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Influence of Magnetic Field on Electron Transfer Reaction in Homogeneous Medium

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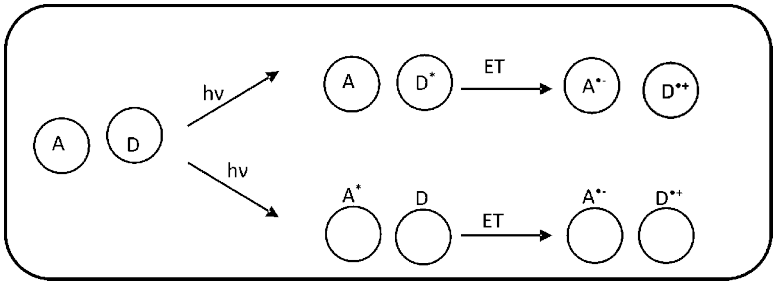
ABSTRACT

The influence of an external magnetic field has energetically very little effect on any reaction. However, during electron transfer reactions, unpaired electrons are generated in the reaction pathway that are susceptible to external magnetic fields. So to understand the mechanism of a reaction, an external magnetic field can be used. To retain the spin correlation between the radicals, either a confined medium like a micelle is required, or the radicals must be covalently attached to each other. However, in the current systems, the radicals are not found in a confined system or covalently bonded; instead, they are attached to each other through non-covalent weak interactions, such as excited-state hydrogen bonding, electrostatic forces of interaction, and hydrophobic interactions. Hence, in such systems, the influence of the magnetic field is watched in a homogeneous medium; that is a rare observation in literature.

Keywords: *Electron Transfer Reactions; Homogeneous; Magnetic Field*

Introduction

The primary reaction on earth, i.e., photosynthesis, which converts solar energy to a utilisable form, involves an electron transfer (ET) process (Stryer, 1999). For many years, scientists were haunted by the challenge of discovering the mechanisms behind the efficiency and control of photosynthesis pathways and various biological processes to replicate those reactions artificially. Photoinduced electron transfer (PET) is one of the fundamental processes in chemistry and biology (Marcus & Sutin, 1985). The most unique aspect of PET is the conversion of light energy into chemical potential. Due to the ubiquitous nature and wide applications of PET reactions,



Scheme 1: A Simplified Outline of the PET Reaction

understanding and controlling them comprise one of the broadest and most flourishing areas of research today.

The PET phenomenon involves photoexcitation of either an electron-rich species (donor, D) or an electron-deficient species (acceptor, A) prior to ET. The following scheme 1, elucidates the process:

The ET between the donor and the acceptor may occur in the singlet state (just immediately after excitation) or may occur in the triplet state (after intersystem crossing from the singlet state). The spin multiplicity of the electron in the excited state is generally conserved during electron transfer, and the memory of this initial spin multiplicity is preserved in the resulting RIP. The nature of the product will depend on its initial spin state; e.g., a singlet-born RIP favours recombination, while a triplet-born RIP prefers escape. However, the spin multiplicity of RIP is not stationary and can coherently evolve between S and T configurations. After the generation of a PET radical ion pair (RIP) or radical pair (RP) that contains unpaired electrons, these pairs become susceptible to an external magnetic field (Gould, Turro & Zimmt, 1984). An applied magnetic field thus alters the fate of the PET reaction by influencing this spin evolution, though it contributes negligibly to the chemical energy.

Photoinduced Electron Transfer Reaction in the Presence of an External Magnetic Field

