17. Magnetic Effects on Chemical Reactions. External Magnetic Field Effect on the Reactivity of Radical Pairs.

The influence of magnetic effects in the radical pair may be classified in terms of the source of the coupling to the electron spins of the radical pair. These sources may be classified as internal and microscopic (spin-orbit, spin-spin and spin-lattice) or external and applied (static and oscillating). Of the internal couplings, the spin-spin hyperfine and exchange coupling are the easiest to manipulate experimentally and will serve as representative of the influence of external couplings on the measurable properties of radical pairs and the products of radical pairs. An applied magnetic field is the most important external coupling available for influencing the behavior of radical pairs. With the specific example of a ACO B radical pair, we shall present examples of how spin-spin couplings and applied magnetic static fields can dramatically influence the behavior of radical pairs.

In zero or very weak magnetic fields, the S and T states of a dynamic radical pair are degenerate when the pair is solvent separated (Region 3, Figure 32). Thus, interconversions of all three T states to S are energetically allowed. Under these circumstances we can consider the three triplet sublevels to be rapidly interconverting and that the ISC step occurs when a T_0 level undergoes rephasing to S or a $T_\pm$ undergoes a spin flip to S. The rephasing or spin flip may be due to any one of the usual couplings (spin orbit, hyperfine, spin lattice, etc.) if angular momentum is conserved. An external magnetic field lifts the degeneracy of the three triplet levels through the Zeeman interaction so that $T_\pm$ is separated from T_0 and S (Figure 33). If the $T_\pm$ pair is rendered completely incapable of ISC in a high field, we conclude that the rate of T-S interconversion of the triplet geminate pair will be reduced by 2/3 compared to that at zero field! Conversely, if a singlet radical pair is the starting reagent (unusual, but known), the magnetic field will close off the $T_\pm$ channels for ISC of the pair and increase its reactivity. Translated into experimental terms, **the probability of the cage effect for a triplet geminate pair is reduced by an applied magnetic field and the probability of the cage effect for a singlet radical pair is enhanced by an applied magnetic field.**

In the presence of a magnetic field, H_Z, the details of T_0-S ISC are clearly distinct from those of $T_\pm$ ISC. In the case of T_0-S ISC, a rephasing of the electron spins is required to achieve ISC from T_0 to S (Figure 22). This rephasing does not induce ISC for $T_\pm$ because it does not induce a change of spin orientation which is required to convert the $T_\pm$ states to S or T_0 (Figure 21). Thus, another magnetic interaction is required to induce $T_\pm$ ISC in a strong magnetic field. Let us suppose this interaction is due to the hyperfine coupling of the electron to the nucleus for our case history pair, ACO· ·B.

The **rate** of ISC from T_0 and $T_\pm$ is directly related to the magnitude of the matrix elements dervied from the spin Hamiltonian evaluated for the S and T wavefunctions. In a simplified version the matrix elements for the T_0-S and $T_\pm$-S ISC are given by Eqs. 42 and 43 (which are related to Eqs. 39 and 40 of the previous section).

$$\text{Rate } (T_0\text{-S}) \sim \Delta g \mu_e \mathbf{H} + aM_I \qquad (42)$$

$$\text{Rate } (T_\pm\text{-S}) \sim aM_I \qquad (43)$$

From Eq. 41 we note that the rate of ISC from the T_0 state is a function of the difference in g factors of the radical partners, the magnetic field strength, the magnitude of the hyperfine coupling and the orientation of the **nuclear** spin, precisely the factors that result in Kaptein's rules for CIDNP. Since hyperfine constants can be negative or positive, the rate also depends on the sign of the coupling constant. For the case history pair, $A^{13}CO$· ·B, the coupling constant is positive. It follows from eq. 41 that in a strong magnetic field, the rate of T_0-S ISC, and consequently the probability of cage reaction of the geminate triplet pair, depends first on the difference in Zeeman energies of the pair ($\Delta g \mu_e \mathbf{H}$), second on the nuclear magnetic moments through the hyperfine coupling constant, a, and third on the orientation of nuclear spin orientation through the quantum number, M_I. The important difference between this discussion and that of CIDNP is that the observed effects are on isolated chemical product yields, not on a spectroscopic measurement pertaining only to pairs containing magnetic nuclei.

