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A Kinetic Study of the Solvent Effect of Tertiary Alcohol on the Thermodynamic Extensive Properties of the Catalysed Solvolysis of Heavy Acetate in Aquo-t-butanol Solvent Systems

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Abstract: ***The solvent effect of a tertiary alcohol was studied on the themodynamic extensve properties of solvolysis of a heavy acetate (butyl acetate) in different aquo-t-butanol reaction media containing 20 to 80% (t-butanol) at different temperatures varying from 20 to 40°C. From the enhancement observed in ΔG* values with simultaneous decrease in the values of ΔH* and AS of the reaction, it is inferred that the organic co-solvent t-butanol acts as entropy controller and enthalpy stimulator solvent for alkali catalysed hydrolysis of butyl acetate From the evaluated values of water moleculex associated with the activated complex of the reaction which are found to increase with increase in the temperature of the reaction, it is inferred that the bimolecular mechanistic path is changed to unimolecular in presence of the organic component (t-butanol) of the reaction media. The numerical value of Iso-kinetic temperature of the reaction which comes to be nearly 287.0 (below 300) indicates that there is weak but considerable solvent-solute interaction in the aquo-t-butanol reaction media***

Keywords: Tertiary alcohol, Extensive, Heavy Acetate, Solvolysis, Enthalpy stimulator, Specific solvation, Dielectric effect, Iso-kinetic temperature.

I. INTRODUCTION

Though a large number of researchers of the kinetic field have reported the effect of different solvents on the rates, mechanism and the thermodynamic properties of hydrolysis of simple esters, but, a little attention has been paid towards the studies of solvent effect of tertiary alcohol on the rate, mechanism and thermodynamic activation parameters of the reaction and solvent-solute interaction for alkali catalysed solvolysis of heavy esters. In order to highlight the above noted facts, it has been proposed to study the kinetics of alkali catalysed hydrolysis of butyl acetate in aquo-t-butanol reaction media.

II. EXPERIMENTAL & CALCULATION

The kinetics of alkali catalysed hydrolysis of butyl acetate was carried out separately in the different aquo-organic co-solvent media (aquo-t-butanol) prepared by adding different volumes of t-butanol (20 to 80%). The strength of the solution was kept 0.1 M with respect of NaOH and 0.05 M with respect to the ester. The reaction was found to follow the second order kinetic equation and the evaluated values of specific rate constants have been recorded in Table - 1. For studying the effect of change of concentration of organic component (t-butanol), the variation of log k values of the reaction with mol% of t-butanol in the reaction media has been enlisted in Table -II. Using Arrhenius equation, the iso-composition and iso-dielectric activation energies values of the reaction were evaluated and are recorded respectively in Table - III & IV. The thermodynamic activation parameters such as ΔH*, ΔG* and ΔS* have been evaluated using Wynne-Jones and Eyring[4] equation and their consolidated values have been shown in Table - V.
For studying the mechanism of the reaction, the evaluated number of water molecules associated with the transition state of the reaction at different temperatures have been depicted in Table-VI

III. RESULTS AND DISCUSSION

A. Effect of Solvent on the Specific Rate Constants of the Reaction

In order to highlight the effect of the solvent on the specific rate constant values of the reaction, the log k values were plotted against the mole % of the organic co-solvent (their values from Table - II) as shown in Fig. 1, and were found to follow decreasing trends. However, the depletion found in the rate with increasing mole % of the organic co-solvent (t-butanol) at all the temperatures follow

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smooth path following two intersecting straight lines at about 18.10 mol% of t-butanol having different numerical values of the slope (of similar nature) before and after the point of intersection (at about 18.10 mol% oft-butanol in the reaction media). From the plots, it wasfound that with increasing the temperature of the reaction, the degree of depletion in the rate constants of the reaction becomes steeper.

However, the possible rate depleting factors in the rate can be listed as follows:

0 decrease in the bulk dielectric constant value of the medium, (n) decrease in the polarity of the reaction media on adding less polart-butanol to it

The above noted two depleting factors are quite in operation and this is quite in agreement with the theory of Hughes and Ingold' that the rate ought to decrease with decreasing dielectric constant of the reaction media.

