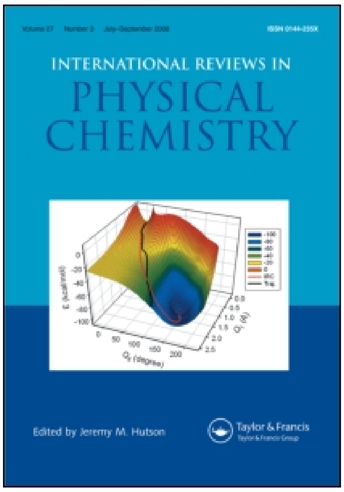

International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Spin correlation effects in radiolysis

B. Brocklehurst[a]
[a] Chemistry Department, The University, Sheffield, England

To cite this Article Brocklehurst, B.(1985) 'Spin correlation effects in radiolysis', International Reviews in Physical Chemistry, 4: 3, 279 — 306
To link to this Article: DOI: 10.1080/01442358509353362
URL: http://dx.doi.org/10.1080/01442358509353362

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1985, VOL. 4, NO. 3, 279–306

Spin correlation effects in radiolysis

by B. BROCKLEHURST

Chemistry Department, The University, Sheffield S3 7HF, England

Radiolysis of liquid hydrocarbons produces radical cations and electrons. Their recombination releases sufficient energy in the solvent, or in the solute if a charge scavenger is added, to produce excited states, Because of the low dielectric constant, most of the recombination is *geminate,* i.e. the positive and negative charges do not separate as far as the Onsager escape distance (~ 30 nm for an alkane at room temperature). For a single ion pair, this means that the two unpaired electrons were initially paired in a molecular singlet state. If recombination is very fast (<1–10 ns), the spin correlation is retained: only singlet products will result. Over longer periods, the correlation decays because of hyperfine interaction between the electrons and magnetic nuclei. This leads to time-dependent magnetic field and magnetic isotope effects on the product yields, easily detected by studying the fluorescence in suitable systems. Spin relaxation randomizes spin orientations but the hyperfine effect is a coherent process and oscillations can be detected. Theory and experiment are in good agreement in most respects. Electron spins can be reversed by absorption of microwaves: the changes in fluorescence can be used for spectroscopic studies of the ions.

Similar arguments apply to pairs of neutral radicals though the dynamic processes are quite different: triplet molecular states are usually repulsive—only singlets react—and diffusive separation is not constrained by coulombic attraction. Recombination is spin-selective which leads to spin polarization, i.e. to CIDNP and CIDEP. These phenomena are described briefly, together with effects of magnetic field on product yields of thermal and photochemical reactions, notably in micelles and in photosynthetic centres, and other related phenomena.

A peculiar feature of radiolysis is the production of spurs consisting of 1, 2, 3 or more radical and radical-ion pairs. Single ion pairs constitute only about 20% of the total. While the overall spin state of a spur should be singlet, recombination with a different partner will give triplet products. The possible consequences are described but this is a controversial area and no clear conclusions have yet been reached.

1. Introduction

When two free radicals meet at random, the unpaired electrons will couple to give singlet and triplet states with a probability ratio of 1 : 3. For neutral radicals the stable recombination product will be a singlet; the corresponding molecular triplet will be repulsive. If then the spin states do not change, the reaction rate should be one-quarter of the encounter rate. Recently this has been confirmed by experiments on benzylic radicals (Claridge and Fischer 1983) but it is not easy to make measurements with sufficient accuracy and, necessarily, there are uncertainties in the effective reaction distance.

The idea of a spin limitation on radical reactions was mentioned in several papers in the 1960s (Lyon 1964, Fox and Hammond 1964, Noyes 1965, for further references see Engel and Bartlett (1970)); the context was usually reaction in a solvent cage of radical pairs generated photochemically from either singlet or triplet precursors. However, the consequences of spin limitations were not realized until 1969.

