Computational Studies on the Effect of External Electric Field on Hydrogen Atom Transfer and Proton Coupled Electron Transfer Reactions

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Submitted By

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Place: PATIALA

Date:

VISHAL SHARMA

CERTIFICATE

This is to certify that the thesis entitled "**Computational study on the Effect of External Electric Field on Hydrogen Atom Transfer and Proton Coupled Electron Transfer Reactions**" being submitted by Vishal Sharma, to the School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala for the award of degree of Masters of Science, is a record of bonafide research work carried out by him. Mr. Vishal Sharma has worked under my guidance and supervision and has fulfilled the requirements for submission of thesis, which to my knowledge has reached the requisite standard.

The results embodied in the thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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SELF DECLARATION

The work embodied in the project entitled "**Computational study on the Effect of External Electric Field on Hydrogen Atom Transfer and Proton Coupled Electron Transfer Reactions"** has been done by me in the partial fulfillment of requirement for the award of degree of **Master of Science in Chemistry,** submitted in the **School of Chemistry and Biochemistry**, **Thapar Institute of Engineering and Technology, Patiala**, is an authentic record of my own carried out under the supervision and guidance **of Dr. Dibyendu Mallick**, Assistant Professor of School of Chemistry and Biochemistry TIET, Patiala. All the ideas and references have been duly acknowledged.

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Date: - - -

Place

This is to certify the above statement made by student concerned is correct and true to the best of my knowledge.

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TABLE OF CONTENT

Abstract

The effect of external electric field (EEF) on the activation energy barrier for two types of H-abstraction reactions, namely, Hydrogen Atom Transfer (HAT) and Proton Coupled Electron Transfer reaction was examined by means of Density Functional Theory (DFT). It has been found that the external electric field affects the PCET reaction significantly as compared to HAT. Two cases of PCET reactions (phenoxyl radical/phenol and *p*-methyl phenoxyl/phenol) have been studied which shows that the barrier for H-abstraction reaction decreases while the external electric field is applied on a preferred direction. Thus external electric field can be used to catalyse the PCET type reactions. On the other hand, three different cases of HAT reactions (methoxy/methanol, benzyl/toluene and *p*-nitro benzyl/toluene) have been studied in presence and absence of external electric field. It has been observed that the HAT barriers for all three reactions remain almost unaffected by the EEF and hence no catalysis is observed in presence of EEF. The Natural Bond Orbital (NBO) charge analysis and the Valence Bond State Correlation Diagram (VBSCD) have been used to rationalize the observations. Our finding of the external electric field catalyzing the PCET can have broader implications in enzymatic conditions where the H-abstraction reaction plays a vital role in various oxidation processes.

Chapter 1

1.1 Introduction

The reaction mechanism which demonstrates the transfer of an electron and a proton in a solitary step can be divided into two categories, namely, hydrogen atom transfer (HAT) and other is proton coupled electron transfer (PCET) processes. In HAT, the proton and the electron are exchanged together, as a hydrogen atom. HAT is a well-known mechanism of free radical chemistry.[1] For example, this mechanism is of fundamental significance in the combustion, partial oxidation, and halogenations of hydrocarbons. PCET is less known however, is of much current significance because of its possible importance in a wide range of biochemical and other processes.[2]Equation 1 depicts a classical H-abstraction process.

In general, classification of H-abstraction reaction as HAT/PCET is not straight forward as there are subtle differences between these two pathways. Hence it had been a topic of debate in the literature for years.[3] The difference between the HAT and PCET pathways arises by the way the transfer of electron and the proton occurs during these two processes.

There are a few descriptors which are used to differentiate between these two processes.[3] The PCET can be compared as a electronically non adiabatic utmost, and the HAT system relates to the electronically adiabatic point of confinement. These differences amongst HAT and PCET have been understood by an examination between the phenoxyl/phenol (PCET) and benzyl/toluene (HAT) self-trade responses.[2] In light of this sort of investigation, the phenoxyl/phenol response, that involves electronically non adiabatic proton exchange, relates to PCET while benzyl/toluene response, which includes electronically adiabatic proton exchange, comparable to HAT. One of the best and elegant descriptors which can differentiate the HAT and PCET pathway is based on molecular orbital analysis. During the HAT process the proton and electron moves simultaneously to the same acceptor orbital whereas in case of PCET the transferring proton and the electron move to different acceptor orbital.[4] The Singly Occupied

Molecular Orbitals (SOMO) in the transition structure for these two processes are shown in the Figure 1.

