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Kinetics and Mechanism of Oxidation of Sodium Nitrite by Quinolinium Dichromate and Chlorochromate in aqueous bisulfate media

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Abstract:* *Kinetics and Mechanism of Oxidation of Sodium Nitrite by Quinolinium Dichromate and Chlorochromate in aqueous bisulfate medium. Increase in bisulfate concentration enhanced the reaction rate with a fractional order dependence (0< n <1). At constant [bisulfate], reaction obeyed second order kinetics with first order dependence on [Nitrite] as well as on [QDC] or [QCC]. Seond order rate constants (k) and activation parameters were evaluated and presented.

I. INTRODUCTION

Nitrite salt is an important inorganic compound which is used as a precursor in the synthesis several pharmaceuticals, dyes and pesticides. Above 330 °C sodium nitrite decomposes (in air) to sodium oxide, nitric oxide and nitrogen dioxide [1].

$$2\ NaNO_2 \rightarrow Na_2O + NO + NO_2$$

Sodium nitrite can also be used in the production of nitrous acid via sulfuric acid. This reaction first yields nitrous acid and sodium sulfate[1]:

$$2\ NaNO_2 + H_2SO_4 \rightarrow 2\ HNO_2 + Na_2SO_4$$

Long ago in 1934 Dhar and coworkers [2] observed that aqueous solutions of $NaNO_2$ or KNO_2 are oxidized to nitrates when exposed to sunlight.

This photochemical reaction is enhanced by the oxides of Ti(IV), Zn(II) and Fe(III), and TiO_2 is a more effective photo sensitzer than other two oxides [2]. Byun, et al [3] explored the ability of themyeloperoxidase-H_2O_2-NO_2^- system to modify nucleic acids, using the nucleoside 2'-deoxyguanosine as a model target. Myeloperoxidase, a heme protein secreted by activated phagocytes, is a potential catalyst for hydrogen peroxide (H_2O_2) and nitrite (NO_2^-) to generate reactive nitrogen species which convert tyrosine to 3-nitrotyrosine. Lister and Rosenblum [4] studied the kinetics of oxidation of nitrite ions by hypochlorite ions in aqueous solution, and revealed that oxidation occurred by hypochlorous acid (HOCl). The slow step of the reaction was,

$$HOCl + NO_2^- + H_2O \rightarrow H_3O^+ + CI^- + NO_3^-$$

The rate constant is given by: $\log k = 7.36 - 6450/RT$ (time in minutes, and the activation energy in calories).

Chromium(VI) reagents with heterocyclic backbone can be placed as effective oxidizing agents in the family of laboratory reagents due to their proven selectivity during oxidation [5-11].

A perusal of literature reveals several novel hexavalent dichromate and halo chromates such as Pyridinium chloro chromate (PCC), Pyridinium flourochromate (PFC), 2,2'-bipyridinium chloro chromate (BPCC), quinolinium chloro chromate (QCC), and quinolinium dichromate (QDC) etc., which were found to be useful as selective oxidizing agents in organic synthesis [12-24].

In recent reports we have accomplished several halogenation and nitration protocols using quinolinium and isoquinolinium bound chromium (VI) reagents like QDC, QCC, IQDC and IQCC for efficient electrophilic aromatic substitution reactions like nitration, in the presence of sodium nitrite, by the oxidation of nitrite (NO_2^-).

Encouraged by the foregoing striking features pertaining to the Onium-bound Cr(VI) reagents, importance of nitrite chemistry[1-6], and catalysis of micelles, we have taken up the present kinetic study, which deals with the oxidation of Sodium Nitrite by Quinolinium Dichromate and Chlorochromate (QDC and QCC) in aqueous acid conditions.

II. EXPERIMENTAL DETAILS

Laboratory distilled water was further distilled over alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$ in a sequence. Quinolinium chlorochromate (QCC) was prepared according to the method of Singh et al [19], while quinolinium dichromate QDC $[(C_9H_7NH^+)_2\, Cr_2O_7^{2-}]$ was according to the method of Bala Subramanian et al. [20,21]. The other chemicals used were of either Annular BDH or Merck samples. Acetic acid has been purified over chromic anhydride and acetic anhydride according to the method of Orton and Bradfield [31]. Binary composition of acetic acid and water has been used as solvent in the present investigation. All the electronic absorption spectroscopic studies were made on double beam Shimadzu recording type spectrophotometer equipped with externally controlled thermostatic arrangement. Matched quartz cells were used to perform the study.

Rate of disappearance of [QDC] or [QCC] was monitored spectrophotometrically by recording absorbance values as a function of time at 425 nm.

