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Physical chemistry through electron spin polarisation. The Bruker lecture †

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New methods are introduced for studying novel physical chemistry through observations of spin-polarized radicals. This includes the photophysics of molecules in solution, including the anisotropy of the rates of inter-system crossing between excited singlet state molecules and excited triplet state sub-levels, and measurement of the re-encounter probabilities of free radicals during the geminate period of their reaction. A simple and quite general method is described for measuring the absolute magnitudes of the spin polarization in both triplet states and radicals in solution.

Introduction

The first successful EPR observations of transient free radicals produced by flash photolysis[1,2] and pulse radiolysis[3] yielded spectra of quite unexpected appearance. The intensities, and sometimes the phases, of the lines were not those familiar from observations on stable radicals, although the line positions were unaffected and still allowed radical identification. Spectra from hydrogen and deuterium atoms observed in steady state concentrations under continuous radiolysis of solutions had shown similar anomalies some years before,[4] but the real-time nature of the new experiments on transient radicals observed as they were formed and decayed enabled the true nature of the phenomenon to be deduced. In particular, the line intensities observed after instantaneous radical formation decayed in time at too fast a rate to be compatible with the re-combination of radicals in bimolecular processes under normal diffusion control. It was soon apparent that this was due to rapid population changes in an ensemble of radicals in which the initial populations of the hyperfine states were not those expected from systems at thermal equilibrium with their surroundings. This physical process would simply be spin-lattice relaxation did it not happen in the continuous presence of a microwave field which helps drive it.[5] The ensemble was said to be 'spin-polarized' when first observed, and it appeared that the polarization arose in the chemistry of the system, a phenomenon called chemically induced dynamic electron polarization, CIDEP.

Confusion was caused by the early flash photolysis experiments yielding spectra with all their lines in a single phase, either absorption or emission according to the molecule irradiated, whereas the radiolysis experiments displayed spectra with equal intensities of lines in absorption (*A*) and emission (*E*), with no overall spin polarization. In the former, the relative intensities of the lines were exactly as would be expected from the degeneracies of the hyperfine states, but in the latter unfamiliar intensities were observed in lines of opposite phase exactly distributed in total intensity between the low- and high-field parts of the spectrum. It was subsequently realised[6] that two separate and independent mechanisms generating polarization were in action, with different implications to the spectral appearance; more are now known, but are much less common.[7]

The spectra of mixed phases were observed from neutral radicals produced in pairs ('radical pairs'), for example in simple bond-scission or atom-abstraction reactions. The polarization originated in magnetic interactions within the radical pair in what has become known as the radical pair mechanism (RPM, see below). Since radicals are always created in pairs it was not obvious why this type of spectrum was not observed in all observations of transient radicals, for example in the flash-photolysis experiments. It happened that the early experiments of this type all involved radical ions, and not neutral radicals, and radical ions may undergo very rapid degenerate electron exchange reactions with their parent molecule. If these are sufficiently fast they average out any difference in phase or intensity between the low-and high-field halves of the spectrum, leaving only the net contribution from the second polarization mechanism.[8] When flash photolysis was used to create neutral radicals, their spectra showed the combined effects of the two independent polarization processes, and could be reproduced by adding the biphasic contribution from the RPM to the single phase one with undistorted hyperfine intensities from the second mechanism. This caused the total signal intensity in one or the other phase to exceed that of the other. Spectra of this type were never, however, observed from the pulse radiolysis experiments, and it became apparent that the net signal arose in a process associated with the photophysics and photochemistry of the parent molecule. It is known as the triplet mechanism, TM.[9]

Analysis of CIDEP results usually involves interpretation of the spectra to identify the chemical natures of the radicals formed, to use the analysis outlined above to determine the origins of the spin polarization, and to use the phase of the signals to deduce the spin multiplicity of the precursor molecule which reacted to form radicals. It has provided a previously non-existent direct link between the photophysics of a molecule and the photochemistry which leads to an identified radical product. It has been used, for example, to demonstrate the predominant formation of a single geometric isomer of a radical from reaction of a singlet state, and another isomer from the triplet state of the same molecule, information which could be obtained in no other way.[10] The time-dependence of CIDEP signals has provided values of reaction rate constants[11–14] and of electron[15] and triplet[16] relaxation times in solution, but CIDEP spectra contain other information of fundamental interest within physical chemistry which has not yet been extracted. Although the RPM and TM have been understood for sometime, and detailed theory given, this theory has not been exploited to yield the properties of the triplet states or the intimate details of radical reactions. This we do here, but we must first summarise the polarization mechanisms themselves in sufficient detail for what follows.

The triplet mechanism

Those photochemical reactions which yield radicals whose spectra exhibit net spin polarization occur *via* reaction of the

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excited triplet states of molecules which are formed by intersystem crossing (ISC) from the excited singlet states which result from light absorption by the singlet ground state with conservation of spin multiplicity. This photophysical process commonly precedes the photochemistry of molecules. The triplet possesses three sub-levels whose energies are non-degenerate even in zero applied magnetic field, as a result of the dipolar ('zero-field') interactions between the two unpaired electrons it contains. ISC occurs within the molecule at different rates into each, a fact known from solid state observations years before the first CIDEP experiments were performed[17]. This implies that at the instant following ISC the populations of the triplet sub-levels differ from those of a thermally-equilibrated triplet, and the ensemble of triplets is spin-polarized. In small molecules ISC is often dominated by spin-orbit coupling which allows change of the spin angular momentum of the molecule at the expense of orbital angular momentum, whilst conserving the whole. ISC links the singlet to a triplet sub-level with the same overall (orbital × spin) symmetry, creating spin polarization because the spin symmetries of the three sub-levels differ.

