

Invited Article

The spin-correlated radical pair as a reaction intermediate

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The concept of the spin-correlated radical pair has been used for some time in the interpretation of the results of magnetic polarization experiments in NMR and in ESR (CIDNP and CIDEP), and of the effects of magnetic fields on chemical reactions. It has, however, a much wider general significance as a reaction intermediate in all radical reactions, including photochemistry. Here the nature of the pair is introduced, and the evidence for it reviewed, and it is further shown how it can be treated theoretically, before some of the consequences of its existence are pointed out. Its recognition, and in particular the understanding of the processes which occur within it, notably the interplay of spin-mixing and diffusion, allow the design of new experiments in the absence or presence of an external magnetic field, and the optimization of reaction yields.

1. Introduction

In recent years new physical techniques have changed and clarified many of the basic concepts of how very fast reactions occur in solution. Where radical recombination reactions are concerned, the fastest reactions had been thought to be those occurring under diffusion-controlled conditions in the classical sense, that is with reaction at each (broadly defined) encounter and on the microsecond to millisecond timescale. It was, however, demonstrated by direct observation of iodine atom recombination in 1974 [1] that an ultrafast reaction preceded this classical process, approximately 90% of the atoms recombining in the first five hundred picoseconds after the photolysis flash which created them. The very fast stage occurs between atoms or free radicals created together, and is known as the geminate reaction [2]. It is not instantaneous but occurs as a result of short term diffusion of the reaction partners together after their initial separation; an important aspect of modelling this phase of the reaction is consequently the use of the relevant diffusion equations from liquid theory. Not all the radicals created together react in the geminate stage, and those that do not react will escape to diffuse through the solution until they encounter similar survivors from different initial geminate pairs, when they undergo the classical 'diffusion-controlled' reaction on a necessarily much longer timescale. Such reactions are said to involve 'freely-diffusing pairs', or 'F-pairs', of radicals. The two stages are differentiated in figure 1.

The existence of separate geminate and F-pair reaction processes raises no new principles, and their recognition simply awaited the development of fast techniques. However, a more fundamental concept came from Brocklehurst [3], in connection

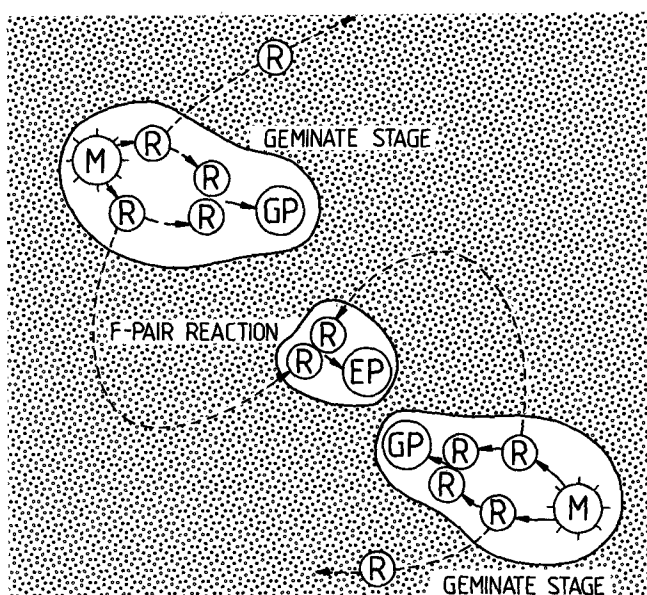


Figure 1. An energized molecule, M, dissociates or reacts to produce a pair of free radicals which may recombine as long as they are in contact, or separate and then diffuse together and react within a few nanoseconds, to form the geminate product, GP. If no reaction occurs the radicals escape from the geminate region and diffuse freely through the solution, where they may encounter radicals which have escaped from different geminate stages. They then form 'F-pairs' and may react to form the escape product, EP. It is this latter type of reaction which represents the classical 'diffusion-controlled' process.

with radiolytic formation of radicals, and from Closs [4] and Kaptein and Oosterhoff [5] in discussion of a novel phenomenon in nuclear magnetic resonance spectroscopy. This was that the NMR spectra of products of free radical reactions, observed while the reaction proceeded, exhibited intensities that demonstrated that the nuclear spin system was not in thermal equilibrium with its surroundings, a phenomenon known as chemically-induced dynamic nuclear polarization (CIDNP). The new realization was that electron spin orientation is conserved on chemical reaction so that thermal dissociation of a singlet ground state molecule, for example, leads to a pair of radicals whose spins, at the instant of radical formation, are themselves singlet-correlated. Similarly, dissociation or reaction of an excited triplet state produces a triplet-correlated pair. Chemical reaction is, of course, spin-selective and it (most frequently) selects radical pairs out of the ensemble with a probability dependent upon their singlet character. Triplet pairs are consequently unable to combine at formation but may do so later if a mechanism exists for changing their spin multiplicity; this same mechanism tends to inhibit reaction of initially singlet pairs as time proceeds. Possible mechanisms are discussed below.

The apparent and widely accepted condition that small radicals which combine with essentially zero activation energy need only to encounter to react is consequently erroneous, for no reaction can occur if the spin multiplicity of the radical pair is inappropriate. This is a much more rigorous condition for reaction than is implied by activation energy or diffusion-based arguments. Spin state interconversion in radical pairs is not instantaneous under the action of a mixing Hamiltonian, and the members of the geminate pair drift apart while it occurs, so that reaction happens only if the

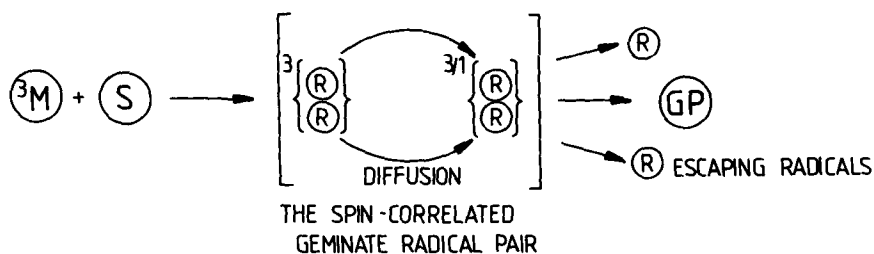


Figure 2. The spin correlated radical pair as exemplified by the triplet case. Reaction of a triplet state, 3M , with a suitable reagent, S , yields a triplet-correlated pair of free radicals, R and R . These are unable to react due to their unfavourable relative spin configurations, and they separate by diffusion. During this process T-S interconversion occurs, and the radicals may react if they then re-encounter when the pair has significant singlet character. Otherwise, they separate completely and undergo reaction in the surrounding medium. The exchange interaction $J(r)$ is of significant magnitude only when the radicals are extremely close together. In the diagram the RP is defined as described in the text.

radicals re-encounter subsequently. Short-term diffusion is an essential part of the reaction process, as above, but now the appropriate timescale can be recognized. For organic radicals, singlet-triplet intersystem crossing occurs within a few nanoseconds, and it is diffusion on this timescale which is all-important; for iodine atoms the spin-orbit coupling provides an efficient source of interconversion and the initially triplet pair is able to react within picoseconds. These times are significant, for the re-encounter probability of two molecules which were together at a chosen zero time falls rapidly thereafter [6], and so does the reaction probability; a higher proportion of geminate radicals react if singlet-triplet interchange is fast.

