

styrenes, and into substituted benzamides.

Though the methodology described in this Account is barely 5 years old, a number of triflate-based transformations have already appeared in the context of

several natural-product syntheses. Enol triflates are proving to be extremely versatile reagents for the synthetic organic chemist, and we look forward to their ever-increasing use.

Flash Photolysis Electron Spin Resonance

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Of the techniques used to detect free radicals in solution only electron spin resonance (ESR) spectroscopy has the resolution to identify them positively. When placed in an external magnetic field the unpaired electron in the radical adopts one of two spin orientations, either parallel or antiparallel to the field, of different energy. In the ESR experiment transitions are caused between them by applying radiation of frequency ν to satisfy the condition

$$h\nu = g\mu_B B$$

where h is Planck's constant, g is a characteristic parameter of each radical, μ_B is the Bohr magneton, and B is the applied field strength. Typically B is 3400 G and ν is ca. 9.6 GHz, and resonance is approached by sweeping the field while keeping the frequency constant.

Rather than the single line expected from this description the ESR spectrum exhibits a hyperfine structure of several lines characteristic of the radical. It arises from the electron coupling to nearby magnetic nuclei in the radical and is analogous to spin-spin coupling in nuclear magnetic resonance spectroscopy. A methyl radical, for example, exhibits an ESR spectrum due to the electron coupling to three equivalent protons and which consequently consists of a quartet of equally spaced lines of relative intensities 1:3:3:1.

The hyperfine structure of an organic radical may extend over 1-200 G, a significant part of the applied field, and is normally displayed by applying an electric current to sweep coils mounted on the magnet. The

inductance of these coils prevents the field from being swept rapidly enough to study the transient radicals produced in flash photolysis experiments, and new methods have been developed to overcome this problem.^{1,2} The radicals are produced not once, in a single flash, but repetitively in a series of flashes that occur at different magnetic field values. Following each flash the signal is sampled either continuously, as in two-dimensional (2D) transient spectroscopy, or for some chosen period, as in time integration spectroscopy (TIS) and boxcar and spin-echo methods. The spectrum at the chosen period is subsequently reconstructed from the data obtained at each field value. The methods can be used within 20 ns of the photolysis flash.

In conventional ESR spectroscopy the transitions are observed in absorption with intensities controlled by the Boltzmann populations of the states at thermal equilibrium. However, when observed within a few microseconds of their creation, transient radicals usually exhibit spectra remarkable for their intensities and phases. They may appear in enhanced absorption, in emission, or with some hyperfine components in one phase and some in the other. This phenomenon is known as chemically induced dynamic electron polarization (CIDEP; see below). It reflects a departure from the equilibrium populations of the states of the radicals which arises at their formation, in the triplet mechanism (TM), or early in their existence, in the radical pair mechanism (RPM), and disappears subsequently by relaxation. CIDEP was first observed in a conventional experiment in 1963.³ Its magnitude is measured by the polarization, P , defined as the difference in the populations of the states connected by the ESR transition divided by their sum. In typical experiments $[P] \sim (10-100)P_{eq}$, where P_{eq} is the value at thermal equilibrium, facilitating radical detection at low concentrations. However, the greatest value of CIDEP is that the phases of the signals disclose the multiplicity of the precursor molecule whose reaction led to radical production directly without further experimentation.⁴

This aspect of CIDEP is covered only briefly here, for it has been the subject of recent articles.^{4,5} We

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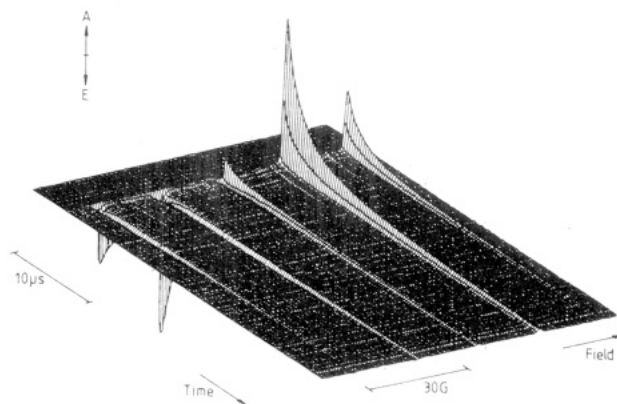


