Original Article

# "Correlation Between Thermal Stability AND Kinetic Parameters OF Metal Complexes"

**Ghanshyam Kumar**

PG Department of chemistry Magadh University Bodh-gaya, Bihar

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## Abstract

Metal complexes are significant in most fields such as catalysis, biology and materials science. Thermal stability and kinetic parameters of the complexes are the key determinants of the structural integrity and reactivity of such complexes. In this paper, the relationship between thermal stability and kinetic values of the selected transition metal complexes has been discussed. The thermal analysis was performed by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) and the calculation of the kinetic parameters (activation energy (Ea)) and (frequency factor (A) and entropy of activation (ΔS)) using Coats-Redfern and Horowitz-Metzker methods. The results indicate the positive relationship that is high between thermal stability and activation energy are high which means that complexes with high activation energy have higher thermal resistance. These findings contribute to the limited literature of correlation between stability and kinetics which plays a crucial role in the development of thermally stable metallic complex to be employed in industries and pharmaceutical market.

**Keywords:** Metal complexes, thermal stability, kinetic parameters, activation energy, Coats-Redfern method, thermogravimetric analysis, decomposition kinetics.

## Introduction:

The coordination compounds or the metal complexes have been of high interest due to their tremendous structural variety and wide-ranging application in both chemistry, biology, medicine and material science. They are those compounds that include structure of which a metal ion in the center is connected with one or more ligands via coordinate covalent bond. Much of the type of metal ion, nature of the ligand and geometry of complex determine chemical, thermal and kinetic properties of a complex. The importance of these factors is required in the study of their influence on the behavior of metal complexes to have compounds of the necessary stability and reactivity.

The ability of a complex to withstand the degradation due to heating is called thermal stability of metal complex. It provides practical information on the strength of metal-ligand bonds, a geometry of the molecules, and the integrity of the structure of the whole complex. In the process of studying decomposition, the stages of weight loss, endothermic or exothermic reactions during heating occurrences, the thermal analysis techniques such as Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) are pretty common in these studies. The techniques aid in the degree and stability of the compound and whether it can be utilized in high temperatures.

In their turn, kinetic parameters provide the quantitative information regarding the process and rate of thermal disintegration. The important kinetic parameters are activation energy (Ea), frequency factor (A) and entropy of activation (Delta S). The minimum amount of energy required to ensure that decomposing occurs and the frequency factor and the entropy give details about the orderliness and the direction of the movement of the molecules in the process. The combination of these kinetic parameters, with thermal stability, can shed a better light into the decomposition process, and such allows chemists opportunities of understanding how their future metal complexes will act under circumstances of thermal stress.

The correlation between thermal stability and kinetic parameters as is, is a significant topic of study by itself as it helps attribute correlation to the physical stability of some compound and its chemical reactivity. High activation energy would typically indicate that metals and the ligand are highly bonded and therefore when the metals are required to be broken down, it would be difficult. Similarly, the negative values of the entropy are informative of that the transition state is more ordered meaning it has a stable structure in the complex. Having the kinetic values, it is possible to use them to make reasonable conclusions about the thermal strength of the metal complexes by comparison with thermal data such as decomposition temperature or the residue percentage.

Indeed, one of the studies has already determined that transition metals complexes of metal, e.g. copper, nickel, cobalt, and zinc, will have different thermal and kinetic properties with varying ligands. However, this direct

correlation between the two aspects is not quantitatively studied to the full extent. Despite research on thermal and kinetic studies, which is carried out independently, little research has the focus of determining the apparent correlation between thermal and kinetic studies. This has been bridged by this present research that documents the association that exists between the thermal stability (as described by the results of TGA/DA) and those of kinetic parameters determined through other methods such as Coats Redfern and Horowitz Metzker.

## Review of Literature

Thermal stability and kinetic behavior of metal complexes have been given much attention as it carries a significant implication in the area of coordination chemistry, catalysis, and materials science. The article by Ali and Verma (2020) has discussed the application of thermal analysis to get to know more about the bonding between metals and ligands and their structure stability. Their article highlighted that both thermogravimetric and differential thermal analysis could come in handy in the research of the trends of decomposition, strength of a metal-ligand bond and the general stability of coordination entities. Similarly, Gupta and Jain (2020) were interested in the perception of metal-ligand interaction in the thermal stability, and decomposition processes of the complexes and demonstrated that the stronger the bond between coordination is, the higher is the temperature of the decomposition of the complex and the more difficult it is to decompose.

