

Effects of Oriented External Field in Organic Reaction

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ABSTRACT

In this chapter, the improvement of the kinetics and thermodynamics of chemical reactions will be reviewed, which have a crucial role in the applied oriented external electric field (OEEF). Also, it is studied that OEEF has catalytic activity in some organic reaction mechanisms and the ability to cleavage hemolytic bonds in a heterolytic way. The use of the Nitroxide radical in the presence of time-dependent fluorescence spectroscopy, the use of Radical mediated Polymerization, and so on are also being investigated. Again, OEEF has a budding area of research, waiting for eventual blossom. In this context, the chemical bond breaking, bond dissociation energy, product selectivity, and how OEEF catalyzes the reaction will be discussed, as well as an overview of fluorescent spectroscopy.

Keywords: Reaction Mechanism; Nitroxide Radical; External Orientation Field

INTRODUCTION

The electron transfer reaction facilitated molecular geometry changes, bonding, and bonding interaction in the presence of an external electric field, affecting homonuclear bonds, heteronuclear bonds, bonds, as well as bond dissociation energy, spin state crossover, and methyl transfer (Menshutkin Reaction). A quantum mechanical concept governs the principle of the external electric field (EEF). EEF along the 'Bond axis' and the 'Reaction axis' facilitated bond breaking and electron pairing changes from reactant to product, respectively. Oriented external electric field (OEEF) provides chemical reaction regioselectivity and allowed the forbidden orbital mixing (Shaik *et al.*, 2018). In we consider a Hydrogen atom, where quantum level $n=2$ is considered, hydrogen possesses four degenerate orbitals that are $2s$, $2p_x$, $2p_y$, $2p_z$ (Shaik *et al.*, 2018). In absence of external electric field all the four levels are degenerate that is they are mutually orthogonal to each other. If OEEF applies along Z-axis $2p_x$, $2p_y$ levels/states remain the same as there is no z-component in $2p_x$, $2p_y$ states split widely, one above and another below the $2p_x$, $2p_y$ orbitals, where $2s$ and $2p_z$ Show mixed hybrid orbitals. Removal of forbiddance is due to the expectation value of the orbital interaction is no longer zero in presence of the z-oriented field.

As the F_z (electric field operator) and z axis have the same symmetry. In this case, it will discuss the space field effect. In presence of OEEF along the z-direction bond axis develops some charge polarization due to the hybridization of σ_g bonding and σ_u^* antibonding orbitals of the bond. This mixing is forbidden in absence of field. At particular field strength the charged species is stabilized, and this stabilization is proportional to the dipole moment of the ion pair.