Such decrease in rate constant with increasing proportion of the organic co-solvent like t-butanol has been reported earlier by Singh & Jha et al[6], Singh & Hafizee et al[7]. and in recent years also by Singh[8] However, the decrease observed in the specific rate constant values with different numerical values of slopes may be attributed partly due to the dielectric effects of the reaction media and partly due to solvation changes taking place in it (aquo-t-butanol reaction media).

B. Effect of Solvent on the Iso-composition Activation Energy (E_C) of the Reaction:

On perusal of the data mentioned in Table III, it is observed that the value of iso-composition activation energy of the reaction go on decreasing from 97.07 kJ/mol to 62.45 kJ/mol with increasing concentration of t-butanol from 20 to 80% (v/v), in the reaction media.

The depletion E_C values of the reaction in water-t-butanol media may be due to either of the following three causes:

(1) The transition state is more solvated than the initial state,

The transition state is less desolvated than the initial state, and

(i) The transition state is solvated and the initial state is desolvated.

Among these three factors, the third factor seems to be operative in this case as from the values of thermodynamic activation parameters of the reaction in Table - V, both ΔH* and ΔS* values of the reaction are found to decrease with increasing proportion oft-butanol in the reaction media (ΔH* values decreases from 92.31 kJ/mol to 60.44 kJ/mol and ΔS* values decreases from 30.27 J/K/mol to 81.94 J/K/mol at 30°C).

Regarding effect of solvent on the E_C value of reaction, similar findings and their interpretations have been found in accordance with the earlier reports of Pathak & Singh et al[9], Singh & Parween et al[10]. and also with the recent reports of Priyanka & Singh et al[11]. and Raghaw & Singh et al[12].

C. Solvent Effect on the Iso-dielectric energy (E_D) of the reaction:

From the values recorded in Table - IV, it appears that E_D values of the reaction go on increasing with increasing dielectric constant values of the aquo-t-butanol reaction media. The E_D value is 78.89 kJ/mol at D value 25 and increases to 98.03 kJ/mol at D value 55. The enhancement in the E_D values with increase in D values of the reaction media is in accordance with depletion in E_C or E_{exp} values of the reaction with increasing mol % of t-butanol in the reaction media. These findings and conclusions have been found in support of the earlier reports of Wolford[13] and also with the recent reportings of Dubey & Singh et al[14].

D. Solvent Effect on Thermodynamic Activation Parameters of the Reaction:

From Table - V, on perusal of the values of thermodynamic activation parameters, namely ΔG*, ΔH* and ΔS* it is observed that ΔG* values (free energy of activation) of the reaction increases with simultaneous decrease in its ΔH* and ΔS* values. At 30°C, ΔG* values have been observed increasing from 83.14 kcal/mol to 85.27 k cal/mol with increasing concentration of t-butanol from 20 to 80% (v/v) in the reaction media. Though this enhancement is not very large, however, it is quite considerable and acceptable too. In order to highlight the effect of changing concentration of the organic content (t-butanol) in the reaction medin, ΔH*, ΔG* and ΔS* values have been plotted against the changing mol% of DMF in the reaction media and their plots are shown in Fig. 2, 3 and 4 respectively. From the plots of ΔG* values against mol % of t-butanol as shown in Fig. -3, it is found that ΔG* values go on increasing non-linearly with gradual addition oft-butanol in the reaction media. This finding is indicative of desolvation of reactants as explained by Elsemongy et al[15].

So far as the variations in ΔH* and ΔS* are concerned on observing their values from Table V and their plots against mol % of t-butanol as shown in Fig. 2 and 4, it is interestingly found that both of them decrease linearly and non-linearly respectively with gradual addition of t-butanol in the reaction media.