III. RESULTS AND DISCUSSIONS

A. Kinetic Observations

Kinetics of the (QDC-NO_2^-), and (QCC-NO_2^-) reactions over all second order with a first order dependence on [Nitrite] and first order in [QDC] and/or [QCC] at constant [Bisulfate]. Typical data are given in table-1.

Table-1 : Order of QDC-NO_2^- and QCC-NO_2^- Reactions in aq.$KHSO_4$ medium
Temp. = 300 K, [**$KHSO_4$**] : (A) = 0. 01 mol dm^{-3}

10^2 [Nitrite]	10^4 Reagent]	$10^2k'$ (min^{-1})	
mol dm^{-3}		QDC	QCC
0.50	1.00	0.760	1.09
1.00	1.00	1.52	2.18
2.00	1.00	3.12	4.40
4.00	1.00	6.20	8.75
5.00	1.00	7.59	10.5
1.00	2.00	1.52	2.23
1.00	4.00	1.60	2.26
1.00	5.00	1.48	2.24

B. Reactive species & mechanism of oxidation by qdc:

Quinolinium dichromate (QDC) resembles the structure of $K_2Cr_2O_7$, it exists as several unprotonated and protonated forms analogous to those of $K_2Cr_2O_7$ [1, 2]. In aqueous acid solutions, $K_2Cr_2O_7$ is known to exist in different anionic and cationic forms like $Cr_2O_7^{-2}$, $HCrO_4^-$, H_2CrO_4, $[HCrO_3]^+$ and $HCrO_3B$ (where B = HSO_4^-, OAc^-, Cl_4^- and Cl^-, etc.). Analogous species with quinolinium bound dichromate have been given according to the following equilibria.

$$(QH)_2Cr_2O_7 + H_2O \rightleftharpoons \underset{(I)}{2(QH)CrO_4^-} + 2H^+ \rightleftharpoons \underset{(II)}{2H(QH)CrO_4}$$

(Where Q = quinoline, QH^+ = quinolinium ion)

$$H\,(QH)\,CrO_4 + H^+ \rightleftharpoons \underset{(III)}{(QH)CrO_3^+} + H_2O$$

$$(QH)CrO_3^+ + BH \rightleftharpoons \underset{(IV)}{[(QH)CrO_3BH]^+}$$

$$(III) + B^- \rightleftharpoons [(QH)CrO_3B] \quad \text{or}$$

$$(II) + BH \rightleftharpoons [(QH)CrO_3B] + H_2O$$

(Where B = HSO_4^-, Cl^-, OAc^-, ClO_4^-; BH^+ : H_2SO_4, HCl, HOAc, $HClO_4$, etc)

On the basis of the foregoing discussions couple with the linearity of plot 1/k' vs. 1/$[H^+]$ with positive slope and intercept on 1/k'-axis most plausible mechanism for the QDC oxidation of Nitrite could be given in the folloeing steps:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \qquad (1)$$

$$H(QH)CrO_4 + H^+ \overset{K_1}{\rightleftharpoons} [(QH)CrO_3]^+ + H_2O \qquad (2)$$

$$[(QH)CrO_3]^+ + NO_2^- \xrightarrow{\text{Slow } (k_1)} [(QH)CrO_3(NO_2)] \qquad (3)$$

$$[(QH)CrO_3(NO_2)] + NO_2^- \xrightarrow{\text{fast}} [(QH)CrO_2(NO_2)] + NO_3^{-} \qquad (4)$$

Cr(VI) *Cr(IV)*

For the above mechanism rate law could be derived according to the following steps:

$$\frac{-d(QDC)}{dt} = k_1 [(QH)CrO_3]^+ [NO_2^-] \qquad (I)$$

Concentration of $[(QH)CrO_3]^+$ could be estimated by considering the equilibrium of its formation. If 'a' and 'b' represent the initial concentrations of $[H(QH)CrO_4]$ or $[QDC]_o$ and $[H^+]$ and x the concentration of complex, the equilibrium constant (K_1) could be written as,

$$K_1 = \frac{x}{(a-x)\,(b-x)} \qquad (\text{Since } b >> a \text{ i.e., } [H^+] >> [QDC]_o)$$

$$K_1 = \frac{x}{(a-x)\,b^2} \implies K_1xb - K_1xb = x$$

$$\implies x(1+K_1b) = K_1ab \implies x = \frac{K_1ab}{(1+K_1b)}$$

$$\implies x = [(QH)CrO_3]^+ = \frac{K_1[H^+][QDC]_o}{(1+K_1[H^+])} \qquad (II)$$

