The role of Chemically-Induced Dynamic Electron Polarization (CIDEP) in Chemistry

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1 Introduction

The presence of transient free radicals as reaction intermediates in solution has been postulated for over fifty years and demonstrated, by direct observation, for twenty. Under normal reaction conditions their concentration is low and they can only be detected when unusually high concentrations are produced, by flash photolysis, pulse radiolysis, or under steady-state conditions. The latter may be achieved by electrolysis, continuous photolysis and radiolysis, and in flow experiments. However, the mere demonstration of the existence of radicals is inadequate: we need to identify them, to obtain their kinetics and to investigate their chemistry. In the past, reaction pathways were inferred from the observed kinetics and the nature of the intermediates and products, but there now exist methods, considered below, with which the chemistry can be exposed directly.

Any of the above methods for producing radicals can be used to investigate their kinetics providing that a means exists for their detection: two major techniques have been used. These are ultra-violet (u.v.) and electron spin resonance (e.s.r.) spectroscopy. The former suffers from the low resolution of u.v. spectra in solution: although the radicals can be detected, only the chromophores they contain are identified and the structure of the radical is uncertain. The latter, in contrast, is a high resolution technique and, from the hyperfine structure of the e.s.r. spectrum, the radical can often be identified exactly. The drawback, until recently, has been that e.s.r. is most readily applied to radicals in steady state concentrations, which can only be obtained for relatively long lived species.

These problems have recently been overcome by the use of pulse radiolysis and flash photolysis techniques together with the development of fast response e.s.r. spectrometers capable of detection and identification of free radicals produced in pulses. This combination affords directly and simply the decay kinetics of identified radicals and, in theory at least, allows one to observe their reaction to form other radicals.

As mentioned above the chemistry of a radical reaction may be inferred from its kinetics and products, but the method is fraught with dangers. There may be several reaction schemes consistent with the observed rate equation, and the mere observation of transient free radicals is inadequate to prove that they are intermediates in the major reaction path. In order to obtain sufficient product for analysis, prolonged photolysis or radiolysis is often necessary, which may result in undesirable side-reactions and products; for example, the initially-formed product in a continuous photolysis experiment may be itself photoactive. Thus, these observations, even when taken together, are insufficient to define the chemistry involved. What is missing is the knowledge of the precise reactions which a radical undergoes to form the observed products. The missing factor has been provided in recent years by two magnetic resonance experiments, chemically-induced dynamic nuclear polarization (CIDNP) and chemically-induced dynamic electron polarization (CIDEP).[1,2] The former involves the observation of the nuclear magnetic resonance (n.m.r.) signals from the products of the free radical reaction as the reaction proceeds. Transitions are observed with unusual intensities, some even in emission, and from the intensity patterns much of the microstructure of the reaction can be deduced, for example the multiplicity of the radical precursor and whether the product results from an in-cage radical reaction or one in which the radicals are scavenged. An extraordinary insight to radical reaction pathways is afforded by direct observation in this well-established method.

CIDEP produces intensity distortions in e.s.r. spectra and is less well known and more complex in that, unlike CIDNP (with a few exceptions), it originates in two quite distinct processes (see next section). It is our purpose in this review to explain how CIDEP too, enlarges our knowledge of radical reactions and also of certain fundamental processes involving paramagnetic species in solution. Mechanistically, CIDEP gives the multiplicity of the radical precursor and complements CIDNP in revealing the pathways of radical reaction not to form diamagnetic products but to form other radicals; the existence of radicals which are too short-lived to be observed directly can be inferred and some of their characteristics measured. This has been particularly significant in radiation chemistry in deciphering the reactions and modes of formation of H• atoms, •OH radicals and solvated electrons. Quantitatively, CIDEP allows measurement of the rate constants involved in the reaction and relaxation of triplet state molecules and radicals, and promises to provide a means for investigating the elusive distance-dependence of the electron exchange interaction. It is already finding application in the investigation of the reactions involved in the photosynthetic processes in plants and bacteria.

CIDEP has been observed under a great variety of experimental conditions[3] ranging from radicals in steady state concentrations, through those observed under intermittent illumination by chopped-beam photolysis[4] to very fast measurements by flash photolysis[5] and pulse radiolysis.[6] To some extent these different techniques provide different information. All the experiments have been analysed in some depth and we give the results of this analysis here with emphasis

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[1] A. R. Lepley and G. L. Closs, 'Chemically Induced Magnetic Polarization', Wiley 1973.

[2] L. T. Muus, P. W. Atkins, K. A. McLauchlan, and J. B. Pedersen, 'Chemically Induced Magnetic Polarization', Reidel 1977.

[3] K. A. McLauchlan, ref. 2, p. 107.

[4] L. T. Muus, ref. 2, p. 205.

[5] K. A. McLauchlan, ref. 2, p. 151.

[6] R. W. Fessenden, ref. 2, p. 119.

on the information which can be extracted; the detailed basis of the theory is to be found elsewhere.[7-11]

We commence this review with a brief description of spin polarization and of the processes which produce it in solution.

2 Chemically Induced Dynamic* Electron Polarization (CIDEP)

CIDEP is the phenomenon of the production of a non-equilibrium distribution of free radicals among their electron spin states by chemical reaction; it affects only the intensities of e.s.r. lines and not their positions. We define polarization as the difference in population of two spin states divided by their sum; at equilibrium at room temperature $P_{eq} \sim 0.00074$. Radicals exhibiting CIDEP can have polarizations several hundred times P_{eq} (which implies that they can be detected in lower concentrations).

There are, in the main, two distinct types of intensity distortions which result from two polarization mechanisms. Both mechanisms produce polarized radicals in pairs although in the majority of experiments only one is observed, usually because of rapid reaction. The first kind of intensity perturbation is due to the triplet mechanism (TM) which causes both radicals to have the same magnitude and phase of polarization (absorption, or more commonly, emission) with no hyperfine dependence. The e.s.r. spectra appear normal in all respects other than their absolute intensities, the relative intensities of the hyperfine structure being preserved. The other type of intensity distortion, due to the radical pair mechanism (RPM), is of a mixed emission–absorption nature. It can be of two kinds: either one radical is observed in emission and the other in enhanced absorption (the 'net' effect), or each radical may have half its spectrum in absorption and the other half in emission (the 'multiplet' effect). The latter is illustrated in Figure 1. A rarer form of the RPM ('$ST_{\pm1}$' polarization) is observed only under special conditions; like the TM it causes both radicals to appear in the same phase but, in contrast to the TM, the polarizations are hyperfine-dependent.

The TM and RPM may occur separately or in the same reaction system. If only one type of polarization occurs both radicals in the pair must be observed to distinguish which mechanism is responsible. If both types occur their relative contributions can be assessed from the time-dependence of the polarized signals. The two processes occur at different times during the reaction history. TM polarization is present in the radicals when they are formed but the RPM operates at a later time, as a result of radical–radical encounters and spin-selective reactions (recombination requires paired electron spins). The two processes consequently produce polarizations with quite different time profiles.

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*The word 'dynamic' in the title is misleading in that the polarization does not result from a dynamic (cross-relaxation) mechanism. although it was once thought to do so.

[7] F. J. Adrian, ref. 2, p. 77.

[8] J. H. Freed, ref. 2, p. 309.

[9] P. W. Atkins, ref. 2, p. 191.

[10] P. W. Atkins and G. T. Evans, *Adv. Chem. Physics*, 1976, **35**, 1.

[11] J. H. Freed and J. B. Pedersen, *Adv. Magn. Resonance*, 1976, **8**, 1.

Figure 1 *Multiplet ST_0 radical pair polarization in the* $(CH_3)_2COH$ *radical formed on the flash-photolysis of benzophenone in propan-2-ol solution* (A. D. Trifunac *et al.*[12]). *The field increases from left to right and the unpolarized central line is distorted by overlap of an emissive signal from the benzophenone ketyl radical. This unusual e.s.r. spectrum was obtained as a field profile (see Figure 7) without field-modulation which normally yields the derivatives of the lines shown. Often in multiplet patterns comparatively small polarizations result in the intensity distribution appearing unsymmetric about the centre, due to significant contributions from equilibrated radicals present*

A. The Triplet Mechanism.—TM polarization arises in systems wherein the radical precursor is a molecular triplet state and has been reported, so far, only in photolytic systems.[3,12] Absorption of a photon by the ground-state molecule yields an excited singlet which may intersystem-cross to a triplet excited state whose Zeeman levels, T_{+1}, T_0 and T_{-1}, are non-degenerate within the magnetic field of the spectrometer. The origin of spin polarization lies in this intersystem crossing (ISC) process since, depending upon the nature of the chromophore, it occurs more rapidly into some of the Zeeman states than into others and yields a spin-polarized triplet.[13–16] This process is of some complexity, for the ISC may be considered to occur within the molecule at zero applied magnetic field and this in itself does not lead to a net magnetization of the triplet; it is only when the zero-field states evolve under the influence of the applied field that magnetization arises. We have considered this and other aspects of CIDEP in a recent review[17] and shall not repeat the arguments here. Once the triplet is produced (within, for carbonyl compounds, 10^{-8}—10^{-11} s of the light being absorbed) two further processes ensue: spin relaxation in the triplet (which is very fast: ${}^3T_1{}^{-1} \sim 10^9$ s^{-1}) and reaction of the triplet with some suitable quencher (Q) to yield radicals. If the latter occurs sufficiently quickly to compete with relaxation the polarization which arose in the triplet is carried, by spin conservation,

[12] A. D. Trifunac, M. C. Thurnauer, and J. R. Norris, *Chem. Phys. Letters*, 1978, **57**, 471.

[13] P. W. Atkins and K. A. McLauchlan, 'Chemically Induced Magnetic Polarization', ed. A. R. Lepley and G. L. Closs, Wiley, 1973, p. 41.

[14] J. K. S. Wan, S. K. Wong, and D. A. Hutchinson, *J. Chem. Phys.*, 1973, **58**, 985.

[15] P. W. Atkins and G. T. Evans, *Mol. Phys.*, 1974, **27**, 1633.

[16] J. B. Pedersen and J. H. Freed, *J. Chem. Phys.*, 1975, **62**, 1706.

[17] P. J. Hore, C. G. Joslin, and K. A. McLauchlan, in 'Electron Spin Resonance', ed. P. B. Ayscough (Specialist Periodical Reports), The Chemical Society, London, 1979, Vol. 5., to be published.

to the radicals where it is effectively frozen by their much slower relaxation rate (*ca.* 10^6 s^{-1}). Only reactions which occur at diffusion-controlled rates are sufficiently fast. The process is summarized in Figure 2. Any other radiative or non-radiative processes which compete for the triplet serve to reduce the observed polarization in the radicals.