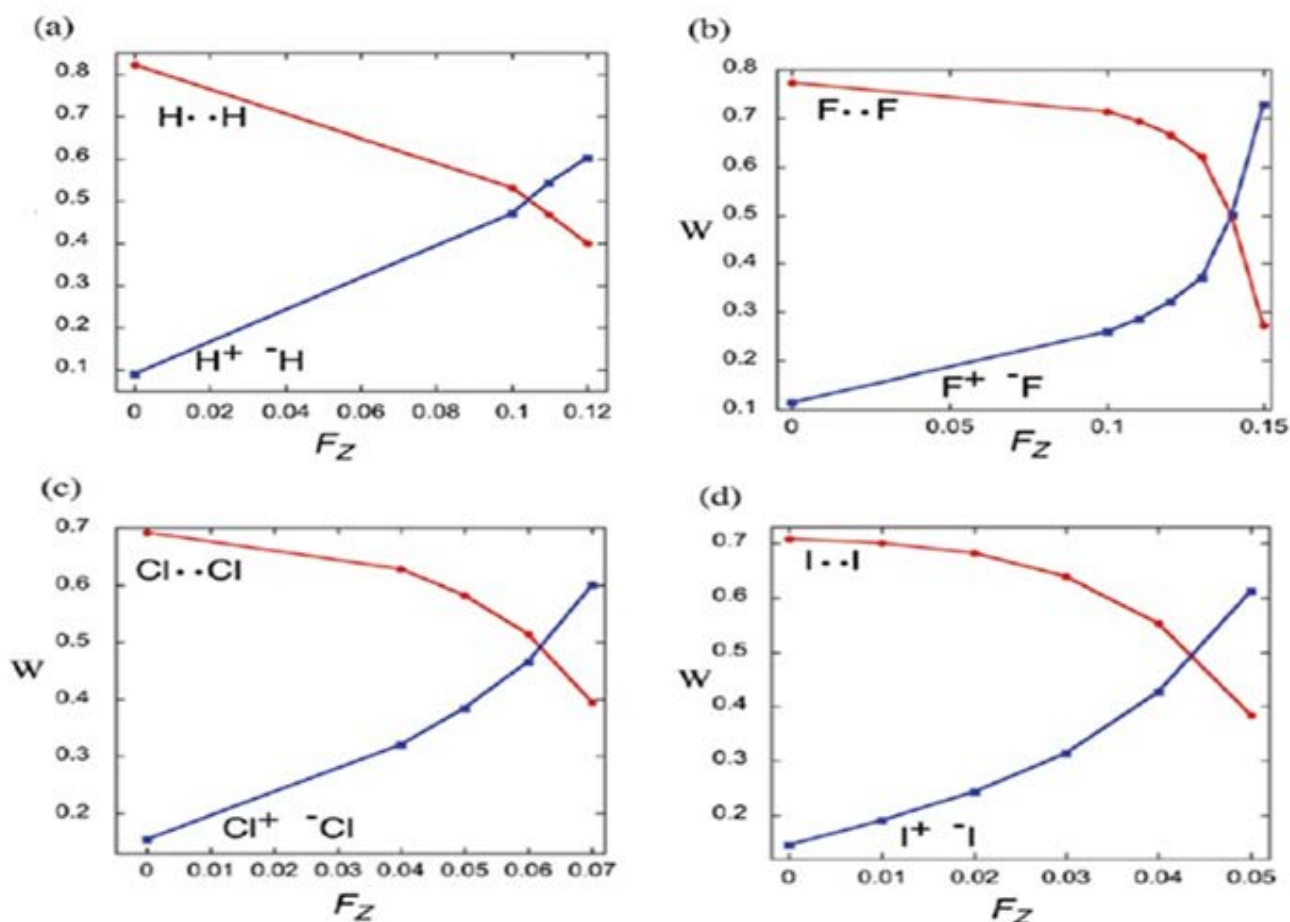
LITERATURE REVIEW

The homonuclear bond cleavage:

The homonuclear bonds undergo heterolysis under increasing OEEF along the bond axis. All bonds elongated and dissociated into ions. i.e $X^+ X^-$ at a certain electric field. This dissociation basically based upon two parameter i.e the difference between ionization energy (IE) and electron affinity (EA) and this difference determines the polarizability of the bond. Now the weight of ionic and covalent structure will be considered corresponding to the bond wave function. In absence of electric field along z axis $F_z=0$ then the bonds are primarily covalent with increasing F_z (i.e electric field along the z- direction)

covalent ionic crossover happens. OEEF can control a variety of named reaction called Diel's alder reaction (Yu *et al.* 2021), Menshutkin reaction etc.

Ionic structure becomes more prominent with the increase in the electric field and overrides the weight of covalent structure. At particular field strength the bond becomes ionic and heterolyze without barriers. (Shaik, Mandal & Ramanan, 2016) For example, H-H, F-F, Cl-Cl, I-I bond will dissociate at field strength stronger than 0.1 au. (Shaik *et al.*, 2018). Off course the difference between IE and EA and hence corresponding polarisability determines the actual critical field at which the bond heterolysis occurred. Na-Na, Li-Li bonds needs much lower fields to dissociate into ions. The figure 1 explained the weight of covalent-ionic structure for bonds under Z-OEEF along the bond axis.



