iJRASET
International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 5 **Issue:** XI **Month of publication:** November 2017

DOI:

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Growth and Calculations of Kinetic and Thermodynamic Parameters for Thiourea Single Crystals

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Abstract*: Crystals are the unacknowledged pillars of modern technology, without crystals, there would be no electronic industry, no photonic industry, and no fiber optic communication. Single crystals of Thiourea (NH_2CSNH_2) were obtained through simple and inexpensive evaporation technique. The crystals are optically smooth and hexagonal and tetragonal in shape and average size of crystals were 40mm×28mm×1mm to 1.5mm×1.5mm×0.5mm.Thermo Gravimetric Analysis has proved useful for evaluating kinetic parameters of various reactions of materials and provides valuable quantitative information regarding the stability of materials. Using the basic relations of thermodynamically variables, Entropy ΔS, Enthalpy ΔH and Gibb's free energy ΔG were calculated using Brood and Coats-Red fernrelations and summarized in present communication. The Differential Scanning Calorimetric analysis was also used to identify the purity and melting point (T_m) of the grown crystal.

Keywords: Thiourea, Thermo Gravimetric Analysis, Kinetic parameter, Thermodynamic parameters, Differential Scanning calorimetric.

I. INTRODUCTION

In recent trends of technology there has been increased need of organic and semi organic materials for Non Linear optical (NLO) applications. The beauty of single crystals is fascinating. The sharpen of their colors and flatness of shape are very fascinating. Stability and reactivity on the surface of grown crystals are utmost important for their applications. Single crystals of Thiourea (NH_2CSNH_2) were grown using simple and inexpensive evaporation technique. The studies of thermal behavior and more significantly the kinetics of degradation is useful in predicting the behavior of crystals stability and a useful aid in the determination of various bonds within the crystals. Methods for determining the Activation Energy ΔE from a thermo gravimetric curves are available in literature. For the case of Thiourea crystals a small quantity of material is employed in Thermal Gravimetric Analysis, and the barriers between the thermal and diffusion processes are very negligible, hence it is reasonable to assume of the Arrhenius relation. In the present work, the methods of Brood and Coats-Red fern relations are used and thermodynamically parameters are calculated.

II. EXPERIMENTAL

The Thiourea (NH_2CSNH_2) crystals have been grown from saturated solution by slow evaporation technique. The saturated solution was prepared by taking 100ml of double distilled water in a beaker and finally powdered 18.75grams of Thiourea. The substance was added slowly and continuously till it gets completely dissolved. For availing the supersaturated solution the solution was stirred well with the magnetic stirrer and process was continued until the last pinch of the substance was dissolved. Then the solution was filtered using filter paper. The filtered solution was kept at room temperature without any disturbance. The single crystals were harvested between 10 to 15 days. In the present work, the thermographs of grown crystals were obtains at a constant heating rate of 10°C per minute in the temperature range from ambient to elevated temperatures 100°C to 600°C.

III. RESULTS

Single crystals of Thiourea (NH_2CSNH_2) a promising organic material is grown through simple and inexpensive slow evaporation technique. This material has good chemical flexibility to provide nonlinearity of organic material and strong mechanical property of inorganic material. The thermo grams of grown Thiourea crystals are shown in Fig:1.

