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Theoretical Calculation of Activation Energy and Heat of Reaction in 1, 2-Migration Step of Selected Migratory Substituents in Dienone-Phenol Rearrangement

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Abstract: ***The purpose of this study is to evaluate the enthalpy change for each step of dienone-phenol rearrangement and to determine activation energy for transition from migration origin to migration terminus. The decrease or increase in enthalpy gives the exothermicity or endothermicity of the rearrangement reaction. Activation energy gives the ease with which migration takes place in the molecular rearrangement. The reaction begins with protonation giving rise to more energetical cationic entity which is stabilized by resonance. The rearrangement has to pass through a transition state so as to accomplish 1,2-migration from C-4 to C-3 therefore calculation of activation energy for forward and backward reaction is necessary to determine the feasibility of the reaction. For enthalpy and activation energy determination computational calculation (AM1, HF and B3LYP) was utilized. Knowing the energy of different structures involved in the reaction, enthalpy and activation energy can be ascertained.***

Keywords: Exothermicity or endothermocity, 1,2-migration, enthalpy, activation energy, cationic entity, dienone-phenol rearrangement

I. INTRODUCTION

Dieneone-phenol rearrangement involve the conversion of dieneone to an appropriate phenol through 1,2-shift of the migrating substituent. The reaction begins with protonation step and ends with deprotonation. Depending upon the nature of the migrating groups, the enthalpy of reaction may vary in different steps of the mechanism. The stabilizing and destabilizing effect of different substituents is also an important determining factors for energy of the transition state in 1,2-shift steps. When 4,4-dialkyl cyclohexadienone is treated with acid, the proton from acid is primarily absorbed by carbonyl oxygen. As the lone pair of oxygen is use up for making sigma bond between proton and oxygen the pi-bond between oxygen and carbon is compelled to break and thus renders formation of positive charge in the ring. Positive charge created in the ring is then stabilized by resonance through delocalization of positive charge in the ring. Deformation of the ring system decreases the stability of di-substituted carbon and cause one of its substituent to migrate to the adjacent carbon (When the migration terminus carbon atom carry positive charge). The shifting of migratory substituent is followed by deprotonation. The residual electron then merge into the ring system and thus promoting aromaticity. The final rearranged product is a phenol derivative with 3,4-disubstituted product. This is reaction commonly known as Dienone-phenol rearrangement.

II. METHODOLOGY

The gradient–corrected electron density functions, geometries, energies and frequencies of the dienone system were calculated by the semi empirical SCF – MO's method of the Gaussian 98 (window version) A . 11 .2 package. Heats of formation from structure II to VI was calculated by taking the difference in energy of the the specified structures and was represented as ΔH_r. It was used as the basis for calculating the energy profile for the reaction pathway in each cases as well as for calculating the enthalpy changes for each successive steps in the reaction . 1,2 – migration step was more focused i.e. Transition from structure-II to IV, where the transition state was located and the activation enthalpy barrier was determined. Transition state was calculated as the differences in energy between structure II and Structure III for the forward reaction and difference in energy between Structure VI and III is taken as activation energy for the backward reaction. Difference in activation energy for the backward and forward reaction give clues to decide the favorability of the reaction condition. In the reaction pathway the initial substrate along with hydronium ion (H_3O) is arbitrarily taken as Zero energy level. Various migrating groups were compared with respect to the facility of undergoing the 1,2 – migration by comparing the calculated values of the activation energies.

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III. RESULT AND DISCUSSION

The first step of dienone-phenol rearrangement involves protonation of dienone. Carbocationic species (Structure-II) is stabilized by two resonating structures. Structure-III represent transition state where partial bond breaking and forming takes place between the migratory substituent with migration origin and migration terminus. In structure-IV the migrating group just migrated from C-4 to C-3, 1,2-shift is followed by deprotonation giving rise to structure-V (3,4-disubstituted phenol)