From first protonation equilibrium of above scheme it could be seen that

$$[QHCrO_3^+] = K_1[H(QH)CrO_4][H^+] / (1+K_1[H^+])$$

Substitution of this in the equation (I) gave

$$\frac{-d(QDC)}{dt} = k_1\, K_1[H(QH)CrO_4][H^+]\,[NO_2^-] / (1+K_1[H^+]) \qquad (II)$$

Upon simplification of above rate equation (II),

$$\frac{-d(QDC)}{dt} = k_x\, [H(QH)CrO_4]\, [NO_2^-] = k_x\, [QDC]\, [NO_2^-] \qquad (III)$$

{where $k_x = k_1K_1[H^+] / (1+K_1[H^+])$}

At constant acidity ($[H^+]$) equation-(III) explains observed kinetics with a first order dependence on [QDC] and $[NO_2^-]$.

C. *Mechanism Of Oxidation Of Nitrite By Qcc*

On the other hand, the most plausible mechanism in QCC (Quinolinium chlorochromate) triggered reactions could be proposed by formulating quinolinium chlorochromate (QCC) in the lines of other "onium halo chromate" species [22-24]. Since the reactions are studied in aqueous acid medium, QCC could exist as ($QHOCrO_2Cl$) and its protonated form $(QHOCr(OH)Cl)^+$, by capturing proton (H^+) from the dissociated bisulphate species according to the following equilibria:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \qquad (1)$$

$$(QHOCrO_2Cl) + H^+ \overset{K_2}{\rightleftharpoons} (QHOCr(OH)OCl)^+ \qquad \ldots(5)$$

The protonated Cr(VI) species thus formed $(QHOCr(OH)OCl)^+$ being a stronger electrophile, may further react with nitrite ion to afford $[QHOCr(OH)(Cl)NO_2]$ species, since the reactions are conducted in excess $NaNO_2$.

$$[QHOCr(OH)Cl]^+ + NO_2^- \xrightarrow{\text{Slow }(k_2)} [QHOCr(OH)(Cl)NO_2] \quad \ldots(6)$$

$$[QHOCr(OH)(Cl)NO_2] + NO_2^- + H_2O \xrightarrow{\text{fast}} [QHOCr(Cl)(NO_2)(OH)] + H^+ + NO_3^-$$

Rate law for the above mechanism comes out as shown in(IV),

$$\frac{-d[QCC]}{dt} = k_x\,[H(QH)CrO_4]\,[\,NO_2^-\,] = k_x\,[QDC]\,[\,NO_2^-\,] \qquad (IV)$$

$$\{\text{where } k_x = k_2K_2[H^+] / (1+K_1[H^+])\}$$

At constant acidity ($[H^+]$) equation-(IV) explains observed kinetics with a first order dependence on [QCC] and $[NO_2^-]$.

D. Temperature Effect And Computation Of Activation Parameters

According to the theory of absolute reaction rates, Eyring's equation can be written as shown below [25]. This equation brings about a relationship between rate constant (k) with free energy of activation ($\Delta G^\#$) at a given temperature. If R is the gas constant; N, the Avogadro number; h, the Planck's constant, Eyring's equation at any temperature (T), could written as,

$(k) = [(\kappa)(RT/Nh)]\exp(-\Delta G^\#/RT)$ ------- (7)

Where and the transmission coefficient (κ) is equal to unity. Upon rearrangement of equation (3), followed by taking natural logarithmic form equation (4) is obtained.

$\Delta G^\# = RT \ln (RT/Nhk)$ ……(8)

Substitution of R, N, and h values in SI units into equation (4), $\Delta G^\#$ simplified to equation (5),

$\Delta G^\# = 8.314 \times T[23.7641+\ln(T/k)]$ ……(9)

Using Gibbs-Helmholtz equation (10), other important activation parameters like enthalpy and entropies of activation ($\Delta H^\#$ and $\Delta S^\#$) could be computed. These values are furnished by the intercept and slopes of the plot, ($\Delta G^\#$) vs temperature (T):

$(\Delta G^\#) = (\Delta H^\# - T\Delta S^\#)$ …… (10)

According to Gibbs-Helmholtz equation, plot of free energy of activation ($\Delta G^\#$) versus temperature (T) should give a negative slope and intercept on ordinate. However, the slope of this plot may be either positive or negative depending the nature and conditions of the reaction (Fig 1 and 2). Magnitude of entropy of activation ($\Delta S^\#$) is positive if the slope is negative, and *vice-versa*. Negative magnitude of ($\Delta S^\#$) generally suggests associative mechanism and greater solvation in the transition state. However, positive ($\Delta S^\#$) shows non-rigid nature of transition state associated with random movement of molecules; this trend often indicates a dissociative mechanism [25,26].