The term 'the spin-correlated radical pair' (the 'RP') is used of the geminate pair from the time that it is formed until it ceases to exist, either as a result of reaction or by the members of the pair drifting apart irrevocably (figure 2). During the very fast initial diffusive process, still within the geminate stage, there is a possibility of several secondary encounters between which singlet-triplet interconversion occurs. For a short period after formation the spins remain correlated as a consequence of the principle of the conservation of angular momentum. This initial correlation is lost in a time determined by the difference of local magnetic interactions at the sites of the separate spins. Such local magnetic differences become particularly effective as the radicals diffuse outside the region where the short-range electron exchange interaction (see below) is significant. Throughout its lifetime it is convenient to describe the overall spin state of the radical pair in terms of a coupled representation of the individual spins, for the reason that the occurrence of chemical reaction depends upon the relative spins of the electrons on the two radicals, and this is summarized in terms of the overall spin state of the radical pair. Although this discussion has been made using geminate pairs, the same concepts apply to F-pairs too. Here the initial spin correlation is via the exchange interaction on encounter, at which reaction tends to remove (normally) singlet-correlated pairs. The subsequent development of the RP spin state, and of the reaction probability, is as in the geminate case.

A fascinating feature common to all RP processes is the interplay between spin-state interconversion and short term diffusion, which implies that the reaction probability can be optimized by control of the diffusion, an important experimental facility. The RP exists in every chemical reaction that involves free radicals, during the

brief period of time between its formation from reactive precursor molecules and the subsequent presence of freely-diffusing radicals. It is a true reaction intermediate which affects the chemistry of the system directly, and its characterization is important to our understanding of that chemistry. Here we attempt to provide a coherent account of its theory and effects, to describe experiments for its direct observation, and to show how it can be manipulated to affect reaction yields. This is by application of external magnetic fields and/or by magnetic isotope substitution, and it forms the basis of many of the field effects on chemical reactions and of magnetokinetic phenomena that have been reported [7]. Here it might be stressed that the interactions which cause singlet-triplet interconversion are weak ones in the sense that their energies are far below the mean thermal energy at room temperature in size; they are effective entirely through their influence on the kinetics, not the thermodynamics, of systems.

2. The electron exchange interaction $J(r)$

The electron exchange interaction plays an important rôle in radical pair phenomena, for it determines the energy separation of the singlet and triplet states (which at all radical-radical distances is given (conventionally) by $2J(r)$) and, consequently, the possibility of spin mixing, which can occur only if a mixing interaction is of comparable size. As can be seen by applying a simple Pauli principle argument to a radical pair formed by two hydrogen atoms, the singlet state is associated with the bonding orbital of the molecule as the atoms approach to bonding distances, and the triplet state with the antibonding one (figure 3*a*). The singlet state of the RP is consequently the lower in energy. The same model allows an explicit calculation of $J(r)$ through the overlap of the 1s orbitals as the atoms approach one another. This simple, isolated molecule, calculation yields;

$$J(r) = J_0 e^{-(r/r_j)}, \quad (1)$$

where r is the inter-radical separation. The exponential form is normally used in solution calculations too, including RP theory [8–10], with typical values of $J_0 = 1.7 \times 10^{17} \text{ rad s}^{-1}$ and the range parameter $r_j = 0.049 \text{ nm}$ [11, 12]. As has been stated, spin-mixing in RP situations often depends upon local field differences, and it is convenient to express $J(r)$ in magnetic field units.

The relations between the quantities used to measure energy in RP theory, and between these and other common measurement units may be summarized in terms of the energy of an electron in a 1 mT field as: $1 \text{ mT} \equiv 1.76 \times 10^8 \text{ rad s}^{-1} \equiv 28.0 \text{ MHz} \equiv 9.36 \times 10^{-4} \text{ cm}^{-1} \equiv 1.86 \times 10^{-8} \text{ aJ} \equiv 4.25 \times 10^{-9} E_h$.

Equation (1) implies that $J(r)$ lies within the 0.1–10 mT range at radical separations of 0.8–0.97 nm. Simple considerations would suggest that it might change sign with radical separation, as a result of superexchange effects, when, for example, a solvent molecule comes between the two radicals during diffusion [13]. Biexponential forms have been used to model this for both radicals [14] and biradicals [15] but knowledge of the form of $J(r)$ in solution remains poor. Nevertheless, it is clear that it falls off very rapidly with radical separation, and it becomes of the same order of magnitude as the interactions which cause spin mixing (see below) at distances of around 1 nm. This occurs within some hundreds of picoseconds in liquids of normal viscosity, and for the greater part of the existence of the geminate pair the radicals are independent of one another.

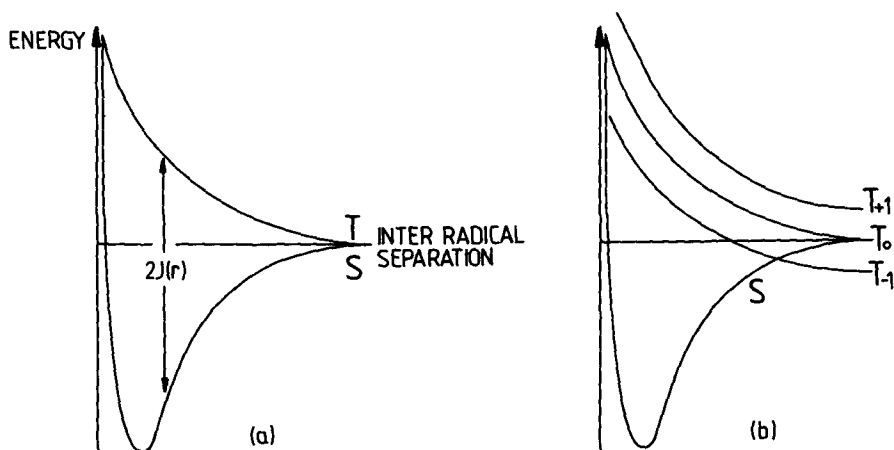


Figure 3. (a) A schematic drawing of the variation of the energies of the singlet and triplet states of the RP as the radicals diffuse apart, as deduced from a simple model of two hydrogen atoms approaching from infinite separation to form bonding (S) and antibonding (T) orbitals. The energy levels are separated by the electron exchange interaction, conventionally $2J(r)$. (b) As in (a), but with the triplet level split by the application of an external magnetic field into its Zeeman components, T_0 and $T_{\pm 1}$. This splitting is shown highly exaggerated for clarity, and it is actually negligibly small compared with $2J(r)$ until the radicals have diffused to about 1 nm apart in a typical system. At large inter-radical distances the $T_{\pm 1}$ levels are so widely separated in energy from the S one that no spin mixing can occur; the ST_{-1} crossing is also ineffective in producing mixing in isotropic solutions of normal viscosity, unless the hyperfine couplings are unusually large, since it is traversed too rapidly as the radicals separate.

This discussion leads to a useful, simple, model of geminate processes. Consider, for example, an RP formed in a triplet state. Spin mixing is inhibited by the size of $J(r)$ until diffusion takes the radicals to the 1–1.5 nm separation, by which time they are too far apart for reaction. The mixing consequently can be approximated as occurring in the absence of $J(r)$, which becomes important again only if and when the radicals re-encounter. In this model the reaction can be summarized as involving a creation stage followed by radical separation while the multiplicity of the RP changes, before reaction may occur at a re-encounter. Those radicals which re-encounter before much spin mixing occurs, or which fail to react at the re-encounter, leave the geminate region and constitute the normal ‘free radicals’ in the system; the ones that re-encounter after spin mixing exhibit chemically induced dynamic electron polarization (CIDEP) in their electron spin resonance (ESR) spectra (see below). This model provides a useful physical picture, but from a theoretical point of view it is unnecessarily restrictive and here the spin evolution of the pair and the relative diffusion of the members of the pair will be considered in the most general sense as occurring continuously. This is through use of the stochastic Liouville equation (SLE, see below), which is model-specific only in its choice of the spin mixing Hamiltonian and in nature of the diffusion operator—no physical restrictions are included in the basic formulation. It should be realized, however, that the understanding of radical reactions in solution is intimately concerned with spin dynamics besides diffusion. The spin-mixing will be considered first.