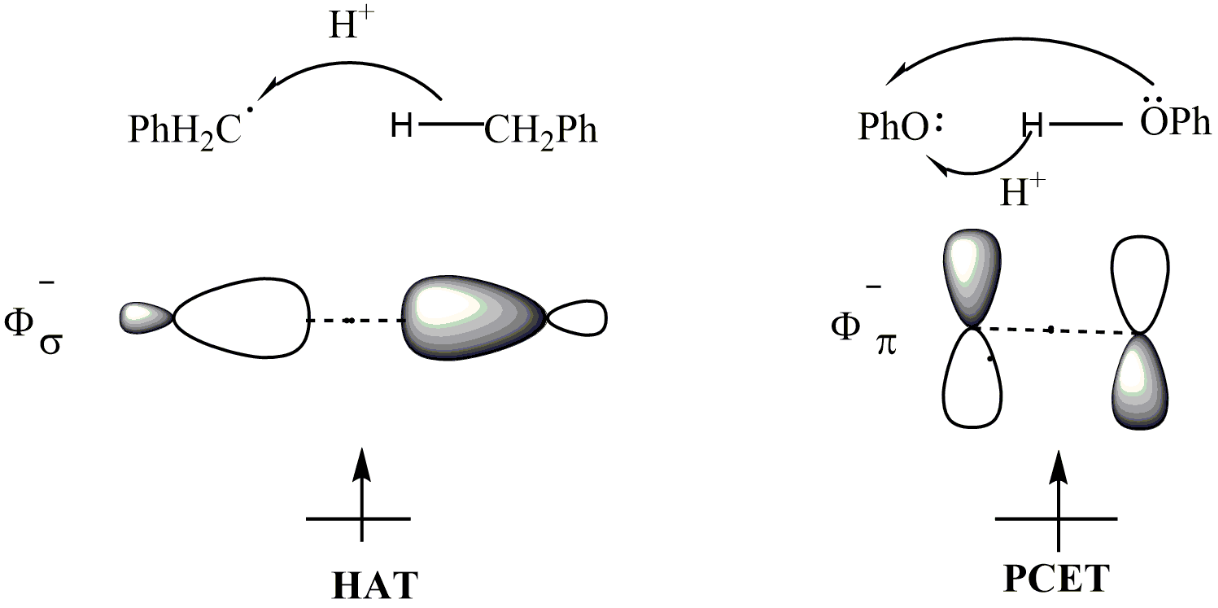

Figure 1: Characteristic Singly Occupied Molecular Orbitals (SOMO) for HAT and PCET

According to the molecular orbital descriptor the orientation of the SOMO of the transition structure with respect to the reaction coordinate which lies along the direction of the hydrogen atom transfer, can be helpful in differentiating the HAT and PCET.[5] If the SOMO, which is dominated by 2p orbitals, is perpendicular to the direction of the reaction coordinate, it is regarded as PCET pathway. The H-abstraction reaction between phenoxyl/phenol system (self-exchange reaction) is an excellent example of reactions which follows PCET mechanism. The SOMO of the reaction is given in Figure 2a. On the other hand, when the 2p orbital of the SOMO lies along the reaction coordinate, it is regarded as HAT. A self-exchange reaction between benzyl/toluene is a classic example of HAT reaction. The SOMO of the reaction is given in Figure 2b.

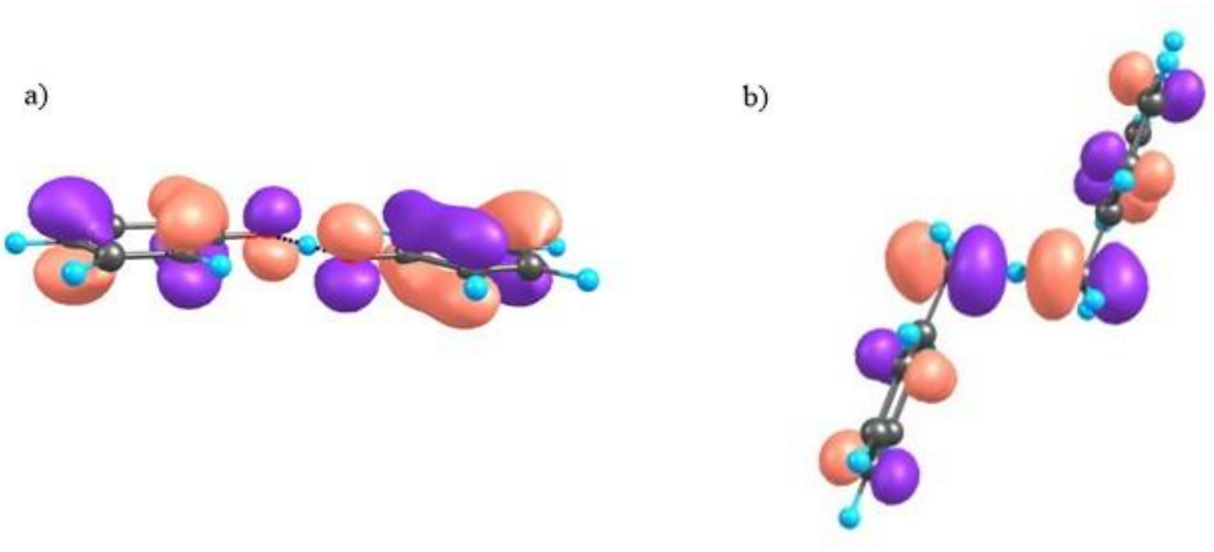

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Figure 2: SOMO of the transition structure for the H-abstraction reaction for (a) phenoxyl/phenol and (b) benzyl/toluene.

1.2 Oriented electric-field as a smart catalytic reagent

In last one decade, the concept of oriented electric field to be used as catalyst has been attracted attention of many chemists.[6] The use of oriented electric field as a smart catalytic reagent was first introduced by Sason Shaik. Shaik and his co-workers have shown an wide range of potential to catalyze the non-redox reaction.[6] They demonstrated that an external electric field can increase or decrease the energy barrier and also change the selectivity by applying external electric field in +ve and –ve direction.