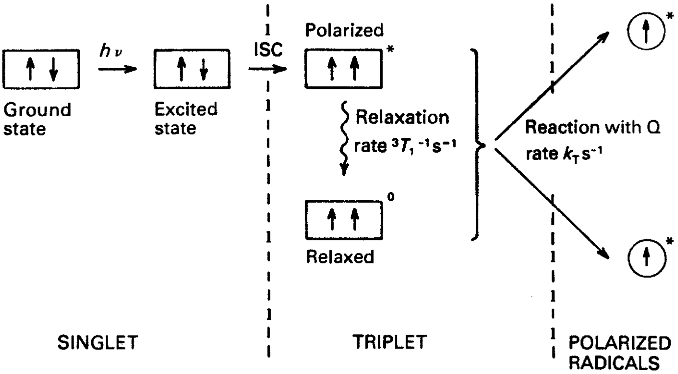

Figure 2 *The triplet model (TM) for radical polarization (schematic), with polarized species denoted by asterisks. Selective intersystem crossing (ISC) from the excited singlet causes overpopulation of one of the Zeeman levels of the triplet (here the upper one). The non-equilibrium polarization so created appears in the radicals subsequently formed provided* $k_T \gg {}^3T_1^{-1}$; *they too are overpopulated in the upper levels and emit*

This basic competition between reaction and relaxation in the triplet is analysed to yield an important expression which we derive in terms of the observable quantity in a flash-photolysis experiment, the polarization ratio γ defined as

$$\gamma = [P_a(\mathrm{I}) - P_{\mathrm{eq}}]/P_{\mathrm{eq}} \ , \qquad (1)$$

where $P_a(\mathrm{I})$ is the initial polarization associated with a hyperfine line labelled by nuclear quantum number '*a*'. $P_a(\mathrm{I})$ and P_{eq} are evaluated at the instant the flash occurs by suitable extrapolation of the experimental curves (see below). Because of fast relaxation in the triplet a fraction ${}^3T_1^{-1}/(k_T + {}^3T_1^{-1})$ relaxes before it reacts, carrying its polarization $P_{eq}{}^{T}$ to the radicals; the remainder $k_T/(k_T + {}^3T_1^{-1})$, with polarization P^T, reacts before loss of excess polarization. Thus the polarization $P_a(\mathrm{I})$ in the radical is the sum of these and is expressed as

$$P_a(\mathrm{I}) = P^{T}{}_{\mathrm{eq}} + (P^T - P^{T}{}_{\mathrm{eq}})\left(\frac{k_T}{k_T + {}^3T_1{}^{-1}}\right) \qquad (2)$$

Now the Zeeman splittings (E) in the triplet and radical are identical and combining $P_{eq}{}^{T} = \frac{2}{3}\frac{E}{kT}$ and $P_{eq} = \frac{E}{2kT}$ we obtain

$$P_{\mathrm{eq}} = \frac{3}{4}P^{T}{}_{\mathrm{eq}} \qquad (3)$$

Thus

$$\gamma = \frac{4}{3}\frac{P_\alpha(\mathrm{I})}{P^{\mathrm{T}}_{\mathrm{eq}}} - 1$$

Combining with equation (2) and using the substitution $\gamma^{\mathrm{T}} = (P^{\mathrm{T}} - P^{\mathrm{T}}_{eq})/P^{\mathrm{T}}_{eq}$,

$$\frac{4}{3\gamma - 1} = \frac{1}{\gamma^{\mathrm{T}}}\left(1 + \frac{1}{k_{\mathrm{T}}\,{}^{3}T_1}\right) \tag{4}$$

Here the triplet reaction rate $k_{\mathrm{T}} = k_q[\mathrm{Q}]$ where k_q is a second-order rate constant and Q is the quencher. This relationship allows determination of γ^{T} and the product $k_{\mathrm{T}}\,{}^{3}T_1$, and is considered below.

Most observations of TM polarization to date have involved the carbonyl chromophore whose symmetry has dictated the ISC process leading, with one possible exception,[18] to over-population of the T_{+1} level of the triplet and thence to the α-states of the electrons in the radicals, causing their spectra to occur in emission.

The inherent assumptions in the theory of the TM have been discussed recently as has the experimental evidence for its essential correctness.[17]

The end-product of the triplet reaction is a pair of free radicals in which further polarization may arise by the second (radical-pair) process although under suitable conditions, for example in flash-photolysis experiments, this contribution is usually negligible. Pairs of radicals can also be produced thermally, by radiolysis or by random encounter of radicals generated separately. In all these situations the RPM may yield polarized radicals.

B. The Radical Pair Mechanism.—The radical pair process[19–22] is more subtle in origin than the TM one and requires a quantum-mechanical description. Furthermore the polarization observed results from all the polarized species in the sample and necessitates averaging over the whole ensemble.

To illustrate it we shall consider the particular example of radical pairs created in a spin-correlated triplet state on reaction of a triplet molecule. Interaction with the applied field of the spectrometer splits the triplet into three sub-states T_{+1}, T_0 and T_{-1} and there also exists an unpopulated singlet state (S). These states have energies which vary with the radical separation (Figure 3); at small distances the S and T levels are split by the exchange interaction $J(r)$ but this is of short range and as the separation increases the S and T_0 levels become degenerate whereas T_{+1} and T_{-1} are removed from them in energy by the Zeeman interaction.

Having a triplet configuration the radicals cannot normally react (since bond formation involves antiparallel electron spins) but rather the radical pair evolves in time so as to attain some singlet character. For the T_{+1} and T_{-1}

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[18] K. Y. Choo and J. K. S. Wan, *J. Amer. Chem. Soc.*, 1975, **97**, 7127.

[19] F. J. Adrian, *J. Chem. Phys.*, 1971, **54**, 3918.

[20] F. J. Adrian, *J. Chem. Phys.*, 1972, **57**, 5107.

[21] J. B. Pedersen and J. H. Freed, *J. Chem. Phys.*, 1973, **58**, 2746.

[22] J. B. Pedersen and J. H. Freed, *J. Chem. Phys.*, 1973, **59**, 2869.

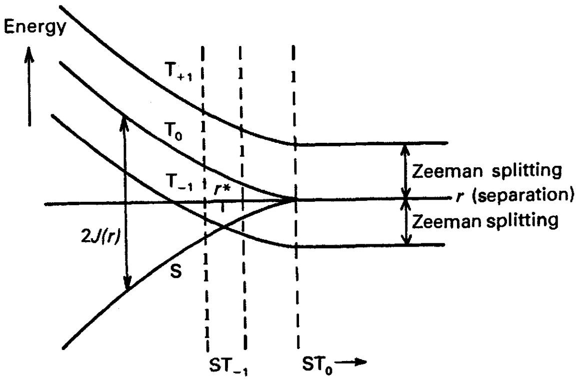

Figure 3 *The variation of the energy levels of the singlet and triplet states of a radical pair as a function of separation. The S and T_0 levels are split by an amount $2J(r)$ due to the exchange interaction which falls off rapidly with distance. ST mixing occurs when the level separations become of the order of the magnetic interactions. At high magnetic field the ST_{-1} region is normally traversed too quickly to allow efficient polarization. Note that ST_0 mixing occurs where $J(r) \rightarrow 0$*

states the energy separation from the S state makes this an inefficient process at normal radical separations and only those radical pairs in the T_0 state need be considered. (In some exceptional circumstances the $T_{\pm 1}$ states are involved and produce '$ST_{\pm 1}$' RPM polarization, see below). The process of $T_0 \leftrightarrow$ S interconversion is easily envisaged in the vector representation shown in Figure 4.

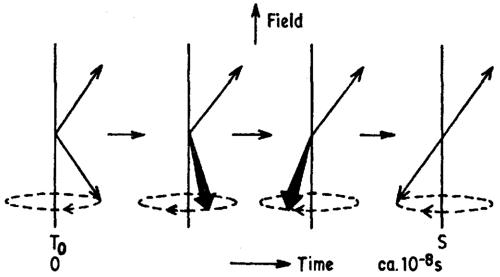

Figure 4 *Conversion of a radical pair born in the T_0 state, with the spin vectors of the electrons on the two radicals in phase, to the S state, where they are exactly out-of-phase. Both vectors precess about the field direction and interconversion occurs if their precessional rates are unequal. The diagram is drawn in a frame rotating at the precessional frequency of one of the vectors*

The electrons on both radicals precess about the magnetic field direction and with a well-defined phase relationship, which causes the two vectors to lie in the same plane. In the T_0 state the vectors are in phase and although the resultant projection in the field direction is zero (hence the label T_0) they have a non-zero projection in the perpendicular directions; in the S state the vectors are opposed and their resultant projection in any direction is zero. To accomplish the transition of a pair in the T_0 state to S it is necessary to cause one of the vectors to precess at a greater rate than the other. This precession rate is simply the resonance frequency of the electron in the local field it experiences within the radical and hence depends both on the *g*-value and the hyperfine coupling constants. The condition for ST_0 mixing is simply that this local field differs at the two electrons and we use the symbol Q to denote this difference. Q is much less than the Zeeman splitting and also than $J(r)$ at short distances, and can affect the development of the radical pair only when the radicals have separated to a point where S and T_0 are almost degenerate. Furthermore using the vector model with known *g*-values and hyperfine coupling constants we can calculate that ST_0 mixing is a slow process (for organic radicals a pure S state would be attained only after about 10^{-8} s, although this is not needed for polarization).

For a pair of electrons the wave functions of the pure S and T_0 states are

$$|\mathrm{S}\rangle = 2^{-\frac{1}{2}}\,(|\alpha\beta\rangle - |\beta\alpha\rangle) \tag{5}$$

and

$$|\mathrm{T}_0\rangle = 2^{-\frac{1}{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle) \tag{6}$$

where $\alpha\beta$ implies that radical 1 has α electron spin and radical 2 has β electron spin, and conversely for radical 2. At a later time, t', a pair born in the T_0 state at time zero has acquired some S character and its wave functions can be written as a linear combination of the two basis functions:

$$\begin{aligned}\Psi(t') &= c_{\mathrm{S}}(t')|\mathrm{S}\rangle + c_{\mathrm{T_0}}(t')|\mathrm{T}_0\rangle \\ &= \{[c_{\mathrm{S}}(t') + c_{\mathrm{T_0}}(t')]|\,\alpha\beta\rangle + [c_{\mathrm{T_0}}(t') - c_{\mathrm{S}}(t')]|\,\beta\alpha\rangle\}\end{aligned} \tag{7}$$

where $c_{\mathrm{S}}(t')$ and $c_{\mathrm{T}}(t')$ are time-dependent coefficients. The latter form is convenient to our discussion because the product of a coefficient with its complex conjugate gives the probability of the state with which it is associated and we can therefore calculate the amounts of α and β spins on the two radicals.

The polarization of one radical is defined in terms of the numbers of $\alpha(n_\alpha)$ and $\beta(n_\beta)$ spins as

$$P = (n_\alpha - n_\beta)/(n_\alpha + n_\beta) \tag{8}$$

where for radical 1 $n_\alpha \propto [c_{\mathrm{S}}(t') + c_{\mathrm{T_0}}(t')]\,[c_{\mathrm{S}}(t') + c_{\mathrm{T_0}}(t')]^*$, and similarly for n_β. Hence

$$P = c_{\mathrm{S}}(t')\,(c_{\mathrm{T_0}})^*\,(t') + (c_{\mathrm{S}})^*\,(t')\,c_{\mathrm{T_0}}\,(t') \tag{9}$$

These coefficients are obtained by solving [7,19] the time-dependent Schrödinger equation for the interaction Q, using the wave-function in equation (7). This yields

$$c_{\mathrm{S}}\,(t') = c_{\mathrm{S}}(0)\cos Qt' - \mathrm{i}c_{\mathrm{T_0}}(0)\sin Qt' \tag{10}$$

and

$$c_{\mathrm{T_0}}(t') = c_{\mathrm{T_0}}(0)\cos Qt' - \mathrm{i}\,c_{\mathrm{S}}(0)\sin Qt' \tag{11}$$

Substitution of these values into equation (9) and remembering that we must take an average over all the radical-pairs present in the system shows that P is zero. That is, although ST_0 mixing has occurred it has not caused spin polarization.