The ensemble of triplets is polarized in the molecular frame of reference, but the eventual EPR experiment is performed inside the external magnetic field of the EPR spectrometer in the laboratory frame. Rapid relaxation in the triplet normally causes line-broadening and precludes its direct observation by EPR (a few exceptions are known[18,19]), and we are reduced to detecting its polarization indirectly in the radicals produced on its reaction through the CIDEP phenomenon. We have to consider, therefore, whether polarization established in the triplet in the molecular frame can become apparent in the same triplet in the laboratory frame. This has been discussed explicitly,[20,21] and is included in the theoretical treatments of the TM.[22,23] At first sight it is not obvious that the polarization can be transferred between the reference frames, since this involves a correlation between the molecular energy levels and the Zeeman levels of the triplet at high field. It has long been known that in a fixed and isolated molecule in the solid state, the relative energies of the triplet sub-levels change as the magnetic field is applied along each of the major axes of the dipole coupling tensor of the molecule. A state which lies above the mean energy in one field-direction may lie below it in another. Although symmetry-selective ISC continues to populate one specific level, this may lie above the barycentre of the system in one field direction, and below it in the other, leading to an emissively-polarized and an absorptively-polarized triplet in turn. In solution, the triplet molecule tumbles freely with respect to the field of the spectrometer, and this tumbling would be expected to average the population differences in the laboratory frame to zero. This is exactly true if the field is sufficiently high as to make the zero-field interaction negligible with respect to the Zeeman one, but at all normal operating fields of EPR spectrometers this is not the situation, and perturbation theory carried to second order shows that some polarization is transferred between the reference frames.[20,21] Selective state population is, however, less specific than in the molecular frame (itself not wholly specific), each molecular frame state correlating to different extents with more than one Zeeman state. The sense of the polarization is preserved, at X-band for instance, but the magnitude depends on the competition between the rates of molecular tumbling and crossing between levels, which causes it to vary with the rotational correlation time of the triplet. The magnitude of the polarization in the triplet ensemble before it reacts to form radicals therefore depends both on the nature of the molecules and their environment. This aspect of the TM has received little attention.

The effect of molecular rotation is summarised in the equation for the magnitude of the polarization in the triplet[22] (defined in an analogous way to that in the free radicals eventually formed, see below), taken to be cylindrically symmetric, [eqn. (1)].

$$P_{\mathrm{T}} = \frac{-4DK\omega_0}{15}\left\{\frac{4}{4\omega_0^2 + [k_{\mathrm{T}} + \tau_{\mathrm{r}}^{-1}]^2} + \frac{1}{\omega_0^2 + [k_{\mathrm{T}} + \tau_{\mathrm{r}}^{-1}]^2}\right\} \qquad (1)$$

Here D is the zero field coupling constant, K the dimensionless anisotropy of the ISC rates into the states perpendicular and parallel to the major axis of the molecule (assumed parallel to the D-tensor axis) defined by eqn. (2), where k is the total

$$K = (k_{\perp} - k_{\parallel})/k \qquad (2)$$

value, ω_0 is the operating frequency of the spectrometer, k_{T} is the reaction rate constant of the triplet molecule (see below), and τ_{r} is its rotational correlation time. For a given triplet system the size of the polarization therefore varies as the viscosity solution is changed, through its effect on τ_{r}, and sometimes k_{T}, in a predictable way.

It remains to consider the production of the polarized radicals which are the species observed. They are formed in pairs by reaction of the laboratory frame-polarized triplets with conservation of electron spin orientation. Thus, if the triplets are over-populated in their upper Zeeman (αα) state, the radicals are formed predominantly in their upper, α, state, and the EPR spectrum observed immediately after radical formation is in emission (Fig. 1). The inverse overpopulation would lead to absorptively polarized radicals; in either case the spectra of the two radicals produced exhibit identical polarizations. But the polarization of the triplets rapidly vanishes as spin-lattice relaxation occurs, usually in a few nanoseconds. In consequence the rate of reaction of the polarized triplet molecules must compete with their rate of spin-lattice relaxation if polarized radicals are to result, implying that the reactions must be very fast. TM polarization consequently only results from unimolecular bond-scission reactions and bimolecular electron and proton transfer ones at high substrate concentrations. Relaxation in the radicals is comparatively slow (with $T_1 \sim 1$ μs typically), and can be neglected during the polarization transfer process. A simple consideration of the competitive kinetics then gives an expression for the spin polarization P_{R} observed in the radicals which is defined (positively for a thermally-equilibrated system) as the ratio of the difference in populations of its electron spin states to their sum (the total number of radicals present), [eqn. (3)].

$$P_{\mathrm{R}} = \frac{P_{\mathrm{T}} k_{\mathrm{d}}[\mathrm{M}] + P_{\mathrm{T}}^{\mathrm{eq}}\,{}^{\mathrm{T}}T_1^{-1}}{k_{\mathrm{d}}[\mathrm{M}] + {}^{\mathrm{T}}T_1^{-1}} \qquad (3)$$

Here $P_{\mathrm{T}}^{\mathrm{eq}}$ is the polarization in the thermally equilibrated triplet, k_{d} the diffusion-controlled rate constant of the triplet molecule with a substrate, M, and ${}^{\mathrm{T}}T_1$ is the spin-lattice relaxation time of the triplet. This equation has been used to extract values of ${}^{\mathrm{T}}T_1$ from independent measurement of the rate constant (see below), although it has not been directly verified. It has recently acquired a new significance. A third polarization mechanism, the radical–triplet pair mechanism (RTPM) can occur in solutions in which radicals and triplets co-exist.[24] It yields polarized spectra which may exhibit both net and hyperfine-dependent biphasic contributions, the same qualitative characteristics as would radicals polarized along the more familiar TM + RPM route. The net contribution can be tested for TM origin by verifying whether the observed polarization varies with substrate in a manner consistent with eqn. (2).

The radical pair mechanism

Whereas the TM arises in the molecule which reacts to form radicals, the RPM results from interactions between the radicals once they are formed; it therefore originates later in time, although usually before observations commence even using fast detection methods (typically 30 ns post flash). This difference in time-origins is exploited below.

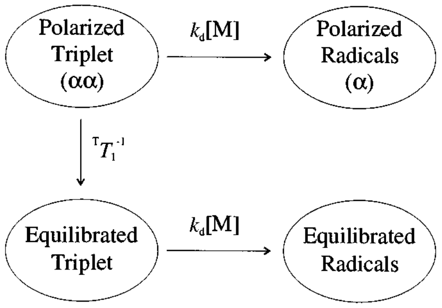

Fig. 1 The final stages of the production of spin-polarized radicals *via* the triplet mechanism. Anisotropic ISC within the molecule following light absorption leads to an ensemble of triplet molecules, here shown with excess population in the αα state, which rapidly relaxes to thermal equilibrium. However rapid reaction with spin conservation competes with the relaxation to form a spin-polarized radical sub-ensemble also with excess α spin. A further sub-ensemble of radicals, now with thermal equilibrium populations, is formed by reaction of the thermally equilibrated triplet. The EPR observation is of the whole ensemble, and therefore the spectra appear in emission, and calculation of the magnitude of the spin polarization in it in terms of the initial polarization in the triplet ensemble yields eqn. (3) of the text.[32] Relaxation of the radicals is assumed sufficiently slow to be neglected when calculating the initial polarization in the radicals.