In 2016, a mutual attempt by scientists in the University of Barcelona, Spain have found a way to utilize the oriented electric fields to catalyze a fundamental chemical reaction.[7] They believed that their hard work will allow the manufacture of a range of significant chemical compound that are rapid as well as cheaper than present technology used. They have set up a device to perform [4+2] cycloaddition reaction by applying an oriented electric field between two nanoelectrodes which contains the reacting molecules.[7] This novel nanochemical synthesis approach involves joining individual molecules to make new molecular backbone. A process that researchers describe as snapping Lego pieces together and then synthesize the chemical compound. While it is often thought that the ability to control reaction rates with an applied electrical potential gradient is decent to redox system, recent theoretical studies suggest that oriented electric fields could affect the results of a range of chemical reactions, regardless of whether a redox system is involved.

This probability emerges in light of the fact that minor charge-isolated resonance can stabilize numerous formally covalent species. At the point when a connected electric field is adjusted to electrostatically balance out one of these minor structures, the level of resonance enhances, which results in the general stability of the particle and transition state. This implies it may be possible to control the energy and thermodynamics of non-redox forms utilizing an outside electric field — as long as the introduction of the applied electric field is aligned properly along the dipole moment of the reacting species.

Therefore, in this thesis we are going to study the effect of oriented external electric field on the reactivity of different H-abstraction reactions which undergo either HAT or PCET pathway. In order to achieve our objectives we will calculate and compare the activation energy of these reactions in presence and absence of external electric field. As we are going to demonstrate that the application of an external electric field in a preferred direction significantly lowers the reaction barrier for the PCET processes whereas electric field has very negligible effect on the reaction barrier for the HAT processes. The H-abstraction processes via HAT/PCET is a fundamental reaction which has been observed in numerous biological processes.[5] Hence it is of great interest to investigate their mechanisms, especially in presence of electric field, which has huge significance as under enzymatic condition proteins are shown to exhibit intrinsic electric field.[8]

Chapter 2

Literature Review

Mayer and his co-workers illustrated mechanism of1the degenerated hydrogen1atom transfer using the DFT method.[2] where they considered the behavior of three type of reaction (i)) benzyl radical and1toluene (ii) methoxyl1radical and methanol (iii) phenoxyl1radical and phenol. The TS of benzyl/toluene hydrogen exchange reaction has C_{2h} but the transition structure of methoxyl/methanol has C_2 symmetry. They have concluded that the first two reactions follow HAT whereas PCET is followed for the reaction of phenoxyl1radical and phenol.[2] **Borden** and his co-workers have performed a density functional theory calculation on phenoxyl with phenol and α napthol also ethanoxyl with ethanol by applying B3LYP and MPW1K method[9]. The comparison shows that the MPW1K gives good result than B3LYP because the MPW1K method calculates the barrier height more accurately than the B3LYP for HAT and PCET mechanisms.[9]

Miller *et. al.* discussed the origins, development, and evolution of the PCET processes mostly linked to applications in organic synthesis.[10] They emphasize on the fact that the PCET can provide a non-classical mechanism for homolytic bond activation under reasonably mild catalytic conditions.[10]

Hummer *et. al.* proposed that a bronsted analysis might distinguish the ground-state PT (proton transfer) and excited state PCET processes.[11] In a theoretical study, **Tantawy *et. al.*** found that water-boryl acid act as a proton coupled electron transfer reagent for its reactions with carbon dioxide, formic acid and formaldehyde, respectively.[12] The elucidated mechanism revealed that the variation in the accompanied activation energy was attributed to the stereo-electronic effect mutually in CO_2 and HCOOH as compared to HCHO.[12]

Hammes-Schiffer and her co-workers have found that the HAT and PCET mechanisms can be differentiated by the analysis of frontier molecular orbitals and topographical characteristics of the potential energy surfaces.[3]They also formulated a more quantitative diagnostic for distinguishing between HAT and PCET in terms of electronically adiabatic and nonadiabatic proton ransfer, respectively. The degree of electron-proton in non-adiabaticity can be evaluated with a semiclassical formalism.[3]

Sason shaik and his co-workers described that HAT/PCET reactivity in various non-heme oxidant complexes like Fe^{IV}–oxo and Fe^{III}–oxo complexes with different substrates[4], such as 9,10 dihydroanthracene, dimethyl formamide etc. They found that for the N-H and O-H activation processes, the change in energy is much superior to the C-H activation reaction. They concluded that the lower barrier for N-H and O-H activation, which follows PCET mechanism, is due to the presence of stabilizing interaction in the transition state fragments.[4]

Coote and her co-workers identified that the polarization and directionality have great role in stabilizing the radical reaction by applying electric-field.[9] They show that electric field leads to lower the bond dissociation energy as well as it decreases the barrier of radical reaction.[9]