Khalil, El-Shobaky and Hussein (2018) investigated the Cu (II), and Zn (II) Schiff base complexes and presented the kinetic specifics of the thermal breakdown. The character of the ligand together with that of the coordination environment as they found impacts heavily on the activation energy and decomposition behavior of the complexes. The article by Kumar and Sinha (2019) provided a comparative analysis of the kinetic parameters associated with thermally-stable coordination compounds thereby showing the applicability of the aspects of activation energy and change of frequency in predictability of thermal stability. Mahajan and Joshi (2021) proceeded to address the topic of mixed-ligand metal complexes, in which the stability of the decomposition process of a given type of ligand and a metal ion, and thermally stable complexes tend to have a higher activation energy and an orderly complex of activation.

Pandey and Tripathi (2020) divided Co (II), Ni (II) and Cu (II) Schiff base complexes and monitored the relationship between the kinetic and thermal stability. Their experiment showed that accurately activated complexes in dormant species having higher activation energies are unraveled at elevated temperatures and hence a positive association between the two variables. In their work, Patil and Deshmukh (2016) used relatively wide categories of transition metal complexes to apply the thermogravimetric analysis, showing that the systematic experiments of the thermo-decomposition are crucial in studying the stages of decomposition and the formation of the complexes that have a chance to be used in practice. Coats Redfern and Horowitz-Metzker methods were employed to determine the kinetic parameters with the help of which the processes of estimating the kinetic parameters was shown to be effective in estimating the behavior of the thermal process (Rao and Singh, 2020).

In particular, Sharma, Bhatt, and Mehta (2021) observed that the correlation between the activation energy and the thermal stability of transition metal complexes are positively (but strongly) correlated, which means that the kinetic parameters are good predictors of stability in transition metal complexes. A bit further, the papers by Zhang and Wang (2021) considered the relationship between the activation energy and the structural stability and have pointed out that a complex understanding of such association must be achieved in order to transform the metal complexes into less thermal and chemical reactive forms. Comprehensively, these references indicate that thermal analysis together with kinetic studies is a viable technique of evaluating the complicated stability of metals and it also provides a provisional basis through which future studies would develop improved and efficient coordination compounds by providing greater stability.

## Objectives of the Study:

- To determine the thermal stability of chosen metal complexes by applying the methods of thermogravimetric analysis and differential thermal analysis.
- To measure the kinetic parameters of activation energy, A and entropy of activation using normal thermal analysis techniques.
- To develop and determine the correlation of the thermal stability and kinetic parameters of the metal complexes.

**Hypothesis:**

- **$H_0$ (Null Hypothesis):** Thermal stability and kinetics parameters of metal complexes do not have any significant correlation.

- **$H_1$ (Alternative Hypothesis):** Thermal stability and kinetic characteristics (activation energy, frequency factor, and entropy) of metal complexes have a significant positive correlation.

## Research Methodology:

1. **Synthesis of Metal Complexes:**

   Metal complexes were synthesized by reacting selected transition metal salts ($Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Zn^{2+}$) with organic ligands under controlled conditions. The obtained complexes were purified and dried.

2. **Characterization Techniques:**

   - **Elemental Analysis:** To confirm metal-to-ligand ratios.
   - **FTIR Spectroscopy:** To identify functional groups and coordination sites.
   - **UV-Visible Spectroscopy:** To determine electronic transitions and geometry of the complexes.

3. **Thermal Analysis:**

   The thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were employed under nitrogen atmosphere to determine thermal stability. The decomposition temperature, stages of weight loss and percentage of residue were noted.

4. **Kinetic Analysis:**

   Coats-Redfern and Horowitz-Metzker techniques were used to calculate the kinetic parameters.

5. TGA data was used to determine the activation energy (Ea), pre-exponential factor (A), and the change in entropy (ΔS).

   - **Coats-Redfern Equation:**

$$\log\left(\frac{g(\alpha)}{T^2}\right) = \log\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{2.303RT}$$

where:

- α= fraction decomposed,
- T= temperature (K),
- β= heating rate (K/min),
- R= gas constant (8.314 J/mol·K),
- $E_a$= activation energy (kJ/mol).

Activation energy ($E_a$), frequency factor (A), and entropy of activation (ΔS) were calculated from TGA plots.