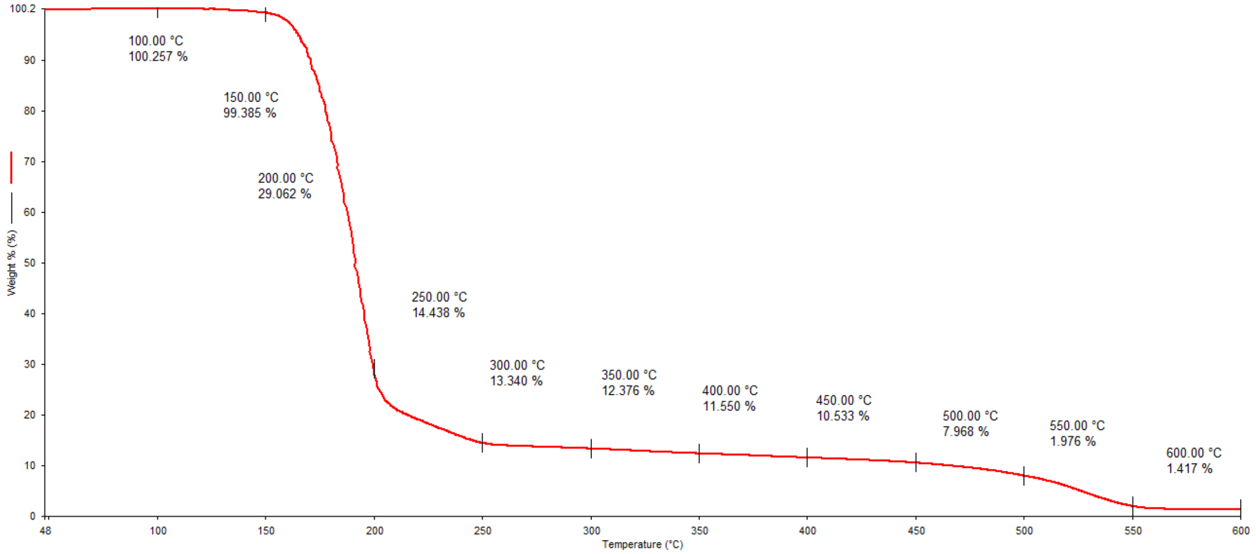

Figure:1: thermogram of thiourea crystal

Differential scanning calorimetry analysis was used to identify the purity and melting point of the grown crystal. In the thermo gram only one endothermic stage was found. At 179.74°C initiation of phase change started and competed at 182.96°C. Area under the curve was 553.372mJ and heat of transition was 197.9865J/g. Fig: 2.

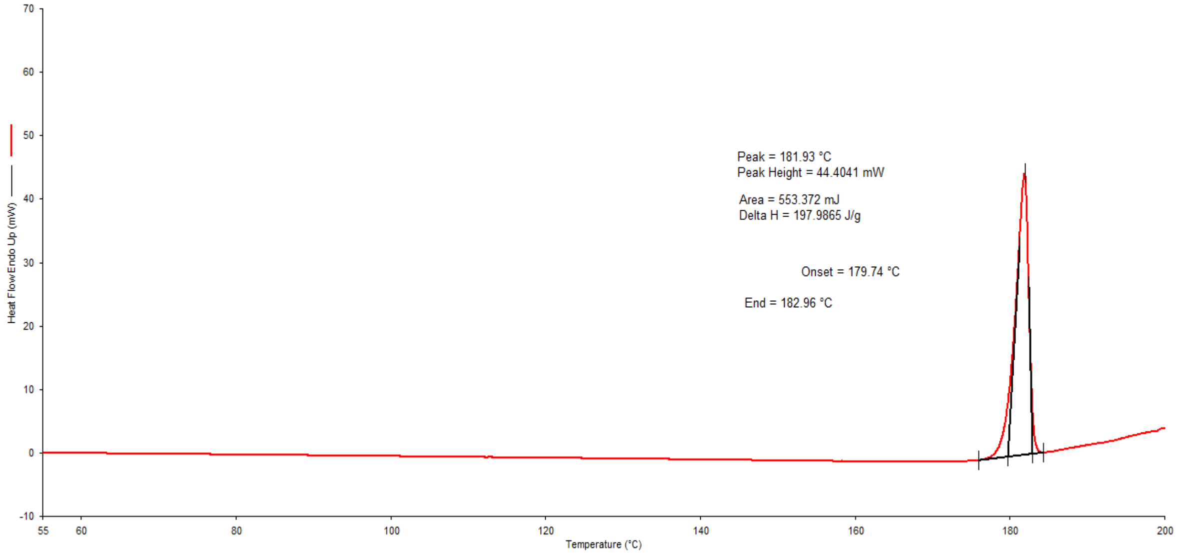

Figure:2: differential scanning calorimetry

In order to understand the kinetics of solid state reactions leading to the gradual, sequential decomposition of the material for calculation of kinetic and thermodynamic parameter following relations are used:

A. Broido Relation

When a pure solid substance is heated in vacuum, it undergoes pyrolysis, in which at least some pyrolysis products are volatile. W_t the weight at any time t, is related to the fraction of the number of initial molecules not yet decomposed, y, by the equation,

$y = \frac{N}{N0} = (W_t - W_\infty)$ = fraction of the number of initial molecules not yet decomposed.

Where, W_t= weight of active material at absolute temperature T.

W_0 = weight of the material taken initially.

W_∞= weight of the material at the end of the reaction.

The reaction rate is given by

$\frac{dy}{dt} = - ky^n$

Where, k = specific rate constant, and n = 1 in present case.

According to the Arrhenius equation;

$K = A_0 e^{-E/RT}$

The graph of lnln(1/y) → 1/T for each steps(first, second and third decomposition) are shown in figure: 3(a),3(b)and 3(c). Then Activation energy is calculated using slopes of the graph and recorded. From the graph it can be seen that the plot gives a good linear fit for n=1.

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

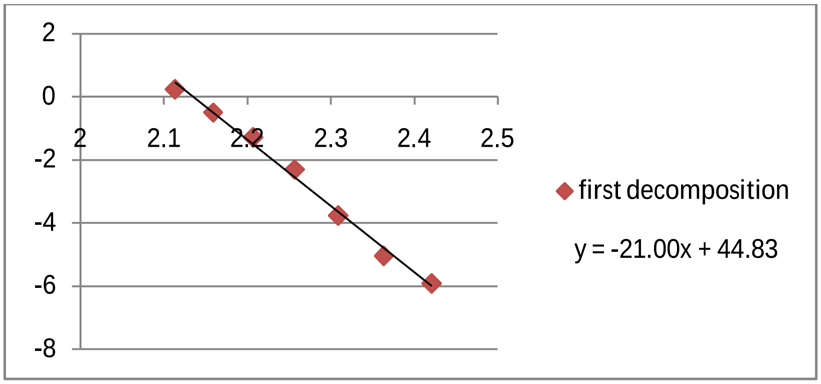

Figure: 3(a): first decomposition plot of lnln(1/y) → 1/T

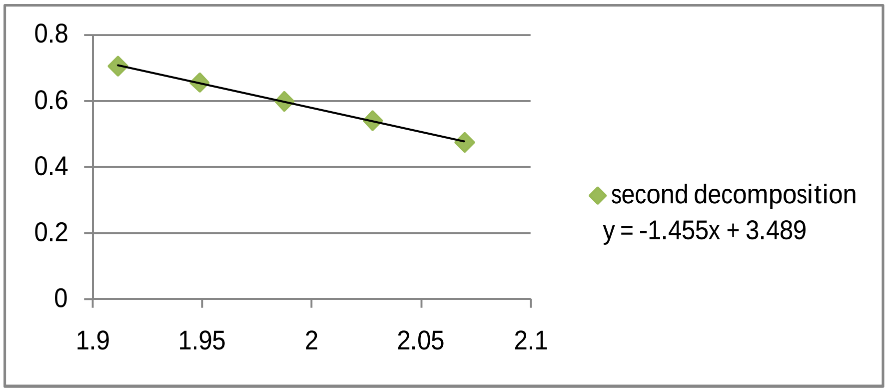

Figure:3(b): second decomposition plot of lnln(1/y) → 1/T

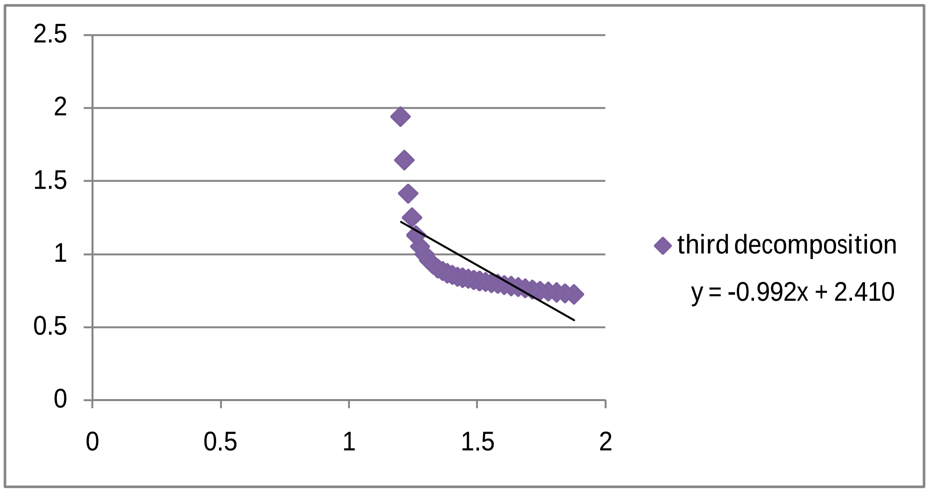

figure: 3(c): third decomposition plot of lnln(1/y) → 1/T