Source: Shaik *et al.*, 2018

Figure 1: Plots of weight of covalent-ionic structure for bonds under Z OEEF along the bond axis

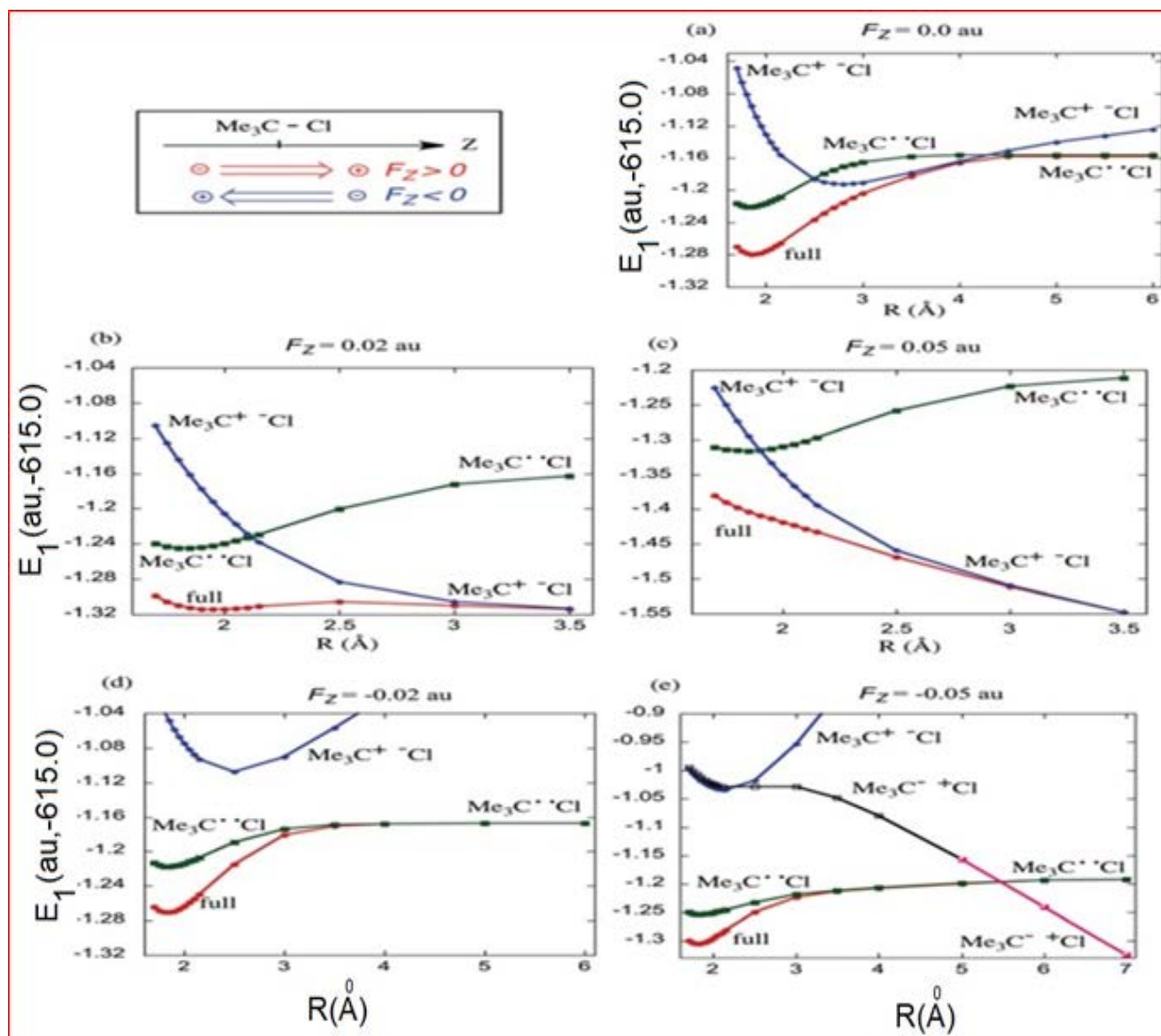
π bond cleavage in presence of OEEF:

In 1859, Breakage of π in OEEF has completely different consequence than in σ bond. When π -bond of ethylene $CH_2=CH_2$ is broken, due to the rotation of C-C bond the C-C bond elongates so that, the dipole moment that is created by the respective ionic structure varies significantly. Experimentally, it is observed that ionic structure ($CH_2^+CH_2^-$) in the π bond wave function mildly increases by OEEF. But huge amount of field is required to lower the π ionic structure. If H is replaced by F in ethylene, the positive charge on C that is in ($CF_2^+CF_2^-$) is stabilized by for its π donation. But huge amount of field in laboratory is impractical (Shaik *et al.*, 2018).

Heteronuclear bond cleavage in presence of orientation external electric field:

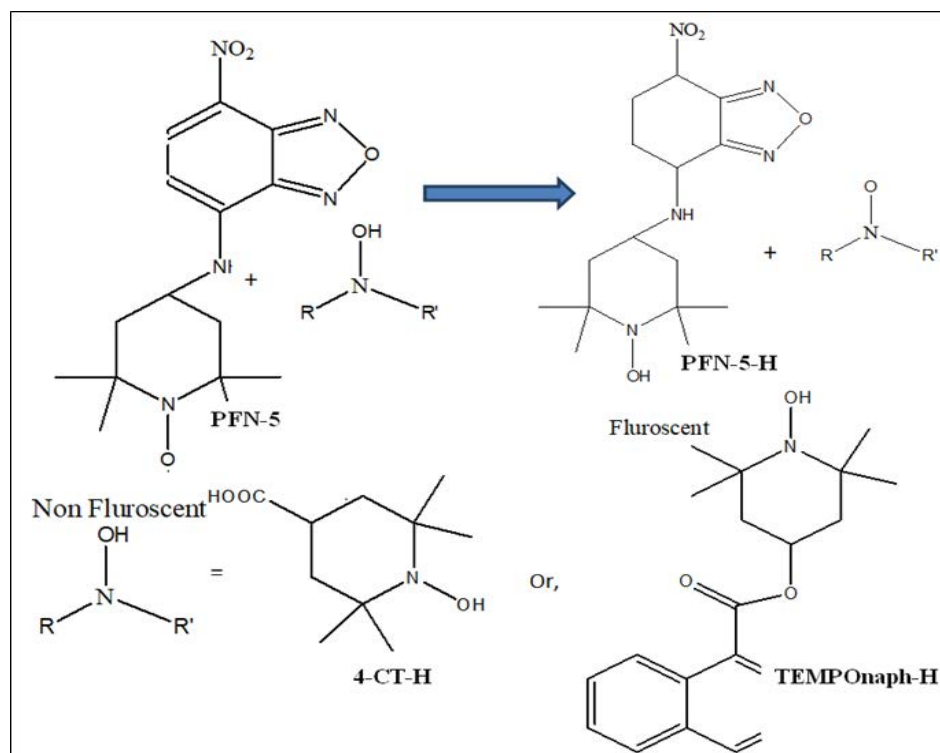
Here, three different types of heteronuclear bonds, i.e., H-Cl, CH_3Cl , Me_3CCl will be considered. In

absence of F_z the covalent bond exists. When F_z field is along the bond axis, H-Cl undergoes bond elongation, then the bond dissociates into $H^+ + Cl^-$ and F_z field applied in the negative direction, the bond shrinks and breaks into opposite ions, $H + Cl^+$. Similarly, the C-Cl bond of CH_3Cl elongates under applied field and breaks into ions $CH_3^+ + Cl^-$. When the opposite direction is applied, the ions break into opposite ions $CH_3^- + Cl^+$. In the case of Me_3CCl , it dissociates, when the electric field is applied into $Me_3C^+ + Cl^-$, whenever the external electric field is applied along the negative Z direction, the ions split into opposite ions i.e. $Me_3C^- + Cl^+$. The figure 2 indicates that the valence bond curves of covalent and ionic structure of C-Cl bond in Me_3CCl . (a) a field free situation, (b) and (c) $F_z > 0$ and (d), (e) $F_z < 0$. The valence bond structures are colored: Green shows covalency, blue shows ionic ($F_z > 0$), Black also shows ionicity but ($F_z < 0$) and red denotes the full wave function.