Immediately after the electron transfer, the new RIP/RPs are sufficiently close so that the singlet-triplet energy difference is significant, making singlet-triplet interconversion impossible. After several diffusive motions, RIP/RPs move apart so that the exchange interaction becomes negligible and singlet-triplet interconversion occurs. On application of an external magnetic field, the degeneracy of the triplet state breaks down, and only the T_0 state remains degenerate with the singlet state, and so intersystem crossing between the $S \rightarrow T_{\pm}$ states no longer remain feasible. Thus, in the presence of a magnetic field, the population of the RIP/RPs increases whether electron transfer occurs in the singlet or triplet state, as spin flipping is required for the $S \rightarrow T_{\pm}$ state, which needs much time and energy. Hence, this study is very crucial in the identification of the RIP/RPs as well as determining the actual mechanistic pathway of an electron transfer reaction, i.e., whether the electron transfer occurs in a singlet or triplet state. Moreover, this method needs optimal closeness between the RIP/RPs, where the exchange integral becomes zero. Excessive closeness between RIP/RPs prevents $S \leftrightarrow T$ inter-conversion due to a significant energy difference from exchange interaction, whereas increased separation between RIP/RPs disrupts the spin correlation. If the donor and acceptor molecules are not covalently linked, then observation of such an effect needs a confined medium like micelles, reverse micelles or vesicles, or a highly viscous solvent at low temperature. In a homogeneous medium, the RIP/RPs disperse more quickly, leading to the rapid disappearance of the spin

correlation between them. In confined systems, after electron transfer occurs, the non-covalently bound RIP/RP can separate slightly due to solvation, resulting in a solvent-separated ion pair where exchange interaction is negligible and intersystem crossing can occur. Hence, due to confinement, the RIP/RPs cannot move far apart where spin correlation is lost. However, non-covalent weak interactions like hydrogen bonding in ground or excited states, electrostatic forces of interaction, stacking, etc., often play a vital role in keeping spin correlation between RIP/RPs. In this review, a few such examples are highlighted, where non-covalent interactions are responsible for maintaining spin correlation in a homogeneous medium.

Radical Ions Associated Through Excited-State Hydrogen Bonding

In its first excited state, Dibenzo[a,c]phenazine (DBPZ) (figure 1) forms hydrogen bonds with various hydrogen bond donating solvents (Dey *et al*., 2007a), a phenomenon that does not occur in its ground state. Upon photoexcitation, the dipole moment of Dibenzo[a,c]phenazine (DBPZ) increases abruptly, resulting in strong hydrogen bonding through its nitrogen atoms. However, the two nitrogen atoms are not very approachable by other molecules due to the presence of hydrogen atoms at 1 and 8 positions. Alcohols with bulkier alkyl groups make less successful hydrogen bonding with DBPZ. Thus, the most efficient excited-state hydrogen bonding is formed with water molecules. This phenomenon is reflected by the enhancement of its fluorescence intensity, with a concomitant red shift from 420 nm to 500 nm compared to non-hydrogen-bonded species in acetonitrile (Figure 2). In the presence of organic amines, photo-induced electron transfer occurs from the amines to DBPZ, resulting in the formation of a radical cation.

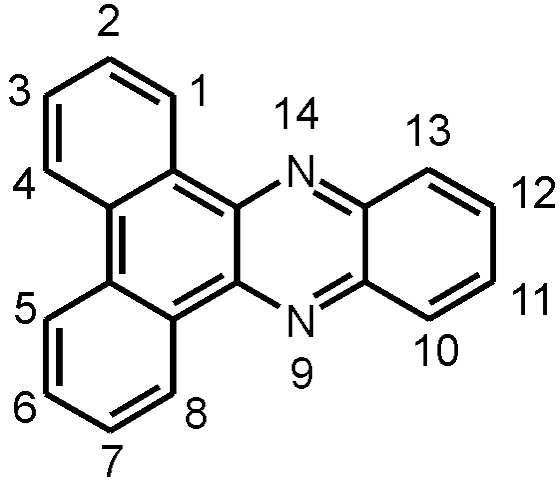


Figure 1: Molecular Structure of DBPZ

The amine and the radical anion of DBPZ are clearly identified in polar solvents, such as acetonitrile (Dey *et al*., 2007b). However, in an acetonitrile-water mixture, those

radical ions remain attached to each other via excited-state hydrogen bonding and show greater intensity in transient absorption spectra in the presence of an external magnetic field. This finding suggests that in the excited state $DBPZ^{\bullet-}$-H_2O-$Amine^{\bullet+}$ remains similar to a linked system via intervening water molecules and shows spin correlation among radical ions even in a homogeneous medium.