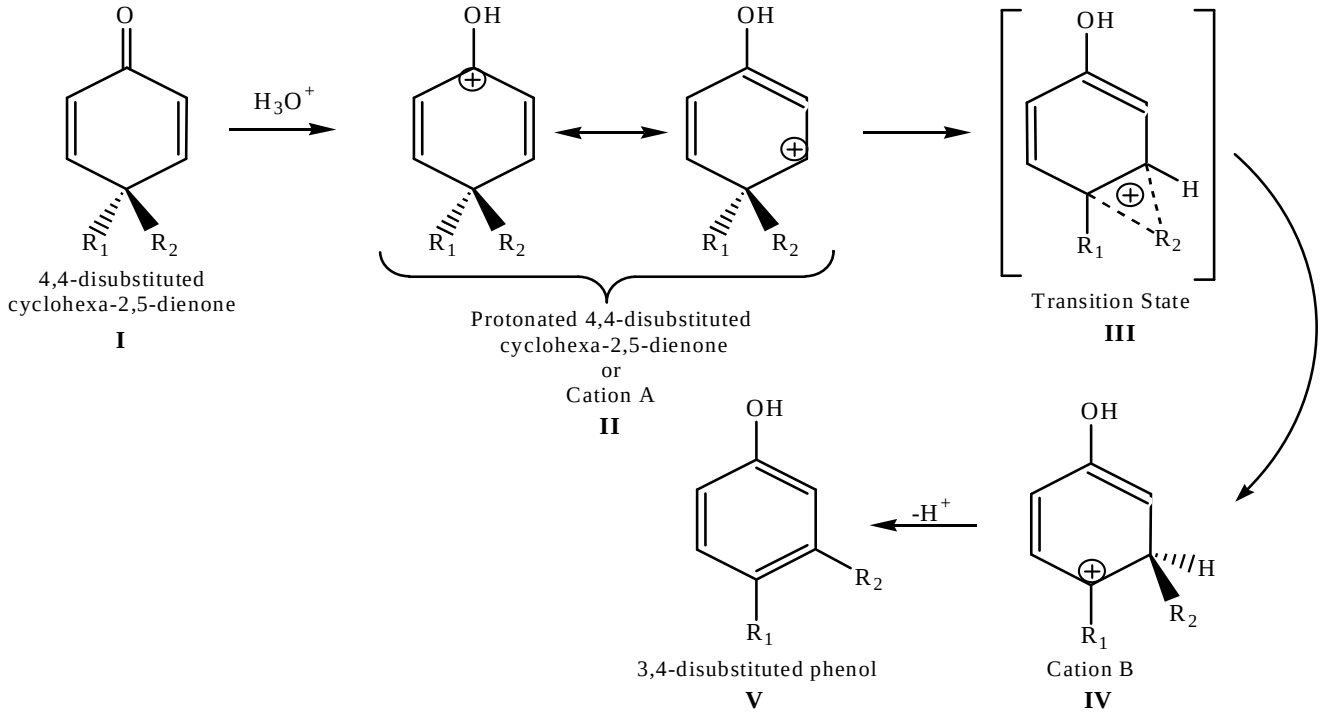

Figure-I: Various Steps Of Dienone-Phenol Rearrangement

Table-I: Energy (Kcal/Mol) Of Variuos Structures Involved In Dienone-Phenol Rearrangement (Am1 Calculation)

Structure	H	Me	Et	i-Pr	t-Bu
I	-7.08	-11.16	-17.18	-20.44	-8.59
II	158.53	158.47	157.65	156.90	159.09
IV	172.26	172.70	171.69	171.01	156.21
III(TS)	190.26	201.17	192.89	184.30	166.36
V	15.24	18.75	18.49	19.18	32.10

Table-II: Energy of the reactions (Δhr), activation energy for forward reaction (ea-1), activation energy for backward reaction (ea-2) and [(ea-1)−(ea-2)] in kcal/mol. (am1 calculation)

	H	Me	Et	i-Pro	t-But
ΔHr (IV−II)	13.73	14.28	14.04	14.11	-2.88
Ea-1[III(TS)−II)	31.73	42.75	35.24	27.4	7.27
Ea-2[III(TS)−IV]	18	28.47	21.2	13.29	10.15
(Ea-1)−(Ea-2)	13.73	14.28	14.04	14.11	-2.88

