre-exponential factor for these complexes do not show any regular change in the series.

**Yttrium and lanthanide nitrate complexes of FAA**

The kinetic parameters of the decomposition reaction of the yttrium and lanthanide nitrates with FAA are given in Table 6.14. The activation energy for the thermal decomposition varies from 84.8 to 140.75 kJ/mol which indicates that the metal-ligand bond is very weak.\(^{166,167}\) The pre-exponential factor observed is in the range 21.17 to \(2.69 \times 10^3\) S\(^{-1}\). The entropy of activation varies from -184.99 to -224.75 J/mol. There is no definite trend in the values of the energy of activation and entropy of activation. But the negative value of the entropy of activation indicates that the activated complex has a more ordered structure than the reactants.\(^{168,169}\)

**Yttrium and lanthanide iodide complexes of FAA**

The activation energy for the thermal decomposition of the iodide complexes of FAA (Table 6.15) varies from 72.74 to 102.93 kJ/mol and the entropy values are in the range -201.03 to -221.2 J/mol. The values of the activation energy are comparable with the activation energy of dehydration of hydrated salts. This indicates that the ligands are loosely bound to the metal ion.
through electrostatic forces since 4f-electrons, shielded by the 5s^25p^6 octet, are not available for covalent bonding.\textsuperscript{166,167} There is no definite trend in the values of the energy of activation and also the entropy of activation like other common physical constants of lanthanide salts viz., boiling point, melting point, etc. But the negative values of the entropy of activation indicates that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal.\textsuperscript{168,169} The pre-exponential factor varies from 9.16 to 3.45 x 10^2 S^{-1}. The variation of these parameters in the series is random.

\textbf{Yttrium and lanthanide perchlorate complexes of TAA}

The activation energy calculated for the first stage of thermal decomposition of perchlorate complexes of TAA is in the range 68.32 to 117.65 kJ/mol and for the second stage 98.91 to 125.88 kJ/mol (Table 6.16). These values are very low and are comparable with the activation energy of dehydration of hydrated salts.\textsuperscript{166,167} This shows weak covalency in the metal-ligand bond due to the nonparticipation of 4f-electrons in bonding. The pre-exponential factor for the first stage varies from 3.83 to 305.01 S^{-1} and for the second stage from 8.38 to
The entropy of activation follows no definite trend. However, these values are negative for all the complexes in both the stages of decomposition. The negative values indicate that the activated complex is having a more ordered structure than the reactants and the decomposition reactions are slower than normal.\textsuperscript{168,169}

The entropy of activation for the first stage is $-203.06$ to $-239.11$ J/mol and for the second stage $-214.89$ to $-234.35$ J/mol. The kinetic parameters give no special regularity among different complexes in the series.

Yttrium and lanthanide perchlorate complexes of NTA

The kinetic parameters of the thermal decomposition of the perchlorate complexes of yttrium and lanthanides with NTA are given in Table 6.17. The activation energy varies from 65.34 to 102 kJ/mol, which are comparable with the activation energy of dehydration of hydrated salts.\textsuperscript{166,167} The very low values suggest that the ligands are loosely bound to the metal ion and the metal-ligand bond is very weak. The pre-exponential factor calculated are in the range 2.34 to 62.96 S\textsuperscript{-1}. The entropy of activation varies from $-216.26$ to $-343.31$ kJ/mol. The negative values of $E$ suggest that the activated complex has a more ordered structure than the reactants.\textsuperscript{168,169}
There is no definite trend in the values of the kinetic parameters of decomposition of the complexes like other common physical constants.

6.3.3 Mechanism of the thermal decomposition reactions

The determination of the mechanism for the solid state thermal decomposition reaction is a complicated one. All the heterogeneous solid state processes can be classified into three categories, viz., (1) nucleation and growth, (2) diffusion, and (3) phase boundary reactions. Several kinetic equations have been proposed corresponding to the above three possible rate determining steps. These equations are based on the assumption that the form of \( g(a) \) depends on the reaction mechanism. In the present investigation nine forms of \( g(a) \) codified by Satava have been used. The form of \( g(a) \) representing best experimental data is considered as the mechanism of the reaction.

Only the first stage of decomposition has been used for kinetic studies in the case of FAA and NTA complexes. The first and second stage of decomposition have been used for kinetic studies in the case of TAA complexes. The nine probable reaction mechanisms suggested by Satava are given in Table 6.7. The correlation coefficients computed using each of this mechanistic equations are presented in...
Tables 6.8 to 6.13. From the above tables it is evident that more than one equation gives good linear curve with a high value of correlation coefficient. But the most fitting mechanism (maximum value of correlation coefficient) in all the five series of complexes is obtained for $g(a) = -\ln(1-a)$. Hence the proposed mechanism in all the five series of complexes is random nucleation with one nucleous on each particle. This represents the Hampel Model.

6.3.4 Summary and Conclusion

All the complexes are thermally stable up to the range 170-240°C which indicates that there are no small molecules like water or solvents present in the complexes. All complexes show two stage decomposition in nitrogen atmosphere. The thermal stability of the complexes are in the following order:

(a) Complexes of FAA
nitrate > perchlorate > iodide

(b) Perchlorate complexes of FAA, TAA and NTA

\[
\begin{align*}
\text{[Ln(TAA)\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2}]ClO\textsubscript{4} > [Ln(FAA)\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2}]ClO\textsubscript{4} >}\nonumber
\text{[Ln(TAA)\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2}]ClO\textsubscript{4}}
\end{align*}
\]

The activation energy calculated are very low and are comparable with the activation energy of dehydration.
of hydrated salts, which suggests that the ligands are loosely bound to the metal ion. The entropy of activation calculated are negative suggesting that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal. It is observed that there is no regular variation in the values of the kinetic parameters of decomposition of the complexes like other common physical constants viz., boiling point, melting point, etc. The mechanism of solid state thermal decomposition of the main stage of all these complexes is random nucleation with one nucleous on each particle, the Mampel Model.