Stage	Activation Energy 10^{20}(eV)	Entropy ΔS 10^{21}eV/K	Enthalpy ΔH 10^{22}eV/mole	Gibb's Free Energy ΔG 10^{22}eV
1	-10.2084	-1.3559	-4.7016	55.3851
2	-0.8012	-1.4894	-5.2303	69.6937
3	-0.4656	-1.5309	-7.1645	98.4276

Table: 1 calculated parameters using Broido relation

The graph is shown in Figure: 3(a), 3(b),3(c) and the calculated parameters are summarized in table: 1

B. Coats-Redfern relation

In Boride's approximation, the order of thermal degradation is considered as first order and the calculations are done accordingly. Assuming the order of equation, Coats and Redfern developed
an integral method for analysis of thermo gravimetric data as follow:

$$log[\frac{(1-(1-a)^{1-n})}{T^2(1-n)}] = log\frac{AR}{aE}[1-\frac{2RT}{E}]-\frac{E}{2.303RT} \quad \text{(for n=0,}\frac{1}{2},\frac{2}{3},\text{ ...)}$$

$$log[-log\frac{(1-a)}{T^2}] = log\frac{AR}{aE}[1-\frac{2RT}{E}]-\frac{E}{2.303RT} \quad \text{(for n= 1)}$$

Where a is the fraction of sample decomposed at time t, n is order of decomposition reaction, a is heating rate in °C/min, T is temperature(K), A is frequency factor (s^{-1}), R is gas constant, E is the activation energy.

Plot of $log[\frac{(1-(1-a)^{1-n})}{T^2(1-n)}] \rightarrow$ 1/T for each steps are shown infigure 4(a), 4(b) and 4(c). The value of activation energy has been calculated from the slops and Z from the intercepts of the graph and the values are recorded. Evidently a fitted linear dependence observed is ½.