From the thermodynamic relation:

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

it can be easily concluded that increase in ΔG* values with simultaneous decrease in both of ΔH* and ΔS* values is only possible when ΔS* values decreases more than ΔH* value. From such findings, it is inferred that in presence oft-butanol in the reaction media, the alkali catalysed hydrolysis of butyl acetate becomes entropy controlled and enthalpy stimulated reaction.

Moreover, linear variation in ΔH* and non-linear variation in ΔS* values with increasing mol% of t-butanol as shown in Fig. 2 and 4 respectively, gives information of the fact that specific solvation is taking place in aquo-t-butanol solvent systems similar to that as reported in the past by Saville et al[16].

However, such solvent effect on thermodynamic activation parameters and extensive properties and their interpretations have also been found in support of the earlier reports of Singh & Priyanka et al[17] and also with the recent reports of Kaushalendra & Kumar & Singh et al[18].

E. Solvent Effect on Iso-kinetic Temperature and Solvent-Solute Interaction in the Reaction Media

The value of the iso-kinetic temperature of the reaction was evaluated by using Barcley-Butler[19] relationship which is expressed as

$$\delta m\,(\Delta H^*) = \beta \Delta m\,(\Delta S^*)$$

It is a straight line equation representing the relationship between enthalpy and entropy of activation values of the reaction. "B' is known as iso-kinetic temperature. From the values of AH and AS values available in Table - V, the plots of AH versus AS at 30°C were made which is shown in Fig. 5. From the slope of the straight line of the plots, the value of the kinetic temperature was evaluated to be 287.32≈287.0 (below 300). Thus, in the light of Leffler's guidelines[20], from the numerical values of the iso-kinetic temperature (which is below 300), it can safely be concluded that there is appreciable change in the structure of the reactant or in the solvent or in both the reactant and solvent due to weak but considerable interaction between solvent and solute present in the reaction media (aquo-t-butanol) in the similar way as reported earlier by Singh & Singh et al[21] and also in recent years by Pathak & Singh et al[22].

F. Effect of Solvent (water concentration) on the Mechanism of the Reaction

Evaluation of the number of water molecules associated with the formation of transition state or activated complex has been done by plotting log k values of the reaction against log [H_2O] values as shown in Fig. - 6 in the light of relation proposed by Robertson[23]

$$\mathbf{\log k = \log k_o + n \log [H_2O]}$$

From Fig. 6, it is apparent that at each temperature two straight lines intersecting cach other at log [H_2O) value approximately 1.453 having different values of slopes are obtained. From the slopes of the plots of log k versus log [HO], the evaluated values of number of water molecules associated with the activated complex of the reaction are noted in Table - VI. From Fig. 6 as well as from Table - VI, it is clear that the number water molecules associated with the transition state increases from 0.236 to 0.771 with increase in temperature above 20 to 40°C before log [H_2O], value 1.453 which corresponds to 51.30% of water concentration in the reaction media. Similarly, in case of above 51.30% of water concentration in the reaction media, the number of water molecules associated with the transition state in its formation increases from 0.520 to 1.145 with rise of temperature from 20 to 40°C. Overall, the number of water molecules involved in the formation of the activated complex of the reaction increases from 0.236 to 1.145 with rise of temperature from 20 to 40°C.

According to observation and findings of Robertson et al[24]. it has been suggested that number of water molecules associated with the transition state is fairly high for unimolecular reaction while that for bimolecular reaction will be very low.

Hence in the light of findings of Robrtson et al[24] it may be inferred that with rise in temperature of the reaction, the mechanistic path of the reaction changes from bimolecular to unimolecular in aquo-t-butanol media. From above noted findings about the increasing number of water molecules associated with activated complex, it may be inferred that in presence of t- butanol in the reaction media and with rise of temperature of the reaction, the structure of water is changed from its dense form to bulky format equilibrium.

$$\mathbf{(H_2O)_d} \rightleftharpoons \mathbf{(H_2O)_b}$$

Earlier Akanksha & Singh et al[25], Singh & Priyanka et al[26]. and also in recent years Kumari & Singh et al[27] and Singh & Hafizee et al[28] have reported similar findings and their interpretations for effect of solvent on the mechanism of the catalysed solvolysis reactions.

