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Determination of Activation Energy and Thermodynamic Functions in Thiourea Single Crystals

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Abstract : The thermal decomposition behavior of Thiourea single crystals was analyzed using Thermogravimetric Analysis (TGA), and the kinetic and thermodynamic parameters were determined through the Piloyan – Novikova Relation. This approach enabled the calculation of activation energy (ΔE), entropy change (ΔS), enthalpy change (ΔH), and Gibbs free energy change (ΔG), providing insights into the thermal stability and degradation mechanism of the material.

Index Terms **: Thiourea, Thermo Gravimetric Analysis, entropy change , enthalpy change , and Gibbs free energy, Piloyan – Novikova Relation**

I. INTRODUCTION

Recent advancements in technology have led to an increased demand for organic and semi-organic materials in nonlinear optical (NLO) applications. Among these, single crystals are particularly noteworthy due to their distinct aesthetic appeal, characterized by well-defined shapes and vivid coloration. The surface stability and reactivity of grown crystals are critical parameters that directly influence their applicability in various technological domains. In this study, single crystals of Thiourea (NH_2CSNH_2) were successfully synthesized using a simple and cost-effective slow evaporation technique. The investigation focused on analyzing the thermal behavior and, more importantly, the degradation kinetics of the crystals, which are essential for predicting their long-term stability and for elucidating the nature of chemical bonding within the crystalline structure. Established methodologies for determining the activation energy (ΔE) from thermogravimetric (TG) curves are well documented in the literature. Given the small sample size typically used in TG analysis of Thiourea crystals, the influence of thermal and diffusion barriers is minimal. Therefore, the application of the Arrhenius model is considered valid in this context. In the present work, the Piloyan – Novikova Relation has been employed to evaluate the thermodynamic parameters associated with the degradation process.

II.EXPERIMENT

2.1:Thermo Gravimetric Analysis: (TGA)

Thermo Gravimetric Analysis(TGA) is a technique in which the mass of the substance is measured as a function of temperature or time while the substance is subjected to a controlled temperature program. In the present study, the Thermo Gravimetric Analysis (TGA) of grown Thiourea crystals were carried out using **Model: Pyris-1 TGA, Make:** Perkin Elmer with nitrogen atmosphere with temperature range 45°C to 600°C. The resulting TGA traces are shown in figure:1.

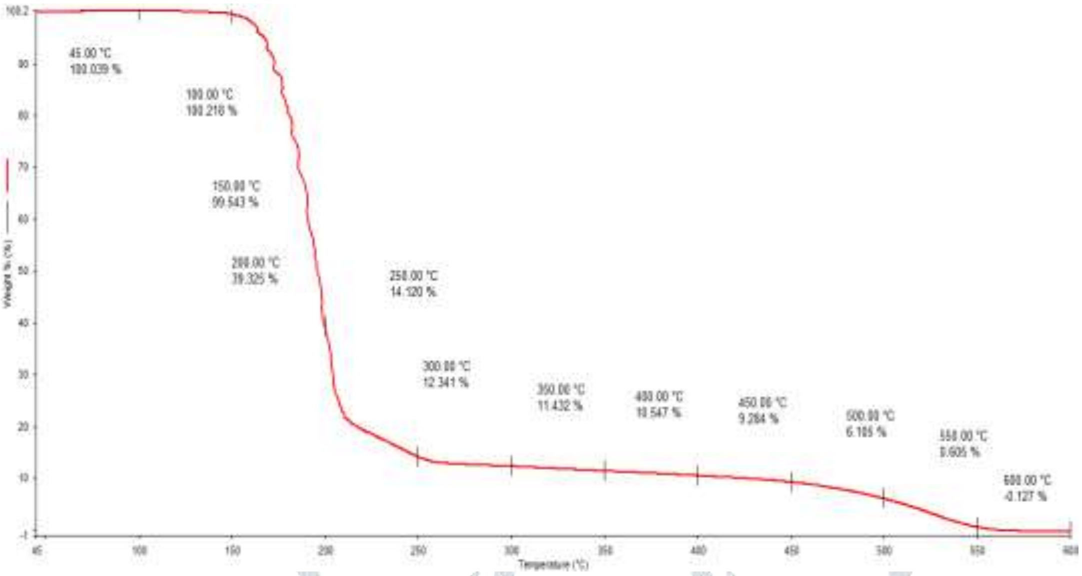


Figure:1: thermogram of thiourea crystal

2.2: Piloyan – Novikova Relation :