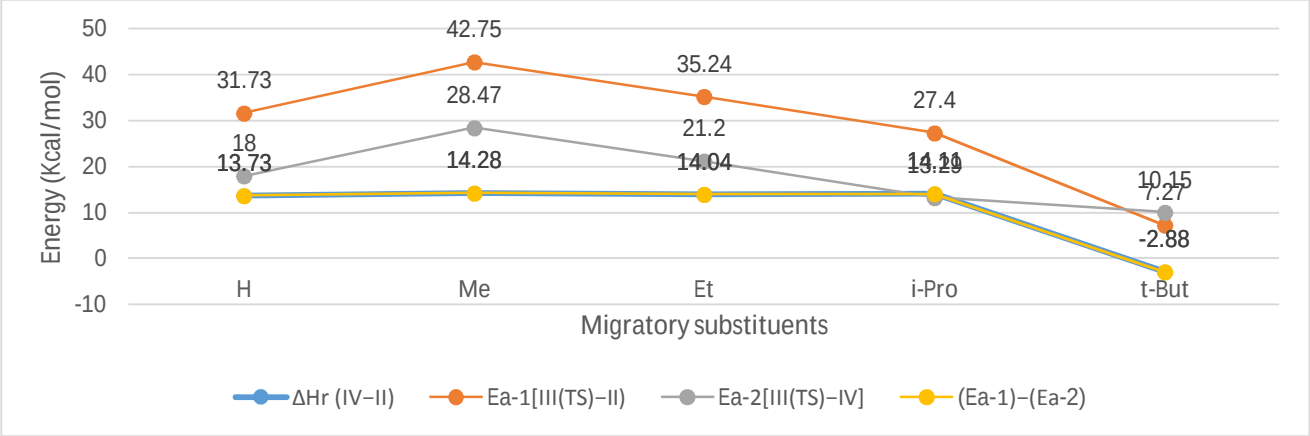

Figure-II: Graph showing energy of the reaction (Δhr), activation energy for forward reaction (ea-1), activation energy for backward reaction (ea-2) and [(ea-1)−(ea-2)] in kcal/mol. (am1 calculation)

The energy required for structure II to climb up the transition state (Ea-1) for different substituents is in the order; Me > Et > H > i-Pro > t-But and activation energy for the reverse reaction is in the order; Me > Et > H > i-Pro > t-But. The order follows the same trend for for forward and backward reaction.

From the order of activation energy (Ea-1) it appears that the substituent that undergoes 1,2-shift with the least probability is methyl substituent while the most probable migratory substituent is tertiary butyl group. Since activation energy for both forward and backward reaction is the minimum for t-butyl group it is more likely to execute equilibrium between structure II and IV among other substituents. This is indicated by the least value of [(Ea-1)−(Ea-2)] which is -2.88. In all substituted structures except for t-But substituted case, Ea-1[III(TS)−II) is greater than Ea-2[III(TS)−IV] this may be an indication of lesser chances of migration from C-4 to C-3 because the activation energy for forward reaction is greater than activation energy for backward reaction.

The heat of formation of structure IV from structure II with different substituents is in the order; Me > i-pro > Et > H > t-But. This order can be interpreted as the endothermicity of different substituents e.i. 1,2-Migration of methyl group is the most endothermic requiring highest amount of energy for 1,2-shift. While, 1,2-shift of t-But is the least endothermic reaction. Negative value of ΔHr for t-But indicates exothermicity of 1,2-shift reaction.

Table-III: Energy (Kcal/Mol) Of Variuos Structures Involved In Dienone-Phenol Rearrangement (Hf Calculation)

Structure	H	Me	Et	i-Pr	t-Bu
I	0	0	0	0	0
II	194.56	135.70	190.32	261.37	115.88
IV	201.67	202.93	204.12	267.45	140.59
III(TS)	222.68	223.94	225.00	288.53	202.05
V	10.16	11.91	12.73	76.76	12.04

Table-VI: Energy of the reactions (Δhr), activation energy for forward reaction (ea-1), activation energy for backward reaction (ea-2) and [(ea-1)−(ea-2)] in kcal/mol. (hf calculation)