Reaction or dissociation of a molecule normally occurs with conservation of spin multiplicity. Since the parent molecule exists in a pure spin state (usually singlet in ground-state chemistry and triplet in photochemistry) this leads at the instant of its formation to a radical pair in that same overall spin state. We shall discuss the spin state of the pair of radicals in the coupled representation in which we ask not what the electron spin state of an individual radical is at a given time after radical pair formation, but rather what the total spin of the pair is. This is even so when the radicals have separated by diffusion and do not interact. This is convenient for discussing radical pair effects in general, for re-combination of radicals, for example, is controlled by a strict spin selection rule: normally electrons must have antiparallel spins to form a bond, implying recombination through the singlet state of the pair. Reaction, however, plays no role in the generation of CIDEP in radicals produced together ('geminate radicals') although it does in that which arises in the encounters of freely-diffusing radicals ('F-pairs'); we are not concerned with these here.

When the pair is formed the radicals are not usually in contact, so that they do not immediately react (even if their electron spins are antiparallel) but diffuse apart (Fig. 2). The geminate pair persists for short periods (usually less than 30 ns, depending upon the solution) and it is diffusion on this timescale we are involved with, not the longer-time diffusion normally considered to control reactions of radicals in solution. Although the pair is created in a pure spin quantum state this is not an eigenstate of the system and so the wave-function evolves in time under the influence of the spin hamiltonian. This can conveniently be separated into a magnetic part, $\mathscr{H}_M$, which contains the Zeeman and hyperfine terms familiar to the EPR spectroscopist, and an exchange part, $\mathscr{H}_J$, representing the (electrostatic) exchange interaction, $J(r)$, between the two spins. After radical formation, the latter is initially completely dominant and it causes the singlet (S) and triplet (T) radical pair states to differ so much in energy that their wave functions are not mixed by the magnetic interactions. However it falls rapidly in magnitude as the radicals drift apart, being of extremely short range, and allows an inexact but convenient simple model in which the two interactions are envisaged to operate over different periods of time.[25]

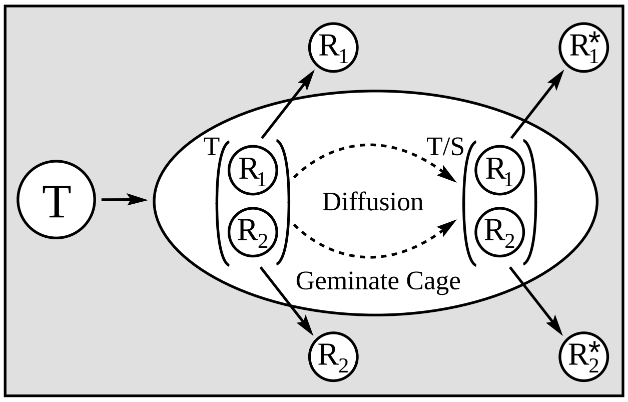

Fig. 2 The molecular dynamics associated with the generation of ST_0 radical pair mechanism spin polarization. In this diagram we assume that the radicals are created as a pair following the reaction of a triplet state of a molecule. Reaction occurs with spin conservation so that when the radicals are first formed their spins are also triplet-correlated. They therefore cannot react and drift apart, some to leave the geminate cage for ever, never to re-encounter their geminate partner. Others do, however, re-encounter during their random diffusion within the cage, and when they do the radical pair exists in a mixed quantum state in which the radicals recombine with a probability proportional to the singlet character of the radical pair. Some therefore survive the collision and escape the geminate region. It is these radicals, denoted by asterisks, which constitute the sub-ensemble which is observed to exhibit RPM spin-polarization in an experiment.

If the triplet state is polarized when it reacts, then the whole ensemble of radicals produced on its reaction may itself be polarized *via* the triplet mechanism before the RPM process commences. A certain fraction of the radicals only undergoes the later re-encounter process in which the RPM polarization is generated and the ratio of the contributions to the observed spectrum from the two mechanisms depends upon this fraction. This is the simple principle on which the estimation of the geminate re-encounter probability described later in the text depends.

In neutral radical pairs $J(r)$ is negative and S underlies the T states in energy. As the pair of radicals separates and $J(r)$ tends towards zero, however, the Zeeman splittings between the triplet sub-levels, T_0 and $T_{\pm1}$ of the radical pair become significant. These cause the T_{+1} state to differ in energy from the singlet, S, state by an amount which prevents spin mixing through the magnetic interactions. The T_{-1} state then must cross the S one as the radicals separate during diffusion, but it does this so rapidly that any spin mixing is negligible; exceptions occur if the diffusion is slowed in a restricted or unusually viscous medium, or if the hyperfine couplings are unusually large. The implication is that with neutral radicals in solutions of normal low viscosity it is only the T_0 state of the radical pair which can mix with the S one, and this happens when the radicals are separated. The wave functions of each contain equal admixtures of the α and β spins on each radical [eqn. (4)] and

$$|S\rangle, |T_0\rangle = 1/\sqrt{2}(\alpha\beta \mp \beta\alpha) \qquad (4)$$

mixing cannot change this. ST_0 mixing does not produce spin polarization in the system but rather causes the eigenstate of the pair to change continuously in time from its initial pure condition.

Polarization of a sort does, however, arise if the radicals then re-encounter during their diffusive excursion. Its origin lies in the action of the exchange interaction, switched back on again as the distance between the radicals decreases. Its generation is a pure quantum phenomenon for which no simple physical model exists, the exchange interaction introducing equal and opposite phase shifts in the S and T_0 contributions to the mixed wavefunctions, which leads in turn to non-zero spin polarizations in the sub-ensembles of each type of radical.[26] If the two radicals differ in chemical type more α electron spin accrues to one, and more β to the other, with the overall polarization necessarily zero; the RPM ST_0 mechanism sorts the spins into different hyperfine states on different radicals rather than produces an absolute polarization. If the two radicals are identical the spectrum exhibits two halves of opposite but equal intensity, for neutral radicals with the low-field half in emission and the high-field half in absorption, an *E*/*A* pattern, if the molecular precursor was a triplet. With chemically-different radicals, one exhibits an *E**/*A* pattern, and the other an *E*/*A** one, where the asterisk denotes an excess of signal in that phase.

