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Kinetics of Oxidation of D-Galactose by Peroxo Complex in Aqueous Medium

M. Anthony Raja[1]
[1]*Centre for Clean Energy and Nano Convergence, Hindustan Institute of Technology and Science, Chennai, Tamilnadu, India*

Abstract: ***The objective of this work is to study the kinetics of oxidation of D-Galactose by μ-peroxo complex in aqueous medium. This kinetics study can be used as the model system for the activation of molecular oxygen with the enzyme peroxidase. The kinetic based investigation is designed so as to study the rate or reaction during the effect of varying concentration of μ-peroxo complex, effect of concentration of substrate, effect of concentration of sulphuric acid, effect of ionic strength and effect of temperature. This work can be extended as a model system for biologically active substance.***
Keywords: D-Galactose, enzyme, μ-peroxo complex, oxidation, rate of the reaction

I. INTRODUCTION

Enzymes are biomolecules that catalyze chemical reactions. In enzymatic reactions, the molecules at the beginning of the process are called substrates, and the enzyme converts them into different molecules, the products. Almost all processes in a biological cell need enzymes in order to occur at significant rates. Since enzymes are extremely selective for their substrates and speed up only a few reactions from among many possibilities, the set of enzymes made in a cell determines which metabolic pathways occur in that cell. The enzymes activities in the living system are considered as an important role. There are varieties of enzymes in our living system and their activities are specific. Peroxidase an important enzyme actively involved in the oxidation of organic molecules as substrates. They are considered as a powerful oxidant.

During the oxidation, the electrons are transferred from the substrate to the metal ion of the enzymes which is at higher oxidation state. As a result of electron transfer, the substrates get oxidized and the enzymes get reduced. Enzymes are large biomolecules which cannot be synthesized and investigated under laboratory conditions. Model systems are necessary to mimic the functions of enzyme. In this context coordination compounds of transition metal with polydentate ligands like ethylenediammine, diethlylenetriammine are used as model systems.

Dioxygen complexes of transition metals are used as model systems for the investigation of Biological oxidation reactions. An important limiting factor in such studies is the tendency for all oxygen complexes to be converted to stable inert complexes in which the coordinated ligand is oxidized to its higher valency and they are no longer able to combine with di-oxygen. In recent years, several studies are made on the structure and function of di-oxygen complexes. In the bi nuclear cobalt III complexes, bridges by oxygen are present. The bridge is found to be either in superoxide or peroxide form. Preparative studies of peroxo complexes of cobalt (III) with different polyamines. They investigated the electron transfer reaction with different substrates.

Ghose and co-workers [1] prepared chromium peroxo complexes and studied the reaction of peroxide and electron transfer. As per the report, the attachment of external carboxylate chromium center does not occur before the electron transfer takes place after the completion of all redox process. Kaizak et al [2] prepared 2-geomentrical isomeric pairs of chromium peroxo complexes and characterized them by the behaviour of the complex by spectral chromatography techniques. The ligand field absorption spectra of these complexes were compared with one another and with those of the corresponding aqua complexes of the same type. Seymour and others [3] prepared the complex μ-peroxodicobalt (III) and studied the chemical and physical properties of these complexes using IR , electronic and NMR Spectroscopy along with conductivity and magnetic susceptibility measurement. Preparation of peroxo complexes was done by bubbling oxygen through a solution containing cobalt(III)nitrate, sodiumperchlorate and the appropriate ligand mixture. Eatom and others [4] studies the oxidation of cobalt(III)amine complexes to mononuclear Cobalt(III) complex by dioxygen. The intermediate is found to be peroxo complex. The suggested mechanism involves reduction of peroxo complexes by cobalt II.