Source: Shaiket al., 2018

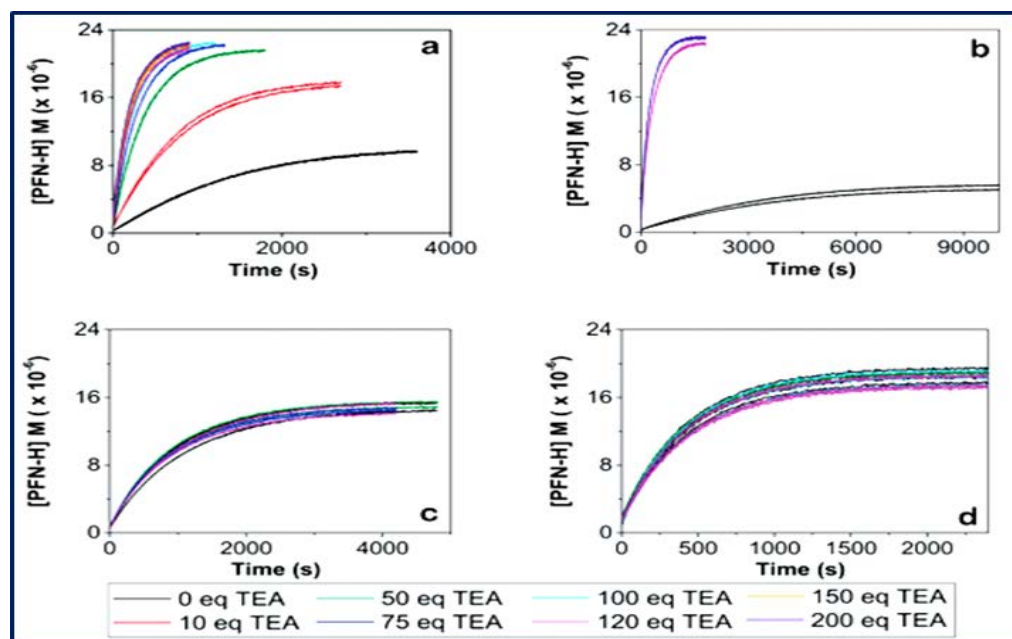
Figure 2: Valence bond curves of covalent and ionic structure of C-Cl bond in Me_3CCl . (a) a field free situation, (b) and (c) $F_z > 0$ and (d), (e) $F_z < 0$. The valence bond structures are colored: Green shows covalency, Blue shows ionic ($F_z > 0$), Black also shows ionicity but ($F_z < 0$) and red denotes the full wave function. i.e., $\psi = C_1\phi_1 + C_2\phi_2$.



Source: Gryn'ova & Coote, 2016

Figure 3: PFN-5H, 4-CT-H, PFN-5, 4-CT

Now Authors have studied the Fluorescence intensity versus Time curve which indicate in the figure 4, Here PFN-5 molecule is Non fluorescent, but PFN-5H molecule is Fluorescent. Fluorescence intensity is shown up to when COOH group of 4-CT molecule is there after a certain time there is no COOH group then a saturation will be seen in the curve with the addition of the base TEA. As no acid remains, it is only noticed the saturated curve of the base. Another study has done with changing the medium of the solvent (Gryn'ova & Coote, 2016).