Table - I : Specific rate constant values of Alkali catalysed hydrolysis of Butyl acetate in water-t-butanol media
$k \times 10^2$ in $(dm)^3\ mol^{-1}\ min^{-1}$

Temp in °C	% of t-butanol (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20° C	49.23	45.85	42.54	40.37	38.04	36.33	33.10
25° C	93.80	86.18	79.03	70.42	64.24	58.05	50.13
30° C	177.01	158.64	144.18	123.94	108.24	95.85	75.88
35° C	323.30	285.30	252.81	208.88	175.95	142.33	112.18
40° C	602.70	504.89	442.69	354.65	286.26	208.22	166.05

Table - II: Variation of log k values of the reaction at different temperatures with mol % of t-butanol in water-t-butanol media.

% of t-butanol (v/v)	Mol % of t-butanol	2 + log k values				
		20°C	25°C	30°C	35°C	40°C
20%	4.53	1.6922	1.9722	2.2480	2.5096	2.7801
30%	7.52	1.6613	1.9354	2.2004	2.4553	2.7032
40%	11.23	1.6288	1.8978	2.1589	2.4028	2.6461
50%	15.95	1.6061	1.8478	2.0932	2.3199	2.5498
60%	22.15	1.5802	1.8078	2.0344	2.2454	2.4568
70%	30.68	1.5603	1.7638	1.9678	2.1533	2.3185
80%	43.15	1.5198	1.7001	1.8801	2.0499	2.2202

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Table - III

Evaluated Values of Iso-composition Activation Energy (E_c or E_{exp}) of the reaction in water-t-butanol media.

% of t-butanol (v/v)	20%	30%	40%	50%	60%	70%	80%
E_c values in kJ/mol	97.07	91.41	89.50	83.30	77.39	67.86	62.45

Table - IV

Evaluated values of Iso-Dielectric Activation Energy (E_D) of the reaction at different desired 'D' values of the water-t-butanol media.

D values	D = 25	D = 30	D = 35	D = 40	D = 45	D = 50	D = 55
E_D values in kJ/mol	78.89	82.38	84.83	88.25	90.01	92.81	95.03

Table - VI

Values of the slopes of the plots of log k versus log [H_2O] at different temperatures

Temperature in °C	Slope - I when log[H_2O] is below 1.453	Slope - II when log[H_2O] is above 1.453
20°C	0.236	0.520
25°C	0.434	0.692
30°C	0.552	0.794
35°C	0.725	0.956
40°C	0.771	1.145

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Table - V

Consolidated Values of Activation parameters (ΔH*, ΔG* and ΔS*) of the reaction in water-t-butanol system at different temperatures.

ΔH* and ΔG* in kJ/mole, ΔS* in J/K/mole

% of t-butanol (v/v)	Mol % of t-butanol	ΔH* in kJ/mole	20°C		25°C		30°C		35°C		40°C	
			ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*
20%	4.53	92.31	83.43	30.30	83.29	30.24	83.14	30.27	83.02	30.14	82.78	30.46
30%	7.52	89.55	83.60	20.29	83.51	20.27	83.41	20.24	83.33	20.19	83.24	20.16
40%	11.23	87.19	83.78	11.62	83.72	11.43	83.65	11.67	83.64	11.53	83.58	11.54
50%	15.95	80.37	83.91	-12.07	84.01	-12.18	84.03	-12.08	84.13	-12.18	84.16	-12.08
60%	22.15	74.69	84.06	-31.97	84.23	-32.03	84.37	-31.96	84.57	-32.06	84.71	-32.02
70%	30.68	65.45	84.17	-63.90	84.49	-62.83	84.76	-63.75	84.11	-63.84	85.54	-64.20
80%	43.15	60.44	84.39	-81.75	84.85	-80.38	85.27	-81.94	85.72	-82.07	86.13	-82.00