In a combined experimental and theoretical study, **Tony *et. al.*** probed the role of electrostatic interaction in enzyme catalysis while the enzymes are binding to the ligand. They gave an example of Escherichia coli dihydrofolate reductase which shows that the change in electrostatic interaction increases the nitrile stretching frequencies.[8] In this study, they calculated the contributions of intrinsic electric fields along the CN axes by decomposing them for specific residues, ligands and solvent molecules that make up the microenvironments around the probes. Moreover, calculation of the electric field along the hydride donor−acceptor axis along with decomposition of this field into specific contributions indicate that the cofactor and substrate as well as the enzyme impose a substantial electric field that facilitates hydride transfer.[8]

Chapter 3

3.1 Computational Methodology

To probe the mechanisms of the five H-abstraction reactions, we carried out the calculations based on density functional theory (DFT). All of the calculations were carried out with Gaussian 09 suite of programs.[13] Unrestricted DFT calculations were performed using Becke's three parameter function and the correlation function of Lee ,Yang and Parr.[14] UB3LYP method and 6-31+G* basis set was used for all the calculations.[15] MPW1K method was also used to see the better energy calculations.[16] For the external electric field (EEF) calculations the direction of the EEF was chosen along the reaction coordinate that is along the direction of H-atom transfer. In all calculations regarding the EEF the z-axis was kept fixed along the reaction coordinate. The strength of the applied EEF is 0.102 V $Å^{-1}$ Natural bonding orbital (NBO) charge densities were obtained with NBO 3.0 implemented in G09 program.[17] All the energies include zero point energy (ZPE) corrections and the frequencies of all the optimized structures were calculated to ensure the nature of stationary points.

The effect of EEF on the activation energy barrier of HAT/PCET was analyzed by Valence Bond State Correlation Diagram VBSCD. The NBO charges with 6-31+G* basis set were evaluated to estimate the charge separation between the H-donor and H-acceptor in the TS of the HAT/PCET reaction in the presence and absence of external electric field. All the inputs for EEF calculation was created in the z-matrix format. We used a Chemcraft 1.8 to view the structures and also the SOMO interactions which are responsible for the electron transfer.

Chapter 4

Objectives

1) To demonstrate the effect of EEF on HAT and PCET process

2) To explain the interaction of the ionic and covalent state for HAT and PCET and their role in catalyzing the aforementioned processes under the EEF

Chapter 5

Results and discussions

We have studied the effect of EEF on the activation energy of HAT/PCET by considering five different reactions out of which two reactions are shown to follow PCET mechanism and rest of the three reactions follow HAT process. A list of all these five reactions is given below along with the types of mechanisms they follow.

1) Phenoxyl /phenol self-exchange reaction (PCET)

2) *p*-methyl phenoxyl/ phenol (PCET)

3) Benzyl/Toluene self-exchange reaction (HAT)

4) Methoxy/methanol self-exchange reaction (HAT)

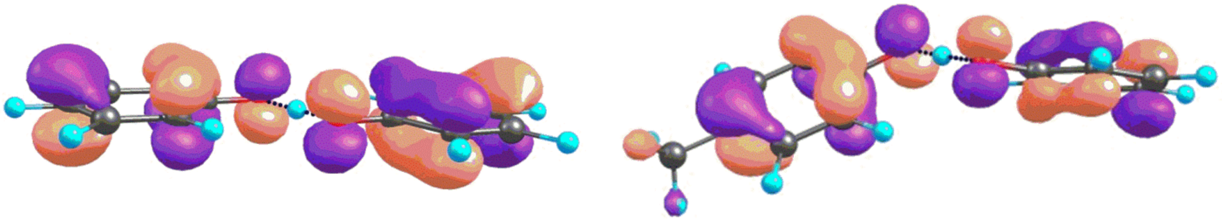
5) *p*-nitro-Benzyl/toluene (HAT)

To investigate the effect of electric field in case of PCET reaction we have identified two reactions which show PCET mechanism. The first one is a symmetrical reaction between phenol and phenoxyl radical and the other one is unsymmetrical reaction between p-methyl phenoxyl radical and phenol. The H-abstraction process for phenoxyl/phenol is shown in Scheme 1 where the phenoxyl radical acts as H-acceptor and the phenol acts as H-donor. On the other hand the H-abstraction reaction scheme for p-methyl phenoxyl/phenol is shown in Scheme 2.

Scheme 1: The hydrogen abstraction reaction by phenoxyl radical from phenol. The important distances are given in angstrom.

Scheme 2: The hydrogen abstraction reaction by p-methyl phenoxyl radical from phenol. The important distances are given in angstrom.

While looking at the SOMOs of the respective TSs for both the reactions which are shown in Figure 3, we can see that all the SOMOs have the characteristic feature of PCET.



(a) (b)

Figure 3: SOMOs of the transition states of the H-abstraction reaction of (a) phenoxyl/phenol (b) p-methyl phenoxyl/phenol.

The activation barrier for H-abstraction for phenoxyl/phenol is 7.25 kcal mol^{-1} and the barrier for *p*-methyl phenoxyl/phenol is 6.36 kcal mol^{-1}. The free energy profiles of phenoxyl/phenol and *p*-methyl phenoxyl/phenol are shown in Figure 4 and 5**.** Application of EEF of strength 0.002 a.u. in the direction along the reaction coordinate (along the direction of the H abstraction) decreases the barriers of both reactions significantly. In case of phenoxyl/phenol (symmetrical reaction) the barrier decreases to 4.70 kcal mol^{-1} and for *p*-methyl phenoxyl/phenol barrier decreases to 1.28 kcal mol^{-1}.