However we remember that ST_0 mixing is a slow process and the radical pair must separate before it becomes singlet and is consumed by reaction. There is consequently a probability that the members of this original pair will re-encounter at a later time. If they are able to, they react but otherwise they experience the strong exchange interaction at this collision before separating once more. This situation differs from that in which the pair was first created in that it now has a mixed S and T_0 character, rather than the original pure T_0 state. When the radicals are inspected as they diffuse away from this second encounter (the 're-encounter') they are found to be polarized.[19]

During the re-encounter, the exchange interaction outweighs the Q one which may be neglected and, to calculate its effect, we solve another time-dependent Schrödinger equation for the interval of the collision, $(t - t')$ s. This yields at the end of the re-encounter

$$c_S(t) = c_S(t')\exp\{-iJ(t - t')\} \tag{12}$$

$$c_{T_0}(t) = c_{T_0}(t')\exp\{iJ(t - t')\} \tag{13}$$

substituting the values from equations (10)—(13) into equation (9) and ensemble averaging gives[17]

$$P = \{\overline{c_S(0)\,(c_S)^*\,(0)} - \overline{c_{T_0}(0)\,(c_{T_0})^*\,(0)}\}\sin 2Qt' \sin 2J(t - t') \tag{14}$$

This, when averaged over the finite lifetime of the radicals, is non-zero provided that $\overline{c_S(0)\,(c_S)^*\,(0)} \neq \overline{c_{T_0}(0)\,(c_{T_0})^*\,(0)}$, that is, providing that there are initially unequal numbers of S and T_0 pairs. This is obviously so in the case of the triplet pair we have considered but the result is in fact a general one.

A common case experimentally is that in which the radicals are created independently and diffuse together to form a radical pair (an 'F' pair). Statistically they have an equal probability of being in either the S or the T_0 state and no polarization would be expected in the radicals as they separate. However, normally the S pairs have a high probability of reaction leaving a preponderance of T_0 pairs which proceed to evolve as above. Thus radicals observed after F-pair formation exhibit qualitatively similar polarizations to those born as triplet pairs.

We should note that throughout the whole RPM ST_0 process there have been no 'spin-flips' and no true spin polarization has occurred. Rather, for a 'net' effect the probability of radical 1, for instance, having an α-spin differs from the probability that it has a β one, but is exactly balanced by the probability that radical 2 has a β-spin rather than an α one. The process is one of spin-sorting into the different radicals.

We summarize the F-pair RPM process with the aid of Figure 5, which clarifies the nature of the diffusion and exchange interaction stages. The relative diffusion of the pair of radicals is considered as a series of re-encounters. Defining the region of separation $d < r < r^*$ as the exchange region, where d is the distance

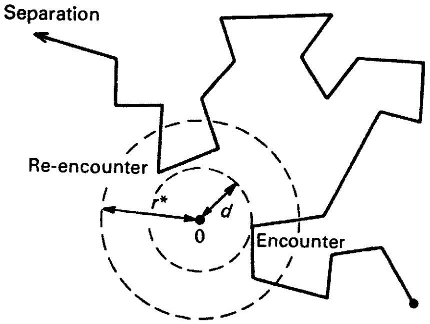

Figure 5 *The relative diffusion of two radicals which encounter to form F-pairs. One is kept in position at* 0 *and the diffusive trajectory of the other with respect to it is mapped. Exchange occurs in the region* $d < r \lesssim r^*$, *where d is the distance of closest approach and* ST_0 *mixing when* $r \gtrsim r^*$

of closest approach and r^* is defined in the figure, the process can be summarized as follows: the independently-created radicals diffuse to $r = d$ (encounter), some react and the others diffuse apart. Of these, some separate for ever (and are not polarized as a result of the encounter), the rest diffuse back into the exchange region (re-encounter) and those that do not react separate again. This cycle of diffusion and re-encounter continues until the pair either react or diffuse apart completely, in which case provided that at least one re-encounter has occurred the radicals are polarized.

The exchange region is defined to be where $J(r) > Q$, that is where exchange dominates the ST_0 mixing interaction. We stress that both the exchange and the mixing interaction are necessary to the generation of spin polarization.

The magnitude of the polarization produced depends on three distinct factors: the difference in the magnetic interactions at the two electrons (their *g*- and hyperfine-coupling constant values), the probability of radical re-encounters (and hence on diffusion) and on the distance-dependence and magnitude of the exchange interaction. The diffusion problem has been considered using both random-walk[19] and random-lattice (stochastic Liouville[8,23,24]) theories but unfortunately the time-scale of ST_0 mixing is such that CIDEP is sensitive only to relatively long-term behaviour; in most cases it is not useful in exploring diffusive motion. However the dependence of polarization on $J(r)$ offers the opportunity of exploring the functional nature of this interaction: Figure 6 shows the polarization expected with $J(r)$ taken both as an exponential function of distance and as a delta function.[8,21] These differ in a region of J_0 which is experimentally accessible.

If the polarization results from encounter of a pair of free radicals created together (in singlet or triplet states) it is termed 'initial' to differentiate it from the random re-encounter (F-pair) type, which occurs independently in the same

[23] R. Kubo, *Adv. Chem. Phys.*, 1969, **15**, 101.
[24] J. B. Pedersen and J. H. Freed, *J. Chem. Phys.*, 1974, **61**, 1517.

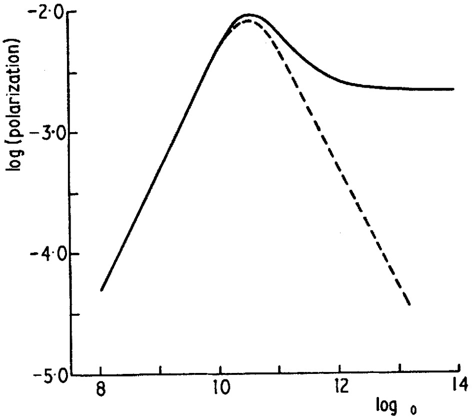

Figure 6 *The predicted variation of radical pair polarization with the magnitude of the exchange interaction, J_0. The solid curve corresponds to an exponential form for $J(r) = J_0 \exp[-\lambda(r - d)]$ and the hatched curve, a delta function $\{J(r) = J_0$ when $r = d, = 0$ otherwise$\}$; λ is a constant. The curves were calculated for realistic values of Q, d, λ and the diffusion constant*[17]

system. Initial polarization is rather rare, probably because of rapid scavenging of one member of the pair.[17]

The qualitative results of RP theory are summarized in two simple sign rules for the phase of polarization:

For the net effect

$$\Gamma^{\mathrm{n}} = \mu J \triangle g \tag{15}$$

where μ is positive for pairs produced in triplet states or for F-pairs and negative for singlet pairs, J is negative when S lies below T_0 and $\triangle g$ is positive for the radical with the higher g-value. A positive value of Γ^{n} implies a spectrum in absorption (A) and a negative value, one in emission (E)

For the multiplet effect

$$\Gamma^{\mathrm{m}} = \mu J \ , \tag{16}$$

and for a positive Γ^{m} the low-field half of the spectrum is in absorption and the high field half in emission (A/E), and conversely for a negative one. F-pairs exhibiting multiplet effects invariably show E/A patterns, independent of the sign of the hyperfine coupling constant. The net effect when present ($\triangle g \neq 0$) is usually dominated by the multiplet one.

If the $T_{\pm 1}$ states participate in the mixing process with the singlet state a true polarization results which originates in their unequal α and β spin state probabilities for the two electrons. $ST_{\pm 1}$ mixing can occur in two ways.[13,25-27] Firstly

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[25] P. W. Atkins, R. C. Gurd, K. A. McLauchlan, and A. F. Simpson, *Chem. Phys. Letters*, 1973, **22**, 209.

[26] F. J. Adrian, *Chem. Phys. Letters*, 1971, **10**, 70.

[27] P. W. Atkins, A. J. Dobbs, and K. A. McLauchlan, *Chem. Phys. Letters*, 1973, **22**, 209.

during the separation of the radical pair the T_{-1} level (if $J < 0$) crosses the S one, which allows efficient mixing save for the fact that it occurs very rapidly in a few diffusive steps; if this diffusion is inhibited, for example in viscous solutions,[28] noticeable polarization can occur. Secondly the unusually large hyperfine interaction in H• atoms results in $ST_{\pm 1}$ mixing, even at normal diffusion rates, since it is not negligible compared with the Zeeman interaction.[6,29–34] The states are mixed by the non-secular part of the spin Hamiltonian to yield a net effect, although the hyperfine interaction produces intensity distortions.[13] The sign rule is

$$\Gamma_{\pm}{}^{n} = \mu J \text{ (positive A, negative E)} \qquad (17)$$

In practice, when it is observed, $ST_{\pm 1}$ polarization occurs concurrently with ST_0 polarization.

C. Secondary Polarization.—A radical produced in a spin-polarized state by either the TM or the RPM may react with a diamagnetic species within its spin-lattice relaxation time, T_1, to yield a secondary radical which, by spin conservation, is itself polarized. This process, is wholly analogous to the reaction of the polarized triplet molecule in the TM but is less restrictive in that the relaxation rates of organic radicals ($T_1^{-1} \sim 10^5$—10^6 s^{-1}) are much slower than those of triplets and most radical reactions satisfy the polarization criterion. Secondary polarization is probably quite common and has been reported several times in those cases where it has been recognized explicitly.[30,35–37]

Qualitatively it provides the chemist with a means for following radical reaction pathways to other radicals and it also enables a wide variety of radicals to be obtained in a spin-polarized state by reaction of one primary polarized radical. This is particularly important in flash-photolysis experiments where flashes short enough to exploit the full time-resolution of the technique can be obtained only by using lasers, which yield light of a single frequency, thus limiting the variety of primary species to those whose precursors absorb in this region. The secondary polarization technique has been exploited predominantly in relaxation studies in which it extends considerably the radical varieties available for study.[38–40]

[28] A. D. Trifunac, *Chem. Phys. Letters*, 1977, **49**, 457.
[29] K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 1186.
[30] N. C. Verma and R. W. Fessenden, *J. Chem. Phys.*, 1976, **65**, 2139.
[31] R. W. Fessenden and N. C. Verma, *Faraday Discuss. Chem. Soc.*, 1977, **63**, 104.
[32] H. Shiraishi, H. Kadoi, Y. Katsumura, Y. Tabata, and K. Oshima, *J. Phys. Chem.*, 1974, **78**, 1336.
[33] H. Shiraishi, H. Kadoi, Y. Katsumura, Y. Tabata, and K. Oshima, *J. Phys. Chem.*, 1976, **80**, 2400.
[34] A. D. Trifunac and D. J. Nelson, *J. Amer. Chem. Soc.*, 1977, **99**, 289.
[35] R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1973, **59**, 4891.
[36] K. A. McLauchlan, R. C. Sealy, and J. M. Wittmann, *J.C.S. Faraday II*, 1977, **73**, 926.
[37] K. A. McLauchlan and R. C. Sealy, *Chem. Phys. Letters*, 1976, **39**, 310.
[38] K. A. McLauchlan, R. C. Sealy, and J. M. Wittmann, *Mol. Phys.*, 1978, **35**, 51.
[39] K. A. McLauchlan, R. C. Sealy, and J. M. Wittmann, *Mol. Phys.*, 1979, in the press.
[40] P. J. Hore, K. A. McLauchlan, L. Pasimeni, and R. C. Sealy, *J.C.S. Faraday II*, 1978, **74**, 1662.

The polarization ratio, γ_S, of the secondary radical is simply related to that, γ_P, of the primary species using the theory given in Section 2A, but with the radical replacing the triplet.

This yields the expression[38]

$$\frac{1}{\gamma_S} = \frac{1}{\gamma_P}\left\{1 + \frac{1}{k[\mathrm{M}]T_1(\mathrm{P})}\right\} \tag{18}$$

where k is the second-order rate constant for reaction of the primary radical with the molecule M and $T_1(\mathrm{P})$ is the relaxation time of the primary radical. Measurement of γ_S as a function of [M] allows γ_P and the product $k\ T_1(\mathrm{P})$ to be determined; an independent measurement of either k or $T_1(\mathrm{P})$ gives an absolute value of the other. The ability to measure γ_P, the polarization ratio of a primary radical which reacts too quickly to be observed, has allowed experimental confirmation of the basic prediction of the TM that both primary radicals should have identical polarizations in sign and magnitude:[36] direct observation of one primary species and deduction of γ_P for the other by a secondary route was possible in the benzophenone–triethylamine–biacetyl system discussed in Section 4A.

Secondary polarization can occur over several reaction steps with the initially-formed secondary species acting in its turn as a source of polarization for a radical formed from it, and so on.