Source: Klinska et al., 2015

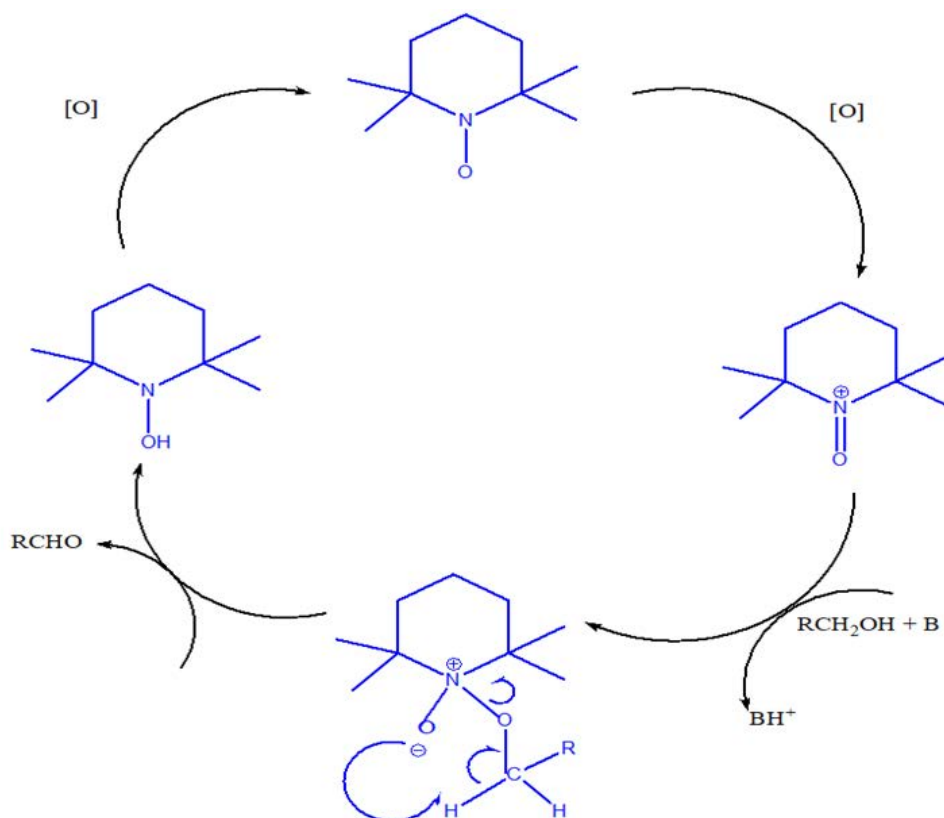
Figure 4: Concentration of PFN-5H vs Time for the addition of TEA at RT, (a) PFN-5 or 4-CT-H in acetonitrile at 25°C (b) the same system at 10°C (c) PFN-5 or 4-CT in acetonitrile at 25°C and (d) PFN-5/TEMPONE-H control in dichloromethane at 25°C

This type of fluorescent intensity vs Time curve surging has broad application in the field of chemistry. The proposed molecule in this study has the same type of property. There have a scope to study that molecule's fluorescent intensity vs time curve.

RESULTS AND DISCUSSION

Application of Nitroxide radical in presence of OEEF:

The figure 5 indicates the scheme. Structure (III) is the polar structure, as N contains the positive charge where O contains the negative charge. Hence, if OEEF is applied in a particular direction (i.e., in a positive direction), this structure will be more stabilized, and the reaction will proceed in a forward direction. Although the TEMPO molecule acts as a catalyst here) OEEF also catalyses the reaction more. By this process, Aldehyde is easily obtained from Alcohol in the presence of a base.



Source: Klinska et al., 2015

Figure 5: Formation of aldehyde from alcohol by using catalyst TEMPO, where OEEF also catalyse the reaction to some extent.

Kinetic Study of reactions accelerated by OEEF:

Polarization is enhanced by resonance stabilization in presence of OEEF which acts as a catalyst (Joy, Stuyver & Shaik, 2020). Where TS is more polar than reactant, It will be needed to apply $F_z > 0$ hence more polarity will stabilize the TS than the reactant and the reaction will be faster, the energy barrier of the reaction can be lowered by this process, and as a consequence, the kinetics of the reactions can be controlled. Importantly, in this case the charges are not optimal for the stabilization of the charge separated resonance contributors to the transition state. When the same charges are placed, they appear in the substrate bound crystal structure, the effects reinforce each other, observe significant catalytic activity. To explore the net effect of charge on radical reaction one can consider a series of Hydrogen transfer reaction and investigate the effect of charge on the TS axis of symmetry

The polar effects of radical reactions will now be considered in the context of standard physical organic chemistry.