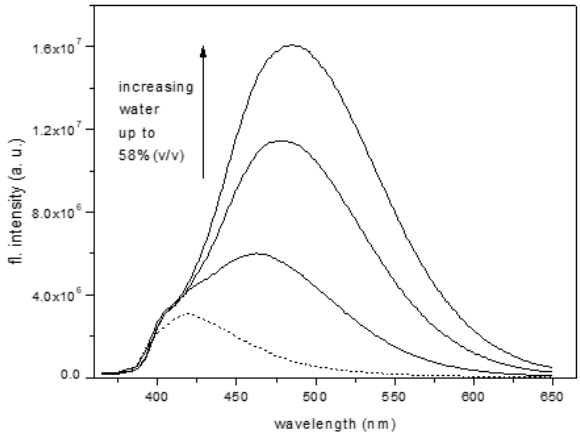


Figure 2: Steady-State Fluorescence Spectra of DBPZ (1 ´ 10-5 M) (lex = 350 nm) in Acetonitrile With Increasing Amounts of Water: 0% (---), 23%, 48%, and 58% (Dey et al., 2007a)

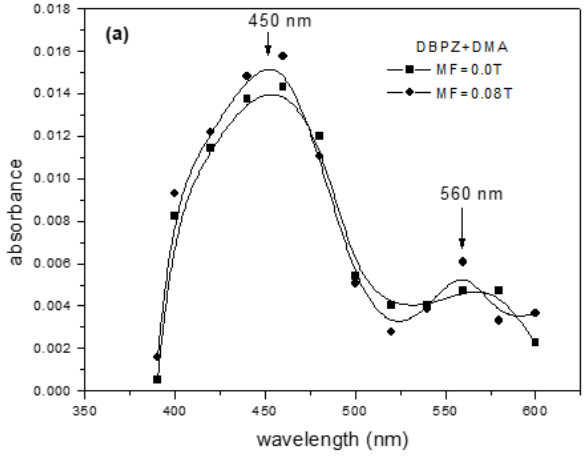


Figure 3: Triplet Transient Absorption Spectra of DBPZ (5´ 10^{-5} M) - DMA (2.5´ 10^{-3} M), in Acetonitrile/H_2O Mixture in Absence (■) and Presence (·) of 0.08 T MF at a delay of 0.6 ms After the Laser Flash (Dey et al., 2007b)

Radical Ions Associated through Non-covalent Weak Interaction

Photoinduced electron transfer reactions are of immense importance in nature, especially during photosynthesis. In living systems, there are innumerable enzymatic reactions that involve electron transfers. Scientists have tried to imitate those in

various environments. The evidence reveals that during the electron transfer reactions, the non-covalent weak interactions, e.g., hydrogen bonding in the ground state, electrostatic attractions, and aromatic ring stacking, etc., play a significant role in maintaining the required distance of separation between the donor and acceptor. They are often present in various drug and DNA interactions and secondarily undergo electron transfer among them. Interaction of transition metal complexes with DNA has attracted scientists since the discovery of cis-platin as an anti-cancer drug. Transition metal complexes primarily interact with double-stranded DNA through electrostatic forces and also undergo electron transfer. Electron transfer among metal complexes and nucleic acids is often initiated by photoinduction. Transition metal complexes with a planar ligand(s) often interact with the base pairs of calf thymus DNA (CT DNA), possibly through partial intercalation. Initially the positively charged complex and the poly-negatively charged DNA come closer due to the electrostatic force of interaction. Then, the insertion of the planar hydrophobic ligand into the DNA base pairs results in partial intercalation, which refers to the attachment of the DNA and the metal complex through non-covalent weak interactions.

In living systems, many proteins undergo electron transfer reactions. The constituent amino acids of the peptides, viz. cysteine, phenylalanine, tyrosine, tryptophan, etc., can act as intermediate charge carriers. These amino acids especially facilitate long-range electron transfer. Amino acids with aromatic side chains are particularly suitable for these phenomena. During long-range electron transfers, the radical ions of tryptophan, phenylalanine, and tyrosine are recognised. Moreover, they have a planar side chain for which they can also participate in non-covalent weak interactions like stacking.