D. Summary.—CIDEP results from two different polarization mechanisms. The TM is recognized in operation by two radicals having the same phase of polarization with no hyperfine distortion, by obeyance of equation (4) with sensible values of the derived constants[41] and by the physical test of the dependence of polarization on the plane of polarization of the light source.[42–44] RPM polarization in its common ST_0 form is identified by the total spectrum showing equal amounts of emission and absorption or, more commonly, by E/A polarization in the only radical observed; in $\mathrm{ST}_{\pm 1}$ polarization an additional single-phase signal, with hyperfine-dependence of intensity, is added to the ST_0 pattern. The expected intensity patterns from any mechanism may however be distorted by differential relaxation effects.[17]

Once the mechanism has been identified the observed polarizations can be interpreted to give a range of physical and chemical data discussed above. For the most part the information obtained from the TM and RPM processes differs, but both yield spin polarized radicals which can act as labelled species for following radical reactions to other radicals or can be used for studies of electron spin relaxation. The uses of CIDEP are summarized below.

In practice the experiment performed largely determines the polarization behaviour.[3] Flash photolysis studies are often dominated by the TM, intermittent

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[41] P. W. Atkins, A. J. Dobbs, G. T. Evans, K. A. McLauchlan, and P. W. Percival, *Mol. Phys.*, 1974, **27**, 769.

[42] F. J. Adrian, *J. Chem. Phys.*, 1974, **61**, 4875.

[43] B. B. Adeleke, K. Y. Choo, and J. K. S. Wan, *J. Chem. Phys.*, 1975, **62**, 3822.

[44] A. J. Dobbs and K. A. McLauchlan, *Chem. Phys. Letters*, 1975, **30**, 257.

photolysis experiments show mixed TM and RPM behaviour and experiments involving continuous creation of radicals or pulse radiolysis usually display only RPM effects. Each experiment needs to be analysed separately and this we proceed to in the next section.

3 Experimental Methods

Electron spin polarization in a radical is ephemeral and disappears in a period of the order of the electron spin lattice relaxation time, T_1 (typically 10^{-4}—10^{-7} s). Its observation must consequently be either in transient conditions by rapid-response time-resolved spectroscopy or in steady-state conditions. The former requires both fast instrument response and a means of creating radicals in a time short compared with T_1; it is associated with flash photolysis and pulse radiolysis. The latter involves production of a steady state in which the formation of polarized radicals is balanced by their reaction and relaxation. In this case a limited time-resolution may be achieved in photolysis experiments by chopping the light source so as to obtain steady states in both the 'light' and the 'dark' periods. Continuous generation of radicals, as in flow experiments, yields no information on the time-dependence of polarization.

The observed e.s.r. line intensities reflect radical concentrations, polarizations, and relaxation rates and their analysis is complex. To interpret their time-dependence recourse is made to the Bloch equations, which may be solved analytically or numerically.[3,30,45–49] This time-dependence depends on a variety of parameters including the radical relaxation times, the microwave field strength at the sample, the off-set of the magnetic field from exact resonance, which polarization mechanism (or mechanisms) operates, and the radical formation and decay kinetics. Also the signal may be observed in the absorption or dispersion mode, with or without field modulation. The fitting of theory to experiment is simplified considerably by removing all modulation, which also allows the response time of the spectrometer to be decreased permitting faster and more accurate measurement of polarizations and relaxation times.[6,17] A general theory has been given,[45] but the parameters are specific to each experiment and rather than describe it here we accentuate the quantities which can be obtained from the analysis.

Two different measures of radical polarization are used: the instantaneous polarization ratio, γ, defined above, which gives a measure of the initial polarization in a pulse experiment, and the enhancement factor, V, which represents the polarization over the lifetime of the radical and is appropriate to all other observations, including re-combination polarization in pulse experiments. The enhancement factor may have two contributions, $V(\mathrm{I})$ and $V(\mathrm{F})$, due to initial polarization, either in a TM or RPM process, and recombination polarization respectively. We define

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[45] J. B. Pedersen, *J. Chem. Phys.*, 1973, **59**, 2656.
[46] J. B. Pedersen, Ref. 11, p. 169.
[47] P. W. Atkins, K. A. McLauchlan, and P. W. Percival, *Mol. Phys.*, 1973, **25**, 281.
[48] H. C. Torrey, *Phys. Rev.*, 1949, **76**, 105.
[49] P. J. Hore and K. A. McLauchlan, *Revs. Reaction Intermediates*, 1979, in the press.

$$V(\mathrm{I}) = \frac{P_a(\mathrm{I})}{P_{\mathrm{eq}}}\,\beta T_1 \tag{19}$$

where $P_a(\mathrm{I})$ has been defined above, $\beta = 1/t_{\frac{1}{2}}$, where $t_{\frac{1}{2}}$ is the first half-life of the radical due to second-order reaction and T_1 is the spin-lattice relaxation time. Similarly,

$$V(\mathrm{F}) = \frac{P_a^*}{P_{\mathrm{eq}}}\,\beta T_1\ , \tag{20}$$

with P_a^* the Fp-air polarization of line a.

The enhancement factors are obtainable directly from experiment and can yield the fundamental quantities $P_a(\mathrm{I})$ and P_a^*, required for comparison with theory, if β and T_1 are known.

A. Steady-state Experiments.—CIDEP has been observed under steady state conditions in flow experiments,[46,47] in which it originates entirely in F-pairs, and in continuous photolysis[5] and radiolysis.[6] It is usually due to the RPM. The observed signal is the sum of contributions from all the radicals present, some of which are polarized and the remainder relaxed: if the latter contribution is dominant then even if the polarization is emissive, the spectrum may be in (reduced) absorption.

Theory predicts[16] that for example $[P_a(\mathrm{I})/P_{eq}]$ may be as high as 600, whereas in normal e.s.r. spectroscopy radicals are detected with their equilibrium polarizations. This implies that CIDEP can be detected in steady-state experiments provided that $\beta T_1 > 1.6 \times 10^{-3}$, which implies $\beta > 10^2$—$10^4\ \mathrm{s}^{-1}$ and $t_{\frac{1}{2}} < 10^{-2}$—$10^{-4}$ s. This condition is not compatible with the attainment of high steady-state concentrations in many systems and it is not surprising that the detection of radicals in this way usually shows them to be unpolarized.

When polarized radicals occur they are produced continuously in time and the signal observed is a complex sum of the solutions of the Bloch equations over the radical formation times. No simple account has been given which allows quantitative interpretation of absolute polarization magnitudes although the relationship of these signals to time-dependent observations of the same systems has been discussed.[31]

The overall enhancement factor,

$$V_a = V_a(\mathrm{I}) + V_a(\mathrm{F}) = (I_a - I_a^0)/I_a^0\ , \tag{21}$$

where I_a is the intensity of the hyperfine line a whose equilibrium intensity is I_a^0, may be deduced. For pure F-pair polarization and assuming $T_1^a = T_1^{-a}$ and $P_a^* = P_{-a}^*$,

$$V_a(\mathrm{F}) = (I_a - I_{-a})/(I_a + I_{-a}) \tag{22}$$

I_a and I_{-a} have opposite signs (F-polarization normally produces an E/A multiplet pattern) but the denominator is non-zero because each contains a contribution from the equilibrium signal in absorption which causes $|I_a| \neq |I_{-a}|$. Steady-state observations sometimes indicate contributions from $\mathrm{ST}_{\pm 1}$ processes.[29]

B. Flash-photolysis Experiments.—All quantitative flash-photolysis experiments have used pulsed nitrogen lasers with flash durations of 3—20 ns, times much shorter than either the instrument response time (0.1—1.1 μs) or the radical spin-lattice relaxation times.[12,48,50] Such experiments involve fast data acquisition after the flash and have the advantage of an unusually well-defined time origin. However, to attain the flash duration the intensity of each pulse is small (1—10 mJ) and signal averaging of the results of many flashes is necessary. The low flash energy produces low radical concentrations (*ca.* 10^{-6} mol dm^{-3} per flash) and the radical half-life is long, preventing any appreciable contribution from F-pair effects to the observed polarization because β is small [equation (20)]. In consequence the polarization is often entirely TM in origin and this single source produced at a highly specified time constitutes a major simplification in the analysis of the experimental results.

A typical experiment consists in setting the magnetic field of the spectrometer on a specific line of the spectrum and following the time profile of the signal following the flash, as shown in Figure 7. The time profile (Figure 8) rises with the response time of the spectrometer (but see below) and then decays by a fast spin-lattice relaxation process to the equilibrium value before decaying much more slowly by chemical reaction. The response function may be de-convoluted from the observed signal to allow more accurate evaluation of γ and T_1.[49]

The analysis of these curves has been discussed recently, for experiments with and without field modulation. When the microwave field amplitude at the sample, $\omega_1 > \frac{1}{2}(T_2^{-1} - T_1^{-1})$, the Bloch equations predict oscillations in both the time and frequency domains.[49,51] The former have been observed in both flash-photolysis[51] and pulse radiolysis[30,52] experiments and at resonance their frequency gives ω_1 directly. With a sufficiently short spectrometer response time ($\sim$ 0.1 μs) the initial rise of the signal corresponds to the time taken for the deflection of the magnetic polarization vector from the magnetic field direction to the orthogonal observation direction.[52]

It has often been assumed that the polarized signal decays exponentially, but this is exact only when $T_1 \gg T_2$; even here the effective relaxation time must be measured at a series of microwave powers and extrapolated to zero power[38,47] to give the true T_1. Outside this limit the decay is exponential when $\omega_1 < \frac{1}{2}(T_2^{-1} - T_1^{-1})$ at times of the order $(3/\omega_1)$ s after the flash, with an effective relaxation time:[49]

$$\frac{1}{T_1^{\text{eff}}} = \tfrac{1}{2}(T_1^{-1} + T_2^{-1}) - [\tfrac{1}{4}(T_2^{-1} - T_1^{-1})^2 - \omega_1^2]^{\frac{1}{2}} \qquad (23)$$

which is again equal to T_1 at zero microwave power. When $\omega_1 > \frac{1}{2}(T_2^{-1} - T_1^{-1})$ (which includes $T_1 = T_2$, the normal situation at low viscosity) the decay is not exponential.

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[50] H. M. Vyas, S. K. Wong, B. B. Adeleke, and J. K. S. Wan, *J. Amer. Chem. Soc.*, 1975, **97**, 1385.

[51] P. W. Atkins, A. J. Dobbs, and K. A. McLauchlan, *Chem. Phys. Letters*, 1974, **25**, 105.

[52] N. C. Verma and R. W. Fessenden, *J. Chem. Phys.*, 1973, **58**, 2501.