Time-resolved E.S.R. measurements following pulse radiolysis (Fessenden and Schuler 1963) revealed unusual spectra, wholly or partly in emission. This phenomenon—an example of chemically induced dynamic electron polarization (CIDEP)—was not understood at the time. Later (Bargon *et al.* 1967, Ward and Lawler 1967) the corresponding phenomenon (CIDNP) was discovered in N.M.R. studies of reacting systems: spectra wholly or partly in emission were observed with considerable intensity enhancements.

This behaviour was explained by Kaptein and Oosterhoff (1969) and by Closs (1969) in terms of radical pair encounters: singlet and triplet states are interconverted by hyperfine interaction between the unpaired electrons and magnetic nuclei in the radicals or by differences in precession rates due to g-value differences; removal of singlet pairs by reaction leads to spin selection, i.e. certain nuclear spin states are removed more efficiently than others, which gives a non-random distribution of nuclear spins in the products (CIDNP) and in the remaining radicals (CIDEP). Since the rate and extent of singlet–triplet conversion is field-dependent, similar arguments lead to predictions of magnetic effects on chemical reactions, first worked out in detail by Lawler and Evans (1971).

Also in 1969, I considered the recombination of radical-ion pairs produced by radiolysis (Brocklehurst 1969). I predicted a magnetic field effect and proposed that the yields of excited state products could be modified by microwave absorption by the radicals—now the basis of one type of optically detected magnetic resonance. However, changes in spin state were described only in terms of spin relaxation: in most cases, hyperfine interaction (measured roughly by the overall width of the E.S.R. spectra of the radicals) produces much more rapid changes than relaxation (measured by the E.S.R. line-width). Subsequently the radical pair theory was applied to radical-ion recombination and a variety of magnetic effects have been observed: this topic will be reviewed in detail.

Encounters between neutral radical pairs are very short (10^{-10}–10^{-11} s): the separation and re-encounter of radicals must be taken into account in explaining the extent of spin-selection (Adrian 1972). Even so, the polarization effects are small but they are very easily observed because normal N.M.R. relies on the thermal difference in level populations of a few parts per million. As a result CIDNP is easy to study experimentally—much easier than measuring field effects on yields—and a great deal of work has been published in the last 15 years. CIDEP is less easily studied; because of the rapid relaxation of electron spins, microsecond time resolution is required. However, a considerable amount of photochemical work has been published by McLauchlan and his co-workers, while Fessenden has greatly extended his pulse radiolysis work.

Fast particles (β-particles, nuclear particles, fast electrons generated by absorption of X- or γ-rays) do not lose their energy in a single event but produce tracks consisting of 'spurs'. Each spur may contain a single pair of radicals or radical-ions, but secondary electrons are often ejected with sufficient energy to produce more ionization: the range of such electrons is very short, so each spur may contain several ion pairs. Magee (1960) pointed out that, though the overall spin state of a spur is likely to be singlet, recombination with a different partner can lead to triplet products. This situation is peculiar to radiation chemistry. Though clusters of ions were observed many years ago in cloud chamber experiments, little is known of their behaviour in condensed phases and this is a very controversial area. Possible spin correlation effects will be discussed.

This review is mainly concerned with radiation chemistry but related topics will be described briefly. (Studies of gas-phase processes will be omitted.) CIDNP and CIDEP have attracted a great deal of attention and a full review will not be attempted. It proved difficult to quantify magnetic field and magnetic isotope effects on the yields of thermal and photochemical reactions of neutral radicals. The effects are normally small, but they are much larger in micelles, which essentially provide a cage for the radical pair. Near ultraviolet light will not ionize hydrocarbon solutions but mixtures of donors and acceptors are readily ionized in polar solvents: field effects on triplet yields from recombination are observed. The same is true of photosynthetic centres, providing complete separation of the charges is prevented by reduction. Another related field comprises the formation and reactions of muonium—the hydrogen 'isotope' formed when fast positive muons are thermalized. Finally, there are magnetic field effects on triplet–triplet annihilation and related processes which depend on the spectral fine structure (zero-field splitting) rather than hyperfine interaction.