3. The sources of spin-mixing

Any process which changes the overall spin state of the radical pair can facilitate the reaction of the members of triplet born pairs or inhibit the reaction of singlet born ones. There exist both incoherent (stochastic) and coherent processes. The first represent the relaxation phenomena long familiar in magnetic resonance studies, and it will be convenient at this stage to introduce the possibility of applying an external magnetic field to the reaction system. This is done since all the indirect evidence for the existence of RPs came from magnetic resonance studies; their direct observation and their manipulation usually involve external magnetic fields. Henceforth the zero field situation will be considered to be the exceptional one. The important fact is that a triplet state interacts with an applied field and the degeneracy of the sub-levels is removed; in a sufficiently high field, there result the Zeeman states T_0 and $T_{\pm 1}$, with T_0 now higher in energy than the singlet state, S, by $2J(r)$ (figure 3b).

The $T_{\pm 1}$ states can be interconverted to the S one by spin-lattice relaxation, which originates in fluctuating local magnetic fields at the electron due to random motion, as can the T_0 state by spin-rephasing relaxation. In normal solutions, and in the absence of electron transfer reactions, these occur with characteristic times of a few μs for organic radicals. They are consequently far too slow to produce sufficient spin mixing before the probability of re-encounter of the members of the geminate pair falls essentially to zero, and these incoherent processes are insignificant in most RP situations. Exceptions occur when the lifetime of the geminate pair is extended [16] by working in micelles or at surfaces, and when orbital degeneracies cause the relaxation to be unusually fast [17] due to their effect on the anisotropy of the g -factor, whose modulation under rotation constitutes the major sources of relaxation in many inorganic systems. In the latter instance relaxation may occur on the nanosecond timescale, and even dominate the interconversion process; it may be field-sensitive through the dependence of the Larmor frequency on the strength of the applied field, although this depends on the motional regime [18].

Coherent singlet-triplet interconversion can be sufficiently fast to occur before diffusion causes the radical re-encounter probability in the geminate cage to be negligible. It happens by the electrons on the two radicals interacting with different local magnetic fields which may originate in the applied field, through different g -factors of the two radicals, or in hyperfine coupling to nearby nuclei. Dipolar interactions average to zero in isotropic solution, even on the timescale of the existence of the RP, but do cause spin mixing in the solid state, for example in the photosynthetic centre [19–21]. The spin mixing is coherent in the sense that it is driven by a constant local field.

It is best understood in the limit that the applied field is sufficient that the $T_{\pm 1}$ states become too widely separated in energy from the S and T_0 ones, by the Zeeman interaction, to mix with them. This leaves only S and T_0 to interconvert, and these are degenerate in the simplest model in which $J(r)$ is zero. A vector representation, whose limitations have been discussed recently by Steiner and Wolff [22], then portrays the two electrons as precessing, one about the applied field direction and the other antiparallel to it (figure 4). The pure S and T_0 states differ in the constant phase differences of the spins, which are exactly out of phase in the former and in phase in the latter. Interconversion happens simply if one spin precesses faster than the other, the angular frequency of each being:

$$\omega = g\mu_{\text{B}}B_{\text{L}}/\hbar \text{ rad s}^{-1}, \quad (2)$$

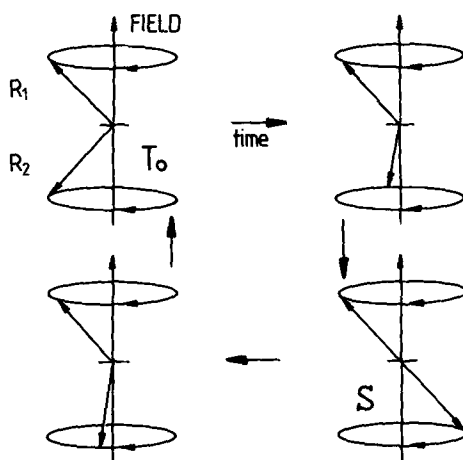


Figure 4. A vector model of spin mixing of the S and T_0 states of the RP. The spin vectors of the two radicals, R_1 and R_2 , precess about the field direction with angular velocities given in the text; if these differ, mixing automatically occurs. The diagram is drawn in a reference frame rotating at the angular frequency of the electron on R_1 and demonstrates how the in-phase T_0 state changes to the anti-phase S one, and back (if no reaction occurs), as time progresses. In between the two extremes the RP possesses both S and T_0 character. Reaction occurs, with a probability depending upon the S character, only if the radicals encounter at the apposite time during their short-term diffusive motion.

where most symbols have their normal significance, and B_L is the local field at the electron; it is the sum of applied and hyperfine terms. Complete S- T_0 interconversion happens in a time Δt related to the difference in precession frequencies, $\Delta\omega$, of the two electrons by:

$$\Delta\omega\Delta t = \Delta g\mu_B B_L \Delta t/\hbar = \pi \text{ rad}, \quad (3)$$

where Δg is the difference in the g -factors of the two radicals. In the same local field of 1 T, a typical Δg value of 0.001 for a pair of organic radicals implies a mixing time of 30 ns, again too long to be effective during the RP lifetime in normal liquids. The figure is, however, field-dependent and this ' Δg ' effect increases in importance as the field is increased, and becomes dominant at field strengths above a few tesla, when the rate of mixing is linearly dependent on the field. Also, Δg values are typically greater for inorganic pairs, and the effect may be important at lower field strengths.

Hyperfine coupling can cause the value of B_L to differ substantially (by an amount ΔB_L) at the two electrons, and so provide an efficient spin mixing mechanism. In a pair of identical radicals complete mixing occurs in a time given by

$$g\mu_B \Delta B_L \Delta t/\hbar = \pi \text{ rad}. \quad (4)$$

In an ensemble, encounters occur between radicals in all possible nuclear hyperfine states and, in an RP created from two methyl radicals, for example in the $+3/2$ and $-3/2$ nuclear spin states, ΔB_L is 6.9 mT, three times the hyperfine coupling constant. Interconversion of the S and T_0 states of this pair occurs in about 1.5 ns, when radical re-encounters in the RP are still probable. This mechanism is directly verifiable in the chemically induced dynamic nuclear polarization (CIDNP) phenomenon, the observation of lines in the NMR spectra of products from free radical reactions which exhibit intensities differing from those expected from populations of the nuclear sub-levels in molecules at thermal equilibrium with their surroundings. Radical pairs

consisting of radicals in different hyperfine states interconvert at different rates. Since the probability of reaction of radicals formed from a triplet precursor depends on the pair acquiring S character while the re-encounter probability is high, this implies that those RPs in the ensemble which are comprised of radicals in significantly different overall nuclear spin states are more likely to react to form the cage product than are the others. The product contains excess, non-Boltzmann, populations in the corresponding nuclear states, and these now control the line intensities. The radicals in the RPs which interconvert more slowly tend to diffuse away and form escape products which are enriched in the complementary spin states. This nuclear spin-sorting process therefore reflects the underlying electron spin-state selective reaction directly. In detail, the cage and escape products exhibit NMR lines in opposite phases, which allows the provenance of the product to be ascertained. CIDNP persists for a period until spin-lattice relaxation establishes thermal equilibrium with the surroundings, and is most commonly observed with continuous radical, and product, generation.

We have chosen to introduce these effects using the vector model because it gives a simple pictorial representation of spin state interconversion. A more strict quantum description of the time-evolution of two states connected by a mixing interaction (summarized in the spin Hamiltonian of the system given, for the situation where $J(r)$ is zero, by equation (15), below), yields the same conclusions as to the relative efficiencies of the different mixing mechanisms. This treatment does, however, emphasize that the system oscillates between the two pure states indefinitely, with a period depending upon Δg and ΔB_L , while the RP is in existence. Damping occurs by removal of radicals from the RP, as a result of reaction or diffusion out of the geminate region.