In actual examples hyperfine coupling will not be the only internal interaction which can induce ISC, and eqs. 41 and 42 must be modified to include contributions due to spin orbit coupling, spin lattice coupling, etc. However, the qualitative aspects of these couplings will be analogous to those introduced by the hyperfine couplings, i.e., they will modify the effect of the Zeeman coupling in eq. 41 and will induce $T_\pm$-S as in eq. 42.

Static Magnetic Field Effects on the Chemistry of the Case History Pair, ACOB.

Let us consider the influence of an applied magnetic field on the products of the photochemistry of ACOB. In this case we will consider the effect for a ketone containing ^{12}C at the carbonyl carbon (which is representative of natural abundance material). At zero field there will be a certain probability that the triplet geminate radical pair produced by α-cleavage will undergo ISC and cage recombination. This process may be monitored chemically through the racemization of a chiral B group. Combination to regenerate (racemic) ACOB will compete with scavenging to form ACOX and BX. The mechanism of ISC at zero field can be envisioned as involving rapid internal interconversion of the triplet sublevels with one another and ISC from T_0 to S. The situation is analogous to the selection of one of several rapidly interconverting conformers, only one of which is chemical reactive.

At high field the T_- and T_+ levels are split so far from T_0 that they stop interconverting with this state and therefore stop undergoing ISC to S. However, the the T_- and T_+ levels can still separate and form free radicals that can be scavenged. Let the probability of geminate combination in zero field be a quantity, ϕ, so that the probability of the scavenging is $(1 - \phi)$. At high field, the probability ϕ will be reduced to ca. $\phi/3$, since two of the three triplet states will become incapable of ISC as geminate pairs and undergo free radical formation and eventual scavenging.

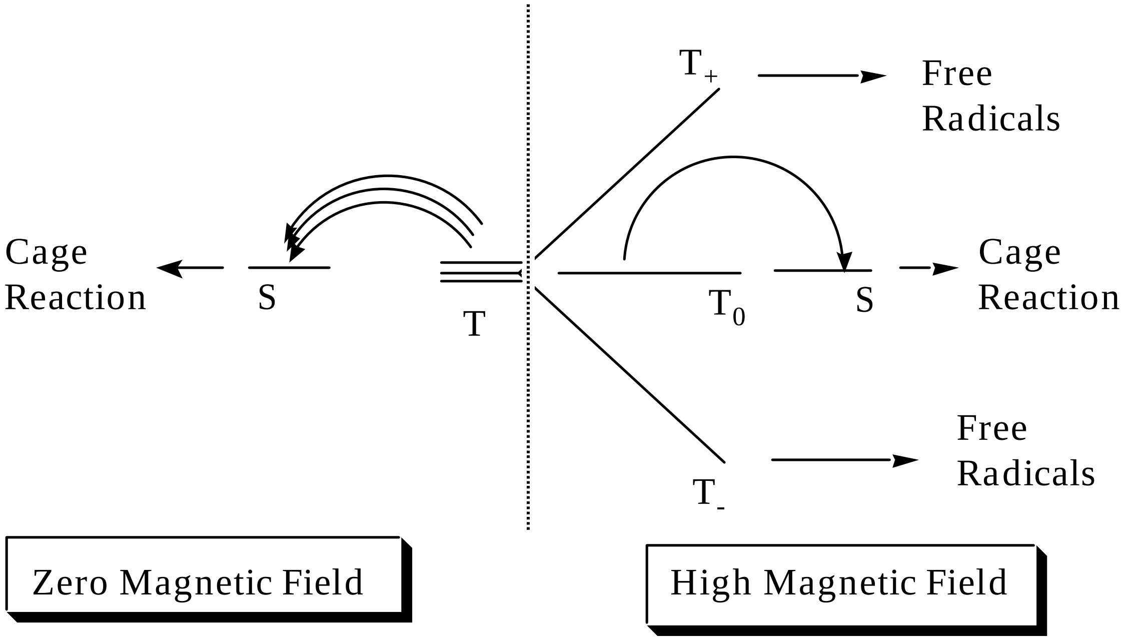

Figure 41. Basis for the magnetic field effect on the cage reaction of triplet geminate radical pairs.