Shinonara and others [5] studied about the cyclic voltametry for dioxygen bridged binuclear cobalt III complexes using platinum electrode at different values of p^H and ionic strength. Reversible electrode reaction occurs particularly for the dioxygen complexes. Decammine complexes show only a cathode peak due to intra molecular charge transfer decomposition in solution after electro reduction. Sayed mohammed and Davis [6] studied about the products sand Kinetics of oxidation of neutral dimeriodo

Cu(I)complex [CUI]$_2$ by dioxygen in nitrobenzene. Saksi and Yoichi [7] studied the mechanism of the deoxygenating and ligand substitution reaction of U- peroxo ethylene diamine cobalt (III) ion in aqueous solution. Rao. B. Madhava et al [8] studied the oxidation of structurally related organic substrates like maleic acid with cerium (IV) sulfate in sulfuric acid medium. The kinetics of oxidation of maleic acid Ce((SO_4) in H_2SO_4 in extending spectrally in H_2SO_4 at 32.5 in 0.10. The rate is inversely proportional to the H^+ concentration and to the SO_4^{2-} ion concentration. Sayet and others [9] studied the catalytic oxidation of maleic acid by hydrogen peroxide by hydrogen in the presence in the presence of manganese II bicarbonate complexes.

In this current study, one of the biologically important substrate D-Galactose was subjected to oxidation by peroxo complex in aqueous medium. The rate of the reaction is measured poteniometrically.

II. EXPERIMENTAL METHODS

A. Preparation of µ-Peroxo bis-ethylene diamine bis -diehtylene triammine dicobalt (III) perchlorate

29 g of Cobalt (II) nitrate and 40g of sodium perchorate was dissolved in 500 ml of H_2O. Then 7.2 g of ethylene diammine and 10.3g of diethylene triammine were added with rapid stirring. A rapid stream of oxygen was bubbled through the stirred solution for one hour. The solution was cooled in ice and bubbling of oxygen was continued for further one hour. The deposited brown crystalline product was collect by filteration and washed successively with 2- propanol, ether and their air dried.

The formula for the complex is **[**$Co_2(en)_2(dien)_2O_2](ClO_4)_4.2H_2O$] and the Molecular weight = 909.88 g.

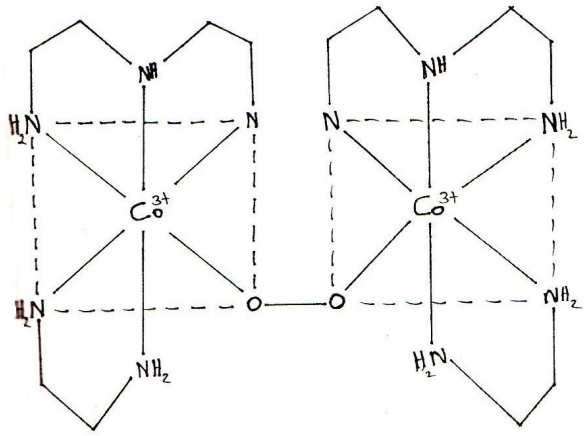

Fig. 1 Structure of µ-Peroxo bis-ethylene diamine bis -diehtylene triammine dicobalt (III) perchlorate

B. Kinetic Methods

All the standard flasks and the reaction bottles were of pyrex glass either ground joint stoppers. The volumetric apparatus, pipettes, burettes and standard flasks were standardised by usual methods. An electrically operated thermostat with a jumo contact thermometer (West Germany) working in conjugation with an electronic relay which maintained temperature accurately with fluctuation not more than ± 0.02º C was used. The bath liquid was water and it was covered with a Layer of thermocole bits to minimize that and water loss due to radiation.

C. Preparation of Standard Solution

The standard stock solution of µ–peroxo complex was prepared by dissolving the required quantity of it in water. This complex solution was found to be invariant in its strength over a period of one month. The substrate (D-Galactose) solution was prepared by dissolving the required quantity of it in conductivity water. The salt (Na_2SO_4) solution was also prepared.

D. Rate Measurements

In a typical experiments the required quantities of the substrate solution, and water were pipetted out into a douple walled beaker provided with inlet and outlet for circulating water from the thermostat set at the derived temperature and the solution were kept in the beaker for nearly an hour to attain the desired temperature.

The reaction was started by pipetting out the required quantity of µ – peroxo complex solution which had also been thermostated for and hour. The total volume of the reaction mixture was kept always 40 ml. A stop watch was started when half the amount of oxidant was added. The reaction was followed by setting up a cell [(Pt)]$^-$. Substrate complex [+ (SCE)] made up of the reaction

mixture into which the platinum electrodes and reference electrode (SCE) were dipped. The emf of the cell was measured periodically using equiptronics digital potentiometer while the reaction mixture was continuously stirred using a magnetic stirrer.