Most RP phenomena at fields below several T, including zero field, are dominated by the hyperfine interaction. In the low field regime all four RP states may interconvert, but the $T_{\pm 1}$ states become uncoupled from the others as the applied field is increased and the Zeeman interaction exceeds the field-independent hyperfine coupling. The effect, from a triplet precursor, is to inhibit reaction of RPs created in these states and the overall reaction probability in the geminate stage falls. Conversely, that for a singlet precursor increases since three unreactive triplet states may be accessed at low field, but only one at high. This exemplifies the action of the field: it does not change the nature of the reaction product, but merely changes the proportions of cage and escape products. Clearly it also affects the rates of formation of them. At very low fields, spin mixing may be enhanced by two separate phenomena. In the first place, if the average value of $J(r)$ over the lifetime of the RP is non-zero and positive, increasing the field inevitably causes the T_{-1} level to cross the non-magnetic S one (figure 5). This serves to couple these states in contrast to the decoupling that occurs at higher field values, and field effects in the opposite sense occur [23]. Figure 5 has been drawn for pure electron states, which are actually effectively broadened by hyperfine coupling in the radicals, leading to a range of fields at which the curve-crossing occurs. The second effect is more subtle. It is derived from the fact that the selection rules of hyperfine-induced spin mixing in the radical pair are more restrictive in zero field than when a field is applied. In zero field, the total spin J of the pair, defined as

$$J = \sum S_i + \sum I_j, \quad (5)$$

where the first sum is over all the electron spins and the second over all the nuclear ones, is conserved, i.e., J^2 and J_z are constants of the motion. Now consider the case, for example, of a radical pair in a hyperfine spin state with the maximum possible

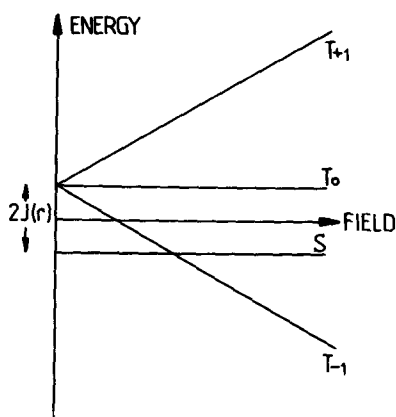


Figure 5. The dependence of the energies of the pure electronic states of the RP as the applied field is increased from zero to about 10 mT, in a situation where the exchange interaction is non-zero. A curve crossing occurs which facilitates mixing of the S and T_{-1} states, but above the field at which this occurs the $T_{\pm 1}$ states become completely decoupled from S. As a consequence, the geminate reaction probability of an RP from a triplet precursor initially increases above that in zero field, as the field is raised, but then decreases. A second, and independent, origin of an identical effect is described in the text.

alignment of electron and nuclear spins. This can only be attained in one way, that is there is only one maximal value of J , although the total angular momentum has $(2J + 1)$ possible different spatial orientations. Since all the spins are aligned, this state belongs to the electronic triplet manifold, and because of the $\Delta J = 0$ selection rule it cannot be mixed with any other hyperfine state. If a magnetic field is applied, this selection rule no longer holds and, since electron and nuclear spins have different magnetic moments, their transverse correlation is lost due to their different Larmor frequencies. This corresponds to a mixing of hyperfine states with different J , but constant J_z . In this way all but the $J_z = \pm J$ components of the hyperfine state with maximal J become connected with singlet-containing hyperfine states. As a result, with increasing field, the hyperfine-dependent S–T mixing receives a positive contribution which, at fields smaller than the average hyperfine coupling constant, may even overcompensate for the negative effect caused by the increased Zeeman splitting of the T_{+1} and T_{-1} states. A small low-field extremum in the field dependence of the overall spin conversion process can ensue. Effects of this type are particularly probably in radical pairs with a small number of hyperfine states (i.e., a small number of nuclear spins), or with a high degree of nuclear spin degeneracy [24]. A clear example of the latter type has been provided in the reaction of t-butyl radicals [25]. Since it has been argued that $J(r)$ is zero for the greater part of the RP lifetime, it may well be that this second type of resonance is likely to be the more common in studies involving neutral radicals in solutes of normal viscosity. In either case, the important implication is that even very low fields may have significant effects on radical reactions. This may be of especial significance in the possible effects of environmental magnetic fields on biological systems. That rather higher, but still low, fields can affect a biochemical reaction is demonstrated in figure 6.

The overall field-dependence of the spin mixing probability when the coherent field processes dominate the behaviour is shown in figure 7. A characteristic plateau region exists from the field value at which the $T_{\pm 1}$ states first become effectively

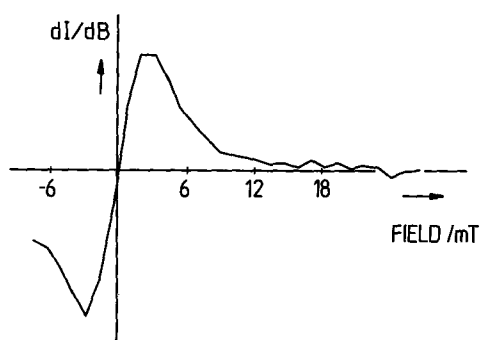


Figure 6. The rate of change of fluorescence intensity I from a bioluminescent reaction with the strength B of an applied magnetic field, showing the reaction yield to be influenced by small magnetic fields. This trace was obtained using a field-modulation technique, developed to have high sensitivity [26], and shows that the effect reaches a plateau value by the time the field reaches about 12 mT, when the derivative no longer changes as the field is increased. The derivative trace exhibits inversion symmetry about the zero-field position as the field is reversed, and the maxima occur at the $B_{1/2}$ values. The behaviour is as expected for the progressive decoupling of the $T_{\pm 1}$ states from the others as the field is increased, but no low-field resonance (see text) is evident in this system. The sample consisted of 7.5×10^{-4} M hemin in 0.44 M hydrogen peroxide, mixed 1 : 1 (vv) in a flow cell with 10^{-3} M luminol in 0.05 M sodium hydroxide solution [27].

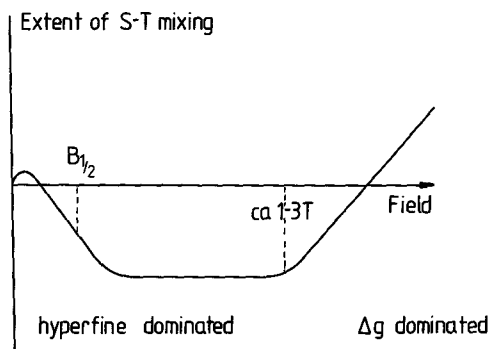


Figure 7. The variation of the extent of S-T mixing with the applied field strength for a typical RP of organic radicals, showing the very low-field resonance, the development of a plateau region as the $T_{\pm 1}$ levels separate off, and the increasing (linear) contribution from Δg mixing at high field. Note that the plateau region extends between roughly 10 m T and 1 T, implying that quite low fields are as effective in influencing reaction as are rather higher ones, provided that hyperfine mixing is dominant (as is usually the case). This makes field effect experiments comparatively inexpensive and convenient to perform. This diagram also broadly represents the probability of geminate reaction of a triplet-born RP, with reaction through a singlet channel, but this depends too on the probability of re-encounter within the geminate period (equation (8)), and it must be remembered that the faster the spin mixing, the greater the number of collisions leading to reaction that occur.

decoupled from the others until the Δg effect dominates at high fields; this shows no saturation behaviour. The important implication is that a field of a few tens of millitesla is as effective in influencing reactions as is one of up to a tesla. The pre-saturation behaviour has the significance that the half-saturation field, $B_{1/2}$, depends upon the natures of the radicals present [28] through the relations:

$$B_{1/2} = 2(B_1^2 + B_2^2)/(B_1 + B_2) \quad (6)$$

and

$$B_i = \left\{ \sum_k a_{ik}^2 I_k(I_k + 1) \right\}^{1/2}, \quad (7)$$

where a_{ik} is the hyperfine coupling of electron i ($= 1, 2$) to nucleus k in the spin state I_k .