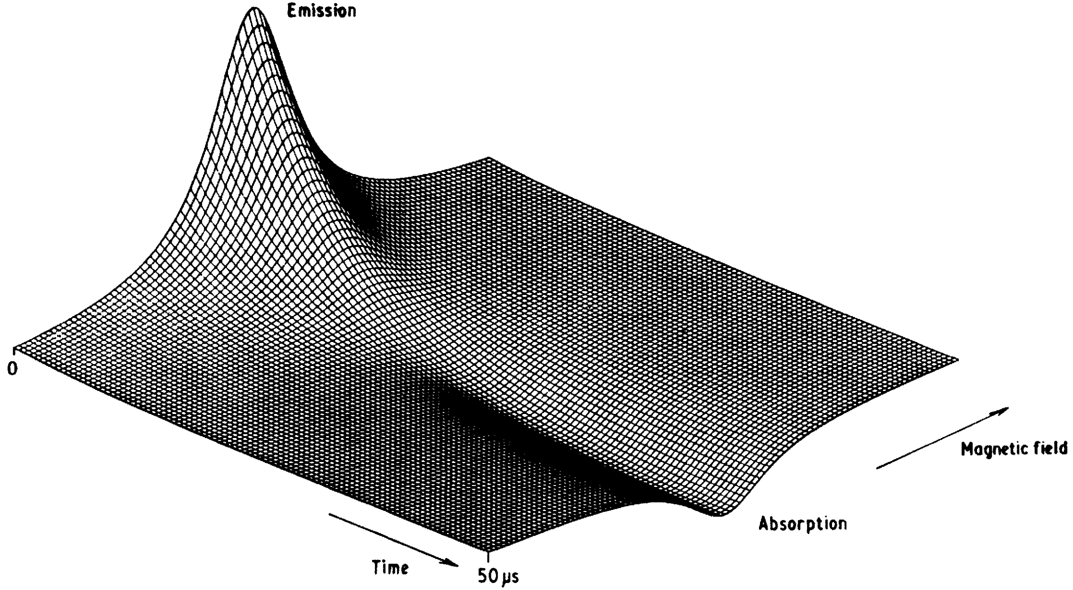

Figure 7 *A computed e.s.r. line, for a pulse CIDEP experiment, as a function of time and magnetic field. The signal, which is initially in emission, decays by relaxation to the equilibrium value (absorption) in ca.* 50 μs. *On the time-scale of this drawing, the decay of the signal due to chemical reaction is negligible. The following values were used in the calculation;* $T_1 = 10$ μs, $T_2 = 1$ μs, $\omega_1 = 10^4$ s^{-1}, $\gamma = -5$. *A typical experiment is to keep the magnetic field constant and follow the e.s.r. signal as a function of time (see Figure* 8*), but at any time the spectra may be obtained by taking a cross-section through the surface parallel to the field axis*

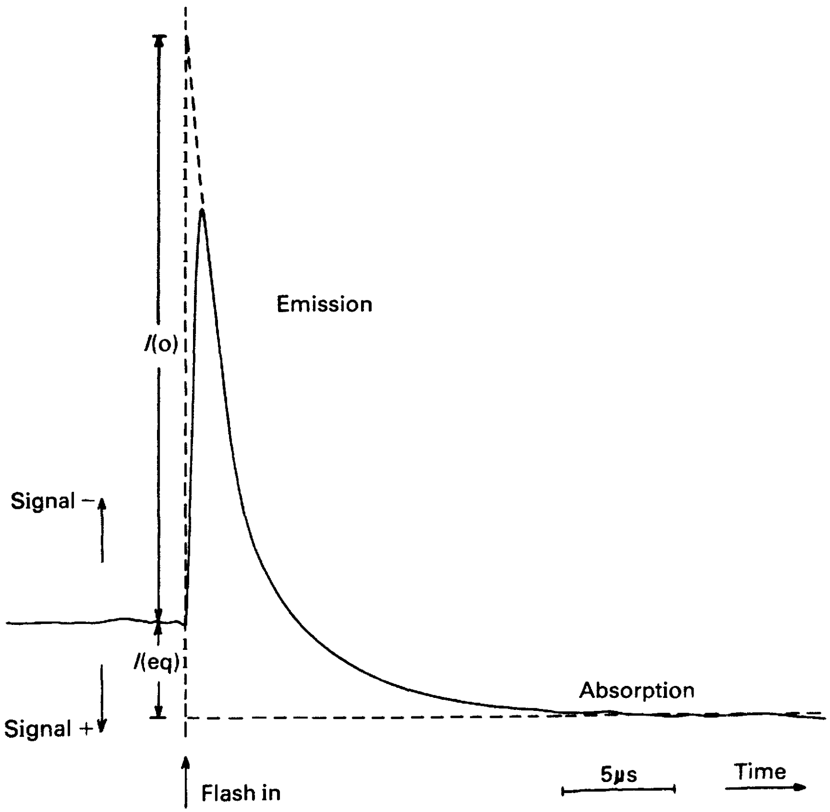

Figure 8 *An experimental time-profile at a point in the spectrum of the emissively-polarized duroquinone radical anion produced by flash photolysis of duroquinone in the presence of triethylamine. The polarization ratio is given by* $\gamma = (I(0) - I_{eq})/I_{eq}$, *where* $I(0)$ *and* I_{eq} *are obtained by extrapolation to zero time. On the time-scale of this diagram the comparatively slow chemical decay of the radicals cannot be observed*

The polarization ratio observed experimentally is also an effective value. It is defined by

$$\gamma_{\text{eff}} = [I(0) - I_{\text{eq}}]/I_{\text{eq}} \ , \tag{24}$$

where $I(0)$ and I_{eq} are the polarized and equilibrium signals extrapolated back to zero time (Figure 8); $P_a(\mathrm{I})$ and P_{eq} are directly proportional to them. In the $T_1 \gg T_2$ limit for unmodulated detection of the absorption signal analysis[49] shows

$$\gamma_{\text{eff}} = \frac{P_a(\mathrm{I})}{P_{\text{eq}}} \left\{1 + \frac{\omega_1^2 T_1 T_2}{1 + \Delta\omega^2 T_2^2}\right\} - 1 \tag{25}$$

where $\Delta\omega$ is the off-set from resonance (if there is one). Thus γ_{eff} is also dependent on microwave power and only becomes equal to γ by extrapolation to zero power. This result is also true when the decay becomes exponential at longer times (see above).

In general, time oscillations are rarely observed, which implies that work is not exactly at the $T_1 = T_2$ limit, but whether the condition $\omega_1 < \frac{1}{2}(T_2^{-1} - T_1^{-1})$ applies is rarely known except for the fact that the decay curves are usually exponential within experimental error. The assumptions are always made that extrapolation of γ_{eff} and T_1^{eff} values to zero microwave power give the true γ and T_1.

The analysis of decay curves from polarized secondary species produced in flash-photolysis experiments has also been presented and its validity investigated.[38] Its importance in extending the number of species available for reaction and relaxation studies has been mentioned above.

C. Pulse Radiolysis Experiments.—Pulse radiolysis is similar in principle to flash-photolysis but involves radical production by electron pulses of typically 1 μs duration in fast-response spectrometers.[6,53] Once again the basic experiment consists of obtaining the time-dependence of the e.s.r. signal at a specific field value but the analysis is complicated in two ways. Firstly the formation pulse is not necessarily negligible in duration, and secondly much higher radical concentrations are produced than in the photolysis experiment. This causes extensive F-pair polarization and implies that the Bloch equations, in contrast to the flash-photolysis case, contain a term in the production of polarization at times following the initial pulse. In some pulse radiolysis experiments polarization contributions are obtained from both recombination and initial processes with, to date, the initial polarization resulting from radical-pair effects.[30]

Whether initial or recombination polarization is dominant is clearly seen by experiment, for the time profiles for the two differ (Figure 9). Initial polarization is observed directly after the flash and decays with T_1 (as is most clearly seen in flash-photolysis) whereas F-pair polarization takes longer to appear and decays with the square of the radical concentration. In the absence of secondary polarization, enhancements existing at times longer than about 5 T_1 s after the pulse originate in RPM polarization in F-pairs.

Pulse radiolysis has disclosed contributions from $ST_{\pm1}$ RPM processes detected, as in the steady-state experiments, as differences in the intensities of the hyperfine lines symmetrically disposed about the spectrum centre.[28,34,54]

D. Intermittent Illumination Experiments.—These involve photolysis with either a rotating sector disc to intercept the light periodically or by square-wave modulation of the light source;[55] in the latter the light intensity is reduced, but not zero, in the dark period. Experimentally, the light pulse is comparatively long and the response time of the spectrometer may be long also: the technique

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[53] A. D. Trifunac, K. W. Johnson, B. E. Clifft, and R. H. Lowers, *Chem. Phys. Letters*, 1075, **35**, 566.

[54] A. D. Trifunac and D. J. Nelson, *Chem. Phys. Letters*, 1977, **46**, 346.

[55] J. K. S. Wan, S. K. Wong, and D. A. Hutchinson, *Accounts. Chem. Res.*, 1974, **7**, 58.

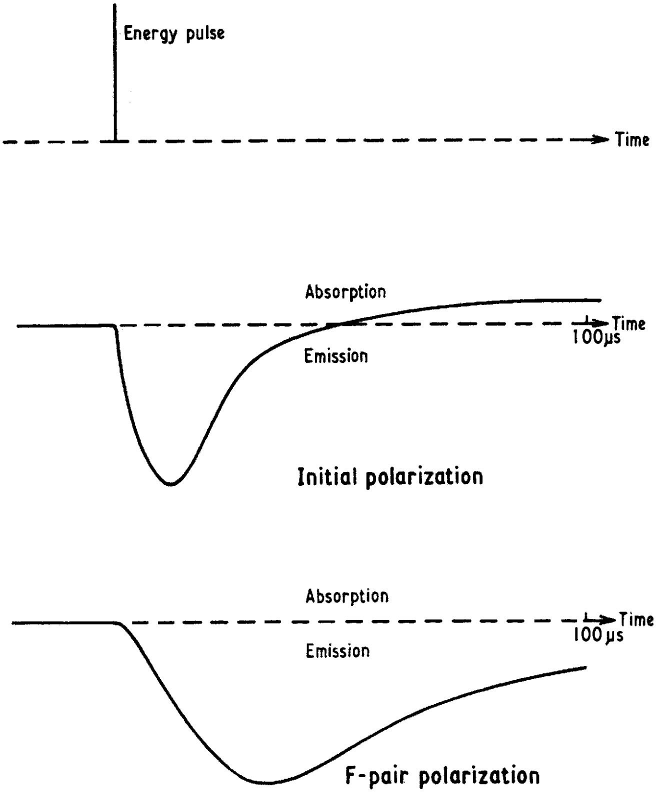

Figure 9 *The time-profiles for pure initial polarization and of pure F-pair polarization observed in a pulse experiment. The pulse is idealised as rectangular with a width less than the response time of the spectrometer and the radical relaxation time (this situation is closely approximated in flash-photolysis experiments). Both curves have been calculated with equal magnitudes of emissive polarization*

is used typically with normal 100 KHz field modulation, producing a higher signal-to-noise ratio than a comparable pulse experiment. The spectrometer response has to be convoluted with the theoretical prediction to compare theory with experiment and this is possible when the response function is of a simple form.[56] The light pulse is never square although this is unfortunately ignored in the analysis.[56,57] Light intensities much greater than in flash photolysis experiments are used and the radical concentrations are comparatively high leading to both initial and F-pair polarization. A unique feature of these experiments is that TM initial polarization and F-pair recombination polarization are usually

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[56] J. B. Pedersen, C. E. M. Hansen, H. Parbo, and L. T. Muus, *J. Chem. Phys.*, 1975, **63**, 2398.