E. Precautions

1) All the experiments reported in this work are done in air.

2) Na_2SO_4 (0.025 N) was used throughout the studies to keep ionic strength constant.

3) All reaction were carried out under pseudo – first order condition with substrate (D-Galactose) concentration is large excess. The rate constants were computed from the linear plots of log (Et-E∞) vs time (sec) using Lotus 1-2-3 macro software and Basic program.

4) All the experiments were duplicated and the velocity constants were reproducible within ±2% error.

5) All pseudo-first order rate constants (k_{obs}) were expressed in $S^{-1.}$

III. RESULT AND DISCUSSION

The rates of reaction have been measured by following the reduction of peroxo complex potentiometrically in aqueous medium. The reaction have been followed under condition were the concentration of substrate was large excess compared to peroxo complex concentration. The result obtained is presented below.

A. Order with respect to µ- peroxo complex

A typical kinetic study of oxidation of galactose by peroxo complex is presented. A plot of log (Et-E∞) Vs Time is linear for even 90% of reaction indicating first order dependence on peroxo complex. A typical kinetic run is shown in table. 1 applying linear regression analysis of these data k was found to be **$k = 9.27 \times 10^{-5} s^{-1}$**

Typical kinetic run for the oxidation of D-Galactose by µ-peroxo complex.

[peroxo complex] = 2.0×10^{-3}M [D-Galactose] = 2.0×10^{-2}M

[Na_2SO_4] = 2.5×10^{-2}M Solvent = Water

[Acid] = 1.5×10^{-2}M Temperaure = 313K

Table 1 Kinetic run for the oxidation of D-Galactose by µ-peroxo complex

S.No	Time (Sec)	EMF (mV)	Log (Et-E∞)
1	300	446	2.347
2	600	439	2.334
3	1200	429	2.320
4	1500	424	2.309
5	1800	419	2.296
6	2100	415	2.283
7	2400	410	2.268
8	2700	405	2.257
9	3000	400	2.243
10	3300	394	2.231
11	∞	221	

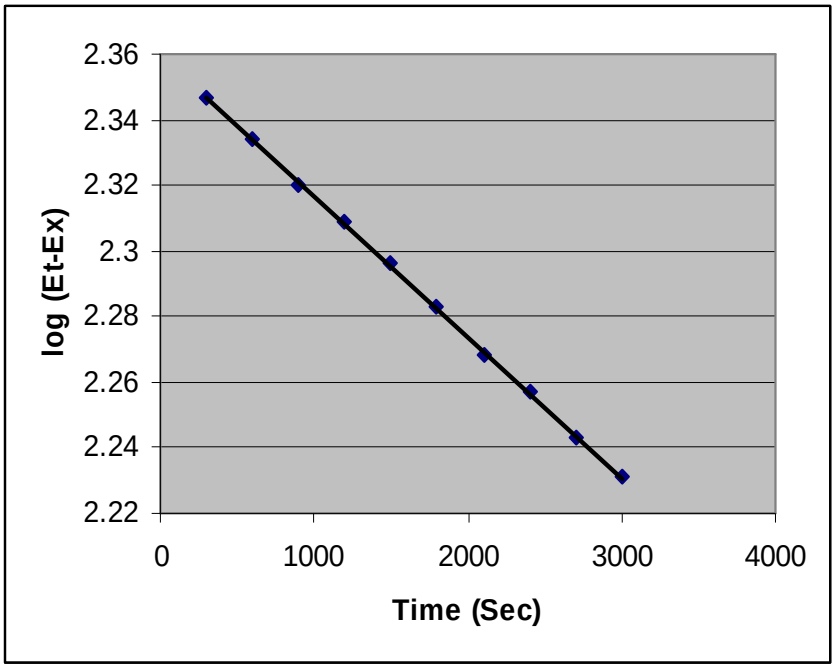

Fig. 2 Graphical representation of a typical kinetic run for the oxidation of D-Galactose by µ-peroxo complex.

B. Effect of concentration of µ-peroxo complex

The oxidation of Galactose was studied by different concentration of µ-peroxo complex. The concentration of Galcatose was kept constant large excess, the result shows that the rate increase with increase in complex concentration but in each kinetic run the reaction shows no deviation what so even from the first order plot.