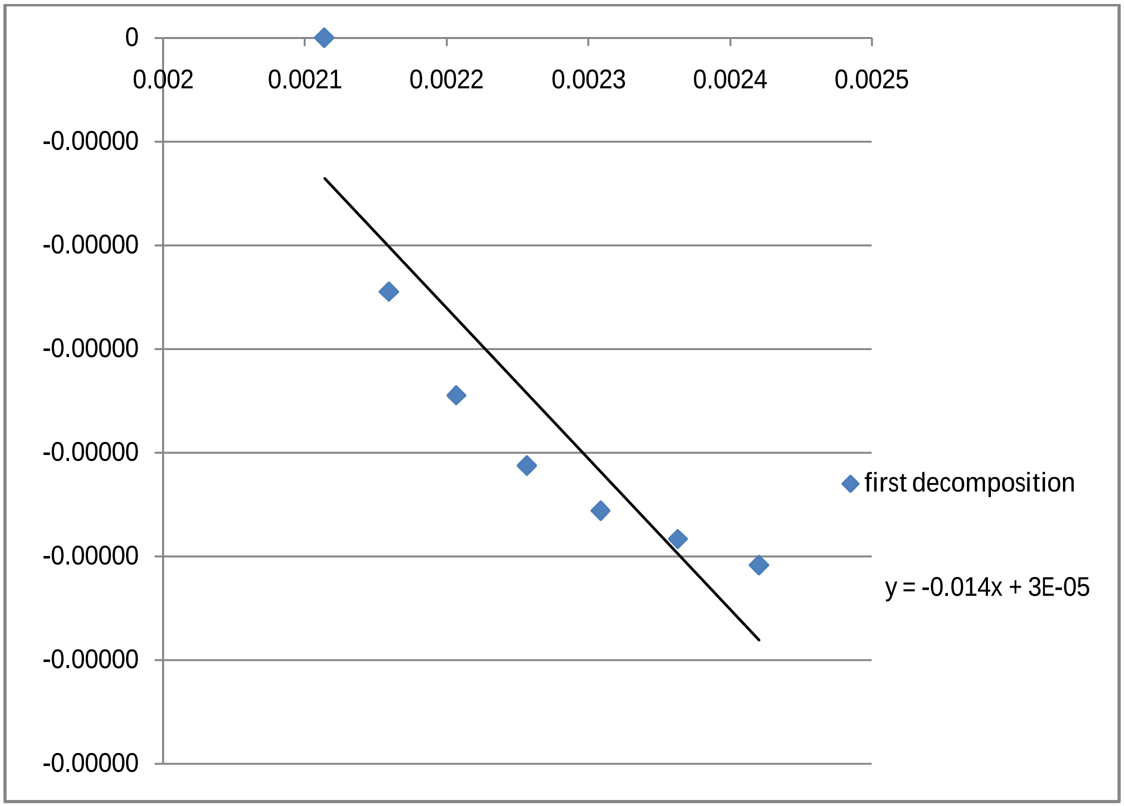

Figure: 4(a): first decomposition plot of Log[1-{SQRT(1-ɑ)}/T^2(1-n)] Vs 1/T

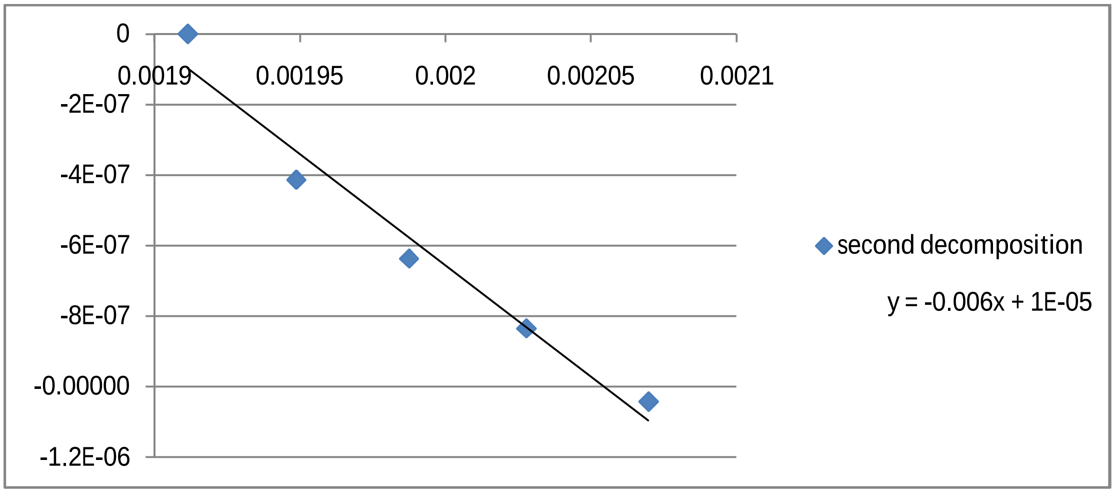

Figure: 4(b): second decomposition plot of Log[1-{SQRT(1-ɑ)}/T^2(1-n)] Vs 1/T

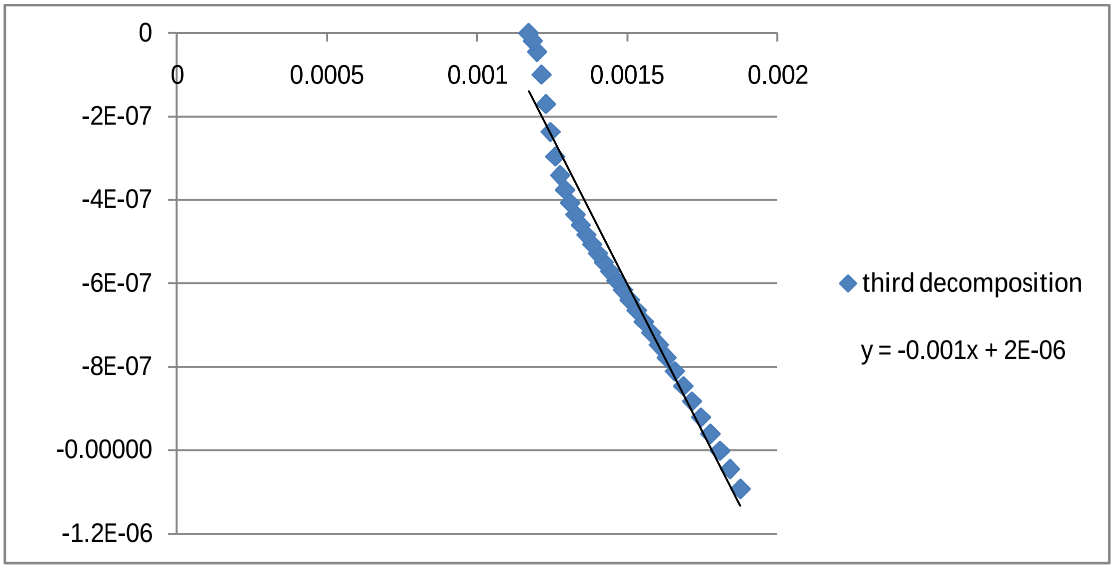

Figure: 4(c): third decomposition plot of Log[1-{SQRT(1-ɑ)}/T^2(1-n)] Vs 1/T

Stage	Activation Energy 10^{20}(eV)	Entropy ΔS 10^{21}eV/K	Enthalpy ΔH 10^{22}eV/mole	Gibb's Free Energy ΔG 10^{22}eV
1	-0.0048	-2.1622	-4.5994	91.2371
2	-0.0033	-2.1538	-5.2222	103.146
3	-0.0007	-2.26596	-7.1942	149.8533

Table: 2 calculated parameters using Coats-Redfern relation

The graph is shown in Figure: 4(a), 4(b), 4(c) and the calculated parameters are summarized in table: 2

IV. CONCLUSION

Thiourea (NH_2CSNH_2) organic single crystals are successfully grown by using relatively simple and inexpensive slow evaporation of aqueous solution technique. This material has good chemical flexibility to provide non linearity of organic material and strong mechanical property of inorganic material. Kinetic parameters like Activation Energy, Entropy ΔS, Enthalpy ΔH and Gibb's free Energy ΔG are calculated using basic thermodynamically relations.