[57] L. T. Muus, S. Frydkjaer, and K. Bondrup Nielsen, *Chem. Phys.*, 1978, **30**, 163.

observed in the same system and their relative magnitudes can be compared directly.[56]

Once again the occurrence of pure initial polarization can be distinguished directly from that of pure F-polarization (Figure 10). The observed signal at, again, a fixed field, rises from its steady state value obtained in the dark period in a time of the order of T_1 and then approaches its steady state in the light period. This has three contributions, from initially polarized radicals, from F-pair polarizations, and from equilibrated radicals. If only the former is present a transient signal with the phase of $V(\mathrm{I})$ is obtained and it decays as the concentration of equilibrated radicals increases until a steady-state is produced. At the end of the light period another transient of opposite phase to $V(\mathrm{I})$ occurs as the polarization decays by relaxation and is followed by decay to the dark

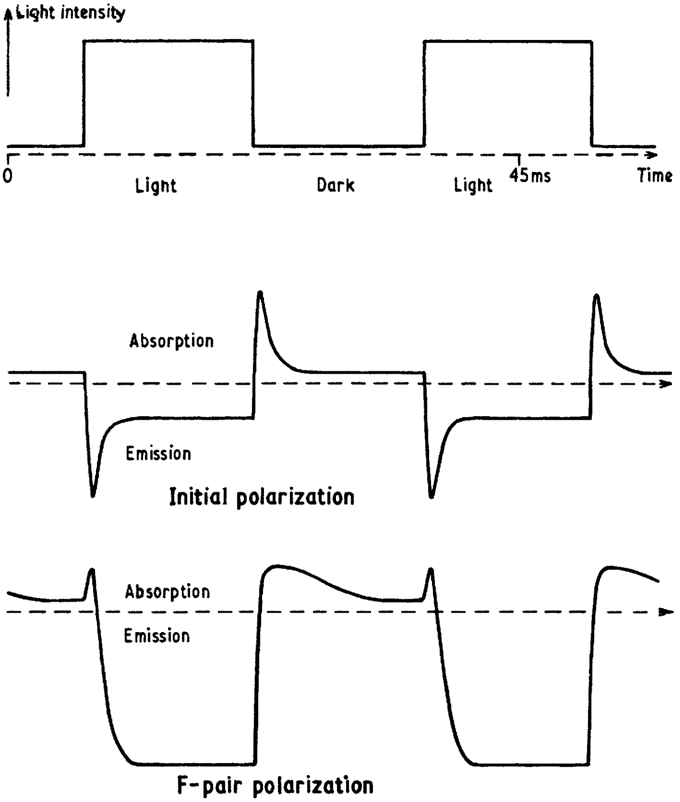


Figure 10 *The observed signals from intermittent-illumination experiments for pure initial polarization and pure F-pair polarization (both emissive and of similar magnitude). The square waves are idealized and, for the case shown, the light is only attenuated in the 'dark' period (as in a light-modulated experiment)*

period steady state. For pure F-polarization the initial rise is slow since the radical concentration is low and polarization is produced at later times as the concentration increases; the decrease of $V(\mathrm{F})$ in the dark period is correspondingly slow. When square wave modulation is used great care must be taken to obtain the true dark-period steady state signal.

The quantities $V(\mathrm{I})$ and $V(\mathrm{F})$ are obtained by curve-fitting whilst the total polarization V is obtained conveniently by observations under systematic attenuation of the light intensity.[4,57,58]

E. Modulation Experiments.—A further method for investigating CIDEP effects quantitatively, used only once, involves the sinusoidal modulation of the photolysis source, with phase-sensitive detection of the e.s.r. signal at the modulation frequency. The amplitudes and phases of the signals contain information on the lifetimes and enhancement factors of the radicals. Both TM and F-pair polarization occurred.[58]

F. Conclusions.—The type of information available from TM polarization studies has been discussed above. The quantities obtained from RP studies are $V(\mathrm{I})$ and $V(\mathrm{F})$ from which the primary quantities relevant to RPM theory $[P_a(\mathrm{I})/P_{eq}]$ and $(P_a{}^*/P_{eq})$ can be derived if the radical decay kinetics (and hence β) and T_1 are known. The kinetics are usually observed to be second-order within experimental error and so β can be determined in principle from the observed curves, although the full chemistry is rarely known. Rather few values of radical T_1's for transient radicals have been measured and they are viscosity- and temperature-dependent; the values used are usually intelligent guesses. The further approximations[56] are made that the relaxation times of all the hyperfine lines of a radical are equal and that $T_1 = T_2$. Even with these assumptions, comparison of experiment with theory is difficult, for the theory itself contains many unknown parameters. Notwithstanding this estimates of $(P_a{}^*/P_{eq})$ for the $\cdot\mathrm{CH_2CO_2}^-$, $\cdot\mathrm{CH(CO_2}^-)_2$, and $\cdot\mathrm{C_6H_6OH}$ radicals[30,59] agree well with experiment although values for α-tetrahydrofuryl[58] and *p*-benzo-semiquinone[56,57] appear to be two—three times those predicted.

F-pair RPM polarization is much more common than initial RPM polarization although theory fails to predict this. A partial explanation is that most time-resolved studies have been made on radicals produced separately (in radiolysis) rather than in pairs. Radicals created in pairs by photolysis may have sufficient kinetic energy to make re-encounter improbable or one radical may be scavenged too quickly for re-encounter to occur.[17] The latter is consistent with experiment in that in those RP systems which have shown initial polarization the observed radical has had a lifetime $> 1\ \mu$s.[18,60,61] Sometimes, however, both radicals are observed and still no initial polarization is evident.[62]

[58] H. Paul, *Chem. Phys.*, 1976, **15**, 115.

[59] R. W. Fessenden, *J. Chem. Phys.*, 1973, **58**, 2489.

[60] S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, 1970, **52**, 5555.

[61] P. W. Atkins, J. M. Frimston, P. G. Frith, R. C. Gurd, and K. A. McLauchlan, *J.C.S. Faraday II*, 1973, **69**, 1542.

[62] R. Livingston and H. Zeldes, *J. Magn. Resonance*, 1973, **9**, 331.

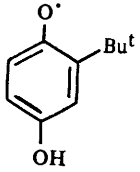
This account has accentuated the type of information available from each experiment rather than provided the detail of how it is obtained because the complexity of the analysis tends to obscure the ends.

4 Applications of CIDEP

The polarization behaviour observed in radicals in solution has been summarized recently, with an indication of the polarization origin in each case.[17] We do not propose to reproduce this here for it is a rationale of results gathered at random whilst the phenomenon was being understood. Rather we wish to accentuate the uses to which CIDEP may be put in chemistry, physics, and biology. Polarization is not an intrinsic property of a radical and a given radical may exhibit TM or RPM effects in different experimental circumstances. CIDEP depends upon the mode of formation of the radicals and their subsequent reactions, and the observations carry kinetic and mechanistic, rather than structural, information; however, since only the intensities of e.s.r. spectra are changed the hyperfine structure still yields the radical identity.

A. Radical Reaction Pathways.—CIDEP has been used to elucidate radical chemistry in a number of ways which we illustrate by examples. Firstly it gives an indication of the spin multiplicity of a radical precursor, and sometimes of a reaction product. If TM polarization is observed the reaction proceeds through an excited triplet molecule, although whether or not this is the major reaction route is best determined by the effect of triplet quenchers on the reaction products. Similar information is available from RPM polarization *via* the sign rules [equations (15) and (16)], although the results are sometimes anomalous. Thus during the pulse radiolysis of some aqueous solutions the hydrated electron e^-_{aq} was detected with a surprising, emissive, F-pair polarization although in these cases the counter-radical had the higher g-value.[63] This is consistent with RPM theory if recombination of e^-_{aq} and the counter-radical is into an excited triplet state of the product. In this situation F-pairs behave qualitatively like singlet, rather than triplet, initial pairs. Triplet formation was rationalized in terms of reaction of the electron by tunnelling and the need to match its energy levels with those of the radical acceptor.[63]

Secondly, CIDEP may be used to label a radical, for example in the photoreduction of t-butyl benzoquinone.[64] On photolysis in the presence of phenol



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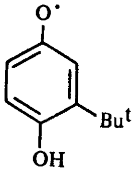

(2)

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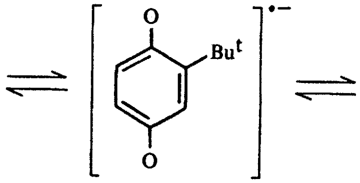
[63] R. W. Fessenden and N. C. Verma, *J. Amer. Chem. Soc.*, 1976, **98**, 243.

[64] T. Foster, A. J. Elliot, B. B. Adeleke and J. K. S. Wan, *Canad. J. Chem.*, 1978, **56**, 869.

this gave the isomeric semiquinone radicals (1) and (2) whose spectra were in complete emission. Independently of how the radicals were produced the concentration of (1) was about twice that of (2), which indicated their equilibration, possibly *via* a radical anion:

(1)



(2)

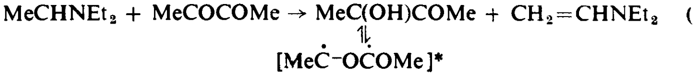
This opens the possibility that only one of them was produced as a primary radical by reaction of the triplet quinone with ground-state phenol, followed by formation of the polarized second radical *via* the equilibration reaction. However the observed enhancement factor (V) was measured for each radical as a function of the concentration of 2-methyl phenol in an intermittent photolysis experiment and V^{-1} was plotted against [phenol]$^{-1}$. Two non-parallel lines were obtained with equal intercepts, which indicates that both radicals are primary species, and the slopes suggested that the rate of reaction to form radical (2) was five to seven times faster than reaction to give (1). This is presumably a result of steric hindrance by the t-butyl group, which also accounts for the greater persistence of (1) than (2).

In a second example, polarization transfer has been used to investigate the reactions of radical intermediates in the production of radicals from α-dicarbonyl compounds in flash-photolysis studies.[36,38] Ketyl radicals from benzophenone in the presence of triethylamine result from two separate routes:

$$^3Ph_2CO + NEt_3 \rightarrow Ph_2\dot{C}OH + Me\dot{C}HNEt_2 \qquad (27)$$

$$Me\dot{C}HNEt_2 + Ph_2CO \rightarrow Ph_2\dot{C}OH + CH_2{=}CHNEt_2 \qquad (28)$$

These cause the quantum yield for ketyl formation to equal two. The initial reaction produces emissively-polarized radicals by the TM process. That the second reaction occurs was demonstrated by increasing the concentration of benzophenone when its rate became sufficiently fast to compete with spin-lattice relaxation in the amine-derived radical (which reacted too fast to be observed); the emission from the ketyl increased but its subsequent absorption signal (proportional to radical yield) remained constant.[37] When conditions were maintained in which the initial radical concentration was constant, addition of biacetyl caused the emission to return to its original value but halved the absorption. It also yielded the biacetyl radical anion in initial emission due to the rapid reaction



$$Me\dot{C}HNEt_2 + MeCOCOMe \rightarrow \underset{\displaystyle [Me\dot{C}{-}O\dot{C}OMe]^{*}}{\underset{\displaystyle \upharpoonleft\!\downharpoonright}{Me\dot{C}(OH)COMe}} + CH_2{=}CHNEt_2 \qquad (29)$$

By measuring the polarization ratio in the radical anion produced *via* the sensitized route, that of the unobserved primary amine radical was obtained [equation (18)] and shown to be equal, within experimental error, to that of the ketyl, as required by TM theory.[36] Unsensitized photoreduction of biacetyl with triethylamine also yielded the radical anion but with its equilibrium polarization, indicating that the reaction

$$^3\text{MeCOCOMe} + \text{NEt}_3 \rightarrow \text{Me}\dot{\text{C}}\text{OHCOMe} + \text{Me}\dot{\text{C}}\text{HNEt}_2 \qquad (30)$$

is too slow to compete effectively with spin-lattice relaxation in triplet biacetyl.

B. Determination of Radical Reaction Rates.—There are two methods that use CIDEP for the investigation of radical reaction kinetics. As discussed in Section 2C, measurement of γ_S for a secondary polarized radical as a function of [M] gives $kT_1(\text{P})$. The other method involves a detailed analysis of the time dependence of e.s.r. intensities which may involve numerical or analytical solution of the Bloch equations.

One of the reasons that the former method has not been widely used is that $T_1(\text{P})$ is often unknown. For example McLauchlan *et al.*[36] found $kT_1(\text{P})$ to be approximately 100 in a study of reaction (28), but since the amine-derived radical could not be observed its relaxation time could not be measured by the method of Section 3B. However, with an estimate of 10^{-6} s for $T_1(\text{P})$, $k \simeq 10^8$ dm^3 mol^{-1} s^{-1} which is not unreasonable for this reaction.[36] As more radical T_1's become available from CIDEP studies this method will become increasingly important.