Effect of [µ-peroxo complex] on rate

[peroxo complex] = 2.0×10^{-3}M [D-Galactose] = 2.0×10^{-2}M
[Na_2SO_4] = 2.5×10^{-2}M Solvent = Water
[Acid] = 4.0×10^{-2}M Temperaure = 313K

Table 2 Effect of concentration of µ-peroxo complex

[µ-peroxo complex] x 10^{-3}M	K_{obs} x 10^{-3} S^{-1}
1	3.32
2	5.56
3	8.81
4	9.21

C. Order with respect to Galactose concentration

The order with respect to Galactose was determined by keeping concentration of peroxo complex constant and varying the excess concentration of Galactose. From the result the linear plot of log(Et-E∞)Vs time has been drawn for each run and the rate constant were calculated. From the table 3 the plot of log k vs log concentration of the D-galactose was drawn and showed the the order with respect to Galactose is one.

Effect of [Galactose] on rate

[peroxo complex] = 2.0×10^{-3}M [D-Galactose] = 2.0×10^{-2}M
[Na_2SO_4] = 2.5×10^{-2}M Solvent = Water
[Acid] = 4.0×10^{-2}M Temperaure = 313K

Table 3 Effect with respect to Galactose concentration

[Galactose] x 10^{-2}M	k_{obs} x $10^{-4}s^{-1}$
1	4.77
2	5.52
3	6.71
4	8.91

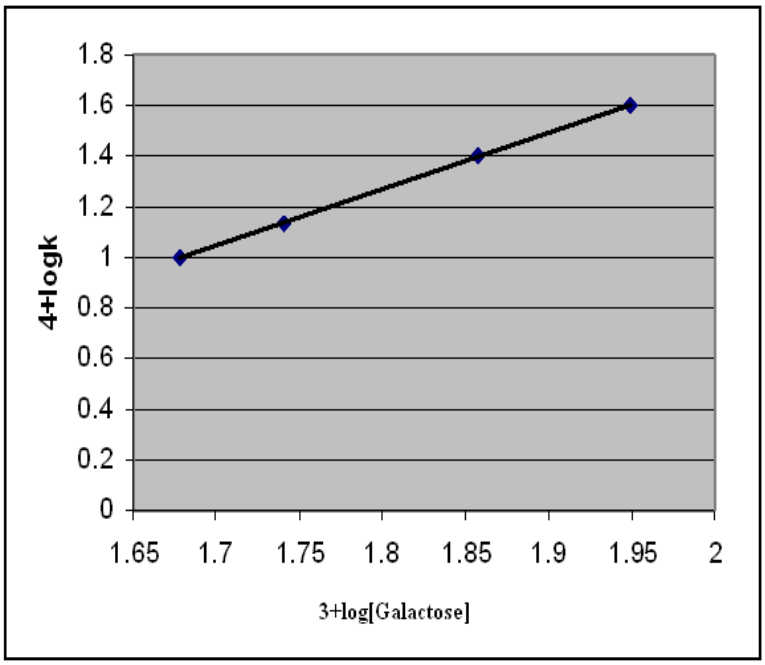

Fig. 3 Graphical representation of Order with respect of [Galactose] on rate

D. Order with respect to H_2SO_4 Concentration

The influence of variation of acid strength on the reaction rate was studied by varying the concentration of added H_2SO_4, from the result table 4. The strong dependence of the rate on the acid increases with increase the acid strength. From the plot of log k_{obs} Vs [H+] fig has ben found to be linear with a slope One. Hence the order with respect to added acid if found to be one.

Effect of H_2SO_4 on reaction rate

[peroxo complex] = 2.0 x 10^{-3}M [D-Galactose] = 2.0 x 10^{-2}M
[Na_2SO_4] = 2.5x 10^{-2}M Solvent = Water
[Acid] = 4.0 x 10-2M Temperaure = 313K