In this paper we are concerned with the RP as a reaction intermediate, but we note that similar magnetic mechanisms are effective whenever paramagnetic pairs of any description are formed, for example in triplet-triplet and in triplet-doublet [29] processes, and they are similarly sensitive to applied fields; here, however, $B_{1/2}$ is determined by the electron spin-spin interaction in the triplet (the zero-field splitting) and is characteristically different from that for the doublet-triplet (RP) processes as given by equation (6). Other field sensitive mechanisms are known in reactions which do not involve RPs, for example by selective reaction of triplet sub-levels in excited state reaction intermediates [30].

We now turn to the second part of the problem, diffusion.

4. Diffusion

It has been stressed that only those encounters are effective in producing geminate reaction in which the RP has the required spin state, which varies in time, and diffusion on the appropriate, very short, timescale is an essential consideration. Using the above model in which spin mixing and diffusion (through the region where the exchange interaction is comparable to the hyperfine interaction) occur on different timescales as a result of the near stepwise nature of $J(r)$, the overall reaction probability within the RP can be expressed as [31, 32].

$$P_R = \lambda \int_0^\infty P_S(t) P_E(t) dt, \quad (8)$$

where λ is the probability that two radicals which encounter in the singlet state react, $P_S(t)$ is the probability of the RP being in the S state at time t , and $P_E(t) dt$ is the probability of a re-encounter during a time interval dt at that time. $P_S(t)$ is directly calculable from the spin Hamiltonian of the system (see below). $P_E(t)$ has been calculated using random walk theory [31, 32], free diffusion theory [33], and refinements of the two [8, 34]. All have in common that the re-encounter probability falls very rapidly in time after RP creation, as directly shown by the iodine atom recombination results described above. In normal solutions geminate re-encounters are essentially over within some 10 ns of radical pair creation. In micellar solutions, where aggregates of surfactant molecules can function as molecular supercages, the geminate stage may be extended up to hundreds of nanoseconds, or even some microseconds [35]. An example of a field effect on RP recombination kinetics in a micellar system is shown in figure 8.

Diffusion has a profound influence on the mathematical form of P_R and, consequently, on its functional dependence on the strength of the applied magnetic field.

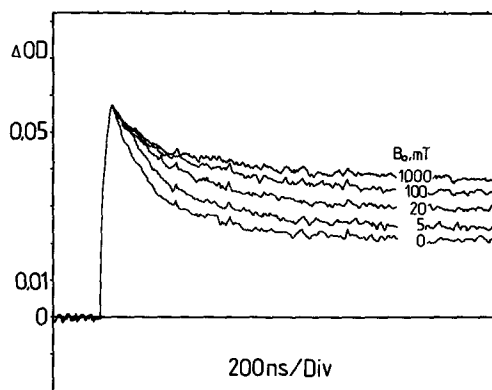


Figure 8. The effect of applied magnetic fields on the transient absorption decays of RPs produced by photoelectron transfer from aniline to triplet excited thionine in reverse micelles of hexadecyldimethylbenzene ammonium chloride in benzene. The micelles, containing water at a molar ratio of 15 per one surfactant molecule, correspond to surfactant-enclosed droplets of about 3 nm radius. The decay on the timescale shown corresponds to intramicellar RP recombination and is slowed in the presence of a field, B_0 . The non-zero absorption at the longer times originates from radicals that escaped the geminate recombination period of the reaction [36].

However in isotropic solutions of normal viscosity this functionality is largely independent of the precise model used. This is because spin mixing only occurs when $J(r)$ has fallen sufficiently as the radicals separate to allow it, and at such times the re-encounter probability is not strongly model-dependent, although it may be so at earlier times. To a good approximation it is found that all models give

$$P_R \propto |Q|^{1/2}, \quad (9)$$

where Q is the matrix element for S-T mixing. In high fields and S-T₀ mixing,

$$Q = \frac{1}{2} \left\{ \Delta g \mu_B B + \sum_k a_{1k} m_k - \sum_l a_{2l} m_l \right\} \quad (10)$$

where m_k and m_l are the magnetic quantum numbers of nuclei in the radicals 1 and 2, respectively, that form the RP. The Δg and hyperfine terms of the previous discussion are evident, and the negative sign ensures that the electrons on the two radicals experience different hyperfine fields. In high fields the singlet probability $P_S(t)$ oscillates periodically with a frequency of $(2Q/\hbar)$. The square-root dependence, symptomatic of RP behaviour in liquids of low viscosity in all of its manifestations, results from the diffusional averaging. At higher viscosities, or in diffusion in confined regions of space, the functional form changes [37–39].

A general theory can be written which includes all possible spin and diffusion trajectories and in which the above model is a special case, assessable by the assumptions made. Reaction is treated as projecting out of the ensemble of radical pairs those that happen to encounter with a reactive spin orientation. We now turn to this treatment.

5. The theory of radical pairs

This theory provides the basis for understanding RP reactions, CIDEP and CIDNP. All are ensemble phenomena and complete information on them is carried

in the density matrix $\rho(r, t)$ which characterizes the spin state of the RP at a time when the radicals are a distance r apart. We shall assume that rotation is sufficiently fast to remove any features which depend on the relative orientations of the radicals, although this may be a limitation in the reactive situation. The density matrix evolves in time according to the rate equation known as the stochastic Liouville equation:

$$\frac{d\rho}{dt} = \{H^* + K^* + L^*\}\rho, \quad (11)$$

where H^* , K^* and L^* are superoperators which describe the effects of coherent spin motion, reaction and stochastic motion in configuration space; a relaxation term to account for a contribution from incoherent spin mixing can be included when necessary.

An important characteristic of RPs is that they are created by spin-conserving reaction in either pure S or pure T states, and these subsequently become mixed. Their electronic nature at any time is described by a density matrix, the elements of which are ensemble averages of products or cross-products of the coefficients characterizing the wavefunctions of the individual radical pairs. As an example, consider an RP in a spin state described by the wavefunction in equation (12), below. It is written as a product of a linear combination of coupled electronic spin states and a nuclear wave function, φ_N :

$$\psi(t) = [c_S(t)|S\rangle + c_T(t)|T\rangle]\varphi_N. \quad (12)$$

The differential contribution of RPs with this wavefunction to the density matrix of the sub-ensemble with the same nuclear spin function, φ_N , is

$$d\rho_{SS}(N) = c_S(t)c_S^*(t) dp(N), \quad (13)$$

and

$$d\rho_{ST}(N) = c_S(t)c_T^*(t) dp(N), \quad (14)$$

where $dp(N)$ is the relative statistical weight of RPs with this wavefunction.

The Liouville operator H^* is related to the spin Hamiltonian of the RP by

$$H^*\rho = -(i/\hbar)[H, \rho], \quad (15)$$

where

$$H = -J(r)(2S_1 \cdot S_2 + 1/2) + \mu_B g_1 S_1 \cdot B + \mu_B g_2 S_2 \cdot B + \sum_k a_{1k} I_{1k} \cdot S_1 + \sum_l a_{2l} I_{2l} \cdot S_2. \quad (16)$$

The reaction superoperator K^* is written in more general terms than might be expected from the discussion above, in that it takes into account the possibility of reaction in either the S or the T state of the RP; although the former is chemically more common, all that is required is that the two probabilities should differ or that S and T reaction should yield different reaction products. This is expressed in terms of the rate constants $k_S(r)$ and $k_T(r)$, written as distance-dependent so that, as in the conventional theory of diffusion controlled reactions, a critical reaction distance can be introduced.

$$K^*\rho = K_S^*\rho + K_T^*\rho = -(1/2)k_S(r)[Q_S, \rho]_+ - (1/2)k_T(r)[Q_T, \rho]_+ \quad (17)$$

The negative sign occurs because reaction removes RPs from the ensemble, and Q_S and Q_T are the projection operators on the S and T manifolds of the spin states. The anticommutators are used to ensure conformation with conservation laws [40].