Fessenden and Verma[31] have used the second method in a detailed investigation of the reactions of hydrogen atoms produced by pulse radiolysis in a spin-polarized state. Since the radical half lives were of the order of their T_1's, the Bloch equations modified to include reaction and polarization effects, had to be solved numerically. In fitting these solutions to the observed time profiles the following parameters were kept constant throughout: the microwave field strength, B_1 (determined from the frequency of oscillations in the time profiles of e.s.r. signals from the radical $^-\text{O}_2\text{CCH}{=}\dot{\text{C}}\text{CO}_2{}^-$); T_1; T_2 (which was set artificially low to include line-broadening by field inhomogeneity); the magnitude of polarization present when the H atoms were formed and that produced (by the RPM) as a result of spin selective H$\cdot$ + H$\cdot$ reaction. The time dependence of the concentration of H atoms was included *via* the kinetic equation:

$$\frac{\text{d}[\text{H}\cdot]}{\text{d}t} = -k_1[\text{H}\cdot] - k_2[\text{H}\cdot]^2 \qquad (31)$$

where k_1 is the pseudo first-order rate constant for H$\cdot$ atom scavenging and k_2 is the second-order rate constant for H$\cdot$ + H$\cdot$ reaction; k_1, k_2 and a scaling factor were used as free variables in the curve fitting.

From the time profiles of the low-field e.s.r. line of H$\cdot$ atoms produced by pulse radiolysis of 0.1 M-HClO$_4$, k_2 was estimated at 2.3×10^{10} dm^3 mol^{-1} s^{-1}, which was slightly higher than the value of 1.5×10^{10} dm^3 mol^{-1} s^{-1} obtained with optical detection.[65] It was also found that the radical half-life increased, but the radical pair polarization remained unchanged, when t-butanol was added to scavenge OH·. These observations are consistent with H· + OH· being much faster than H· + ·CH_2CMe_2OH (produced by Bu^tOH + OH·), and H· + OH· producing little or no polarization (see Section 2C). Rate constants, k_1, were subsequently determined for the reactions of H with methanol, ethanol, propan-2-ol, and succinic acid, and, from linear plots of k_1 against the quencher concentration, the second-order rate constants were found. The results are shown in Table 1 together with those from other sources. The agreement between the different methods was good apart from the steady-state[66] value for methanol and that of Smaller *et al.* for ethanol,[67] both of which were low.

Table 1 *Rate constants for reaction with* H· *atoms*

$k \times 10^{-6}/dm^3\ mol^{-1}\ s^{-1}$

Reactant	*Pulse radiolysis* (*ref.* 31)[a]	(*ref.* 67)[b]	*Steady-state e.s.r.* (*ref.* 66)[c]	*Chemical competition* (*ref.* 68)
methanol	2.5	2.4	1.6	2.9
ethanol	21	13	26	25
propan-2-ol	68	79	65	78
succinic acid	3.0	—	3.5	2.3

[a]Full Bloch analysis; [b]kinetic (inexact) analysis; [c]assumed initial polarization

In these studies it is important that the source of polarization is known. In a previous study of H atom reaction rates,[66] the steady-state e.s.r. signals were analysed assuming that the polarization observed was present when the radical was formed, rather than being created during the radical lifetime as a result of the recombination radical pair process. The values so obtained, however, were in reasonable agreement with measurements by other methods. Similarly, Smaller *et al.*[67] assumed that the signal intensity was proportional to radical concentration in a time-resolved study of H· atoms.

C. Fundamental Processes in Radiation Chemistry.—All CIDEP results in radiation chemistry[6] have involved radical and atom formation by the fast-electron irradiation of aqueous solutions. These electrons interact with water molecules and are slowed by successive collisions until their energy is degraded to less than 100 eV, when they cause chemical events. The energy is deposited in small isolated regions called spurs, which contain only a few pairs of radicals. The most important primary event is

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[65] P. Pagsberg, G. Christensen, J. Rabani, G. Nilson, J. Fenger, and S. O. Nielson, *J. Phys. Chem.*, 1969, **73**, 1029.
[66] P. Neta, R. W. Fessenden, and R. H. Schuler, *J. Phys. Chem.*, 1971, **75**, 1654.
[67] B. Smaller, E. C. Avery, and J. R. Remko, *J. Chem. Phys.*, 1971, **55**, 2414.
[68] P. Neta, G. R. Holdren, and R. H. Schuler, *J. Phys. Chem.*, 1971, **75**, 1449.

$$\begin{array}{l} \mathrm{H_2O} \xrightarrow{e^-} \mathrm{H_2O^+} + e^- \rightarrow \mathrm{e}^-_{aq} \\ \qquad\qquad \downarrow \text{rapid} \\ \qquad\qquad \mathrm{H^+} + \cdot\mathrm{OH} \end{array} \tag{32}$$

The hydrated electron is formed by solvation after the electron has travelled a little way from the reaction centre. The hydroxy-radical and the hydrated electron may either diffuse together and react to form $\mathrm{OH^-}$ ions, or may diffuse apart; approximately equal proportions go by each route. Other processes are possible, such as the excitation of water which yields small amounts of hydrogen atoms on dissociation:

$$\mathrm{H_2O} \xrightarrow{e^-} \mathrm{H_2O^*} \rightarrow \mathrm{H}\cdot + \cdot\mathrm{OH} \tag{33}$$

The radicals produced in the spur are known as the primary species. On average the $\bullet$OH radicals are displaced by <1 nm from the centre of the spur while the lighter electron may travel 2—3 nm. Eventually, as diffusion occurs no further reaction with spur partners is possible and the distribution in the solution becomes uniform after about 0.1 μs.

Of the three primary paramagnetic species, only H$\bullet$ and e^-_{aq} are directly observable by e.s.r., since the $\bullet$OH radical relaxes too fast and experiences severe line-broadening. However, secondary radicals produced by reaction of these primary species with added solutes are observable from all three initial entities. These can be used to monitor the polarizations in the primary radicals if reaction competes favourably with their spin-lattice relaxation rates (Section 2C). These reactions can be sufficiently fast to compete with the spur reactions themselves. The polarization is invariably of a radical pair nature and in general we may expect the polarization of the secondary radical to have two contributions: the polarization it obtains on formation as it effectively samples the polarization of the primary species and further polarization it acquires by virtue of subsequent radical re-encounter.[6] We shall be concerned only with the former here. Most of the information has come from detailed analysis of the time profiles from pulse-radiolysis experiments.[30]

The hydrated electron is found to be produced in an unmagnetized state;[30,53] that is with essentially equal spin populations corresponding to a polarization $P_a^*/P_{eq} = 0$. This was shown, for example, in the irradiation of aqueous solutions of bromomaleic acid[30] at pH 9:

$$\begin{array}{l} \mathrm{e}^{-*}_{aq} + {}^-\mathrm{O_2CCH{=}CBrCO_2}^- \rightarrow [{}^-\mathrm{O_2CCH{=}CBrCO_2}^-]^{\cdot\,-*} \rightarrow \\ \qquad\qquad\qquad\qquad\qquad {}^-\mathrm{O_2CCH{=}}\overset{\cdot\,-}{\mathrm{C}}\mathrm{CO_2}^* + \mathrm{Br}^- \end{array} \tag{34}$$

Observation was of the polarized maleate radical, which implies that decomposition of the initially-formed adduct was over in a time short compared with the spin-lattice relaxation time (*ca.* 1 μs). The result has also been obtained by direct observation of e^-_{aq} in $\mathrm{Na_2SO_3}$ solutions at pH4 but the secondary polarization method gave the more accurate measure. The result is remarkable for e^-_{aq} undergoes encounters with $\bullet$OH (of much higher g-value) in the spurs, but these collisions apparently produce no polarization[6,31,53] (see below). The observation appears simply to reflect a production of electrons with random spins.

In contrast the $\cdot OH$ radical exhibits an equilibrium polarization in secondary-polarization experiments, which implies that it relaxes completely before it reacts.[30,53] This has been shown very clearly by a comparative study of the $\cdot CH_2CO_2^-$ radical produced by $\cdot OH$ attack on acetate ions and by reaction of the aqueous electron with chloroacetate ions; the behaviour observed was quite different.[30] Analysis of the time profiles gave the results. In a similar experiment with lactic acid at a concentration of 1 mol dm^{-3}, a measured rate constant of 3×10^8 mol^{-1} dm^3 s^{-1} for the reaction implied that $T_1(OH) < 1$ ns. This suggests that $\cdot OH$ in solution is in an orbitally-degenerate state, presumably the gas-phase ground state $^2\Pi$. This is a unique example of CIDEP providing information on the electronic state of a molecule.

The polarization in primary $H\cdot$ atoms has also been investigated by direct observation and, more accurately, by secondary polarization methods, the latter especially in studies of the reaction[30]

$$\cdot H^* + {}^-O_2CC{\equiv}CCO_2 \rightarrow O_2\dot{C}CH{=}C^-CO_2^* \qquad (35)$$

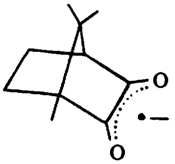
In this case, analysis of the time profile indicated that the primary species did have an initial polarization $P_a(I)/P_{eq} \sim 3$. An independent study of the irradiation of 0.1 M-$HClO_4$ in the presence and absence of a hydroxy-radical scavenger showed that the polarization observed was independent of the presence of $\cdot OH$ radicals: $H\cdot + \cdot OH$ encounters also do not lead to spin polarization. The explanation of the observed polarization must lie either in the fundamental processes of $H\cdot$ atom production or in spur reactions;[30] at present it is unclear which.

The lack of polarization from radical pairs of which the hydroxy-radical forms one member has not been explained previously and deserves comment. In any radical pair, polarization can be thought to be a consequence of the correlation which exists of the S and T_0 states of the pair with the states of the separated radicals, $\beta(1)$ $\alpha(2)$ and $\alpha(1)$ $\beta(2)$ respectively (where radical 1 has the higher g-value). If this was complete, as in an adiabatic separation of a pair created in a pure S or T_0 state, large polarizations would arise. The observed ones are small because the process is non-adiabatic and the correlation is imperfect, but is not negligible.[7] However the severe uncertainty broadening of the energy levels of the hydroxy-radical, occasioned by its extremely rapid spin-lattice relaxation, destroys any remaining discrimination in the crossing from the radical pair states to the radical ones. This leaves the state populations of the second radical unaffected by the encounter and its polarization is independent of it.

D. Radical Relaxation Studies.—As discussed in Section 3B, the spin-lattice relaxation times of radicals can be extracted from the time profiles of polarized e.s.r. spectra, most conveniently from flash-photolysis experiments. This method of T_1 determination has the advantage that transient radicals are studied making it complementary to all other methods, which use either stable radicals or steady-state conditions. In addition, the low concentration of radicals usually produced in each flash implies that the values obtained are independent of exchange effects.

The method was first tested using the modulation-broadened resonance from the perdeutero-benzophenone ketyl radical produced by photolysis of the parent molecule in liquid paraffin solution.[47] In these high-viscosity conditions the decay is accurately exponential and the true T_1 was obtained by extrapolating the observed effective relaxation time to zero microwave field. If the microwave field amplitude at the sample is known (and it can be measured directly from the oscillations observed at resonance for a sample in which $T_1 \approx T_2$) the spin–spin relaxation time T_2 can also be obtained without recourse to line-width measurements, which may be affected by exchange and by magnetic field inhomogeneities.