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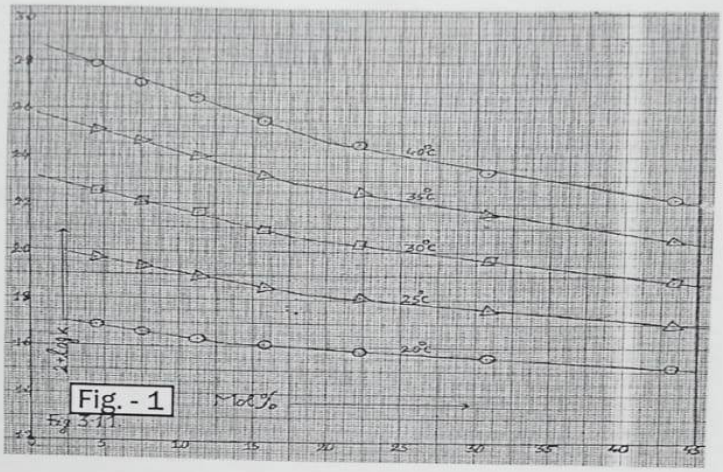
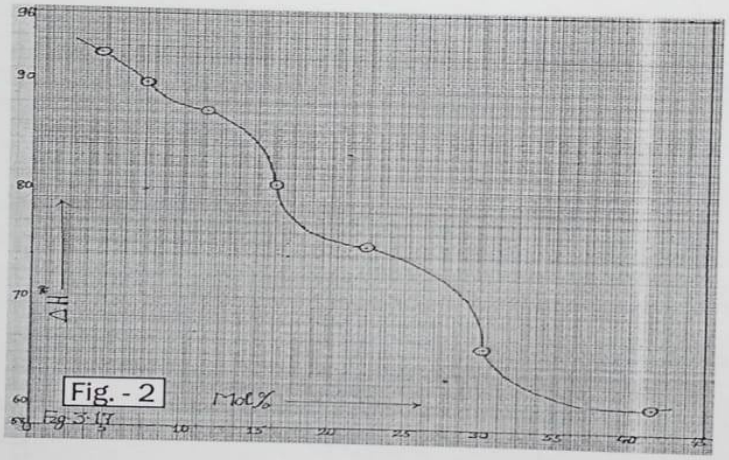


Fig. - 1
Mol%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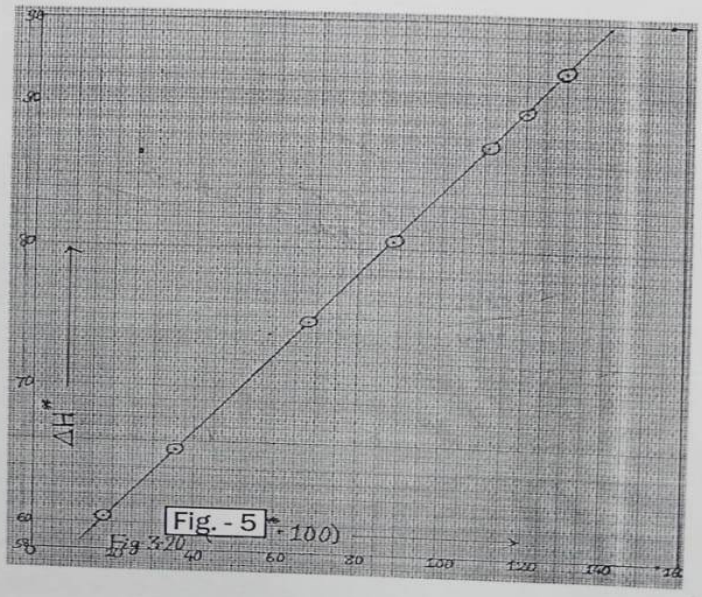
Mol%
ΔH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ΔH