These predictions of magnetic field effects have been difficult to verify in homogeneous non-viscous solutions because in these cases the probability of cage reaction is very small for triplet geminate pairs because rapid formation of free radicals (rapid pair separation in space) is much faster than ISC. However, when radical pairs are placed in restricted spaces that inhibit pair separation, magnetic field effects on geminate pair reactions can be substantial. It is particularly interesting that only relatively weak fields are needed to effectively shut off ISC from T_- and T_+. This is because the magnetic coupling between these states and T_0 is relatively weak, so that the size of the applied field required to decouple T_- and T_+ from T_0 is often of the order of a few hundred gauss (the field provided by magnetic stirrer bars!).

Influence of Oscillating Magnetic Fields on the Dynamic Radical Pair. Reaction Yield Detected Magnetic Resonance.

Static magnetic fields cause the direct splitting of magnetic energy levels and the inhibition of T S ISC. Interestingly, this inhibition can be reversed by the application of the oscillating magnetic field of electromagnetic radiation. For example, the $T_-$and T_+ states that are split away from T_0 by an applied field can be converted to T_0 by the application of microwave radiation (which provides the oscillating magnetic field) of the correct frequency. Figure 42 schematically shows the basis of the use of microwaves to influence the behavior of dynamic radical pairs (throughout the discussion we shall assume $J = 0$, i.e., we are dealing mainly with interactions involving solvent separated pairs).

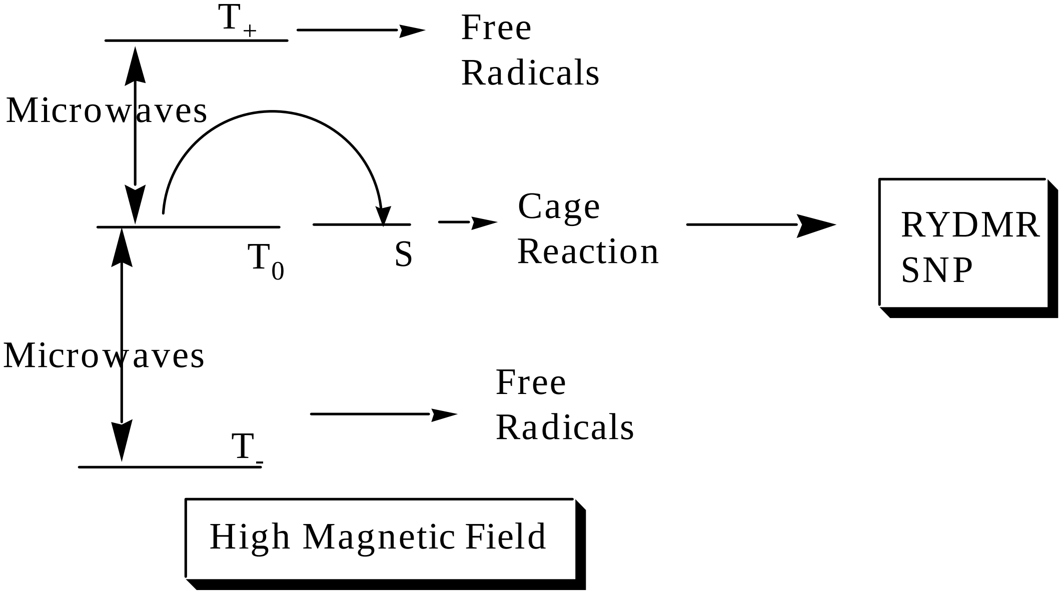

Figure 42. Energy diagram basis for the RYDMR and SNP phenomena. In both cases microwaves are employed to stimulate T ∅ T_0 transitions, which in turn lead to ISC to S. In one case the products of cage reaction are monitored (RYDMR) and in the other case nuclear polarization is monitored (SNP).