Figure 1. 2D spectrum of the cycloheptan-1-oxyl radical produced by photolysis of cycloheptanone in cycloheptanol. The surface is composed of individual decay curves produced by creating radicals at a series of different magnetic field values. The spectrum exhibits ST_0 RPM effects of an E/A nature.

concentrate rather on the analysis of flash photolysis ESR spectra which allows these applications to be made. The qualitative interpretation of CIDEP spectra can be misleading and a full analysis must be performed if proper conclusions are to be reached. The analysis includes a consideration of line shapes pertinent to our own 2D and TIS techniques and also to boxcar ones if the experimental conditions are properly set. An extension of the analysis to systems undergoing chemical exchange demonstrates that the spectra obtained are sensitive to exchange effects at rates at which normal ESR spectra are not.

Experimental Techniques

All techniques involve the repetitive creation of free radicals by laser pulses performed at different field values. In 2D⁶ and TIS⁷ techniques the field is advanced in discrete steps while with current boxcar^{2,8} and spin-echo⁹ methods it is swept continuously but slowly. The former allow an exact theoretical description. The signals are detected directly and field modulation is not employed.

Following each flash the signal decays with time and is sampled as it does so. In the 2D and TIS experiments the entire decay curve is stored digitally in a transient recorder before the field is advanced and the process repeated. In the 2D version the entire curve is transferred to a computer but in TIS the signal at a chosen time after the flash is summed over a preselected period and only the integrand is stored, to give a single point on the eventual spectrum. The cycle continues for many field positions and at its finish the computer in the 2D version contains a matrix of intensity, time, and field position values from which the surface shown in Figure 1 can be reconstructed. As with all methods, the experiment was performed to discriminate against any stable radical present and to display only the pulse-correlated spectrum. From this surface the spectrum at any given time after radical creation can be obtained

by taking a cross section perpendicular to the time axis. If required, its signal-to-noise ratio may be improved by summing the signal over a selected time interval so as to perform TIS off-line. In this way spectra can be obtained at times after the point-sampled signals have disappeared below the noise level. The advantage of the 2D technique, besides it giving the nature of the radical and the time dependence of its spectrum, is that it yields all the information required on the system at the temperature of study, and this can be examined without further use of the spectrometer.

The TIS technique was developed originally to overcome a basic problem in flash photolysis ESR, that the sudden production of radicals in a resonant microwave field may induce oscillations in the time-domain signal and consequent spurious sidebands in the spectrum.¹⁰ Their observation depends, inter alia, on the strength of the microwave field, which was set too low when obtaining Figure 1 to observe them. However, they are commonly observed in point-sampled experiments and summing the signal over a period of time, as in TIS, then tends to remove them. This also occurs in boxcar experiments, which involve continuous sampling over a chosen period.

An entirely different method, spin-echo spectroscopy, is the fastest of the available techniques but has proved useful only during the first few microseconds of the radical's lifetime. This has prevented its use in the study of time-dependent effects such as exchange.

Chemically Induced Dynamic Electron Polarization^{4,11,12}

CIDEP originates in two independent processes, the TM and the RPM, each of which produces its own characteristic intensity pattern; both often influence the spectrum simultaneously (Figure 2). The TM arises on reaction of a photochemically produced triplet molecule which is itself spin-polarized as a result of a spin-selective intersystem crossing (ISC) from the excited singlet state created on light absorption by the ground-state molecule; that is, ISC occurs at different rates into its three Zeeman levels. Reaction, with conservation of electron spin alignment, within the spin-lattice relaxation time of the triplet then yields a pair of spin-polarized radicals. They are identically polarized, in phase and magnitude, and may exhibit spectra either in emission or in enhanced absorption dependent upon the specific levels connected in the ISC process. TM polarization occurs within a few nanoseconds of light absorption and produces spectra whose lines have the relative intensities expected of equilibrated radicals; only their absolute intensities are changed.

The more general RPM originates in the pairwise production of radicals, or their pairwise encounter during random diffusion in solution. The former are termed "geminate pairs" and the latter "freely diffusing" or "F-pairs". Since reaction occurs with conservation of spin alignment, geminate pairs are created with a definite correlation between the electron spins on the two radicals, to give singlet or triplet radical pair states depending upon the spin multiplicity of their precursor.