Figure-1: Gibbs-Helmholtz plot for QDC-Nitrite reaction in $KHSO_4$

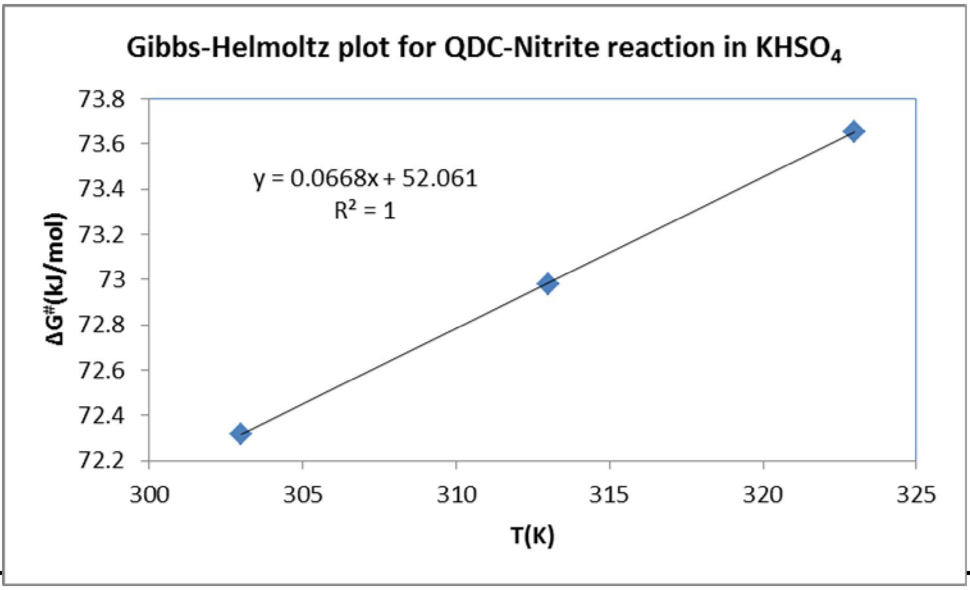

Figure-2: Gibbs-Helmholtz plot for QCC- Nitrite reaction in $KHSO_4$

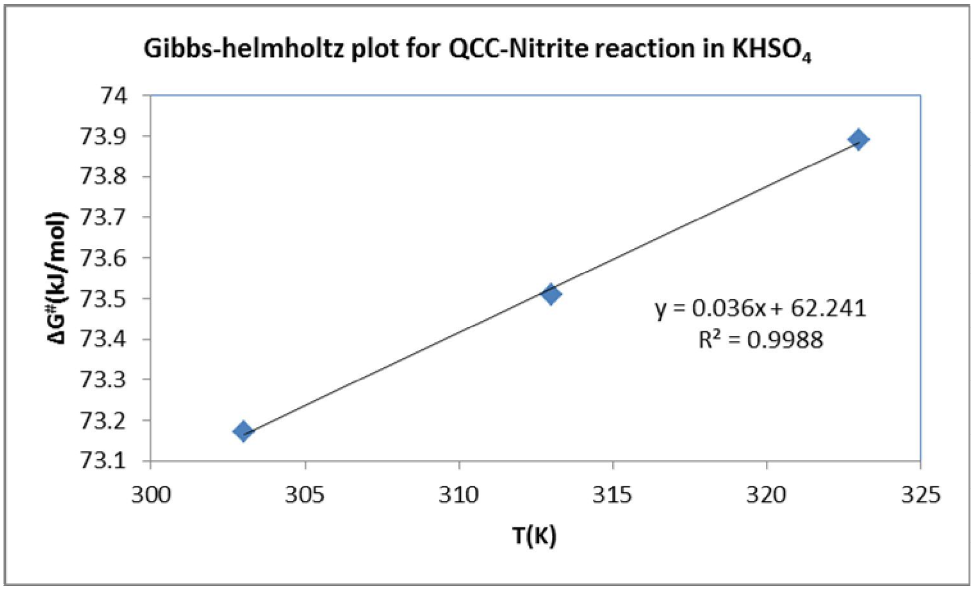

Table-2: Activation parameters for the oxidation of Nitrite by QDC and QCC in aq. KHSO4 medium

Reagent	Temp (K)	(k_x) dm^3/mol min	$\Delta G^\#$ (kJ/mol)	$\Delta H^\#$ (kJ/mol)	$-\Delta S^\#$ (J/Kmol)
QCC	303	1.52	73.2	62.2	36.0
	313	3.55	73.5		
	323	7.56	73.9		
QDC	303	2.18	72.3	66.8	52.1
	313	4.30	73.0		
	323	8.14	73.7		

IV. CONCLUSIONS

Oxidation of Nitrite by “quinolinium bound- Cr(VI) reagents” (QDC and QCC) obeyed second order kinetics with first order in [Cr(VI) reagent] and [NO_2^-] in aqueous bisulfate media at constat ionic strength (μ), and temperature. Reactions appeared to follow dissociative mechanism.