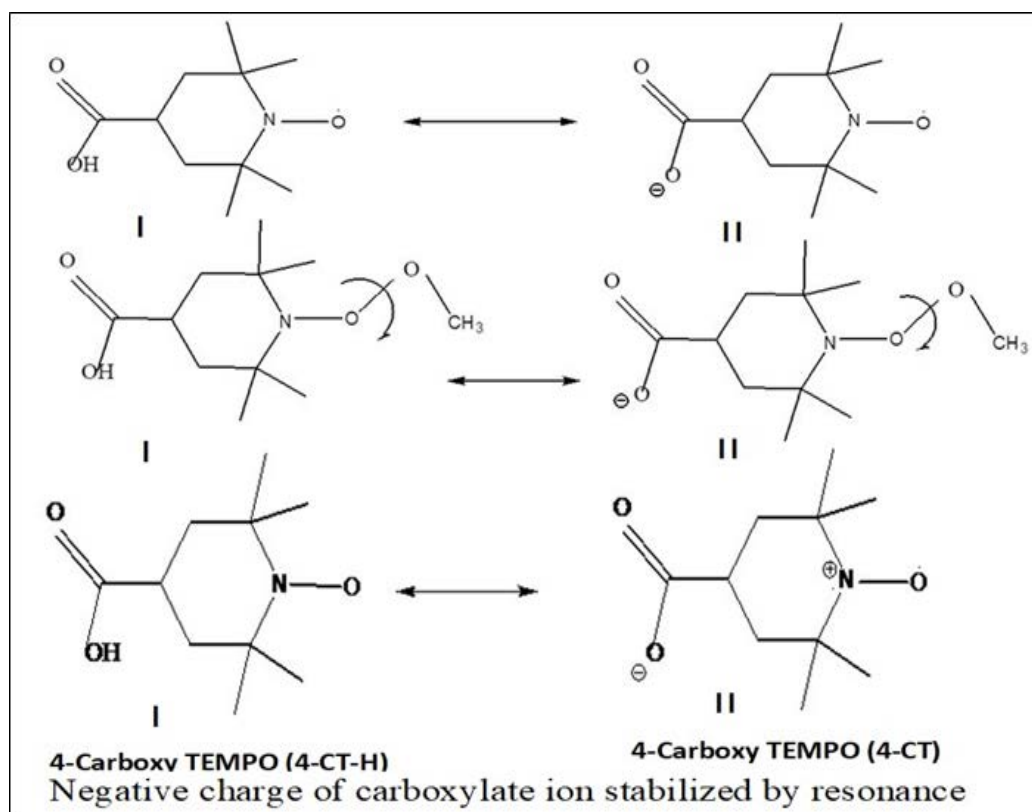
There are three types of polar effects are there. Firstly, the interaction between a charged functional group and a radical. This interaction additionally stabilized by resonance. Resonance is restricted when charged functional group is absent or where this charged functional group is replaced by point charge.

Second type of interaction is that where the radical itself is stabilized by valence bond in absence of charge. Here resonance stability can be enhanced by protonation or deprotonating (Gryn'ova & Coote, 2016).

The third type of interaction is the subject matter of this study. Here the resonance stabilization of radical is enhanced or disrupted not via direct orbital interaction but through space electric field effects. It will be said that the third type of polar effect does not require direct orbital overlap and is replicated by replacing the charged functional group with an equivalent external electric field.

Following the above concept, the following mechanism will be proposed, in which resonance is stabilised via space orbital interaction. In the presence of the charge transfer resonance contributor of electrostatic stabilization, the carboxylic acid group leads to significant of the nitroxide radical (which is formed due to breakage of the peroxide bond).