The rate of dehydration can be expressed by the kinetic equation :

$\frac{d\alpha}{dT}$ = Z* exp($\frac{-E}{RT}$) $(1-\alpha)^n$

Where α = degree of conversion = loss in weight at a given temperature/ total weight loss at the step involved

n = order of reaction for constant heating rate β, we can write

$d\alpha/dT = (Z/\beta) * \exp(-E/RT)(1-\alpha)^n$

Integration of this equation leads to the following expression,

$[\frac{1-(1-\alpha)1-n)}{1-n}] = (Z/\beta)\int_0^T \exp(-E/RT)\, dT$

Expansion of the integral in the asymptomatic series as proposed by Murry and White [26] and rearrangement for E >> RT and n ≠ 1 gives,

$[\frac{1-(1-\alpha)1-n)}{1-n}] = ZRT^2 / (E\beta)\, e^{-E/RT}$

This can be simplified, by assuming that E is determined at a ≤ 0.5 to 0.05

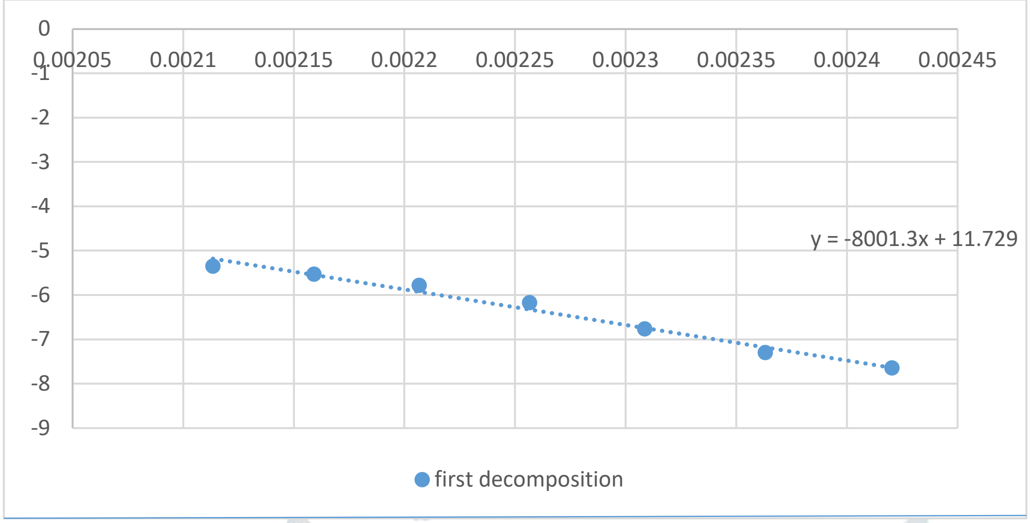
$\log(\frac{\alpha}{T^2}) = \log(ZR/(E\beta)) - E/2.303\, RT$

Where, α = 0.05 to 0.5

The graph of log ($\frac{\alpha}{T^2}$) → 1/T for each steps are drawn. The value of activation energy E for all the steps has been calculated from the slope and frequency factor from the intercept and recorded. Figur: 2, 3,4.

Activation energy E (eV) = slope * 2.303 * R (R= Gas Constant)

And Intercept = log (ZR/ βE)



Figur:2: Plot of Log(α/T^2) Vs 1/T (first decomposition n=1/2 We=70.966)