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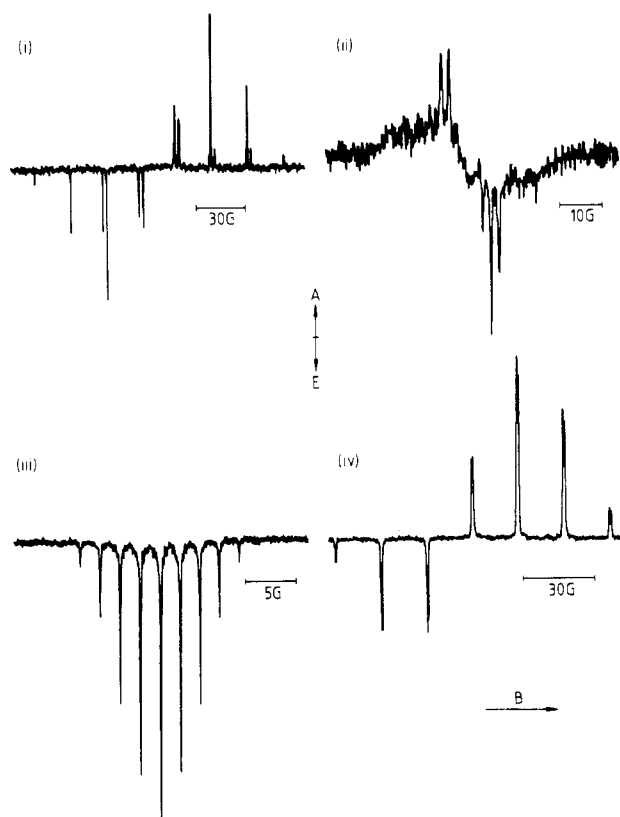


Figure 2. The appearance of electron spin polarized spectra soon after radical creation. (i) Spectrum of the $(\text{CH}_3)_2\text{CH}$ radical produced upon photolysis of diisopropyl ketone, showing an E/A RPM pattern characteristic of a triplet precursor. (ii) Spectra of the radicals formed upon irradiation of nitrosobenzene in the presence of di-*tert*-butylphenol. The spectra show the A/E RPM characteristics expected for the reaction of a singlet precursor. (iii) Pure emissive TM behavior shown in the spectrum of the radical anion produced upon the photolysis of duroquinone in the presence of triethylamine. (iv) Mixed E/A RPM and absorptive TM behavior shown in the spectrum of the propan-2-oxyl radical produced by the photolysis of acetone in propan-2-ol. The contribution from both polarization mechanisms is recognized by an excess of one phase of signal over the other.

Radicals that encounter to form F-pairs usually react if they form singlet pairs, leaving triplet pairs to behave qualitatively as they would have done had they been created as triplet geminate pairs (but see below).

In the magnetic field of the ESR spectrometer the radical pair may exist in singlet, S, one of three Zeeman triplet states, T_0 and $T_{\pm 1}$, or some mixed state. The S and T_0 states differ in energy at small interrational separations due to the short-range electron-exchange interaction, $J(R)$, and as the radicals diffuse apart the S and T_0 states tend toward degeneracy (Figure 3). Radical pairs created in these two pure states subsequently become mixed as a result of the electrons on the two radicals experiencing different local magnetic fields due to the Zeeman and hyperfine interactions. If they then experience the electron-exchange interaction, ST_0 spin polarization is produced. This is most efficient if the radicals initially separate and then reencounter within the geminate cage, for this allows appreciable spin mixing before they experience the J interaction; at this reencounter J is again nonzero. However, the S and T_0 states each contain equal admixtures of the α and β spin states of the radicals and mixing cannot change this. In consequence no absolute polarization

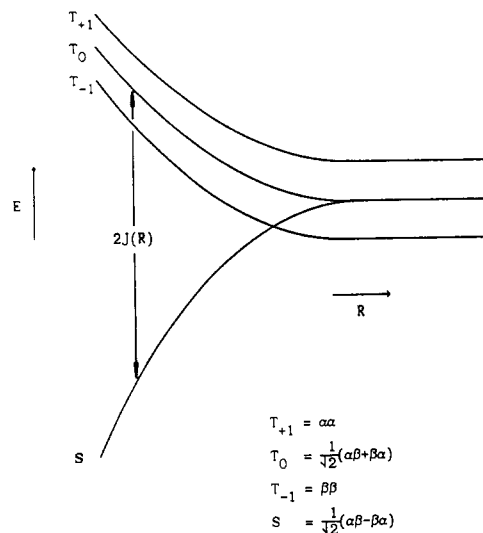


Figure 3. Spin energy levels of a radical pair separating diabatically in the presence of an external magnetic field.