This type of radical formation can be enhanced from other previous method by the addition of peroxide bond which can replace the any electron donating group like CH_3 , C_2H_5 etc. Figure 6 explain the 4-CT molecule stabilize through space interaction, 4-CT-H where OH group is present.



Source: Shaik, Mandal & Ramanan, 2016

Figure 6: 4-CT molecule stabilize through space interaction, 4-CT-H where OH group is present

Bond dissociation energy is lowered in case of (B) Structure due to presence of through space resonance stabilization of carboxylate ion and NO (Nitroxide radical) this is due the effect of deprotonation of the carboxylic group and resonance stabilization is enhanced.

The gas phase room temperature bond dissociation Gibbs free energy decreases from 261.1 to 242.2KJ/mol due to deprotonation of the carboxylic acid group. It is known that with the increase in

proton donation, the medium will be more acidic. Hence this system is called "pH switch".

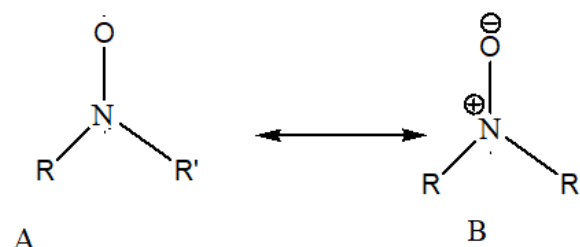
Application of Radical mediated Polymerization:

Nitroxide radical has a wide variety of practical applications. Nitroxide radicals are utilized as spin trap can act as a control agent for free radical polymerization and active species when hindered amine light stabilizers used as a radical trapping antioxidant. It has an application in the redox mediators for dye sensitized solar cell and organic batteries and useful in a variety of imaging and structure determination application. External conditions could be greatly enhanced the utility of nitroxide radicals to manipulate the stability of it. Nitroxide mediated polymerization for the application such as sequence control, block polymerization and end group synthesis can be done by simple pH change (Klinska *et al.*, 2015).

Application of this nitroxide Radical in the field of Chemistry:

Nitroxide radical has a wide variety of practical application. It can act as a effective traps for carbon centered radicals during the self-terminated product formation. Most importantly it can act as a free radical polymerization and are the active species when hindered amine light stabilizers are used as radical trapping antioxidant. In addition they show a redox mediator for dye sensitized solar cells and organic batteries. Nitroxide has the ability to act as a "Radical protecting groups" (Klinska *et al.*, 2015).

By changing the pH in Nitroxide mediated polymerization, it will be able to tune the stability of the radical and can apply it in sequence control, block copolymer synthesis or end group exchange. Figure 7 indicates the two different resonance structures of the nitroxide.



Source: (Klinska *et al.*, 2015)

Figure 7: Resonance contributing structure is B

Here Structure B is more polar than that of structure A. Its effect is strongly dependent on the polarity of the medium, experimental studies shows that while the gas phase pH switches on radical stability should be largely preserved in low polar solvent such as Toluene. The electrostatic pH switches are effectively quenched in water. As in the gas phase solute –solvent interaction is less.

CONCLUSION

OEEF has a budding area of research, waiting for eventual blossom. In this context, the chemical bond breaking, bond dissociation energy, the product selectivity, how OEEF catalyze the reaction, and an overview of fluorescent spectroscopy will be discussed. OEEF can control a variety of named reactions called Diel's alder reaction, Menshutkin reaction, etc. Analysis of radical stabilization in presence of an external electric field can be a potentially useful tool for manipulating the chemical process. By changing the orientation, the ionic charge of the particular ion will be manipulated.

As a consequence, polarizability changes. It can vary from case to case, as it is discussed in the introductory part. The proposal of radical stability through space in the presence of EEF polarity becomes a major parameter in determining the reaction's forward mechanism and future. Although this type of approach has some drawbacks, that is, the field associated with charged functional groups is progressively quenched by polar solvent and lower polarity or lower field is required for the optimum stabilization. All the possibilities are waiting for experimental data, which can be done by computational methodology, which has immense potential in this field.

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