Table 4 Effect of [H^+] on reaction rate

[H_2SO_4] x 10^2M	k_{obs} x 10^{-4} s^{-1}
1.5	3.31
2.0	4.42
2.5	5.31
3.0	6.62

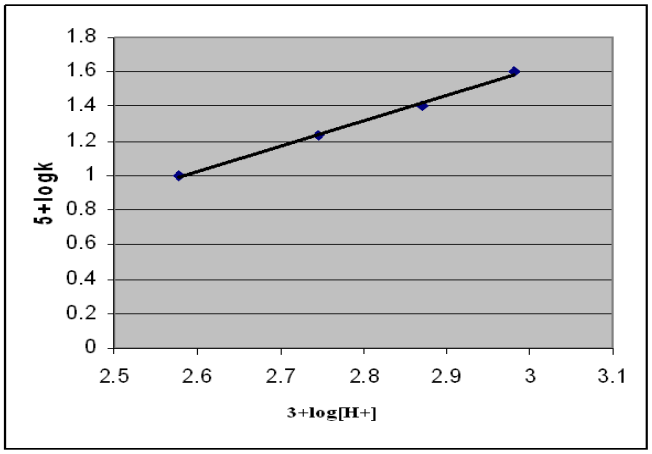

Fig. 4 Graphical representation of Effect of $[H^+]$ on reaction rate

E. Effect of sodium sulphate Concentration

The influence of variation of ionic strength on the reaction rate has been studied by varying the concentration of sodium sulphate. The result is given in the table 5. In all cases the reaction rate had been found to be constant with increasing ionic strength. Hence the sodium sulphate has a neglible effect on the reaction rate.

Effect of Na2SO4 on reaction rate

[peroxo complex] = 2.0×10^{-3}M [D-Galactose] = 2.0×10^{-2}M
$[Na_2SO_4]$ = 2.5×10^{-2}M Solvent = Water
[Acid] = 4.0 x 10-2M Temperaure = 313K

Table 5 Effect of sodium sulphate Concentration

$[Na_2SO_4] \times 10^{-2}$M	$k_{obs} \times 10^4$ S^{-1}
2.5	5.23
3.5	5.32
4.5	5.23
5.5	5.39

F. Effect of Temperature on reaction rate

The oxidation of Galactose was carried out at different temperature ranging from 313K to 328K the result are shown in the table 6.

[peroxo complex] = 2.0×10^{-3}M [D-Galactose] = 2.0×10^{-2}M
$[Na_2SO_4]$ = 2.5×10^{-2}M Solvent = Water
[Acid] = 4.0 x 10-2M Temperaure = 313K

Table 6 Effect of Temperature on reaction rate

Temperature (K)	$K_{obs} \times 10^4 S^{-1}$
313	28.01
318	34.64
323	41.5
328	48.01

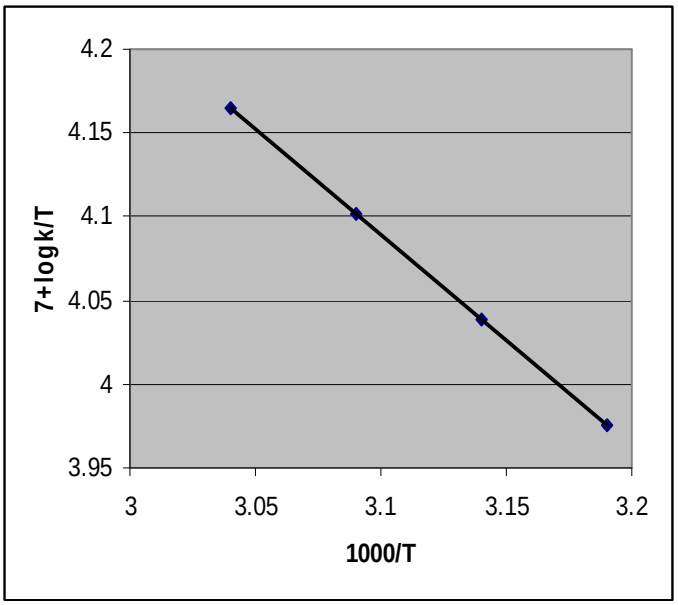

Fig. 5 Graphical representation of Effect of Temperature on Rate

IV. CONCLUSION

The Co (III) polyamine peroxo complex has been prepared. One of the biologically important substrate D-Galactose was subjected to oxidation by peroxo complex in aqueous medium. The rate of the reaction is measured poteniometrically. The rate of oxidation of substrate by peroxo complex showed a first order with respect to Peroxo Complex. The rate constant was found to increase with increase in concentration of the complex. The reaction was found to be first order with respect to the substrate concentration. The rate of reaction was found to increase with increase of H^+ ion concentration and the order was found to be one. The rate of oxidation remained unaltered by the addition of sodium sulphate. This kinetics study can be used as the model system for the activation of molecular oxygen with the enzyme peroxidase.