	H	Me	Et	i-Pro	t-But
ΔHr (IV−II)	7.11	67.23	13.8	6.08	24.71
Ea-1[III(TS)−II)	28.12	88.24	34.68	27.16	86.17
Ea-2[III(TS)−IV]	21.01	21.01	20.88	21.08	61.46
(Ea-1)−(Ea-2)	7.11	67.23	13.8	6.08	24.71

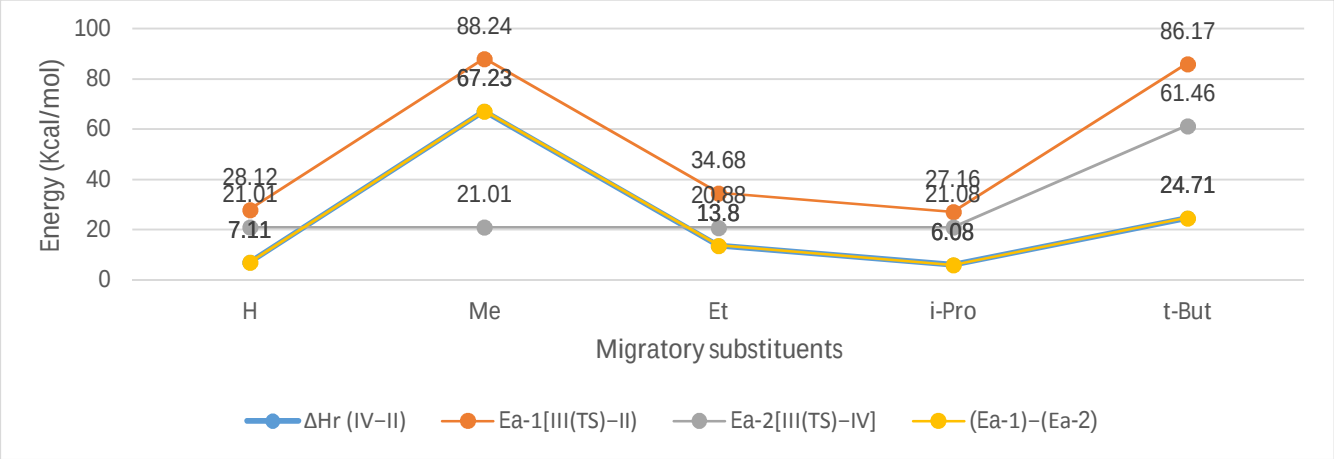

Figure-III: Graph showing energy of the reactions (Δhr), activation energy for forward reaction (ea-1), activation energy for backward reaction (ea-2) and [(ea-1)−(ea-2)] in kcal/mol. (hf calculation)

The energy required for structure II to climb up the transition state (Ea-1) for different substituents is in the order; Me > t-But > Et > H > i-Pro and activation energy for the reverse reaction is in the order; t-But > i-Pro> Me = H > Et. The activation energy of 1,2-shift for forward reaction and backward reaction does not follow the same trend. As shown by the order methyl has least chance to overcome the transition state energy for 1,2-migration while i-Pro has the least energy required for climbing up the transition state. For backward reaction t-But requires the least chance for climbing up the transition state and is likely to undergo reverse reaction with most difficulty while Et- has the highest probability.

The heat of formation of structure IV from structure II with different substituents is in the order; Me > t-But > Et > H > i-Pro. Here, ΔHr values indicates that methyl group requires maximum amount of energy for 1,2-shift among other substituents while i-Pro require the least amount of energy. This is the sign of highest endothermicity of 1,2-migration for methyl group while i-Pro migration would be the least endothermic.

Table-V: Energy (Kcal/Mol) Of Variuos Structures Involved In Dienone-Phenol Rearrangement (B3lyp/6-31g Calculation)

Structure	H	Me	Et	Pr	Bu
I	0	0	0	0	0
II	197.22	166.08	199.42	206.63	193.27
IV	206.88	189.57	210.14	211.89	131.00
III(TS)	222.68	194.71	225.50	226.63	209.32
V	13.76	16.43	17.05	18.06	16.36

Table-VI: energy of the reactions (Δhr), activation energy for forward reaction (ea-1), activation energy for backward reaction (ea-2) and [(ea-1)−(ea-2)] in kcal/mol. (b3lyp/6-31g calculation)