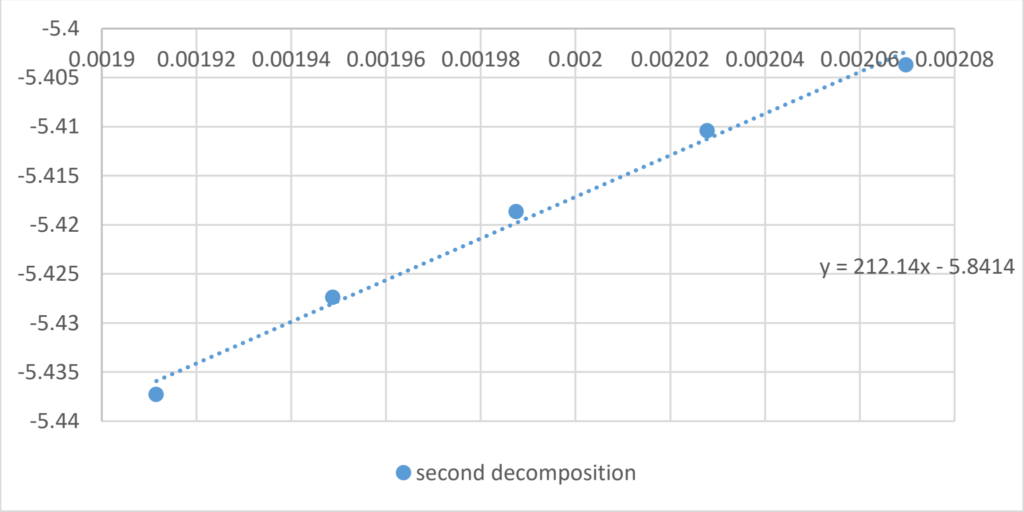


Figure:3: Plot of Log(α/T^2) Vs 1/T (second decomposition n=1/2 We=85.59)

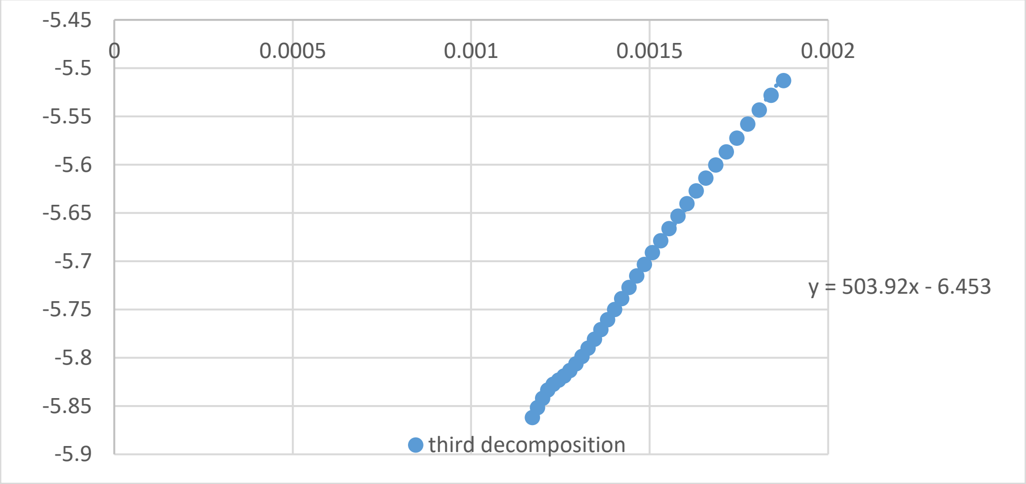


Figure:3: Plot of Log(α/T^2) Vs 1/T (third decomposition n=1/2 We=98.642)

III. RESULT

The Activation Energy, Entropy, Enthalpy and Gibb's Free Energy for all stages of thermo gram were ccalculated and summarized in Table:1.

Table: 1 Summary of calculated thermo dynamical parameters

Stage	Activation Energy (eV)	Entropy ΔS eV/K	Enthalpy ΔH eV/mole	Gibb's Free Energy ΔG eV
1	653.40×10^{20}	-1.6676×10^{21}	1.8826×10^{22}	87.5240×10^{22}
2	98.24×10^{20}	-1.6474×10^{21}	-4.2397×10^{22}	78.2265×10^{22}
3	350.05×10^{20}	-1.6853×10^{21}	-3.7974×10^{22}	106.0531×10^{22}

IV.CONCLUSION

The variation in activation energy across the three stages suggests distinct mechanisms governing each phase of thermal degradation. The negative entropy values in all stages indicate a decrease in randomness during the decomposition process. The Gibbs free energy values, being significantly positive, further confirm the non-spontaneous nature of the degradation reactions under the experimental conditions.

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