is produced, but rather a spin-sorting process occurs that yields some lines in absorption and some in emission, in contrast to TM effects. Radicals created from triplet precursors, and with a negative J value in the pair, yield spectra with their low-field lines in emission and their high-field ones in absorption, an E/A pattern. The converse occurs for singlet precursors, demonstrating that CIDEP identifies the precursor multiplicity directly (Figure 2). If the radicals are unidentical one exhibits more emission and the other more absorption, yielding E^*/A and E/A^* patterns from a triplet precursor, where the asterisk denotes a predominance.

The $T_{\pm 1}$ levels are removed in energy from S by the Zeeman interaction at those interrational separations where ST_0 mixing occurs and normally remain unmixed. However, at shorter distances the T_{-1} and S levels cross and, in exceptional circumstances the two may mix. When this happens true emissive spin polarization is produced in radicals formed from a triplet precursor. Mixing occurs through the hyperfine interaction and yields a hyperfine-dependent polarization, in contrast to emissive TM effects.

Geminate ST_0 polarization occurs within the geminate cage and, as with the TM, is complete before observations commence: spectra observed at early times often exhibit contributions from both and require careful analysis. In the absence of ST_{-1} polarization, an excess of one phase of signal over the other in the complete spectrum is diagnostic of the action of both mechanisms. The initial polarization decays in time due to relaxation, and the effects of F-pair encounters become more obvious (although their contribution maximizes quite early on). From above, they would be expected to cause an E/A (triplet) polarization pattern in the radicals but in every case that radicals have been observed sufficiently long after creation the observed phase is A/E. This remains incompletely understood but is largely invariant on the nature of the radical.¹³ Confusion has arisen on this point since it is not always realized that only some of the experimental techniques are capable of observations on the long time scale. The

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phase of the signals in true F-pair polarization remains controversial.

In viscous solutions, in micelles, and when radicals have unusually large hyperfine coupling constants, ST_{-1} mixing can also occur. The spectra must then be analyzed in terms of several independent contributions.¹⁴ This is a rare complication in carbon-centered radicals at room temperature. In viscous solutions and micelles also a different polarization behavior causes individual lines temporarily to exhibit E/A characteristics. This results from direct observation of the ESR spectrum of the radical pair itself, rather than of the separated radicals.^{15,16}

Calculation of CIDEP Spectra

Analysis proceeds by constructing "stick spectra", consisting of δ functions of calculated intensity, and imposing a line shape onto them. The former requires the g values and hyperfine coupling constants of the radicals, to determine the resonance positions, and polarization theory to yield the intensities. In theory the relative contributions from TM and RPM processes could be calculated, but in practice we calculate the basic patterns from each and vary their proportions in a summed spectrum empirically until agreement with experiment is reached.

The TM causes no difficulty: the relative intensities of the lines are normal and the correct phase can be recognized directly from the experimental spectrum. Whether it is absorption or emission may disclose whether the triplet state is $n\pi^*$ or $\pi\pi^*$ in character.⁴

ST_0 polarization in solutions of normal viscosity can be written

$$P_a \propto \sum_b (Q_{ab}^{1/2} - cQ_{ab}) \quad (1)$$

where c is a constant, dependent on the radical concerned and the viscosity and temperature of the solution, and

$$Q_{ab} = \frac{1}{2}(g_1 - g_2)\mu_B B + \frac{1}{2}\sum_i A_{1i}m_{1i}^{(a)} - \frac{1}{2}\sum_j A_{2j}m_{2j}^{(b)} \quad (2)$$

Here i and j refer to the nuclei in radicals 1 and 2 that exist in the overall nuclear spin states (a) and (b); the other symbols have their usual significance. These equations expose polarization as an ensemble phenomenon that results from the average effects of radicals in a particular Zeeman and hyperfine state forming radical pairs with second radicals in all of their possible states, weighted for their degeneracies. The constant c is normally zero but becomes significant in radicals with large spectral widths. The exponent on the first term decreases in solutions of high viscosity.^{14,17} The first term originates in radical reencounters inside the geminate cage and the second during the initial separation of the radicals.¹⁸

The line shape is obtained from the Bloch equations, initially applied to the calculation of the decay curve observed at a specific magnetic field position. Exten-