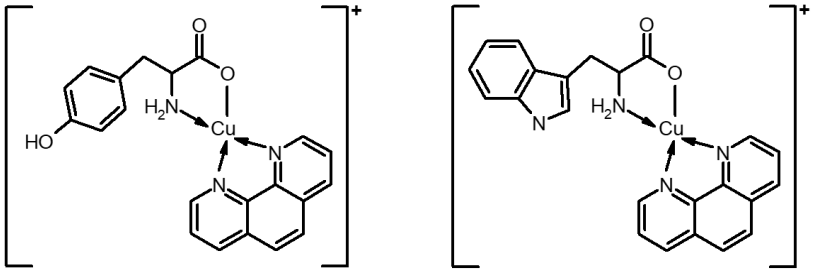


Figure 4: Schematic Diagram of Complex (1) and Complex (2)

It has been observed that tyrosine involves proton-coupled electron transfer in ribonucleotide reductase and oxidises cysteine residues almost 35 Å away via multiple aromatic residues (McCaslin *et al*., 2019). Very recently it has been found that when Cu^{2+} is exchanged with redox inactive Zn^{2+} in blue copper protein azurin, a neutral tryptophyl radical is formed with a longer lifetime (Rivera, Trinh & Kim, 2022). Hence, the study of ternary metal complexes comprising aromatic amino acids, e.g., tyrosine and tryptophan, and a second ligand which contains a planar moiety such as '2,2'-bipyridyl or 1,10-

phenanthroline, is important to understand the electron transfer reactions between the amino acid and heterocyclic molecules in aqueous solution.

$[Cu(phen)(Htrp)]^+$ (1), $[Cu(phen)(Htyr)]^+$ (2) (phen: 1,10 phenanthroline; Htrp: tryptophan; Htyr: tyrosine) Both complexes contain a planar phen ligand that interacts with DNA through partial intercalation (Dey, Pramanik & Basu, 2009; Dey & Basu, 2011). This partial intercalation can be proved by a quenching study with ethidium bromide (EtBr), a known intercalator of the DNA double helix. The fluorescence intensity of EtBr increases many times when it intercalates between the DNA base pairs compared to the free molecule in aqueous medium. On addition of both the complexes, the fluorescence intensity of DNA intercalated EtBr decreases, suggesting that both complexes can displace EtBr from DNA base pairs and itself interact with the nucleic acid (figure 4).

On photoexcitation, the amino acid complexes (1) and (2) undergo intra-molecular electron transfer from amino acid to phen ligand, resulting in $phen^{\bullet-}$, $trp^{\bullet+}$, and $tyr^{\bullet+}$ radical ions. As phen and amino acids are both covalently attached to copper, the radical ions remain spin correlated for a longer time and show greater transient absorption in the presence of an external magnetic field (Scheme 1).

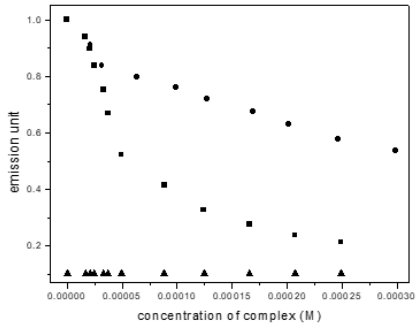
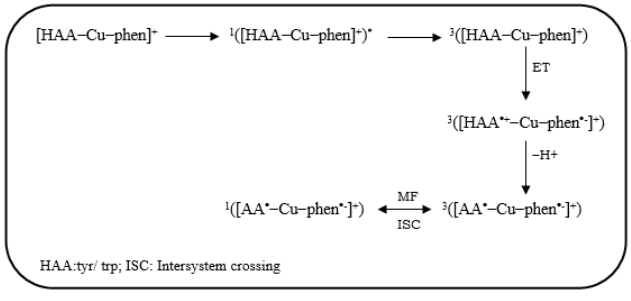
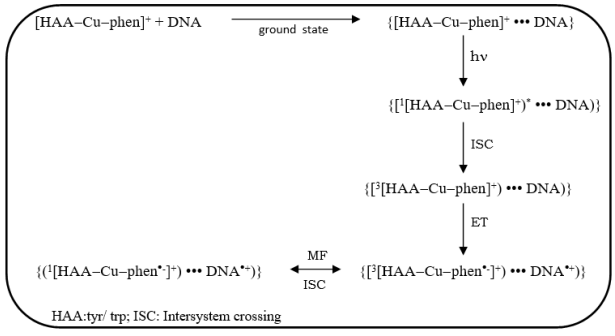