More recently chemical sensitization (secondary polarization) has been used to produce a high quantum yield of the camphorquinone (CQ) radical anion (3) in a spin-polarized state[39]



$C\dot{Q}^{-}$

(3)

The reaction scheme is shown in Scheme 1, where BP represents benzophenone and the asterisks denote electron spin-polarized species.

$$\mathrm{BP}(S_0) \xrightarrow{h\nu} {}^1\mathrm{BP}(S_1) \xrightarrow{\mathrm{ISC}} {}^3\mathrm{BP}^*$$
$$ {}^3\mathrm{BP}^* + \mathrm{Et_3N} \rightarrow \mathrm{Ph_2\dot{C}OH}^* + \mathrm{Me\dot{C}HNEt_2}^*$$
$$\mathrm{Me\dot{C}HNEt_2}^* + \mathrm{CQ} \rightarrow \mathrm{C\dot{Q}H}^* + \mathrm{CH_2{=}CHNEt_2}$$
$$\mathrm{CQH} \rightarrow \mathrm{C\dot{Q}}^{-*} + \mathrm{H}^+$$

Scheme 1

T_1's were measured in several alcoholic solvents at room temperature and as a function of temperature in octan-2-ol. The relaxation times in all the solvents studied could be accounted for by just two relaxation mechanisms: modulation of the anisotropic *g*-tensor and spin rotation. The results are plotted as a function prediction in Figure 11.

T_1's were also obtained[39] for $C\dot{Q}^{-}$, from optically active (+)-CQ, in the enantiomeric solvents (+)- and (−)-octan-2-ol (in the presence of BP and Et_3N). Above 260 K the relaxation times in the two solvents were equal within experimental error; however at 240 K there was a difference of 5 μs with an average T_1 of 41 μs. This interesting effect is presumably due to differential solvation.

In the first study of T_1's in an homologous series,[39] chemical sensitization

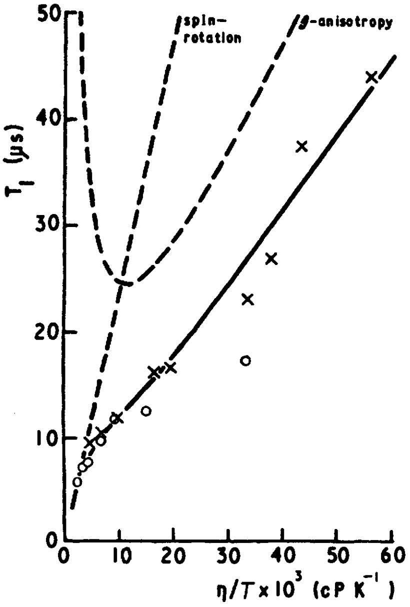


Figure 11 *The relaxation time of the camphorquinone radical anion as a function of viscosity* (η) *over temperature.*[39] *The crosses correspond to experiments at varying temperatures in octan-2-ol and the open circles to ones at room temperature in several alcohols. The two circles with highest* (η/T) *values correspond to cyclic alcohols in which the micro-diffusional motion may be different from in straight-chain alcohols (all other circles). The solid line represents the theoretical relaxation times corresponding to the relaxation contributions from spin-rotation and from g-anisotropy shown in the hatched curves*

was used to investigate the radical anions of the series MeCOCOR where R = Me, Et, Pr^n, or Ph. Relaxation times increased with viscosity, although the correlation was not good, and also, in general, with increasing chain length.

One of the features of the CIDEP method is that it allows the investigation of the hyperfine dependence of relaxation times. This is important for the interpretation of polarization behaviour, especially when TM and RPM contributions occur simultaneously. In a study of the radical anion of 2,3,5,6-tetraisopropylnitrobenzene,[40] produced by BP–amine chemical sensitization, a small variation in T_1 and T_2 among the hyperfine lines was observed. This could not be accounted for entirely in terms of modulation of the anisotropic Zeeman interaction, the electron–nuclear dipolar couplings, and the spin–rotation interaction.

E. Triplet Relaxation Times and Reaction Rates.—As discussed in Section 2B, information on the relaxation and reaction of triplet molecules may be obtained from the dependence of TM polarization on the quencher concentration [Q]. Plots of either $4(3\gamma - 1)^{-1}$ against $[Q]^{-1}$ or $4(3\gamma - 1)^{-1}[Q]$ against [Q] give γ^T

and $k_q\,{}^3T_1$ from the gradient and intercept. If either is known, or is measured independently, the other can be determined; alternatively relative rate constants for different triplet quenchers may be obtained.

This method has yielded the only direct measurements of triplet relaxation times in solution, from a flash-photolysis study of the polarization of the radical anion of duroquinone ($DQ\cdot^-$) as a function of triethylamine concentration in several alcoholic solvents.[69] The polarized anion was produced in the reactions in Scheme 2.

$$DQ(S_0) \xrightarrow{h\nu} {}^1DQ(S_1) \xrightarrow{ISC} {}^3DQ^*(T_1)$$

$$^3DQ^* + Et_3N \xrightarrow{k_q} DQH\cdot^* + \dot{C}H_3CH^*NEt_2$$

$$DQH\cdot^* \rightleftharpoons DQ\cdot^{-*} + H^+$$

Scheme 2

The rate constant k_q was measured by conventional flash-photolysis.[41] The values of ${}^3T_1$, together with the T_1 values for the radical $DQ\cdot^-$ (obtained from the time profiles of the spectra), are given in Table 2. The viscosity-dependence of ${}^3T_1$ indicates that the triplet was in the slow-motion region ($\omega_0\tau > 1$). With the dipolar coupling constant taken to be *ca.* 0.3 ω_0, a ${}^3T_1$ value of 3 ns implies a plausible value of 3×10^{-10} s for the rotational correlation time, τ. Neither the ${}^3T_1$ nor the T_1 values correlate well with the bulk viscosity but the approximate constancy of their ratio suggests that the two relaxation processes depend upon the same molecular motion. It was assumed in this work that the solution viscosity and therefore ${}^3T_1$ were independent of Et_3N; this is unlikely to be true. A similar approximation was made in the determination of relative quenching rate constants to be described below.

Table 2 *Spin-lattice relaxation times in triplet duroquinone and duroquinone radical anion*[27]

Solvent	*viscosity*/cP	${}^3T_1$/ns	$T_1/\mu s$	$\frac{{}^3T_1}{T_1}$
CH_3OH	0.61	2.7	2	1.4×10^{-3}
$(CH_3)_2CHOH$	2.2	9.7	8	1.2×10^{-3}
$(CH_3)_3COH$	4.8	7.7	9	0.9×10^{-3}
$\overline{CH_2(CH_2)_4C}HOH$	57	17	18	0.9×10^{-3}

These values of ${}^3T_1$ have been used to obtain absolute rate constants from a rotating sector study of duroquinone.[70] This yielded k_q values of 2, 4, and 2×10^8 dm^3 mol^{-1} s^{-1} for the reaction of ${}^3DQ$ with, respectively, phenol, 2-methylphenol, and pentachlorophenol; these compare with 3.6×10^8 dm^3

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[69] A. T. Bullock, *Ann. Reports* (B), 1976, **73,** 81.

[70] A. J. Elliot and J. K. S. Wan, *J. Phys. Chem.,* 1978, **82,** 444.

$\text{mol}^{-1}\ \text{s}^{-1}$ for triethylamine[71] and 2—4 × $10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ for durohydroquinone.[72-74]

Approximate relative rate constants may be obtained in two ways. Determination of $k_q\,{}^3T_1$ by the above procedure for a given triplet and a number of different quenchers is an obvious method. Alternatively, if more than one quencher is present and they compete for the triplet molecule, then careful analysis of γ as a function of the quencher concentrations gives ratios of k_q's. Both these methods involve the doubtful assumption that ${}^3T_1$ is constant and require a detailed knowledge of the chemistry of the system studied; they may be unreliable if the radical observed is produced (polarized or unpolarized) by unknown pathways. Thus, the reactions of the triplet states of a number of substituted benzo- and naphthoquinones in propan-2-ol with phenols as hydrogen donors were also investigated.[69] The measurements were analysed in terms of Scheme 3 for the production of the semiquinone radical (QH·):

$$\begin{gathered}
{}^3\text{Q}^* + \text{ArOH} \rightarrow \text{QH}\cdot^* + \text{Ar}\dot{\text{O}}^* \\
{}^3\text{Q}^* + \text{Me}_2\dot{\text{C}}\text{HOH} \rightarrow \text{QH}\cdot^* + \text{Me}_2\dot{\text{C}}\text{OH}^* \\
\text{Ar}\dot{\text{O}} + \text{QH}_2 \rightarrow \text{QH}\cdot + \text{ArOH} \\
\text{Q(S}_0) + \text{Me}_2\dot{\text{C}}\text{OH}^* \rightarrow \text{Q}\dot{\text{H}}^* + \text{Me}_2\text{CO}
\end{gathered}$$

Scheme 3

It was assumed that the semiquinone radicals produced by the third reaction of Scheme 3 were unpolarized. The importance of this step was not known and the results were analysed both with and without it. It was found that pentachlorophenol reacted about three times faster than the other phenols studied, and two orders of magnitude faster than propan-2-ol. These results contrast with those for duroquinone which was most efficiently quenched by 2-methylphenol and reacted very slowly with propan-2-ol. The quantitative results may not be very accurate due to the number of assumptions involved.

F. Photosynthesis.—CIDEP has been observed in radicals produced during both plant and bacterial photosynthesis. These differ in that in plants two photosystems, 'one' and 'two', act in tandem whilst in bacteria only one exists. Each, however, depends on a similar primary step, the absorption of a light quantum by a pigment (P) which yields a radical ion pair *via* an excited intermediate. It is the constituents of the pair which exhibit polarization.

In a study of deuteriated algae[75] two separate signals, assigned to the positive ion of the primary donor of photosystem two, P680 (the figure denotes the maximum in the u.v. spectrum), and to the negative ion of the primary acceptor, probably a plastoquinone, were observed in emission. This suggests that their precursor was an excited triplet state. However, a study of plant chloroplasts[76]

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[71] P. W. Atkins, A. J. Dobbs, and K. A. McLauchlan, *Chem. Phys. Letters*, 1974, **29**, 616.

[72] D. R. Kemp and G. Porter, *Proc. Roy. Soc.* (A), 1972, **326**, 117.

[73] E. Aymosyal and R. Bensasson, *J.C.S. Faraday I*, 1976, **72**, 1274.

[74] J. Natisi-Movaghar and F. Wilkinson, *Trans. Faraday Soc.*, 1970, **66**, 2268.

[75] A. R. McIntosh and J. R. Bolton, *Nature*, 1976, **263**, 443.

[76] R. Blenkenship, A. McGuire and K. Sauer, *Proc. Natl. Acad. Sci. U.S.A.*, 1975, **72**, 4943.

revealed only the signal of the positive ion of the primary donor of photosystem one, the P700 pigment, and following an initial interpretation of its polarization as originating in the TM, subsequent work[77] on oriented samples made an RPM explanation more tenable. In this case the radical precursor was an excited P700 singlet state.

An early report of CIDEP in a bacteriochlorophyll-quinone sample at low temperatures was interpreted on the TM model.[78] A similar low-temperature study of the bacterium *rhodopseudomonas sphaeroides*[79,80] displayed no CIDEP from untreated material but strong absorption and emission from bacteria treated with a detergent. In the former the primary acceptor is an iron-ubiquinone complex but the iron is removed by the detergent to leave ubiquinone in this role. The signals were assigned to the positive ion of the pigment in absorption and the negative ion from ubiquinone in emission. Despite the experiments being performed in a solid at 100 K the reaction centres were fully photo-active and showed similar behaviour in almost all respects to chromatophores at higher temperature. The polarization was interpreted consequently as a radical-pair effect.

The interpretation of the results on algae, which apparently give the best evidence for TM polarization, has been questioned recently and current thought is that polarization arises in RPM processes in both plants and bacteria. Further work is clearly necessary before the nature of the radical precursor is established completely.

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[77] G. C. Dismukes, A. McGuire, R. Blenkenship, and K. Sauer, *Biophys. J.*, 1978, **21**, 239.
[78] J. R. Harbour and G. Tollin, *Photochem. and Photobiol.*, 1974, **19**, 163.
[79] A. J. Hoff, P. Gast, and J. C. Romijn, *F.E.B.S. Letters*, 1977, **73**, 185.
[80] A. J. Hoff and H. Rademaker, ref. 2, p. 399.