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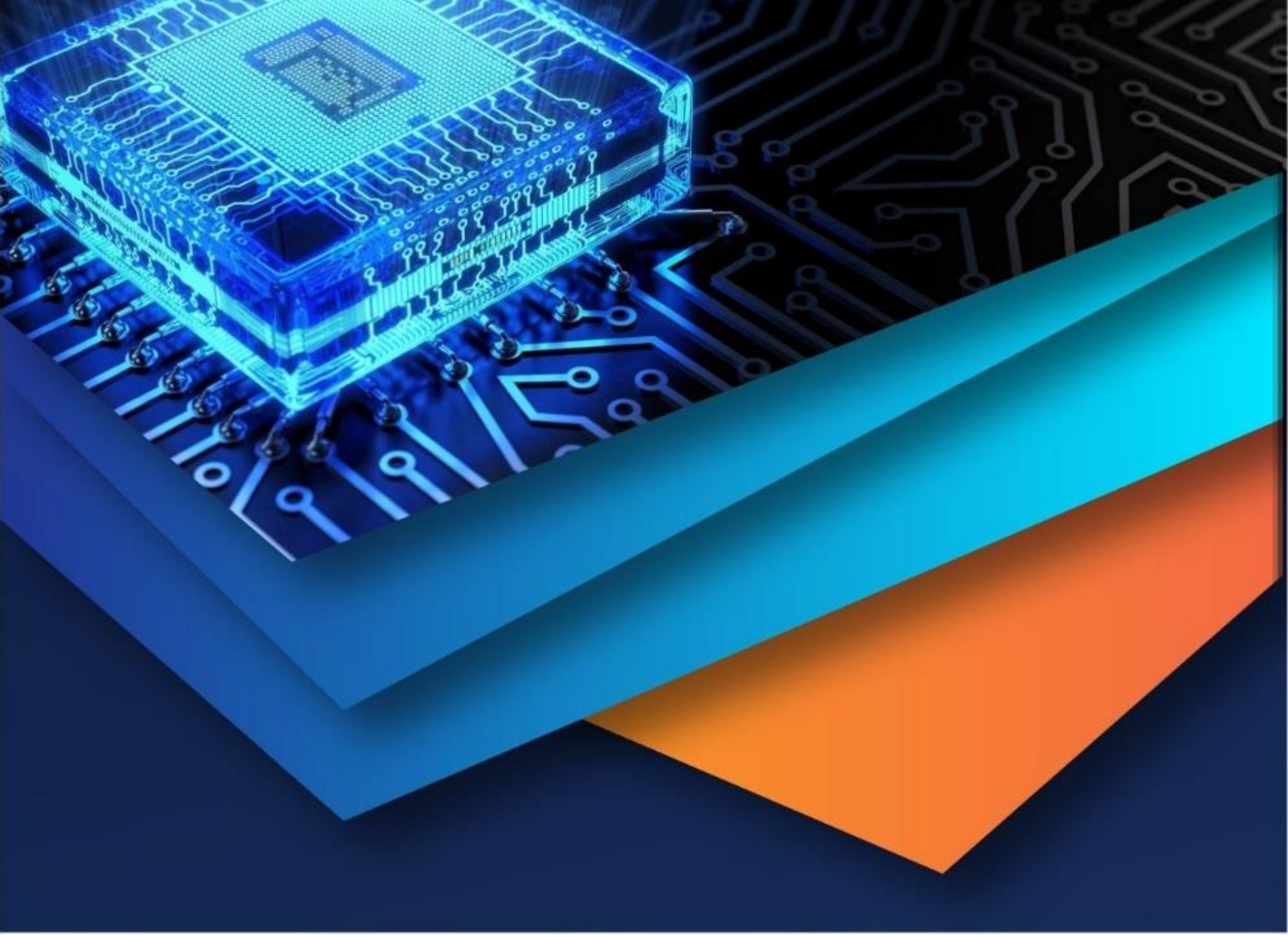

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