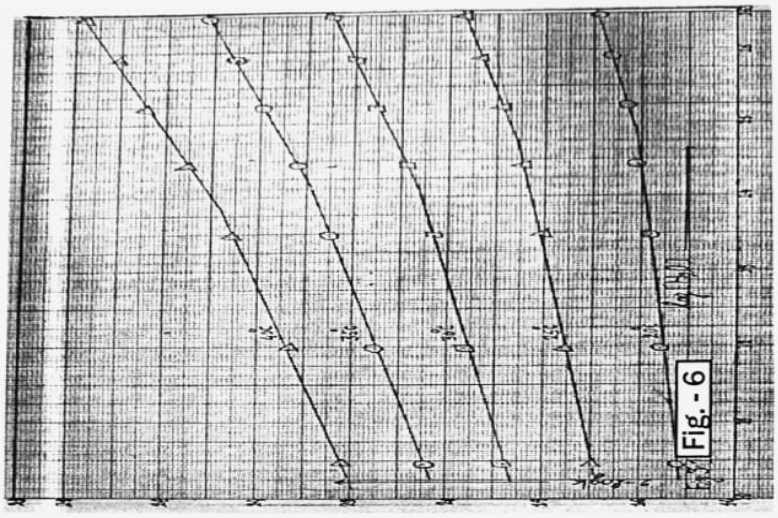
Fig. - 6

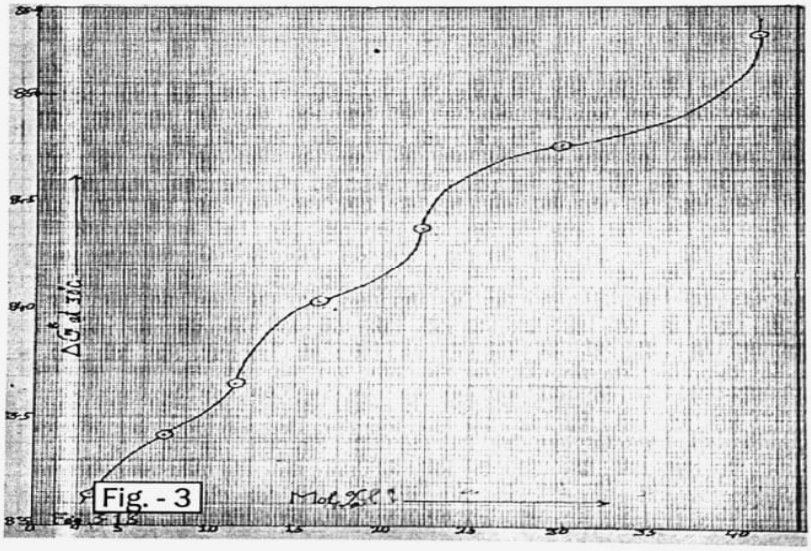
Fig. - 3

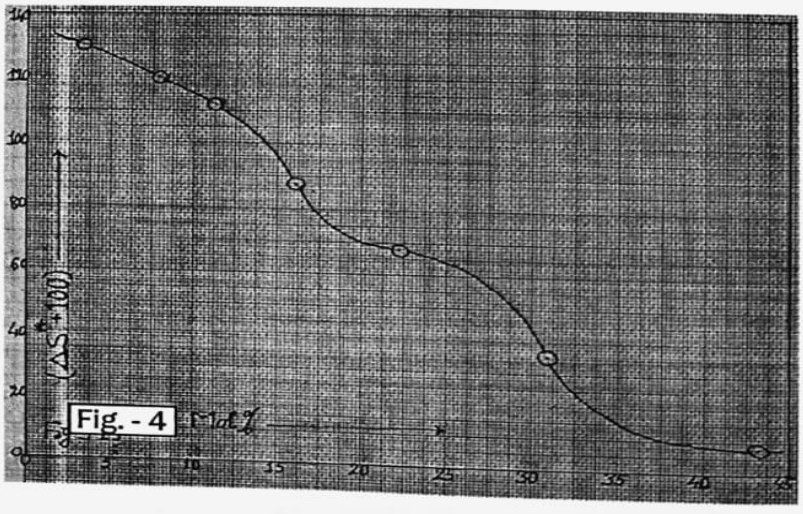
Fig. - 4

