

Magnetic Field Effects in Chemistry and Biology*

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Summary: Chemical and biological photoprocesses which involve bimolecular reactions between non-zero spin intermediates, e.g. doublet molecules $^2A + ^2B$, often produce the intermediate molecular pair in a pure overall spin state, e.g. a singlet state $^1(^2A + ^2B)$, and select for the reaction channels again such spin states, e.g. a triplet state $^3(^2A + ^2B)$. The necessary transition $^1(^2A + ^2B) \rightarrow ^3(^2A + ^2B)$ is affected by magnetic interactions (hyperfine, Zeeman, zero field splitting) and can be influenced by magnetic fields. Examples are photoinduced electron transfer processes, e.g. the primary reaction of photosynthesis.

1 Introduction – Magnetic Field Effects on Chemical Systems

The study of possible influences of magnetic fields on chemical and biological processes with claims of rather odd effects had been for long an activity of ill repute; the proponents of this activity were those unable to comprehend a simple argument: the strength of magnetic interactions is much smaller than thermal energies kT and, hence, on thermodynamic grounds chemical and biological processes cannot be influenced by magnetic fields to any measurable degree.

This argument appears to be completely valid. However, it has to be realized that a chemical reaction cannot only be affected by alterations of potential energy surfaces through external forces but also by the perturbation of a coherent quantum mechanical process, for which purpose interactions much weaker than kT will suffice. In fact, there had been a variety of observations [1] which demonstrated by means of altered intensities in NMR and ESR spectra that chemical reactions can lead to products with electron (in case of doublets) and nuclear spins strongly perturbed from their nearly uniform thermal orientational distribution. The correct explanation of this phenomenon [1] involves the occurrence of a pair of doublet molecules in a pure singlet or triplet quantum state, the magnetic hyperfine interaction between electron and nuclear spins coherently altering the spin motion, i.e. mixing singlet and triplet states and concomitantly polarizing the nuclear spins (see below). This explanation known as 'Chemically Induced Dynamic Spin Polarization' opened the avenue for an experimental technique to detect chemical reaction routes involving doublet intermediates.

Our own interest [2] in the role of magnetic interactions in chemical processes came about through observations regarding the photochemical process illustrated in

* Dedicated to A. Weller on the occasion of his 60th birthday.

Fig. 1: A polar liquid contains two kinds of molecules, electron acceptors A and electron donors D. The molecules selected, A = pyrene and D = dimethylaniline acquire the ability for electron transfer only after photoexcitation $^1A \rightarrow ^1A^*$. When $^1A^*$ collides in the liquid with 1D an electron is transferred and the pair of doublets $^2A^- + ^2D^+$ is formed. Energetically two routes are open for the back transfer, either to the ground state $^1A + ^1D$ or to the triplet excited state $^3A^* + ^1D$. When we entered the field in 1975 a dispute raged if, in fact, a population of the $^3A^*$ state had been observed as early as a few nanoseconds after photoexcitation and formation of the ionic doublets $^2A^- + ^2D^+$, and whether that would be physically possible at all. The point of the discussion was that the precursor of the doublet pair is a singlet state, i.e. $^1A^* + ^1D$, and, therefore, electron transfer creates the doublet pair also in a singlet alignment, i.e. $^1(^2A^- + ^2D^+)$. In case a third partner, either $^2A^-$ or $^2D^+$, intercepts the original pair, the mutual electron spin alignment between the new reaction partners is random, i.e. 25 % singlet and 75 % triplet, and, hence, such events can populate the triplet state. However, because of the existing low concentration of doublets the mean time for such events to occur is about 10^4 ns. The claim of a triplet population $^3A^*$ at considerably earlier times necessitates a magnetic perturbation which realigns the electron spins in the original $^1(^2A^- + ^2D^+)$ pair. Because of the Brownian motion of the molecular partners the average time an ionic pair $^2A^- + ^2D^+$ spends together in a close neighbourhood in a polar liquid is limited to a few nanoseconds and, hence, the magnetic interaction has to be effective in such short time. However, because the singlet and triplet alignments of a doublet pair not in direct contact, i.e. with negligible exchange interaction, are energetically degenerate a perturbation energy of 10^{-7} eV suffices to produce a spin realignment on this time scale. 10^{-7} eV is, in fact, the size of magnetic interactions, e.g. the hyperfine coupling in organic compounds or the Zeeman interaction for electron spins in fields of a few Gauss.

Fig. 1

Cyclic electron transfer in a polar liquid: the process is induced by a ns laser flash, the concentrations of the participating compounds 1A , $^3A^*$, $^1A^*$, 1D , $^2A^-$ and $^2D^+$ are monitored through their absorption spectra by means of a probe light; the initial electron transfer $^1A_i^* + ^1D_i \rightarrow ^2A_i^- + ^2D_i^+$ is followed by a reverse transfer either between the initial partners (i+i) or between random partners (i+r); the reverse transfer between the initial partners $^2A_i^- + ^2D_i^+ \rightarrow ^1,^3A_i + ^1D_i$ has a duration of a few nanoseconds, after which time the initial pairs are irreversibly separated by Brownian motion; the subsequent reverse transfer between random partners $^2A_i^- + ^2D_i^+ \rightarrow ^1,^3A_i + ^1D_i$ proceeds on a longer time scale of microseconds, the retardation being due to the low concentration of $^2A^-$ and $^2D^+$ which results in such long time for a random encounter to occur.