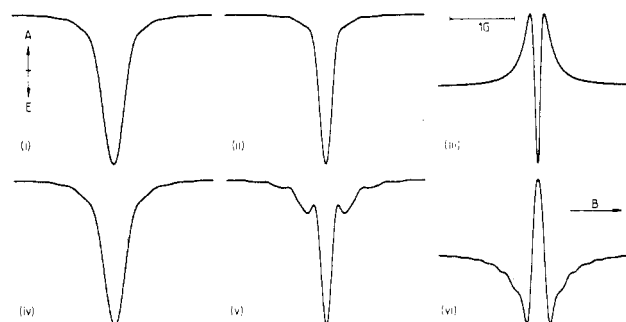


Figure 4. Time dependence of TIS line shapes calculated with $T_1 = 5 \mu s$, $T_2 = 0.6 \mu s$, and $P_1/P_{eq} = -6.5$. Set i-iii corresponds to sampling at 0.1–1.0 μs , 1.0–2.0 μs , and 10.0–11.0 μs post flash, with a microwave field strength of 0.05 rad·MHz. Set iv-vi is for similar times but with $\omega_1 = 1.75$ rad·MHz. All lines are normalized to the same absolute intensity.

sion to yield a point-sampled spectrum, e.g., from a 2D surface, is straightforward, as is its summation to yield the TIS line shape. For a slowly decaying radical of initial polarization P_1 , the signal at time t is proportional to the y component of the magnetization

$$M_y(t) = [P_1 g_y(t) + P_{eq} T_1^{-1} G_y(t)] n(t) \quad (3)$$

where $n(t)$ is the radical concentration, $g_y(t)$ is a function of the relaxation times T_1 and T_2 , the microwave field strength (ω_1), and the offset from resonance, and $G_y(t)$ is the time integral of $g_y(t)$ between 0 and t .¹⁹ Our line shape discussion is based upon the analytical expressions for these quantities under the conditions common experimentally. For systems involving F-pair polarization only numerical solutions are possible while most situations that involve exchange processes can be treated semianalytically. Equation 3 shows that the signal can be thought of as a sum of "polarized" and "unpolarized" terms. The line shape and the signal size consequently depend upon the polarization ratio (P_1/P_{eq}) and vary with time as the second term increases relative to the first. This causes some remarkable changes since the polarized and unpolarized contributions to the signal have different line widths (Figure 4). The lines appear normal (although they sharpen for about 1 μs after the flash) until some remarkable features appear when the signal is sampled near the time when an initially emissive signal relaxes through zero to absorption. At low microwave field strengths the two terms in eq 3 then have opposite phases but are of similar size and a composite line shape is observed that exhibits a broad absorptive outer component with a sharp emissive inner one. At higher microwave field strengths the transient oscillations are incompletely averaged out by the TIS experiment and another composite form, the inverse of the first, is obtained. Both line shapes are sensitive functions of the polarization ratio and allow its accurate measurement.²⁰ The behavior shown is general and the precise line shape at a given time depends upon many parameters. It differs from spectrum to spectrum and time to time in ways without analogy in conventional ESR, and the need for full analysis is obvious.

The final part of the calculation of the spectrum involves the numerical convolution of the line shape to the stick spectrum.²¹ Since effects exist to change the

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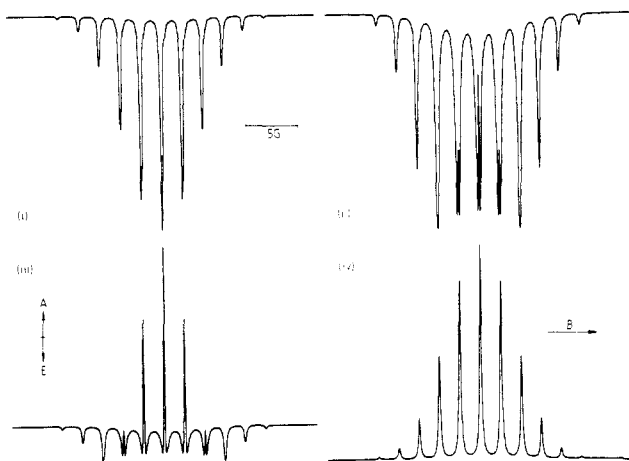