When microwaves corresponding to the resonance frequency that will interconvert T_- and T_+ with T_0 are applied to the dynamic geminate triplet radical pair, resonant transition to T_0 is stimulated by the electromagnetic field. If T_0 to S ISC is rapid, then the microwaves take the "inert" T_- and T_+ levels into the S state and effectively "catalyze" ISC of these states. The S state undergoes cage reaction. This enhancement of the cage reaction by applied microwaves may be detected experimentally. Varying the external field, H_Z allows the detection of the energy gap corresponding to the resonance condition. This is the same energy gap that is detected in the ESR spectroscopy of the triplet, but is detected by measuring chemical yields of products and is a form of "chemical spectroscopy"! Such measurements of ESR through the yields of products is termed "Reaction Yield Detected Magnetic Resonance" of RYDMR. In the case of the case history dynamic radical pair, the yield of geminate cage products would be monitored and would be increased by the application of resonant microwaves.

Influence of Oscillating Magnetic Fields on the Dynamic Radical Pair. Stimulated Nuclear Polarization (SNP).

We have seen that hyperfine interactions of the dynamic radical pair can lead to nuclear spin orientation dependent ISC of cage products and escape products which results in CIDNP. It is possible to use microwaves to selectively induce ISC of the nuclear spin states of a dynamic radical pair and thereby produce nuclear polarization. This phenomena is termed stimulated nuclear polarization (SNP).

The basis of the SNP phenomena may be understood for the concrete example of our case study dynamic radical pair, $A^{13}CO\cdot \ \cdot B$ through consideration of the ESR of the pair (Figures 37 and 39). The ESR line of the $A^{13}CO\cdot$ radical consists of a line at low frequency ($\omega_1{}^{\beta}$) and a line at high frequency ($\omega_1{}^{\alpha}$) separated by a frequency corresponding to the hyperfine coupling constant (ca 120 G). Irradiation of the dynamic radical pair at the frequency $\omega_1{}^{\beta}$ will stimulate radiative transitions selectively to $T_0{}^{\beta}$, which will in turn convert selectively to S^{β}. **These singlet pairs will, in turn, produce cage combination products enriched in β nuclear spins**. Thus, if the NMR of the combination product is monitored as the microwaves are applied, at the resonance frequency corresponding to the $T_{\pm} \varnothing T_0$ transitions an emission corresponding to the selective formation of $A^{13}C_{\beta}OB$ will be observed. The reverse effect will be observed if the ω_{α} transition is irradiated with microwaves. The SNP experiment perhaps most elegantly shows the relationships of spin chemistry (spin selective formation of geminate cage products) and magnetic resonance (ESR of precursor dynamic radical pair and NMR of geminate cage products). These relationships are shown schematically in Figure 43.