L^* represents the diffusion in the system, and it describes the time evolution of the RP probability distribution over r . It is chosen to be appropriate for the physical system under consideration, and in isotropic solution is often given the Smoluchowski form,

$$L^*\rho(r, t) = D[\nabla^2\rho + (1/kT)\nabla(\nabla U(r))\rho], \quad (18)$$

where D is the sum of the diffusion coefficients of the radicals and $U(r)$ is an inter-radical potential, for example the Coulomb potential if the radicals are charged. L^* does not usually operate on the spin part of $\rho(r, t)$, although care must be taken if the exchange interaction is included in $U(r)$ [41].

The SLE corresponds to a set of coupled linear partial differential equations and, in general, no closed analytical solution can be obtained of them because, with H^* and K^* r -dependent, the spin and diffusional parts of the equation cannot be separated. Only numerical solutions are then possible [37, 38, 42], although their results have been described in approximate analytical form [37]. By making the assumptions described in the simple model discussed above, separation is obtained and the SLE can be solved, but closed expressions have been presented only for cases involving S-T₀ mixing at high field [43, 44]. A detailed comparison of the results of analytical solutions using cage and free diffusion models of motion within the RP has been made recently [45]. The $Q^{1/2}$ dependence of equation (9) was shown to be specific for the case of rapid free diffusion. Other terms appear if diffusion is slow or if the system involves strong cages. RP phenomena in photosynthetic reaction centres have been reproduced satisfactorily using further simplified treatments [46–49]. A theoretical treatment of magnetic effects on RPs in micelles with particular consideration of spin relaxation, the influence of which becomes significant owing to the lifetime of the RP, has also been given [50].

6. The consequences of RP existence

Here we separate the observation of effects that follow as a consequence of the existence of RPs from those experiments that interact with or draw information from or about the RP directly. The latter are covered below. The subjects covered in this section are (1) CIDNP, (2) CIDEP, (3) the observation of geminate reaction products from radicals created from triplet precursors, (4) magnetic isotope effects and (5) the effect of magnetic fields on chemical and biochemical reactions. This section could fill books on its own and here we simply attempt a broad summary.

6.1. CIDNP

The origin of CIDNP has been described briefly above. Interestingly, the basic mechanism does not involve the electron exchange interaction but relies upon spin mixing, followed by spin-selective reaction, only. However, the magnitude of the polarization is predicted [10, 51], and observed [10] to depend upon $J(r)$.

6.2. CIDEP

A similar phenomenon, CIDEP, is observed, now as a non-Boltzmann distribution amongst the electron energy levels, in the ESR spectra of transient free radicals [52, 53]. It is more fleeting than CIDNP since it persists only for a period of the spin-lattice relaxation time in the radicals, and this is normally of the order of a few microseconds (contrast the seconds in NMR spectroscopy). Its common observation

and recognition consequently awaited the development of techniques for obtaining ESR spectra on this timescale after radical creation, although its influence was apparent in previous studies of continuously generated radicals. It originates in two different processes, the reaction of spin-polarized precursor triplet molecules and interactions within the RP. It is the latter, more common, form which is relevant here. In high-fields it arises, as does CIDNP, in spin mixing of the S and T_0 states of the RP only but, by contrast with CIDNP, its creation requires both the spin mixing and the $J(r)$ interaction. No electron polarization results from simple spin mixing since the S and T_0 states, and their spin-mixed combinations, contain equal amounts of α and β spin character on each radical. CIDEP owes its origin not to a simple spin-sorting process, as does CIDNP, but rather to the action of the $J(r)$ interaction producing a phase shift in the spin-mixed electronic wavefunction of the radical pair. The full theory is closely analogous to that of the RP given above and, since CIDEP has formed the subject of several recent articles by one of the authors [52–54], it will not be discussed further here. We note, however, that CIDEP and CIDNP are both valuable sources of information on $J(r)$.

6.3. Geminate products from triplet reactions

Chemically, formation of geminate products from the reactions of triplet excited states may be the most extraordinary consequence of RP activity, particularly because it has not previously been appreciated as being remarkable. It underlies, of course, much of photochemistry which, in contrast to our other examples, is performed usually in the absence of an external magnetic field. Nevertheless, it is apparent from the above discussion that no reaction can occur between triplet-correlated radicals at the instant of their creation, and that geminate recombination occurs only as a result of spin mixing under the action of the hyperfine interactions.

This implies that we should now consider the zero-field situation in more detail. In normal solutions diffusion is, to all intents and purposes, independent of whether a field is applied or not, and this side of the problem is unchanged from the situation discussed above. The coherent spin mixing originates in the hyperfine terms of the spin Hamiltonian, each of which involves the scalar product of the spin vectors, and it is useful now to expand this product and to introduce the raising and lowering operators, S_{\pm} and I_{\pm} . These change the electron and nuclear spin angular momenta, respectively, by one unit, and conservation of angular momentum is maintained by the changes occurring in opposite directions for the two coupled particles.

$$aI \cdot S = a[I_x S_x + I_y S_y + I_z S_z] \quad (19)$$

$$= a\{I_z S_z + (1/2)[I_+ S_- + I_- S_+]\}. \quad (20)$$

The wavefunctions of the zero field states can be written using the high-field states as basis functions, and the first term in this equation serves to mix the S and T_0 contributions, whereas the others serve to mix in the $T_{\pm 1}$ states. The effect of S– T_{-1} interconversion is observable at high fields too, if the hyperfine coupling is strong or if diffusion is inhibited to maintain the members of the RP at the inter-radical separation where the levels cross (see figure (3b) for comparatively long periods of time. The coupled nature of the spin flips is then manifest in the CIDEP intensities of the ESR spectra of the radicals concerned; in contrast to S– T_0 CIDEP spectra, these are entirely in emission for radicals from triplet precursors, with a characteristic hyperfine dependence [55, 56].

We conclude therefore that the requisite spin-state interconversion necessary for the occurrence of triplet state photochemistry in many reaction systems is caused by the hyperfine interaction. It should be remembered, however, that spin mixing can occur in zero field, as in high, only when the mixing interaction is not swamped by the exchange one. This consideration, and the interplay of spin mixing with diffusion, suggests a whole new dimension to photochemistry in zero field which is largely unexplored at present. Indeed it is one of the objects of this article to bring this possibility to the attention of photochemists and kineticists.

In some systems, of course, the hyperfine interaction is not the source of the spin mixing necessary for the formation of geminate products from triplet precursors; atoms or radicals lacking magnetic nuclei, for example, cannot interchange their spin states in this way. Here other mechanisms play their part, and they may be dominant even where hyperfine-driven mixing is possible. A common example is spin-orbit coupling, the origin of the very rapid reaction of the iodine atoms mentioned in the Introduction, for these are formed from reaction of an excited triplet state of the iodine molecule. In general, if RPs are involved as intermediates in reactions, the spin-orbit mechanism is effective only if the members are in close contact [57].

6.4. Magnetic isotope effects

An obvious consequence of the hyperfine interaction representing the main source of spin mixing in many RPs is that kinetic changes are expected if magnetic isotopes are substituted into the radicals. As a corollary, it is to be expected that in radical ensembles containing magnetic isotopes in natural abundance, those that actually contain these nuclei will react at different rates from those that do not. Most experiments that have utilized this principle have been concerned with the effects of $^{12}\text{C}/^{13}\text{C}$ or $^1\text{H}/^2\text{H}$ substitution [7, 58–60] but possible evidence for hyperfine influence has been provided for reactions involving an atom as heavy as Ge [61, 62]. It is noteworthy that, although isotope effects dependent upon isotopic mass usually follow a $M^{1/2}$ dependence, and thus produce little discrimination between the isotopes of the heavier elements, nuclear moments show no corresponding regular trend. They vary between zero and several nuclear magnetons amongst the isotopes of the same element, with concomitant variations in the strengths of their hyperfine interactions, and may cause much more significant kinetic discrimination.