The degree of spin-sorting depends upon the amount of spin mixing which has occurred prior to the encounter, and in the ensemble radicals encounter at different times after their creation during random diffusion. Each subset of encounters at a specific time contributes differently to the polarization than do those at different times, and the effect must be integrated over the distribution of encounter times. Independent of the model taken for diffusion (all predict the same long-term dependence relevant to polarization development) the result is given by eqns. (5) and (6), where radical (1) is in the overall nuclear spin

$$P_R \propto |\langle S|\mathscr{H}_M|T_0\rangle|^{1/2} \qquad (5)$$

$$\langle S|\mathscr{H}_M|T_0\rangle = 1/2[g_1 - g_2)\mu_B B + \sum_n a_{1n}m_{1n}^{(a)} - \sum_m a_{2m}m_{2m}^{(b)}] \qquad (6)$$

state (a) and radical (2) in (b), and the other symbols have their usual meanings. The implication is that each different hyperfine line has an unique polarization which depends on its nuclear spin magnetic quantum number. The square root is the result of the diffusional averaging, and does not appear in a static model. These equations suffice to calculate the relative intensities of the lines due to the RPM mechanism for the purposes of this paper, although a fuller treatment[27] is needed to introduce the sign information which allows us to predict that lines corresponding to different signs of *m* (giving lines on opposite sides of the spectrum centre) exhibit opposite phases (assuming little difference in *g*-factors), as observed.

Finally it must be remembered that in the whole ensemble radicals in a given hyperfine state encounter counter-radicals in all possible hyperfine states, and each encounter gives rise to a different contribution to the polarization, as is evident from the above equation. The polarization must consequently be summed over all possible encounters, with due attention paid to the degeneracies of the hyperfine states of both radicals.

Although the origin of RPM polarization lies in the quantum world, we may summarise the physical picture of the processes necessary to its creation, from which novel physical chemistry can be extracted. The model we have is of spin-mixing and of molecular diffusion to bring the radicals back together after an initial separation, within the geminate period of the reaction. The diffusion has a profound effect on the relative intensities of the lines, which are fully calculable, and CIDEP spectra are potential sources of information about molecular diffusion within the geminate cage. Absolute calculations of polarization magnitudes remain difficult due to uncertainties in precise modelling of both the diffusion and the exchange interaction processes, but the strategy introduced in this paper circumvents this to yield unique information.

Experimental

All experiments have been performed using the continuous wave flash photolysis EPR technique with digital field advance invented in this laboratory,[28] but running in the mode in which all the information following each photolysis flash is stored and output as a three dimensional surface of signal plotted against field and time. Spectra over specific periods after the photolysis flash were extracted from the data off-line using the 'time integration spectroscopy (TIS)' technique.[29] In the experiments reported here our interest was in the polarization patterns observed immediately after the flash and over a narrow time-window, so as to be sure that the contributions to the observed polarization arose from interactions in the original pair of radicals created, with no contribution from later F-pair events. Inspection of the spectrum at a series of times post flash ensured this, the F-pair contributions becoming apparent at later times in experiments producing approximately 10^{-5} M radical per flash from an excimer laser operating at 308 nm with feed-back control of the average pulse intensity. Having selected appropriate sample periods, the spectra were re-run using on-line TIS with sufficient field-sampling points to ensure correct and reproducible intensity information; using digital sampling systematic errors accrue if too few are used.

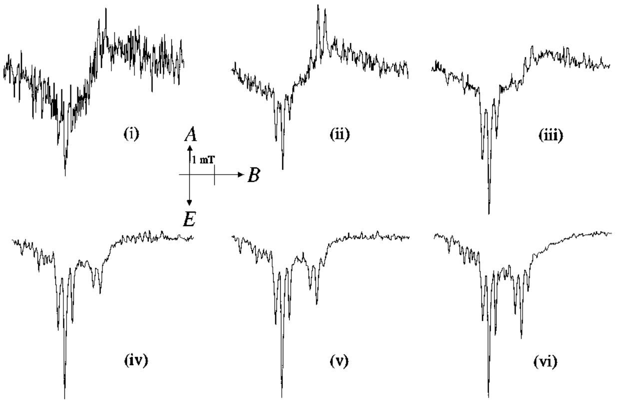

Fig. 3 Irradiation of tetramethylpyrazine in the presence of 2,6-di-*tert*-butylphenol produces the radical product of H-addition to the pyrazine, with a broad spectrum, and the phenoxyl radical, with a spectrum consisting of a doublet of triplets. The spectra shown are displayed with the amplitudes of the signals normalized, although their absolute intensities which are used in the calculations vary substantially. The series is obtained at various phenol concentrations in benzene solution (i) 4×10^{-3} M, (ii) 0.024 M, (iii), 0.119 M, (iv) 0.34 M, (v) 0.485 M and (vi) 1.212 M. At low concentrations there is a strong biphasic contribution to the signal from the RPM mechanism, although one phase preponderates over the other, due to a TM contribution. As the concentration increases this becomes greater and the spectrum swings entirely into emission, although with some RPM distortion even at the highest concentration used. Since the RPM does not produce an absolute spin polarization, the integral across the whole spectrum yields a value which is proportional to the TM contribution alone. It is the variation of this with changing concentration which is used in the analysis, the integration process also improving the signal-to-noise ratio of the measurements.

All chemicals were used as supplied, with experiments conducted on flowing solutions at room temperature.

Applications to physical chemistry

Calculations of the relative intensities of the contributions from the TM and the RPM to a spectrum are straightforward, and spectra are usually reproduced by adding the two in empirically-adjusted proportions to reproduce the observations. This approach is necessitated by many of the parameters required to calculate the absolute magnitude of each being unknown, whilst the magnitude of the observed polarization can only be measured with difficulty.[30,31] In this paper are described methods for overcoming these limitations, so as to abstract physical chemical information directly from the spectra. The first involves the verification and application of TM theory.