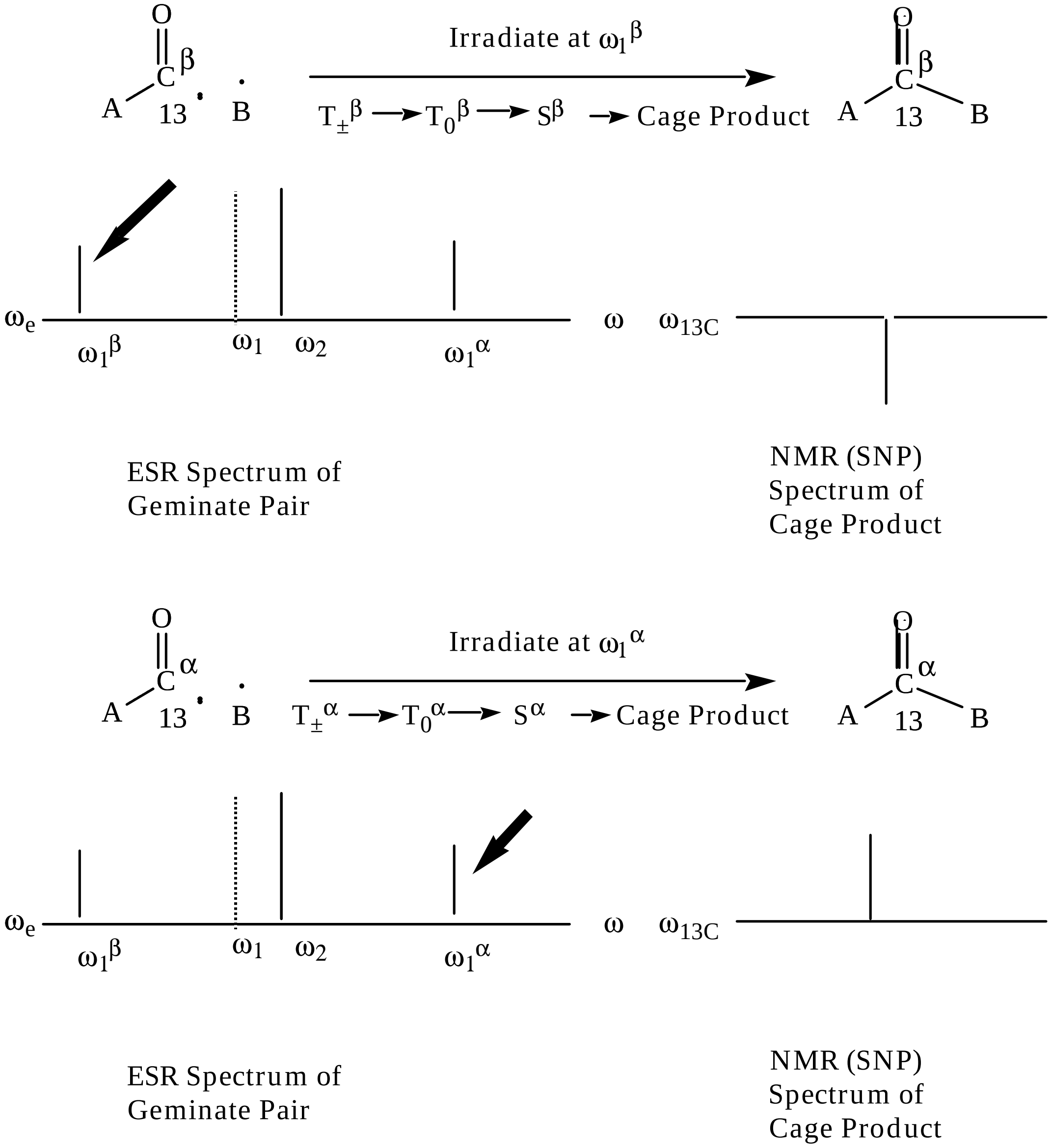

Figure 43. Schematic representation of the SNP phenomena. CIDNP emission results from selective irradiation at $\omega_1\beta$ and CIDNP enhance absorption results from selective irradiation at ω_1.

Summary

Magnetic interactions in correlated dynamice radical pairs control the spin dynamics and therefore the multiplicity of the radical pairs. Both applied static and dynamic magnetic fields can influence the rates of interconversions of various spinomers and therefore result in magnetic field effects on photochemical processes involving radical pairs. These magnetic field effects are most pronounced when the geminate pair possesses a significant lifetime. Experimentally, the lifetime of the pair can be enhanced by a high solvent viscosity or by creating the pair in a small microhetergeneous confined space such as that provided by a micelle. The reactions and lifetimes of biradicals, which are contrained to remain geminate during their entire lifetime, are found to be significantly influenced by the application of applied magnetic fields.