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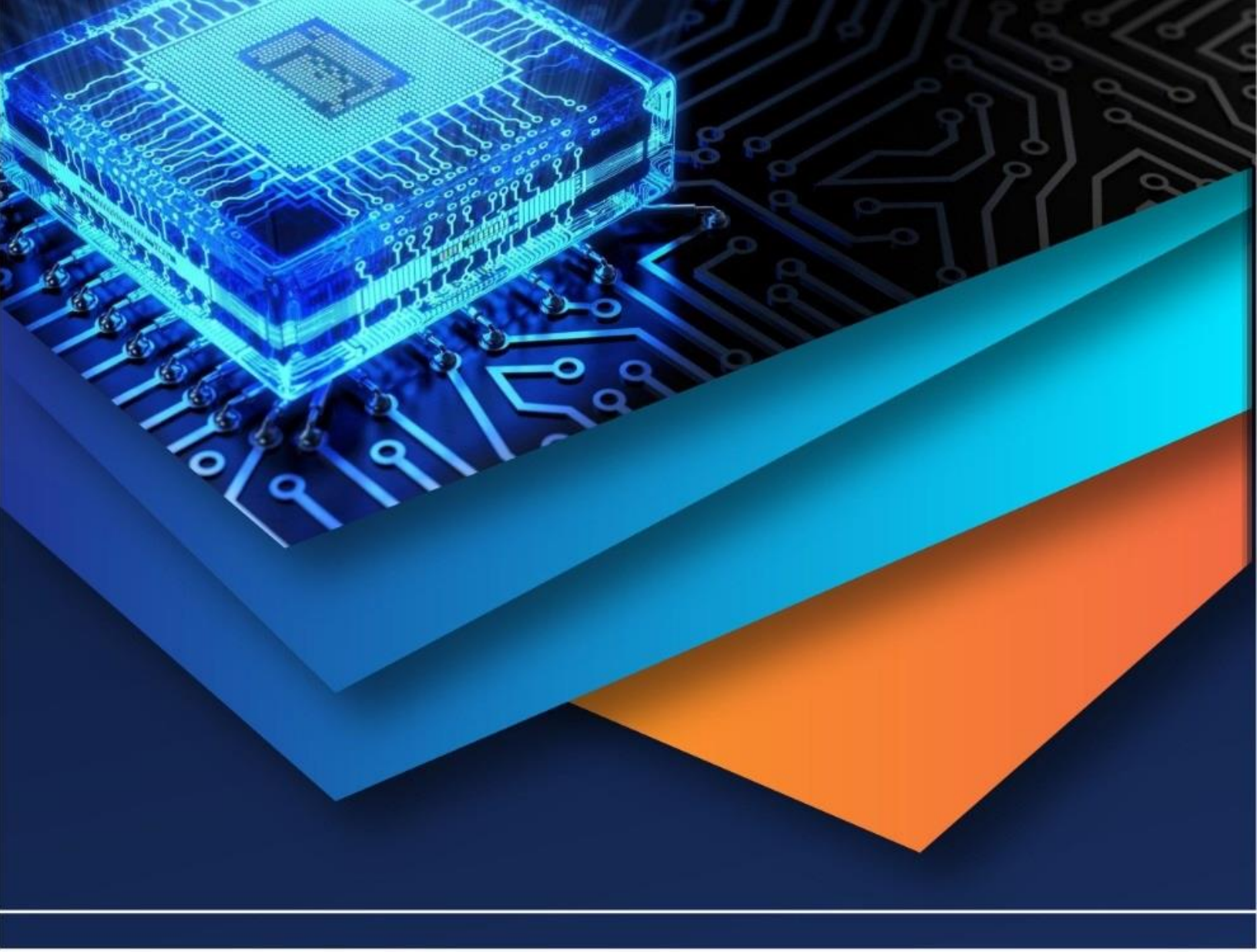

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