Investigation of the photophysics of molecules in solution[32]

The largely untested eqns. (1) and (2) for TM polarization offer the opportunity for determining the polarization in the triplet state itself before it reacts to form radicals, and through this to investigate the dynamics of the ISC process in solution. We introduce a new strategy for obtaining the absolute value of the polarization in the triplet state and in the radicals. Rather little firm evidence exists for the operation of the TM in fluid solution, since the observation of a single-phase contribution to polarization without hyperfine intensity distortion is, with the advent of the RTPM, only consistent with the mechanism rather than diagnostic for it. A second object of our studies is to

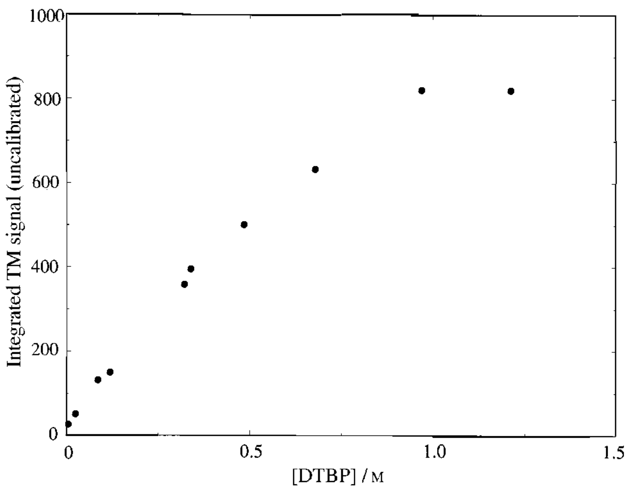

Fig. 4 A plot of integrated signal intensity, that is the signal due to the TM contribution alone, *versus* phenol concentration in benzene solution. As predicted from eqn. (3), at low concentrations this exhibits a linear dependence, from the slope of which the parameter $(k_d/{}^{T}T_1^{-1})$ can be obtained, whilst at high concentrations a plateau is observed. Working at constant optical density, and constant laser intensity, the ratio of the plateau value to the intercept on the zero concentration axis gives the polarization in the triplet molecule in terms of the equilibrium polarization, and this can be made absolute by using the Maxwell–Boltzmann distribution to calculate the latter. The absolute polarization in the radical can also be deduced (see text).

In this introductory paper a full fit of the observations to eqn. (3) is not attempted since several parameters within it are viscosity-dependent, and the viscosity of the solution increases as the phenol concentration is increased.

confirm its operation in a sample of historical importance. Some years ago we used group theoretical arguments to predict that the phase of signal produced through the TM should vary between radicals produced by reaction of two closely related molecules with identical chromophores and similar chemistry, pyrazine and quinoxaline;[33] the opposite phases of the signals in the two cases appeared to provide incontrovertible evidence for the TM, but the approach depended upon assumption of the orbital symmetries of the molecules in their excited states. We have consequently studied the reaction of excited tetramethylpyrazine (selected to yield strong signals, whilst not changing the symmetry[34]) with 2,6-di-*tert*-butylphenol (DTBP) to yield the radical formed by H-addition to the pyrazine, and the phenoxyl radical. DTBP has the advantage of being extremely soluble in the benzene solvent used, whilst the phenoxyl radical spectrum consists of a sharp doublet of triplets which enable the polarization contributions to be identified simply. In this study, however, this is immaterial since, although TM and RPM polarization both occur (Fig. 3) we are interested only in the size of the net signal, which is obtained by integration of the whole spectrum, a procedure which eliminates any ST_0 RPM contribution. As with thermally-equilibrated radicals, the signal is proportional through an apparatus constant (c) to the concentration of the radicals times the magnitude of the spin-polarization:

$$S = cP_R[\mathrm{R}] \qquad (7)$$

It follows that if the optical density of the solution is maintained constant (0.2 mol dm^{-3} methyl pyrazine in benzene), that a constant intensity of laser light is used, and that the triplet concentration is so low (*ca.* 10^{-5} M per flash) that all the triplets formed react to create radicals even at the lowest phenol concentration used, then the radical concentration remains unchanged and $S \propto P_R$. The experiment then consists of varying the concentration of the phenol [M in eqn. (3)], and observing the change in S.

In Fig. 4 is shown a plot of the integrated signal intensity as a function of phenol concentration in benzene solution. Its general shape is consistent with eqn. (3), which confirms the TM to be the origin of the net signal. So long as the phenol concentration is sufficiently low to make $k_d[\mathrm{M}] \ll {}^{T}T_1^{-1}$, then P_R and S are linearly dependent on phenol concentration. As [M] is increased, however, P_R eventually becomes independent of it and the curve approaches a plateau value. The concentration at which this is attained is controlled by the magnitudes of k_d and ${}^{T}T_1^{-1}$ which depend upon the viscosity of the solution through the translational diffusion coefficient, and the rotational correlation time, respectively. In consequence, the plateau is attained at lower concentrations in a low-viscosity solvent, such as benzene, than it is in a higher viscosity one, such as octan-2-ol, although the effect is not great. This, and other differences in behaviour in the two solvents will be reported in detail in a forthcoming paper.

Extrapolation of the lower part of the curve to zero phenol concentration gives an intercept on the signal axis which is directly proportional to the thermal equilibrium polarization in the triplet state. In the high concentration region $k_d[\mathrm{M}] \gg {}^{T}T_1^{-1}$, and provided that $P_T k_d[\mathrm{M}] \gg P_T^{eq}\,{}^{T}T_1^{-1}$, the asymptotic signal is directly proportional to P_T. This is automatically the case under the first inequality, since $P_T > P_T^{eq}$. The ratio of this signal to that at the low-concentration intercept, with [R] constant, therefore gives the polarization in the triplet when it reacts in terms of the polarization in the relaxed triplet. From the curve, we obtain a value of $P_T = 42 \pm 1 P_T^{eq}$ in the most viscous solution (P_T varies with viscosity as discussed above). We stress that this is the polarization in the (unobservable) triplet, rather than that in the radicals themselves, although this (P_R) can also be obtained at any concentration of phenol using the intercept as a calibration, and remembering to correct for the difference between the radical and triplet Boltzmann equilibrium values. Less directly, but interestingly from a theoretical point of view, eqn. (8) can be obtained from eqn. (2) with the aid of the equations valid at low viscosity, where μ_0 is the permeability of free space, μ_B the Bohr magneton, d is the distance between the electrons and τ_r is the rotational correlation time given by eqn. (9), where a is the molecular radius and k_B the Boltzman constant.