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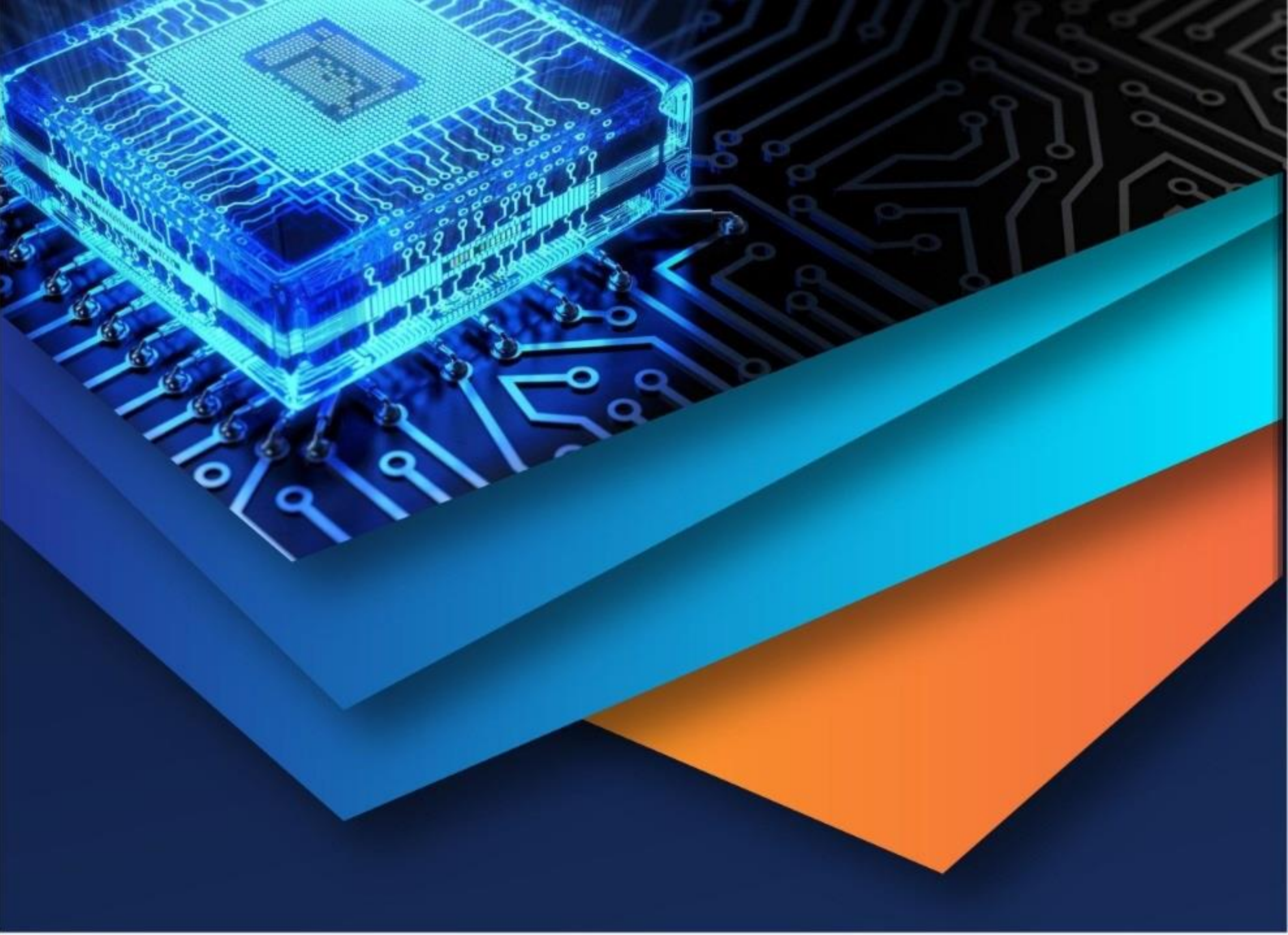

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