Figure 4: Free energy profiles for the H-abstraction reaction by phenoxyl radical from phenol calculated at B3LYP/6-31+G(d) level of theory.

Figure 5: Free energy profiles for the H-abstraction reaction by *p*-methyl phenoxyl radical from phenol calculated at B3LYP/6-31+G(d) level of theory.

To investigate the effect of electric field in case of HAT reaction we have identified three reactions which show HAT mechanism. We have considered two symmetrical reactions which are benzyl/toluene and methoxy/methanol and the other one is unsymmetrical reaction which is *p*-nitro-benzyl/toluene. The H-abstraction processes for these three reactions are shown in Schemes 3-5 where the reactants, TSs and products for each reaction are mentioned.

Scheme 3: The hydrogen abstraction reaction by benzyl radical from toluene.The important distances are given in angstrom.

Scheme 4: The hydrogen abstraction reaction by methoxy radical from methanol. The important distances are given in angstrom.

Scheme 5: The hydrogen abstraction reaction by *p*-nitro benzyl radical from toluene. The important distances are given in angstrom.

While looking at the SOMOs of the respective TSs for all the three reactions which are shown in Figure 6, we can see that all the SOMOs have the characteristic feature of HAT except for the methoxy/methanol (Figure 6b) which shows mixed PCET/HAT character.

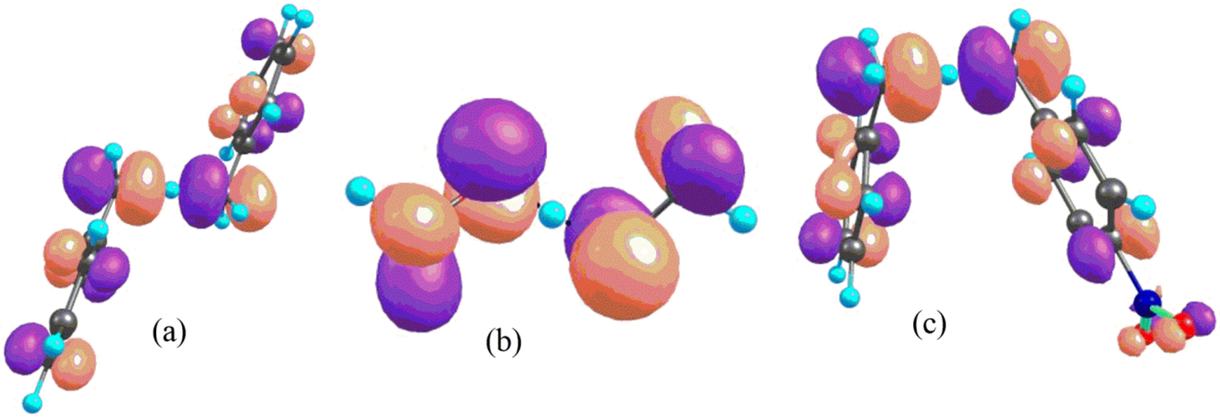


Figure 6: SOMOs of the transition states of the H-abstraction reactions of (a) benzyl/toluene (b) methoxy/methanol (c) *p*-nitro benzyl toluene

The activation barrier for H-abstraction for benzyl/toluene is 20.78 kcal mol^{-1} and the barrier for the same for *p*-nitro benzyl/toluene is 20.98 kcal mol^{-1}. The H-activation barrier for the methoxy/methanol is quite small (8.40 kcal mol^{-1}) as compared to the previous two cases. The free energy profiles for these three reactions are shown in Figure 7-9. Application of EEF of strength 0.002 a.u. in the direction along the reaction coordinate (along the direction of the H abstraction) does not affect the barriers of these three reactions significantly. In case of benzyl/toluene (symmetrical reaction) the barrier is 19.99 kcal mol^{-1}, for *p*-nitro benzyl/toluene barrier is 21.9 kcal mol^{-1} whereas for methoxy/methanol the barrier is 7.59 kcal mol^{-1}.

Figure 7: Free energy profile for H-abstraction reaction by benzyl radical from toluene calculated at UB3LYP/6-31+G(d) level of theory.

Figure 8 : Free energy profile for H-abstraction reaction by methoxy radical from methanol calculated at UB3LYP/6-31+G(d) level of theory**.**

Figure 9: Free energy profile for H-abstraction by p-nitro benzyl radical from toluene calculated at UB3LYP/6-31+G(d) level of theory.

When we compare the activation energies of the all five reactions that we have studied we found that the application EEF along the reaction coordinate significantly reduces the barriers for those reactions which follows PCET mechanism, whereas HAT barriers remain almost unaffected by the EEF. Below are the tables (Table 1 and Table 2) which summarize the activation energies for these two types of reaction in presence and absence of the EEF.

Table 1: Free energy of activation ($\Delta G^{\ddagger}$) and reaction energy (ΔG_r) for the HAT processes which are considered in this study calculated at B3LYP/6-31+G* level of theory.