An important consequence of magnetic isotope-dependent RP kinetics is that RPs of different isotopic constitution differ in the ratio of geminate cage to escape products that they form. As a result, when subjecting an isotopic mixture of molecules to a reaction involving RP intermediates, an enrichment of magnetic and nonmagnetic isotopes takes place into different types of product. In this way single-stage isotopic enrichment factors much larger than those expected from kinetic mass isotope effects are obtained. In some cases, the enrichment factors can be enhanced by applying suitable external magnetic fields [63].

6.5. Magnetic field effects on chemical reactions

The origins of the effects of magnetic fields on chemical reactions which involve RPs have been described above; a detailed description requires use of the full Hamiltonian, rather than just its high-field form, as above. Examples of such effects on chemical kinetics ('magnetokinetics') and on reaction yields have been summarized in a recent review article [7]. They have been observed in isotropic solution, in micelles and at surfaces and here we simply stress two aspects. First, they can be enhanced by

suitable choice of reaction conditions by recalling spin evolution takes time, and that only encounters in the appropriate overall spin state are effective in leading to reaction; the stratagem is simply to optimize the number of such re-encounters, for example by extending the geminate period of the reaction. This is important when such effects are to be exploited in synthesis, and the ability to manipulate the RP in this way provides a novel tool to the chemist. Magnetokinetic effects can often be detected in normal solutions, and themselves have great significance: they may be used to detect a free radical stage in a reaction pathway, and to determine the kinetics of this stage uniquely. In this way a part of an overall complex reaction can be delineated. This has enormous potential use when the radicals may be at very low concentrations in which they may not be observable directly, for example in enzyme reactions, many of which proceed through radical pair-like steps. Second, field effects have several different origins which optimize at quite different field values, and even extremely small fields can produce significant effects, the magnitude depending on the diffusive conditions besides the spin mixing ones. A study of the field-dependence of the effect allows the spin mixing mechanism to be identified, and the chemical mechanism to be confirmed.

7. Direct observation of the radical pair (see also [64, 65])

Although the circumstantial evidence for the existence of the RP is convincing, further progress demands that it should be detected directly and characterized via its spectroscopy. There are already a number of ways in which this has been done. The most obvious is to obtain its ESR spectrum using fast time-resolved methods [66–68]. Inspection of the RP Hamiltonian in equation (16) shows it to differ from that of two isolated radicals only in the presence of the exchange term. This extra term is in the coupling of one electron to the other and, for small values of $J(r)$, it simply splits the normal hyperfine levels into two. Each transition in the ESR spectrum of the RP, obtained, as normal, using low resonance field strengths, should consequently be split into a doublet, of separation $|J(r)|$. Observation of this splitting constitutes direct evidence for the existence of the RP. It has been observed in micellar and in viscous solutions, in which the RP lifetime is enhanced over normal solutions; a spin-polarization effect (not the usual RP one [66, 67]) causes the two components (which are absorptive in the magnetic resonance sense of involving detection of the out-of-phase part of the Bloch susceptibility) to be observed with opposite phases of their signals. An elegant and detailed analysis has recently been given of similar experiments performed using a pulsed spectrometer [69]. Here the authors demonstrated the detection of a dispersive (in-phase) contribution to the signal and showed that its intensity allowed calculation of $J(r)$ from its amplitude and from a knowledge of the escape rate of radicals from the geminate cage.

The fact that a non-zero value of $J(r)$ is obtained under the conditions described is interesting. In our discussion above it was argued that $J(r)$ is negligible for the majority of the time that the RP exists, and the implication is that in these situations there exists a potential ($U(r)$ in equation (18)) which tends to hold the members of the pair together; this is instinctively the case in a micelle, although the nature of the potential may not always be obvious. The significance of the value obtained experimentally from measurements based upon RP effects, including CIDNP and CIDEP, deserves comment: it is the average value detected on the timescale of the particular experiment, or, more strictly, on the timescale of the production of the observable. It

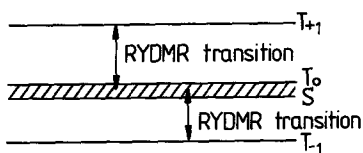


Figure 9. A schematic drawing of the energy levels of the RP as they exist, in a large applied field, for the greater part of the lifetime of the RP, when $J(r)$ is small or negligible; the hatched region is supposed to represent that the S and T_0 states are mixed by the hyperfine interaction, and that the RP population is entirely in these mixed states, if the RP is created in singlet form. This would be the situation if the RP was created from a singlet precursor, and if no diffusion occurred out of the RP eventually all radicals would form geminate products. This can be prevented by inducing resonant transitions from these mixed states to the unreactive $T_{\pm 1}$ ones, which cannot spin-mix with the others on account of their energy separations from them. The geminate product yield consequently falls. In the actual experiment, the resonance condition is approached by sweeping the applied field at a constant irradiation frequency, and it is detected by optical monitoring of the molecules leaving the geminate RP, either the product or the escaping free radicals. It is known consequently as reaction yield detected magnetic resonance (RYDMR). The same principle is the basis of the stimulated nuclear polarization (SNP) experiment, in which detection is by NMR spectroscopy, see text.

is arguably this average over the period of time for which spin mixing can occur, i.e., that period for which the magnetic interactions are of the order of $J(r)$, and this depends on the hyperfine coupling in each individual case. It promises to be difficult to interpret in detail.

The ESR experiment has been discussed in terms of the spins on the individual radicals of the pair. That is, we have assumed that the spins are only weakly coupled, and we have made no use of the coupled representation. Now we reverse this and discuss transitions which concern the coupled states of the pair itself. It has been seen above that in applied magnetic fields which exceed the hyperfine couplings only the S and T_0 states can interconvert, and the $T_{\pm 1}$ ones are decoupled (figure 9). It is possible to recouple them by applying a resonant fluctuating field of the requisite frequency to cause spectroscopic transitions between them and the spin-mixed S and T_0 states. Since RPs in triplet states (normally) cannot react, this serves to affect the reaction probability in the ensemble of RPs in the opposite sense than does the application of a static field. For example, for an RP created in a singlet state such transitions produce triplet RPs and inhibit geminate reaction. Since the RP lifetime is short, these experiments require high radiation intensities, often at microwave frequencies, and ESR detection cannot be used. Instead, the resonance is detected by the continuous optical monitoring of the geminate product yield (or the concentration of free radicals escaping the cage) as the resonance condition is swept through. The experiment is known consequently as reaction yield detected magnetic resonance, RYDMR [70, 71].

At low microwave field strengths the RYDMR spectrum would be expected to be identical to the ESR one of the same radical pair but, in practice, the strength of field required to effect the transitions to an appreciable extent during the RP lifetime causes line-broadening, and lack of spectral resolution (figure 10a). At higher field strengths the microwave field is no longer a weak perturbation which simply causes transitions, but it mixes the levels it connects and produces new, and even inverted, lineshapes (figure 10b). These have a complex origin involving both the state