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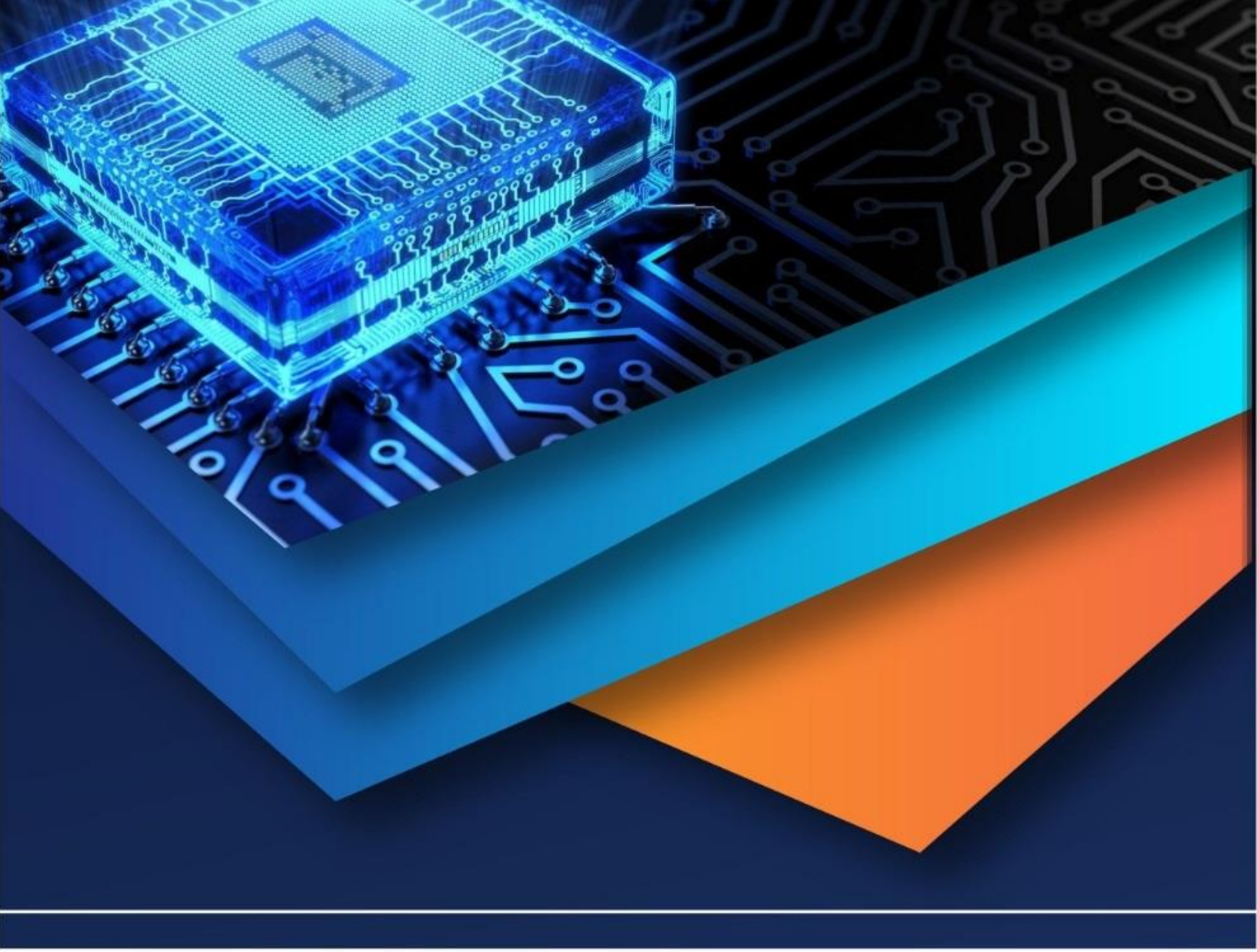

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