	H	Me	Et	i-Pro	t-But
ΔHr (IV−II)	9.66	23.49	10.72	5.26	-62.27
Ea-1[III(TS)−II)	25.46	28.63	26.08	20.00	16.05
Ea-2[III(TS)−IV]	15.8	5.14	15.36	14.74	78.32
(Ea-1)−(Ea-2)	9.66	23.46	10.72	5.26	-62.27

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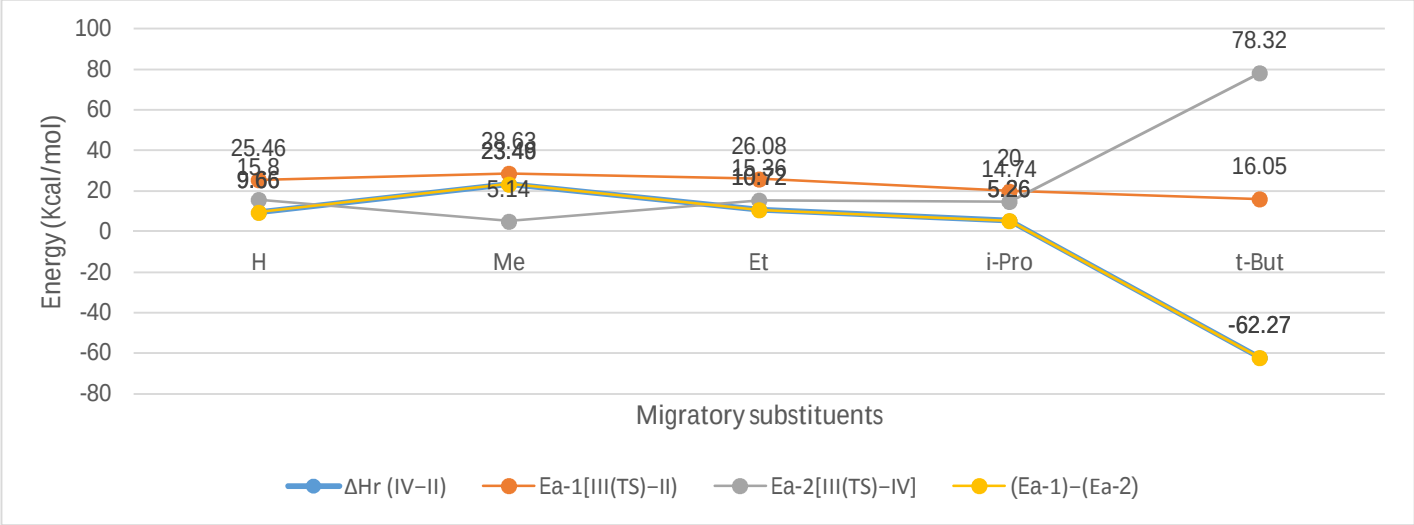

Figure-iv: graph showing energy of the reactions (Δhr), activation energy for forward reaction (ea-1), activation energy for backward reaction (ea-2) and [(ea-1)−(ea-2)] in kcal/mol. (b3lyp/6-31g calculation)

The energy required for structure II to climb up the transition state (Ea-1) for different substituents is in the order; Me > Et > H > i-Pro > t-But and activation energy for backward reaction is in the order; t-But > H > Et > Me > i-Pro . The order of activation energy for forward reaction shows that t-But has the highest probability of 1,2-migration while methyl group has the least.

The heat of formation of structure IV from structure II with different substituents is in the order; Me > Et > H > i-Pro> t-But. From the order of ΔHr value, 1,2-migration of methyl group is the most endothermic among other substituents. It is likely to happen with most difficulty. While migration of t-But is the least endothermic which implies that tertiary butyl group has the highest migratory aptitude among other substituents.

IV. CONCLUSION

Although all observations in different calculations do not follow the same trend in both activation energy and ΔHr, a general pattern can be drawn for energy involved in the reaction with different migratory substituents. In all calculations methyl group has the highest activation energy as well as highest heat of formation for forward reaction. This is an indication of the least migratory aptitude for 1,2-migration i.e. from C-4 to C-3. Whereas, In all calculations except for HF, tertiary butyl group has the minimum activation energy as well as heat of formation. This is an indication of the highest migratory aptitude of tertiary butyl group for 1,2-migration compared to other selected substituents. This theoretical work suggests that higher is the stabilizing effect of migratory substituent to the positive charge in the transition state larger is the migratory aptitude of the substituent in dienone-phenol rearrangement.