$${}^{T}T_1^{-1} = \frac{3}{2}\left\{\frac{g_e^2\mu_0\mu_B^2}{4\pi\hbar d^3}\right\}^2 \tau_r \qquad (8)$$

$$\tau_r = (4\pi\eta a^3)/(3k_BT) \qquad (9)$$

The experiment provides an accurate and rather simple method for measuring P_R, independent of measurement of the concentration of radicals present, which can be made absolute (as can the P_T value) by calculating the magnitude of the polarization in the thermally-equilibrated triplet in a given magnetic field, using the Maxwell–Boltzmann distribution to calculate the populations of the levels. By this route an absolute value for the electron spin polarization due to the TM is obtained. Since with neutral radicals formed from triplet precursors the observed polarization usually results from both TM and RPM mechanisms, and the observed spectrum may be reproduced by adding empirically-adjusted contributions from both, the absolute value of the RPM polarization can in turn be measured. This provides a general method of wide application, and provides an opportunity for studying the polarization processes, and the dynamic processes involved in them, in detail.

Knowing the value of P_T, fitting of eqn. (2) to the experimental curve appears to involve the single parameter $(k_d/{}^{T}T_1^{-1})$, from which a value of either k_d or ${}^{T}T_1$ can be obtained if the other is measured independently, or calculated. In practice, a difficulty is encountered. The addition of large quantities of the phenol significantly affects the viscosity of the solution, and this implies, through eqn. (1), that the value of P_T is not constant. This will be discussed elsewhere.

Direct measurement of the polarization in the triplet precursor to the radicals allows this species itself to be investigated. Referring to eqn. (1), the absolute value of P_{T} is now measured, whilst the motional term in brackets can be evaluated from estimates of the reaction rate constant of the triplet, k_{T}, and of its rotational correlation time. We take k_{T} to be the pseudo-first order rate constant $k_{\mathrm{d}}[\mathrm{M}]$, and calculate this using the Stokes–Einstein relation and a value of [M] in the plateau region of the curve. Here, as in calculating τ_{r}, it is assumed that the bulk viscosity may be used. Having calculated the motional term, and using the measured value of P_{T}, the anisotropy in the rates of ISC, K, can be obtained from eqn. (1) if the zero-field coupling constant D is known, or conversely. This provides an unique method for measuring these quantities in solution, and it will be interesting to investigate how they vary with the phase of the sample. D is often known from solid state measurements, and K less frequently so. For tetramethylpyrazine D has been reported to be 0.0963 cm^{-1} [35] and 0.099 cm^{-1} [36] in different crystal hosts, yielding a value of K of ~0.63. In the solid state observations in host crystals of durene at low temperatures yielded a value of ~0.38,[37] but this medium is known to cause the molecular axis system to differ from that of the zerofield coupling tensor, and it is not apparent whether the figures are directly comparable. Nevertheless this first solution-phase value seems not unreasonable.

Radical re-encounter probabilities in solution[38]

As explained above, radicals are created in pairs with conservation of spin angular momentum. If it is a triplet state which reacts to form them then the spins of the radicals are themselves triplet-correlated, and the radicals cannot react immediately after they are formed, but must separate. If a singlet radical pair is formed the energy of the reaction tends to separate the radicals, and they also do not recombine immediately. In both cases a ‘spin correlated radical pair (SCRP)’, has been formed, and in both cases the initial production of radicals is followed by molecular diffusion through the solution. During this period the spin wave function of the pair evolves and becomes mixed, and if the geminately-created radicals re-encounter at a later time then they react with a probability which depends upon the singlet character of the pair, reaction normally occurring through the singlet state according to the strict selection rule for bond formation. This short-term diffusive process, together with the spin mixing, therefore determines the probability of product formation in the geminate cage. It also controls the magnitudes of all the phenomena (not all of which involve reaction) now known collectively as spin chemistry, including chemically-induced dynamic electron and nuclear polarization (CIDEP and CIDNP), reaction yield detected magnetic resonance (RYDMR),[39] stimulated nuclear polarization (SNP),[40] and magnetic field effects in chemistry (MFE or magnetic effects on reaction yields, MARY).[41,42] It is therefore of interest to measure the fraction of the free radicals created together that subsequently re-encounter within the geminate period of the reaction, and how this varies with experimental conditions. This has received theoretical attention[43,44] but has proved difficult to investigate experimentally. We demonstrate here how this may be done using CIDEP phenomena.

The principle of the experiment lies in TM polarization existing in the ensemble when the radicals are created, whereas RPM polarization arises later in time as a result of magnetic interactions within the SCRP and radical re-encounter. Not all the radicals which are produced together do, however, re-encounter since during their random motion in solution some simply diffuse apart for ever. This means that a smaller sub-ensemble is involved in the RPM polarization-generation process than in the TM one. The size of this sub-ensemble, determined by the fraction of the original radicals which re-encounter, depends upon the viscosity of the solution, and we wish to monitor it as this is changed. This can be done without measuring the absolute value of the polarization (*i.e.* without using the method described above) by using the polarization from the TM as an internal standard.