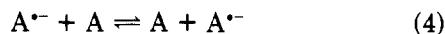
Figure 5. Time evolution of a theoretical TM-polarized spectrum in which the radical undergoes slow electron exchange, calculated with $T_1 = 6.7 \mu\text{s}$, $T_2 = 0.66 \mu\text{s}$, $\omega_1 = 0.5 \text{ rad}\cdot\text{MHz}$, and an exchange lifetime of $3.0 \mu\text{s}$. The initially emissive signals decay in the order of their degeneracies (i-iv) and exhibit the line-shape effects at crossover shown in Figure 4 in turn.

phases of lines under certain operating conditions, qualitative analysis of a CIDEP spectrum obtained over a single time period may lead to erroneous conclusions.

Chemical Exchange

For a radical created with initial polarization, the effects of exchange can be analyzed conveniently by using the McConnell extension to the Bloch equations.²² This has been applied to radicals undergoing electron exchange, proton exchange, and conformational isomerism. In the fast-electron-exchange and proton-exchange cases the results are similar to those observed in stable radicals but the analysis demonstrates that exchange rate constants can be extracted from the spectra of highly transient species and extends the range of such studies considerably.²³ Under the conditions of slow exchange new phenomena are observed as the spectrum varies in time, and it becomes possible to study reactions at rates hitherto impossible using magnetic resonance methods.²⁴ Conformational exchange yields novel polarization patterns in RPM-polarized radicals and allows study of very slow processes.²⁵

The degenerate electron-exchange reaction involving a species A may be written



Its effect is to transfer the electron from a radical that exists in a certain hyperfine state onto another molecule whose hyperfine state at the time is random. The electron usually experiences a different coupling in the two molecules, and the modulation of this coupling in the exchange process is the source of relaxation effects. The systems that undergo electron exchange normally display pure TM polarization.

In the slow-exchange limit the line separation is greater than the line width and the exchange rate, and the spectra vary in time as shown in Figure 5. The

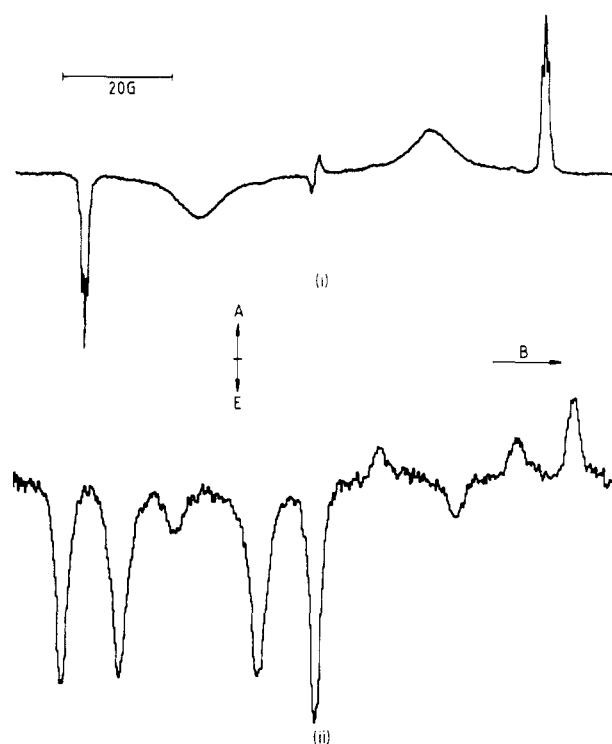


Figure 6. Spectra of the cyclohexan-1-oxyl radical produced from reaction of the triplet state of cyclohexanone with cyclohexanol: (i) at room temperature with pure ST_0 RPM polarization; (ii) at 223 K, where exchange has slowed to allow resolution of all the hyperfine lines and an ST_{-1} RPM contribution causes the low-field lines to be more intense than the high-field ones.

early-time spectra of emissively polarized radicals appear normal but as time progresses each line changes its phase in turn in the order of its degeneracy, the strongest line first and the weakest last. This is the characteristic and diagnostic behavior of a polarized radical undergoing slow electron exchange. As the phase change occurs the line shape exhibits the characteristics discussed above. Experimentally, such spectra commonly occur in low-concentration solutions of anions.²⁴

The physical origin of the phenomenon lies in the hyperfine components having different effective relaxation rates. In the slow-exchange limit only one transition is excited at a time and the upper electron state, overpopulated in the TM process, loses population at a rate determined by relaxation and the rate at which transitions are driven by the resonant microwave field. However, due to exchange this state is simultaneously refilled by electrons hopping from a large reservoir of radicals in different original hyperfine states. The net rate of population gain depends upon the degeneracy of the state concerned and the total degeneracy of the radicals, and overall the strongest line has the fastest effective relaxation rate. The inherent competition between exchange filling the level and microwave pumping emptying it causes a dependence upon the microwave field strength, which may be adjusted to detect the exchange process while the radical exists in its spin-polarized state.