Sr. No	**Reaction**	**Reaction condition**	**$\Delta G^{\ddagger}$ (kcal mol^{-1})**	**ΔG_r (kcal mol^{-1})**	**Reaction Condition**	**$\Delta G^{\ddagger}$ (kcal mol^{-1})**	**ΔG_r (kcal mol^{-1})**
1	Methoxy/Methanol	Without EEF	8.40	0.0	With EEF	7.56	-2.14
2	Benzyl/Toluene		20.78	0.0		19.94	-2.00
3	*p*-Nitro-benzyl/Toluene		20.98	-0.77		21.95	-1.02

Table 2: Free energy of activation ($\Delta G^{\ddagger}$) and reaction energy (ΔG_r) for the PCET processes which are considered in this study calculated at B3LYP/6-31+G* level of theory

Sr. No	**Reaction**	**Reaction condition**	**$\Delta G^{\ddagger}$ (kcal mol^{-1})**	**ΔG_r (kcal mol^{-1})**	**Reaction Condition**	**$\Delta G^{\ddagger}$ (kcal mol^{-1})**	**ΔG_r (kcal mol^{-1})**
1	Phenoxyl/Phenol	Without EEF	7.25	0.0	With EEF	4.70	-4.43
2	*p*-methyl phenoxyl/Phenol		6.36	-1.78		1.29	-7.22

To explain the effect of EEF on the activation energy barriers for HAT/PCET processes we have considered the archetypical valance bond state correlation diagram as shown in Figure 10.

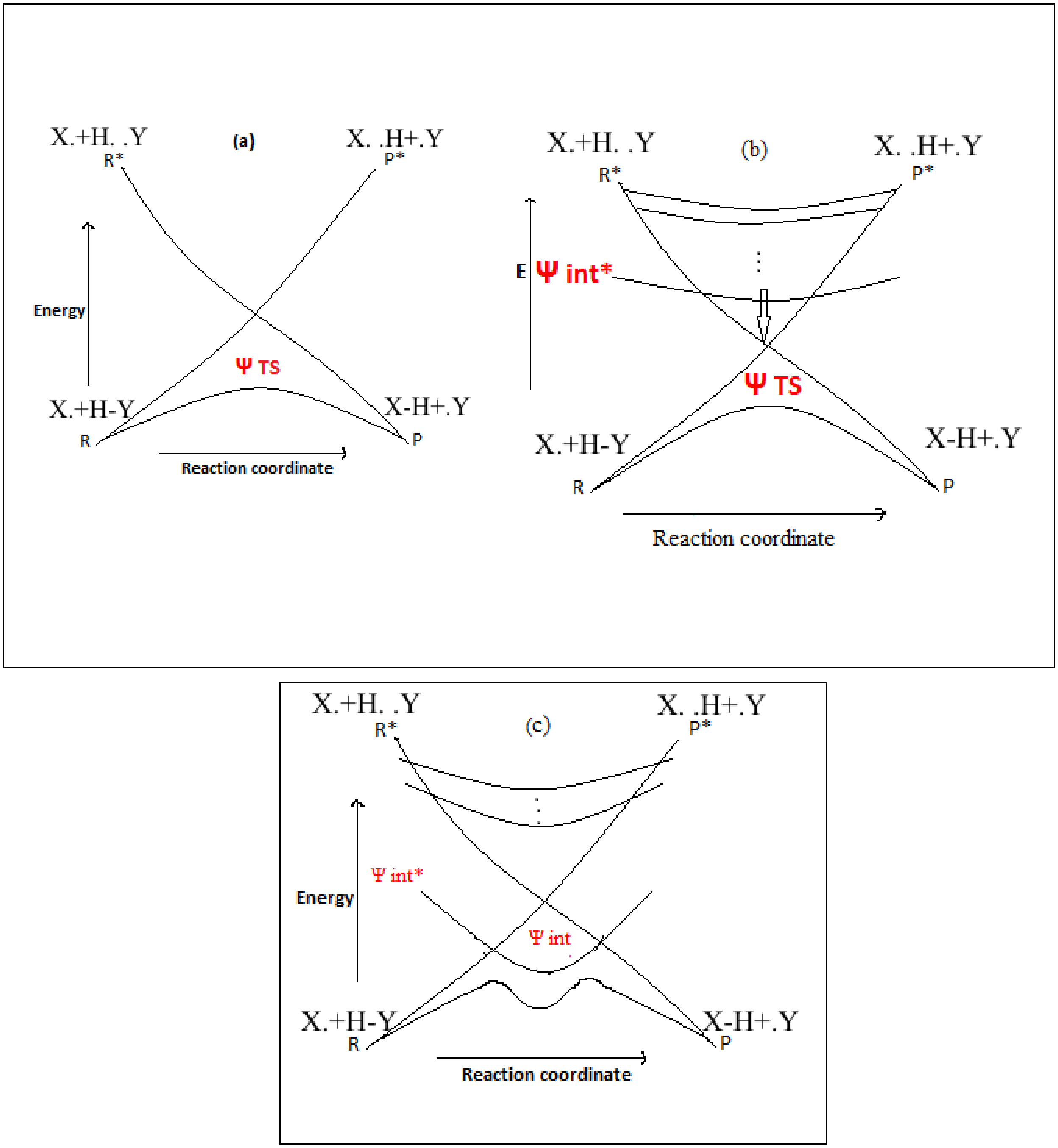


Figure 10: Valance Bond State Correlation Diagram (VBSCD) (a) When there are no ionic state, (b) ionic states mixes with covalent state to stabilize the TS, (c) ionic states mixes with covalent state to generate an intermediate for H-abstraction reaction.