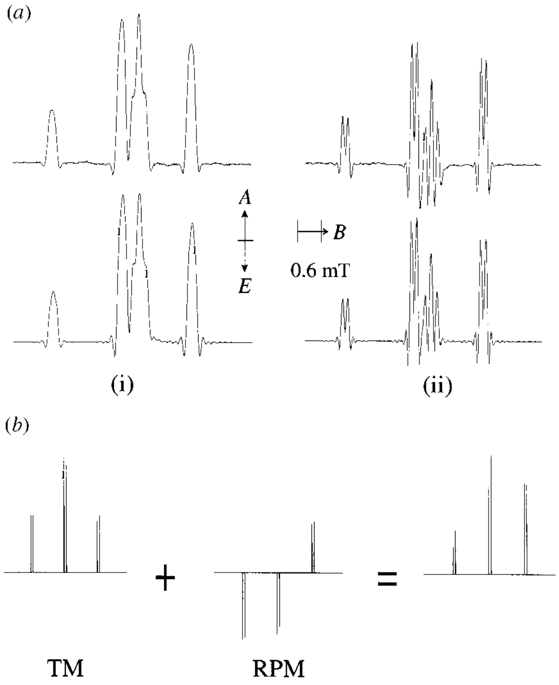

Fig. 5 (*a*) Observed (above) and calculated spectra from the $^{\bullet}$CH$_2$OH and $^{\bullet}$COCH$_2$OH radicals produced on photolysis of 1,3-dihydroxypropanone in ethandiol solution (i) 0.14–0.26 μs post flash and (ii) 0.26–0.37 μs post flash. The two spectra are reproduced using the same ratio of contributions from the TM and RPM mechanisms, where the RPM contribution is calculated for the geminate pair of radicals; this shows the absence of F-pair contributions over the two sampling periods and confirms the identities of the radicals which must be used to calculate the RPM contribution. The later time spectrum in particular shows the effects of Torrey oscillations, not wholly eliminated by the TIS method using the narrow sample window selected for these measurements,[29] whilst the earlier one exhibits the familiar line-broadening inherent in the continuous wave technique. The relaxation times needed to calculate the lineshapes, and the relative sizes of the signals from the radicals as time evolves, were taken from our previous studies.[15]

(*b*) The intensity patterns calculated from TM and RPM polarization for the hydroxymethyl radical. Addition of the two in the ratio *a*/*b* reproduces the observed spectral intensities. In the case shown the ratio has been set equal to one. The experiment consists in observing the changes in the spectrum as the viscosity of the solution is varied, and analysing each for this ratio.

Our requirements for production of TM polarization in the radicals observed are now quite different from above. We need to produce radicals by direct, and very fast, bond scission so that to a good approximation the magnitude of the TM polarization is independent of the viscosity of the medium (although we correct for the small change that does occur). This requires an unimolecular decomposition which competes in timescale with the rotation of the triplet so as to trap a constant fraction of the molecular frame polarization in the laboratory frame. It is a simple matter to choose a suitable system experimentally because possible competing atom abstraction reactions of the triplet are bimolecular. These may, however, be very fast if the triplet can react with the solvent. A simple test is to observe the spectrum and see whether only those radicals formed by bond scission are present {in the case where reaction of the triplet with the solvent is possible, this immediately allows a lower limit on k_{T} [eqn. (1)] to be deduced}. In this study we have used photolysis of 1,3-dihydroxypropanone which fulfils this condition in all the solvents investigated to produce $^{\bullet}$CH$_2$OH and $^{\bullet}$COCH$_2$OH radicals, and has been the subject of two detailed CIDEP studies so that its chemistry and its polarization and relaxation behaviour are well established.[45,15]

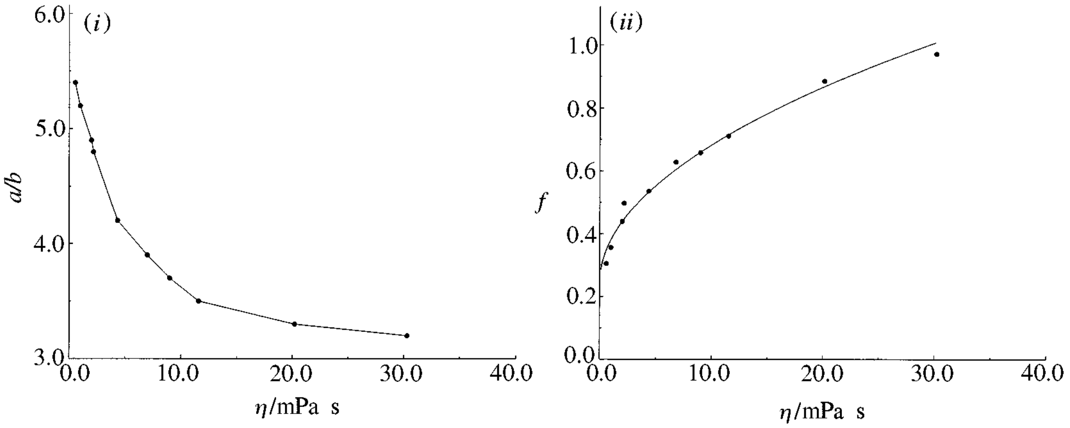

Fig. 6 (*i*) Direct experimental data showing the decrease in the *a*/*b* ratio as the viscosity in the solution is increased. This is due to a greater contribution from the RPM and reflects an increasing fraction of those radicals which are created together which eventually re-encounter within the geminate cage. The ratio tends towards an asymptotic value at high viscosity.

(*ii*) The fraction, *f*, of re-encounters, obtained from the corrected data according to eqn. (10) of the text, plotted against viscosity. The experimental points fit well to a square root dependence [eqn. (12)] expected from a simple model of the liquid. The intercept on the *f*-axis gives the fraction of re-encounters in an infinitely mobile fluid, and is consistent with expectations from a random-walk model. It is interesting that the probability of a re-encounter increases by only a factor of 4–5 in going to an infinitely viscous medium.

The observations consist of observing the changes in the spectrum as the viscosity is varied, in the experiments reported here by altering the solvent; some sample spectra are shown, together with their theoretical simulations, in Fig. 5(*a*). There are large variations in appearance as the viscosity is changed, but they can be reproduced by adding the contributions from TM and ST_0 RPM sources alone. Although the whole spectrum can be reproduced, the short relaxation time of the acyl radical makes it more convenient to use the spectrum of the hydroxymethyl radical only in our analysis; its spectrum is also more sensitive to the ratio than is that from the acyl which has a lower RPM contribution. The TM contribution is in the absorptive phase from this molecule, and the relative intensities of the three doublets are 1 : 2 : 1. The relative intensities of the doublets expected from ST_0 RPM polarization were calculated using the measured parameters for the radical pair (for $^{\bullet}CH_2OH$, g = 2.003 23, $A_{CH} = 1.739$, $A_{OH} = 0.114$ mT; for $^{\bullet}COCH_2OH$, *g* = 2.000 75, $A_{CH} = 0.152$ mT); the two low-field doublets are predicted in emission and the high field one in absorption, due to the radicals originating in a triplet reaction, and having quite different *g*-values. The TM and RPM patterns are shown in stick spectrum form in Fig.5 (*b*), where they are added in proportions of *a* and *b* to reproduce a typical observed spectrum.