**Table 1: Thermogravimetric Analysis (TGA) Data of Metal Complexes**

| Metal Complex | Decomposition Stages | Temperature Range (°C) | Total Weight Loss (%) | Residue (%) | DTA Peak (°C) | Thermal Stability (°C) |
|---|---|---|---|---|---|---|
| Cu (II)-complex | 3 | 100–650 | 78.2 | 21.8 | 345 | 345 |
| Ni (II)-complex | 3 | 110–640 | 76.5 | 23.5 | 360 | 360 |
| Co (II)-complex | 2 | 120–600 | 80.4 | 19.6 | 325 | 325 |
| Zn (II)-complex | 2 | 90–580 | 82.1 | 17.9 | 310 | 310 |

**Interpretation:**
Ni (II)-complex showed the highest decomposition temperature (360°C), indicating maximum thermal stability. Zn (II)-complex decomposed earliest, suggesting lower stability.

**Table 2: Kinetic Parameters of Metal Complexes (Coats–Redfern Method)**

| Metal Complex | Activation Energy (Ea, kJ/mol) | Frequency Factor (A, $s^{-1}$) | Entropy of Activation (ΔS, $J \cdot mol^{-1} \cdot K^{-1}$) |
|---|---|---|---|
| Cu(II)-complex | 96.5 | $1.82 \times 10^8$ | -115.2 |
| Ni(II)-complex | 102.8 | $2.04 \times 10^8$ | -108.6 |
| Co(II)-complex | 89.2 | $1.55 \times 10^8$ | -120.4 |
| Zn(II)-complex | 83.7 | $1.34 \times 10^8$ | -125.0 |

**Interpretation:**

- Ni (II)-complex has the highest activation energy (102.8 kJ/mol), corresponding to its highest decomposition temperature (360°C).
- The more negative ΔS values indicate a more ordered activated complex and stronger bonding between metal and ligand.

**Table 3: Correlation Between Thermal Stability and Activation Energy**

| Metal Complex | Thermal Stability (°C) | Activation Energy (kJ/mol) |
|---|---|---|
| Cu (II) | 345 | 96.5 |
| Ni (II) | 360 | 102.8 |
| Co (II) | 325 | 89.2 |
| Zn (II) | 310 | 83.7 |

## Pearson's Correlation Coefficient (r):

$$r = 0.986$$

## Interpretation:

There is a strong positive correlation (r = 0.986) between activation energy and thermal stability. This means that as the activation energy increases, the complex becomes more thermally stable.

## Discussion:

The results evidently indicate that kinetic parameters and thermal stability mutually relate. Among the complexes which were examined, the Ni (II)-complex was the most complex and activated with the highest energy which is as a result of a high binding between the metal and the ligand and a square-planar shape. The next appearance was of Cu (II)-complex, and the stability of Co (II) and Zn (II)-complex were not so high.

The profiles show negative values of the entropy of activation (S) of all complexes that means the process of decomposition is preceded by an activated complex that is more organized than reactants. This coincides with the large degree of coordination amid the metal centre and the ligand atoms.

The findings are similar to the other sources (Rao and Singh, 2020; Sharma et al., 2021) and prove the point that the more significant the activation energy and the less disorderly the activated complex is, the more thermal stability is ensured.

## Conclusion

Thermogravimetric (TGA) and differential thermal analyses (DTA) showed that complexes with greater activation energies (Ea) break up at much higher temperatures, thereby indicating that strong metal to ligand interactions are very important in improving thermal resistant ability. The Ni (II)-complex was the most active and the highest temperature of decomposition between the studied complexes, which suggests that the type of ligand, the coordination geometry, and the strength of the initial metal-ligand bonds contribute to the overall stability of the complex. On the contrary, with lower activation energies complexes like Zn (II)-complex exhibited lower decomposition temperatures, and so weaker bonding leads to lower thermal stability.

The decomposition mechanisms were further explained with the help of the kinetic analysis that was conducted with the Coats Redfern and Horowitz Metzker method and enabled the attainment of the frequency factors and entropy of activation. The observed negative values of $\Delta S$ in all the complexes indicate that the activated decomposition state is more organized than the starting reactants further supporting the fact that coordinated interactions of the ligand leads to stabilization of the complex under thermal stress. The research also found that energy of activation is a good indicator of thermal stability with an objective of creating a quantitative approach towards evaluating the strength of metal complexes during high temperatures.

On the whole, the results obtained in the course of this work can be used to determine that precise knowledge of the kinetic parameters can inform the rational design of metal complexes with a high thermal stability. This understanding can be used in catalysis, where complexes of metals that are thermally resistant can be used to carry out reactions at high temperatures; in material science, where stable metal complexes are needed in polymers, coats and removed electronics; and in pharmaceutics, where drugs made with metals must be stable and resistant to degradation.

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