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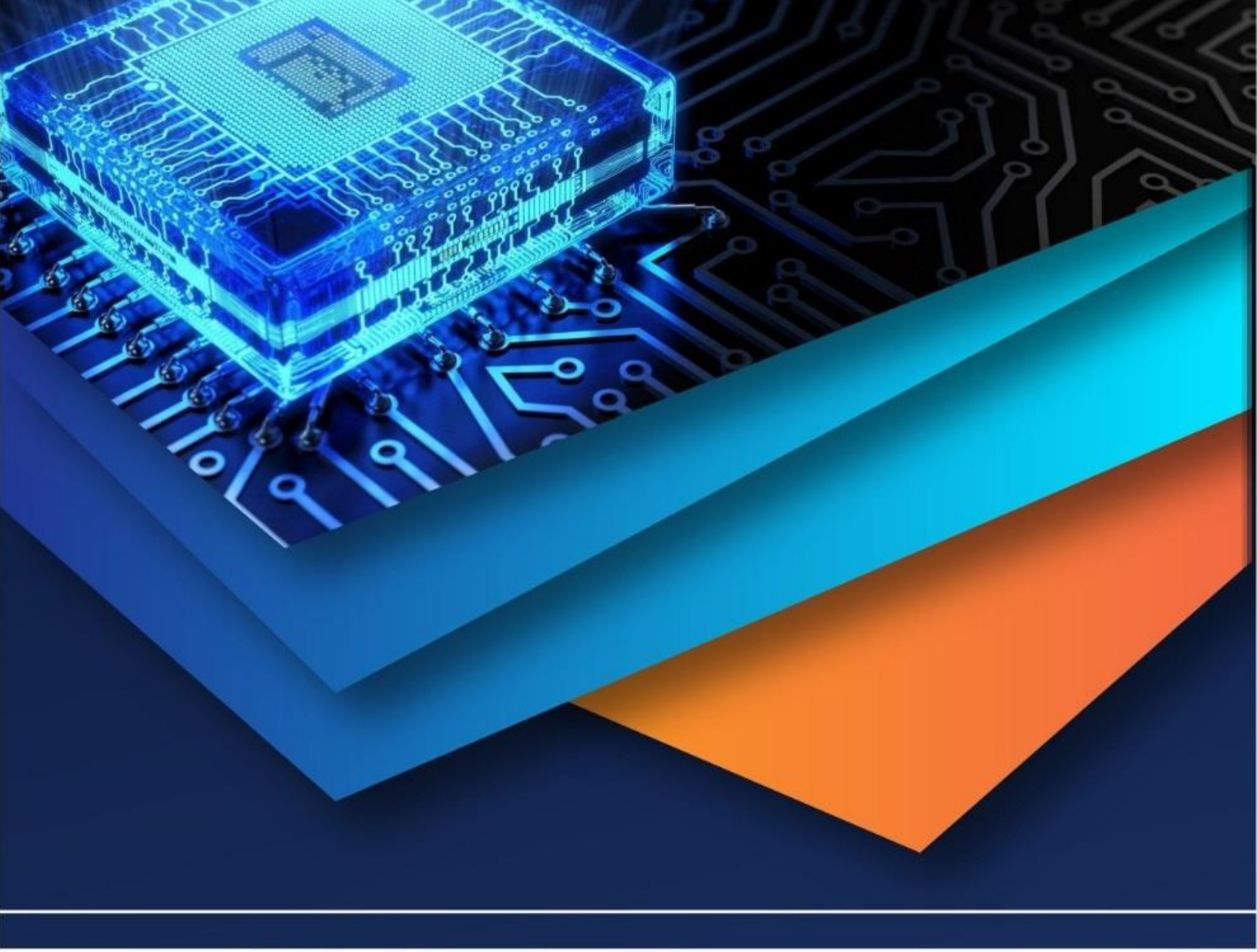

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