In this valance bond correlation state diagram, Figure 10a defines that there is only covalent character in the transition state and there is no ionic state which can mix with the covalent states. Such type of diagram is valid for HAT reaction. Here curve (R) stands for reactant and (P) stands for product, where R* and P* are the electronic images of excited reactant and product states. In Figure 10(b) Ψint* acts as an ionic state which can mix with the covalent state which in turn decreases the energy of the transition state and hence gives rise to lower activation energy as compared to the case shown in Figure 10a. This type of diagram is suitable for PCET. In figure 10c, there is a formation of an intermediate as the ionic state which can go down to the principle curve and form two types of transition state.

In case of PCET, when we apply external electric field (EEF), the electric field stabilizes the ionic-state. The stabilization of the ionic state leads to more chance of inter-mixing of covalent state and ionic state which causes the increase in the resonance energy of the transition state and also stabilizes it. Thus we observe a decrease in the activation energy barrier for the PCET process while an external electric field is applied in a preferred direction. We can validate this theory by comparing the NBO charges of H-donor and H-acceptor of a PCET process at the transition state in presence and absence of EEF. We have observed an increase in the charge separation from 0.448 to 0.526 between the H-donor and H-acceptor in the TS for the phenoxyl/phenol reaction as we apply an EEF. The higher charge separation between the H-Donor and H-acceptor in the TS in presence of applied external electric field suggest that the TS gains more ionic character. The higher ionic character in the TS in presence of EEF indicates the higher mixing of the ionic state with the covalent state which validates our theory. The tables (Table 3 and 4) shown below provide the charge separation between the H-Donor and H-acceptor for all five reactions in presence and absence of EEF. As we have seen earlier that H-abstraction barrier for the HAT processes remain unaffected by EEF can be rationalized from the NBO charges show in Table 4. We have observed that all three HAT reactions have very less charge separations between the H-donor and H-acceptor in their corresponding TSs.

Table 3: NBO charges of the H-donor and H-acceptor in the TS of different PCET reactions

		Without EEF			With EEF		
Sr. No	**Reaction name**	**H donor**	**H acceptor**	**Charge separation**	**H donor**	**H acceptor**	**Charge separation**
1	Phenoxyl/Phenol	0.224	-0.224	0.448	0.262	-0.264	0.526
2	*p*-methyl Phenoxyl/PhOH	0.291	-0.291	0.582	0.359	-0.357	0.716

Table 4: NBO charges of the H-donor and H-acceptor in the TS of different HAT reactions

		Without EEF			With EEF		
Sr. No	**Reaction name**	**H donor**	**H acceptor**	**Charge separation**	**H donor**	**H Acceptor**	**Charge separation**
1	Benzyl/toluene	0.124	-0.125	0.249	0.126	-0.125	0.251
2	Methoxy/Methanol	0.256	-0.255	0.511	0.272	-0.271	0.543
3	*p*-nitro-benzyl/toluene	0.07	-0.068	0.13	0.035	-0.035	0.07

Results shows that the charge separation of H-donor and H-acceptor in the transition state of PCET will be more. By comparison between without EEF reactions and with EEF reactions. Where HAT will show similar type of charge separation in both the cases .which state that HAT will unaffected by applying EEF.

Chapter 6

Conclusions

We have studied the effect of external electric field on the activation energy for the H-abstraction reaction of two types, namely HAT and PCET by using DFT method. We have considered five different H-abstraction reactions for this study in which three of them follow HAT and the other two follow PCET. We have observed the lowering of H-abstraction barrier for both the PCET reactions once the EEF is applied whereas the EEF does not affect the activation energies of the HAT processes. The above observation is explained by using valence bond state correlation diagram and NBO charges of the H-donor and H-acceptor in the TS. It is found that the EEF stabilizes the ionic states of the TS for PCET process which in turn reduces the energy of activation energy. This result has strong implications on many biological processes where the H-abstraction process is one of the key steps for many oxidative processes.

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Supporting Information

In order to supporting the results, the Spin densities value of HAT/PCET reactions with respect to their individual atom of the TS (transition - state) have study in the table S1 to S5.

Table S1 :- Spin Densities of Benzyl radical/Toluene in the presence or absence of EEF

Spin Densities of atom in the absence of EEF	
Atoms	**Spin Density**
H1	-0.087
C2	0.479
C3	0.132
C4	-0.071
C5	-0.071
H6	0.002
C7	0.119
C8	0.119
H9	-0.005
H10	-0.005
C11	-0.113
H12	-0.006
C13	0.479
H14	-0.018
H15	0.002
H16	-0.018
H17	-0.018
H18	-0.018
C19	-0.113
C20	0.119
C21	0.119
C22	-0.071
C23	-0.071
C24	0.132
H25	-0.005
H26	-0.005
H27	0.002
H28	0.002
H29	-0.006