Spectra were obtained using identical photolysis flash energies over the same period after the flash from 0.5 M solutions of 1,3-dihydroxypropanone in solutions of 10 different viscosities measured using a calibrated pyknometer. These consisted of methanol, ethanol, propan-2-ol, ethanediol, propane-1,2-diol and mixtures of ethanol with ethanediol and with propane-1,2-diol in various proportions. They were fitted to give the ratio *a*/*b* for each, and this ratio was plotted against the viscosity [Fig.6 (*i*)]. As expected from theory, the RPM contribution becomes progressively comparatively greater as the viscosity is increased and *a*/*b* falls, tending to an asymptotic value of approximately 3.1 at high viscosity.

Although the optical density of the solution and the flash energy were maintained constant, so that the absolute value of the concentration of radicals was the same in each solution, this is unimportant to the analysis. In any solution, we assume that a concentration of radicals [R] is produced with TM polarization, but that only a fraction '*f*' of these radicals re-encounter within the geminate cage after an initial diffusive separation. The RPM polarization therefore arises in a concentration of *f*[R] radicals. With an obvious extension of the nomenclature in eqn. (6) it follows that the ratio of the contributions to the observed spectra from the two mechanisms is given by eqn. (10).

$$S_{TM}/S_{RPM} = a/b = P_{TM}/(fP_{RPM}) \qquad (10)$$

If the polarization ratios are known in each solution, *f* can be extracted quite straightforwardly. However both P_{TM} [through eqns. (1) and (2) as discussed above] and P_{RPM} ($\propto \eta^{\frac{1}{2}}$ through the diffusion process) are viscosity-dependent, and the equation should be written as eqn. (11).

$$(S_{TM}/S_{RPM})_\eta = 1/f(P_{TM}/P_{RPM})_\eta \qquad (11)$$

We now assume that the value of 3.1 observed at the highest viscosity used represents the true asymptotic value which, in the limit, corresponds to all the radicals which are created together re-encountering inside the geminate cage, *i.e.* to $f = 1$. This implies that at this viscosity the ratio of polarizations is 3.1 and we can use this as a datum point to correct the polarizations, and their ratios, observed in all the other solvents. To do this we need a value of the unimolecular decay constant of the triplet which we expect to be in the range 10^{10-12} s^{-1}. Using the mean value of 10^{11} s^{-1}, the magnitude of P_{TM} is predicted to increase by a factor of only 1.3 between the least viscous, and most viscous solutions: as expected with a rapidly-dissociating triplet the correction (although made) is a minor one. The correction to P_{RPM} for change in viscosity is, however, more significant.

The corrected values of *a*/*b* then allow the fraction of re-encounters in all the other solutions to be assessed from eqn. (10). There is an interesting feature to this. In our experiments we observe the effects only of ST_0 RPM polarization, which through spin-mixing involves only one half of the total number of radicals present, and it would seem that the asymptotic value of *f* for these should be 0.5. But this would not give the total number of radicals which re-encounter since there are silent collisions which involve that half of the radical pairs which are in the $T_{\pm 1}$ states and produce no such polarization. We therefore correct for this by putting $f = 1$.

The fraction of radicals which re-encounter is plotted against the viscosity of the solution in Fig.6(*i*), where it is seen that it varies by a factor of four between non-viscous and very viscous solutions. Over the viscosity range in which random-walk theory is applicable the probability of re-encounter of a pair of radicals created together at a later time varies as the square root of the time between diffusive steps, and through this as the square root of the viscosity. The solid line in the figure is a least means squares fit of a curve of the form eqn. (12) to the

$$f = c\eta^{1/2} + d \qquad (12)$$

observed points, where *c* and *d* are constants, and *d* represents the fraction of re-encounters in an infinitely mobile liquid in which there is un-restricted random walk. The fit is very satisfactory, although at some viscosity the relationship must break down since *f* cannot exceed unity; it is possible that the highest viscosity points should not be included in the fit, which would affect the value of *d* extracted. Furthermore this initial analysis has used the value of the signal ratio observed in the highest viscosity solution as the asymptotic value, and this will need further experiment to confirm. Under these circumstances the value of 0.24 obtained for *d*, whilst approximate, seems reasonable since a simple random walk calculation for a hexagonally close-packed liquid gives a value of 0.2. This adds confidence to the interpretation.

Fig. 6(*i*) has many implications to spin chemistry and radical recombination chemistry, and it will be interesting to compare the re-encounter probability obtained in this way with the reaction probability in the geminate cage. If it is assumed that the probability of reaction at a re-encounter depends simply on the singlet character of the SCRP, then the ratio of the two probabilities gives this character, integrated over the distribution of re-encounter times of the radicals in the geminate cage. This is calculable assuming a theory of the liquid, and provides a possible route for confirming the assumption or, alternatively, for measuring the reaction probability in an encounter involving two radicals forming a pure S state of the SCRP. Interpretation of the parameter '*c*' in terms of the model of the liquid used is also possible, but will await a more sophisticated treatment than that provided here for purposes of illustration.

Another polarization experiment might give similar information, one in which ST$_{-1}$ polarization contributes to the observations. This does not depend on diffusion in the same manner as does ST$_0$ polarization, but its magnitude depends on the different number of radicals which are polarized through this mechanism as the radicals initially diffuse apart to the number which are polarized by the same mechanism when they re-encounter at any later time.[46]

Conclusion

Whereas in the past observations of spin-polarized radicals have yielded information on their reaction and relaxation rates, the specific opportunity they offer to investigate basic physical processes in the liquid phase has not been exploited. Here it has been shown that they can be used to illuminate the photophysics of molecules in solution, on the one hand, and the re-encounter probabilities of radicals inside the geminate cage, on the other. These are both novel measurements, seemingly only possible through polarization studies.

But further possibilities exist which depend upon the absolute measurements of the spin polarization which arises in chemical and photochemical processes. Such measurements have proved difficult in the past, and few have been made so that the opportunities have largely gone un-exploited. Here a new and rather general simple method has been introduced for determining the absolute polarization in triplets and radicals in solution, which opens the possibility for further studies of the intimate details of reaction processes and of photochemistry and photophysics in solution.

In this Bruker Lecture a broad account has been provided to introduce these new methods in a transparent fashion so as to establish the principles involved, and to indicate their application. Fuller and extended descriptions will appear elsewhere.

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