Conformational exchange, as in the interchange of the cyclohexan-1-oxyl radical between its degenerate chair forms, introduces new phenomena in a now RPM-polarized spectrum. Coupling of the electron to different extents to the equatorial and axial protons should give

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a triplet of triplets spectrum but the ring flip modulates these couplings and an alternating line-width effect occurs (Figure 6i). The positions of the outermost lines and, largely, the central one are unaffected while the more intense lines to low field interchange, as do their high-field counterparts, and exhibit line broadening. The individual lines can be observed at low temperatures (Figure 6ii). Exchange also interchanges the two inner lines of the outer triplets, which are on opposite sides of the center. Figure 6i exhibits the CIDEP characteristic of a radical from a symmetric radical pair, formed from a triplet precursor, with pure ST_0 RPM polarization. The low-field lines are in emission and the high-field ones in absorption, and this latter exchange connects lines of opposite phase. At exchange rates too slow to cause line broadening, population is transported between the two environments and a line is observed in each position whose intensity is the average of the original ones. For radicals with symmetric ST_0 polarization this average is zero.

As the temperature is lowered ST_{-1} polarization, asymmetric in its hyperfine dependence, is added to the ST_0 effects and the low-field signals become more intense than those at high field. Now exchange produces a nonzero emissive average and the innermost members of the outer triplets in the spectrum both appear in emission. A novel CIDEP pattern is observed with a single emissive line among the absorptive high-field ones (Figure 6ii). The entire exchange behavior from very slow exchange affecting line intensities, to line broadening, and eventual line sharpening is predicted by a simple two-site exchange model.²⁵

Concluding Remarks

Flash photolysis ESR provides positive identification of transient free radicals shortly after their formation. CIDEP in turn provides a direct link between the photophysics of the system and its photochemistry. The multiplicity of the precursor involved in forming a precise radical is obtained.

RPM polarization arises in both ESR and NMR (CIDNP) in spin-correlated pairs. These are essential reaction intermediates between the excited state of the molecule produced in the flash and the subsequent free radicals. The spin evolution that occurs within them controls the amount of geminate product formed and the future course of the reaction. These intermediates have not long been recognized but they can now be studied directly in new experiments.^{26,27} Thus microwave transitions can be induced in the radical pair held within a magnetic field to affect the S-T mixing within it and, consequently, the product or escaping radical yield. This is the radical yield detected magnetic resonance (RYDMR) technique. Similar experiments can be performed by measuring the yield as a static magnetic field only is applied, since S-T₀ mixing occurs via the different magnetic fields at the electrons of the two radicals in the pair. This is why high magnetic fields affect radical reactions.

Previous accounts of CIDEP have been concerned with basic polarization effects and their interpretation. Here we have discussed some of the further information available from the study of the time dependence and line shapes of polarized signals. It has been shown that spin-polarized radicals provide the opportunity for a wide range of exchange studies, opening up new possibilities in the slow-exchange, and very-slow-exchange, situations. The analysis of the spectra, and their time dependence, is more involved than with conventional ones but is well understood. CIDEP is a common phenomenon and it yields complex information in a direct manner. The experiment is not difficult to perform and has a remarkably wide range of applications. It should be one of the major weapons in the armory of the photochemist and, at a fundamental level, it provides a continuous challenge to the physical chemist and theoretician.

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Modifications of Transition-Metal Reaction Patterns through the Manipulation of Superexchange Couplings

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Our training as chemists conditions us to think in terms of orbitals and even to construct mechanistic arguments based on the presumed properties of orbitals. In keeping with this bias it would be natural to expect

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that electronic selection rules and symmetry requirements be clearly manifested in the observed variations of single-electron-transfer rates. Certainly there have been a variety of attempts to attribute specific electron-transfer rate patterns to variations in electronic factors.¹⁻⁶ However, the work required to move nuclei

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