Spin Densities of atom in the presence of EEF	
Atoms	**Spin Density**
C1	0.474
H2	-0.087
C3	0.135
C4	-0.073
C5	-0.072
H6	0.002
C7	0.119
C8	0.122
H9	-0.005
H10	-0.005
C11	-0.115
H12	-0.006
C13	0.484
H14	-0.019
H15	0.002
H16	-0.018
H17	-0.018
H18	-0.019
C19	-0.112
C20	0.118
C21	0.115
C22	-0.070
C23	-0.070
C24	0.130
H25	-0.005
H26	-0.005
H27	0.002
H28	0.002
H29	-0.005

Table S2 :- Spin densities of Methoxy/methanol in the presence or absence of EEF

Spin densties of atom in the absence of EEF	
Atom	**Spin Density**
C1	-0.014
H2	0.001
H3	0.018
H4	0.042
O5	0.473
H6	-0.045
O7	0.473
C8	-0.014
H9	0.018
H10	0.042
H11	0.001

Spin densties of atom in the persence of EEF	
Atom	**Spin Density**
C1	-0.045
O2	0.499
C3	-0.012
H4	0.001
H5	0.017
H6	0.040
O7	0.446
C8	-0.015
H9	0.019
H10	0.046
H11	0.002

Table S3 :- Spin densities Nitro benzyl radical/toluene in presence or absence of EEF

Spin densities of TS in absence of EEF	
Atoms	**Spin Density**
C1	-0.082
H2	0.477
C3	0.112
C4	-0.064
C5	-0.060
C6	0.002
H7	0.109
C8	0.113
C9	-0.004
H10	-0.004
H11	-0.104
C12	0.432
H13	-0.018
H14	0.002
H15	-0.017
H16	-0.017
H17	-0.018
C18	-0.112
C19	0.120
C20	0.122
C21	-0.076
C22	-0.074
C23	0.138
H24	-0.005
H25	-0.005
H26	0.002
H27	0.002
H28	-0.006
H29	-0.002
O30	0.021
O31	0.020

Spin densities of TS in presence of EEF	
Atoms	**Spin Density**
C1	0.427
H2	-0.083
C3	0.483
C4	0.106
C5	-0.061
C6	-0.056
H7	0.002
C8	0.104
C9	0.107
H10	-0.004
H11	-0.004
C12	-0.095
H13	-0.018
H14	0.002
H15	-0.018
H16	-0.017
H17	-0.018
C18	-0.111
C19	0.119
C20	0.1237
C21	-0.076
C22	-0.073
C23	0.139
H24	-0.005
H25	-0.005
H26	0.002
H27	0.002
H28	-0.006
H29	-0.002
O30	0.020
O31	0.019

Table S4 :- Spin densities of para-methyl phenoxyl radical/ phenol in the absence or presence of EEF

Spin densities of TS in absence of EEF	
Atoms	**Spin Density**
C1	-0.061
C2	0.132
C3	0.218
H4	-0.006
C5	0.001
C6	-0.084
H7	0.002
C8	0.141
H9	-0.006
H10	0.001
O11	0.180
H12	-0.008
O13	0.183
C14	-0.014
C15	0.141
C16	0.137
C17	-0.075
C18	-0.083
C19	0.215
H20	-0.006
H21	-0.006
H22	0.002
H23	0.002
H24	-0.009
C25	-0.018
H26	0.000
H27	0.008
H28	0.011

Spin densities of TS in Presence of EEF	
Atoms	**Spin Density**
O1	0.183
H2	-0.008
C3	-0.072
C4	0.147
C5	0.237
H6	-0.006
C7	0.016
C8	-0.072
H9	0.002
C10	0.129
H11	-0.006
H12	0.001
O13	0.175
C14	-0.022
C15	0.134
C16	0.128
C17	-0.073
C18	-0.077
C19	0.194
H20	-0.006
H21	-0.006
H22	0.002
H23	0.002
H24	-0.008
C25	-0.019
H26	0.012
H27	0.011
H28	0.000

Table S5 :- Spin Densities of phenoxyl radical / Phenol in the absence or presence of EEF

Spin densities of TS in absence of EEF	
Atoms	**Spin Density**
C1	-0.078
C2	0.144
C3	0.224
H4	-0.006
H5	-0.009
C6	-0.010
C7	-0.086
H8	0.002
C9	0.142
H10	-0.006
H11	0.002
O12	0.186
H13	-0.008
O14	0.186
C15	-0.010
C16	0.144
C17	0.142
C18	-0.078
C19	-0.086
C20	0.224
H21	-0.006
H22	-0.006
H23	0.002
H24	0.002
H25	-0.009

Spin densities of TS in the presence of EEF	
Atoms	**Spin Density**
O1	0.157
H2	-0.008
C3	-0.067
C4	0.122
C5	0.198
H6	-0.005
H7	-0.008
C8	-0.004
C9	-0.075
H10	0.002
C11	0.124
H12	-0.005
H13	0.002
O14	0.217
C15	-0.017
C16	0.166
C17	0.160
C18	-0.089
C19	-0.097
C20	0.249
H21	-0.007
H22	-0.007
H23	0.002
H24	0.003
H25	-0.011

Figure 11: Arrangement of atom in the transition states ,to demonstrate the numbering of reaction axis which quantified with Table S1 to S5 in the absence or presence of EEF for HAT/PCET reactions.