Figure 5: Fluorescence Quenching of EtBr (4.5 μM) Bound to CT DNA (100 μM) at Different Complex (1) (●) and (2) (■) Concentrations (λex = 512 nm)

The intrinsic fluorescence of EtBr is not quenched with the concentration of both complex (1) and (2) (▲)



Scheme 1: Mechanism for Photoinduced Intramolecular ET within the Complexes (Dey, Pramanik & Basu, 2009; Dey & Basu, 2011)



Scheme 2: Illustrates the Mechanism for Photoinduced Intermolecular Electron Transfer (ET) Between DNA and the Specified Complexes (Dey, Pramanik & Basu, 2009; Dey & Basu, 2011)

In the CT DNA-bound copper complexes, the electron transfer occurs from the guanine base (G) instead of the amino acids to $phen^{\bullet -}$ at first, giving rise to $G^{\bullet +}$ and $phen^{\bullet -}$ for both the complexes. Thus, primarily the electron donor is guanine instead of amino acids. The reduction potential of guanosine radical is 1.29 v, considerably higher than both tryptophan (1.01 v) and tyrosine (0.9 v). It has been well investigated that DNA damage can be repaired by proteins. More specifically, amino acids that are susceptible to redox reactions, like cysteine and tyrosine, play an important role in this aspect. Theoretical studies using density functional theory also revealed that radiation- induced DNA damage can be recovered by amino acids of proteins (Jena, Mishra & Suhai, 2009). Milligan *et al.* (2003) reported that in oxidative damage guanyl radicals are produced in plasmid DNA. Derivatives of cysteine, methionine, tyrosine and tryptophan react and repair the guanyl radical in plasmid with a time scale ranging from 105 to 107 $dm^3\ mol^{-1}\ s^{-1}$. For the copper complexes also, there is a possibility of repairing the guanyl radical by the amino acid. The repair of the radicals will take a longer time, within which the radicals will separate out, forming individual solvent- separated ion pairs. In other words, the geminate characteristics of the primarily produced radicals will be lost. For such an e, an external magnetic field cannot have any influence on the RIP/RPs. Actually, a prominent increase in transient absorption spectra was observed for primarily generated $G^{\bullet +}$ and $phen^{\bullet -}$ radical ions only (scheme 2). No influence of an external magnetic field was observed for the time-delayed repaired radicals.

Conclusion

The RIP/RP produced during electron transfer bears free electrons and is susceptible to external magnetic fields. After generation, the RIP/RP undergo diffusive movement, and when they are separated by a certain distance, the exchange interaction between them becomes negligible, allowing for $S \leftrightarrow_T$ intersystem crossing to occur. If an external magnetic field is applied under such conditions, the T state splits into T_+, T_0, and T_-, making intersystem crossing possible only between S and T_0. Thus, whether the electron transfer occurs in a singlet or triplet state, the forbidden intersystem between S

and $T_{\pm}$ increases the population of the RIP/RP in their initial spin state. This increment in RIP/RP population is reflected as greater transient absorption of the RIP/RPs. In a homogeneous medium, if the donor and acceptor are not covalently bound, the RIP/RPs move apart and become separately solvated, which causes them to lose their geminate characteristics; consequently, no change occurs in the presence of a magnetic field. In this review excited- state hydrogen bonding and non-covalent weak interactions (electrostatic force of interaction and intercalation) are responsible for keeping the geminate characteristics of the RIP/RPs even in a homogeneous medium, which is a rare observation in literature.

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