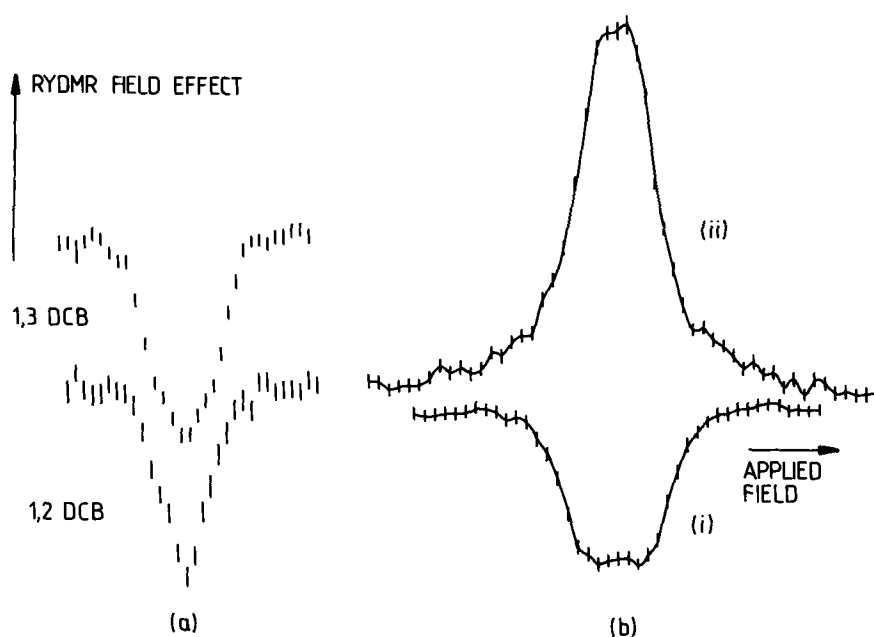


Figure 10. (a) RYDMR spectra, obtained at low irradiating field strengths, of the RPs formed on irradiation of pyrene in the presence of 1,3-dicyanobenzene (1,3-DCB) and 1,2-DCB. Although individual hyperfine lines are not resolved, the spectrum of the former is broader as a result of higher coupling constants in the 1,3 isomer. Hyperfine structure has been resolved for larger couplings in other systems [72], but no line-splitting due to $J(r)$ has been reported as yet in solution observations. (b) As the irradiation field strength is increased in the 1,3-DCB solution, the RYDMR spectrum broadens, and begins to split (i), and then inverts (ii) to attain a constant amplitude as this field is increased further; in between, complex lineshapes are observed [76].

separation and the mixed wavefunction of the RP, both of which vary as resonance is approached [73–75]. Understanding these, and the origin of the inversion at high microwave field strengths, requires further consideration of the principles involved, and we move into the familiar rotating frame of magnetic resonance theory. It is a standard result that in a reference frame rotating at the resonance angular frequency the effective static magnetic field in the direction of the applied field falls to zero, and the spin system experiences only the resonant field, which is stationary in this frame of reference. In consequence quantization is now with respect to its direction rather than the applied field one, and we need to ask how the T_0 state, for example, transforms into this new axis system. It becomes distributed over two spin components, t_+ and t_- , which are quantized in the direction of the resonant field. As the strength of the microwave field is increased, these two rotating frame states, which contain T_0 completely (although not exclusively), become progressively separated in energy until their hyperfine mixing with the S state is entirely suppressed. This therefore causes a change in reaction yield at high microwave field strength in the opposite sense from that produced by a weak irradiation field, described in the basic introduction to the RYDMR phenomenon above.

In cases where the average value of $J(r)$ differs from zero, analysis of RYDMR spectra yields its magnitude, besides the rate constants of the singlet and triplet

reaction channels of the RP, and hence its lifetime. Different experimental systems can yield qualitatively different lineshapes, as for example between observations of the photosynthetic reaction centre and of reactions involving exciplexes [76], although all forms are encompassed by the same basic theory.

A closely related experiment is stimulated nuclear polarization (SNP) [77, 78]. It involves magnetic resonance at two different frequencies, with the observations made by NMR rather than by optical spectroscopy. The RP is created outside of the magnetic field of the NMR spectrometer but in a subsidiary field in which the resonant transitions between the RP electronic states described above are caused by radiation of the appropriate frequency. The experiment is performed in a flow system, and after irradiation the sample flows, within the spin-lattice relaxation time of the nuclei, into an NMR spectrometer where the spectrum of the reaction products is recorded. The SNP phenomenon is most easily understood in the high field limit (although in most SNP studies reported to date the strength of the field in which the transitions are induced has not exceeded 50 mT). In this limit, it is the T_0 spin state of the RP which is most strongly mixed with the S one, so that the geminate recombination causes a relative underpopulation of the T_0 state relative to the $T_{\pm 1}$ states, if the RP has been created from a triplet precursor; a relative overpopulation results from singlet reaction. Inducing hyperfine-dependent electron transitions between the triplet spin states causes changes in the populations of the hyperfine sub-levels of the T_0 state and results in an increase (or decrease, depending upon the spin multiplicity of the precursor) in the corresponding nuclear populations of the geminate product. These are detected as induced nuclear polarizations in the NMR spectrum of this product. If the intensity of an NMR line is monitored as the irradiation frequency of the sample in the external field is swept through resonance (or the field is swept with the frequency maintained constant), the SNP spectrum is obtained. As with the RYDMR experiment this constitutes the ESR spectrum of the RP itself providing that low field strengths at the frequency of the radiation causing the transitions are employed. With the small applied static magnetic fields currently used in the irradiation region, it may be strongly influenced by second-order spin coupling effects besides by additional spin-mixing between the different RP spin states, both in contrast to the RYDMR experiments described above, which are usually performed in a high external field. At high static field strengths, the SNP and RYDMR observations of the spectrum of the RP are directly comparable. Similarly, the line-shape changes observed as the strength of the irradiation field which induces the spin mixing in the RP is increased are identical in the two experiments. Values of $J(r)$ can be obtained, in principle, from the analysis of the results of either.

It is noteworthy that although the observation of SNP depends upon spin-mixing and reaction within the RP, the effect is completely separate from the generation of nuclear polarization by reaction alone (i.e., CIDNP); in consequence, there is no requirement for the NMR lines monitored to exhibit CIDNP. This is best seen by an example. We consider an RP, created from reaction of a triplet precursor, with coupling to a single proton in one radical and to none in the other; furthermore we shall take Δg to be zero. Inspection of equation (9) then shows that $|Q| = a/2$ for RPs containing nuclei in either the α_N or the β_N spin states. In both types of RP therefore, S- T_0 spin mixing is equally effective and yields equal quantities of cage products, but these have opposite, but identical, nuclear spin polarizations. In consequence, over the whole ensemble, any polarization cancels and no net CIDNP effect results. Nevertheless, two lines appear in the SNP spectrum since this results from transitions

in the RP monitored by their effect on the intensity of the single NMR line. Thus if the RPs containing nuclei in the α_N nuclear state are brought into resonance, they will form the cage product more efficiently, and in its NMR spectrum the line is observed in enhanced absorption. On the other hand, as the resonance condition of the RPs containing β_N is satisfied they will in turn lead to more efficient production of cage product, now to yield the same line in emission. The SNP spectrum obtained by continuous monitoring of the intensity of the line consequently consists of a doublet, the components of which are in opposite phase.

8. Conclusion

In this paper we have attempted to demonstrate that the spin-correlated radical pair exists, and is a genuine reaction intermediate which exerts a profound influence on the chemical kinetics and product formation of radical reactions. It is in its infancy as a species to be studied but it underlies all radical combination chemistry, and reactions, such as polymerizations [79], which stem from initial radical-creating events. It also underlies the bulk of photochemistry, including photosynthesis. Its major importance is therefore in the normal situation in which reaction proceeds without an external magnetic field applied. Nevertheless, we have attempted to present the evidence for its existence in the context of the magnetic resonance experiments which gave the first hints for it, we hope in a coherent way, and to show the relation of these studies to the zero field situation. This has been to expose the basic magnetic origins of the essential spin-mixing process, and, in particular, the seminal role of the hyperfine interaction in normal radical reactions. We have also attempted to sum up the existing knowledge of the species, and to describe the overall theoretical approach to it. Nevertheless, the greatest impact of the existence of the RP is practical, and experimental, and its recognition as a reaction intermediate will open up new areas of chemical thought and achievement. This will happen particularly where the significance of magnetically driven spin-mixing, and also its interaction with fast diffusion, have previously gone unappreciated in the context of chemical reaction. Not the least, the existence of spin-correlated radical pair provides a firm basis for believing that effects of magnetic fields will be important in biological systems, even at environment field strengths.

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