The older literature on magnetic field effects has been reviewed by Atkins and Lambert (1975). A comprehensive account of both field effects and spin polarization studies by Salikhov *et al.* (1984) covers the literature up to 1980, while Buchachenko (1984) has recently reviewed magnetic isotope effects.

2. Basic concepts

Once neutral radicals have separated by a few molecular diameters, recombination is unlikely; at the short distances that matter, the exchange interaction, J, is significant; its rapid variation with distance leads to considerable complexity in treating CIDNP, etc. Ion recombination in hydrocarbons is much simpler in this respect; the ion pair spends most of its lifetime at large separations (up to the Onsager escape distance, $\sim 30\,\mathrm{nm}$ at room temperature) yet must eventually react because of the coulomb attraction. The final stage of approach is probably very rapid with the electron jumping from one ion to another at separations $\sim 2\,\mathrm{nm}$ (Brocklehurst 1973).

The Zeeman energy of an electron in a magnetic field, B, is $\pm\frac{1}{2}g\mu_B B$, where μ_B is the Bohr magneton, g the Landé splitting factor; for a free electron $g\mu_B = 28{\cdot}026\,\mathrm{GHz\,T^{-1}}$ (1 tesla $= 10^4$ gauss). The magnetic interaction between electrons and nuclei is measured by the hyperfine coupling constant: an in electron spin resonance spectroscopy where it gives the familiar hyperfine structure, only the isotropic part, a, need be considered for mobile liquids. Values of a for aromatic hydrocarbon ions are usually a few tenths of a millitesla; $0{\cdot}35\,\mathrm{mT} \sim 10\,\mathrm{MHz}$: this gives an indication of the time-scale of spin evolution.

Before a full theoretical treatment is presented, a simple classical model will be used to explain the evolution of the spin states. It is easiest to start with the high-field case, i.e. $g\mu_B B \gg a$. A vector representation of the electron spins is shown in figure 1: the vectors precess independently around the direction of the field. Note that the T_0 triplet component differs from the singlet only in the phase of the precession. If the two electrons precess at different rates the system will oscillate between S and T_0. This can happen if the g values are different: if the system is in a singlet state at time zero, then the probability, ρ, of it being singlet at time t is:

$$\rho = \tfrac{1}{2}[1 + \cos\{(g_1 - g_2)\mu_B B t\}] \tag{1}$$

If the g values are the same, but a magnetic nucleus (spin one-half interacts with one of the radicals, its precession rate is $\frac{1}{2}g\mu_B \pm \frac{1}{4}a$ and

$$\rho = \tfrac{1}{2}\{1 + \cos(\tfrac{1}{2}at)\} \tag{2}$$

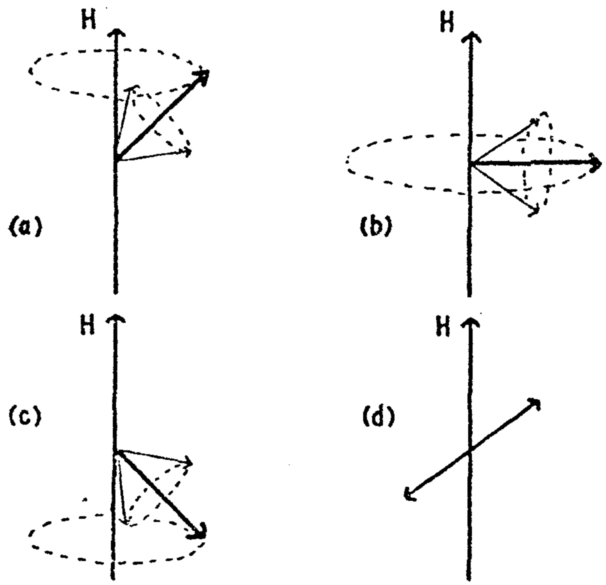

Figure 1. Motion of two electron spin vectors in a magnetic field: S, M_s: (*a*) 1, 1; (*b*) 1, 0; (*c*) 1, -1; (*d*) 0, 0. Reprinted by permission of Macmillan Journals Limited (Brocklehurst 1969).

(For simplicity a and $g\mu_B B$ are taken to be in angular frequency units, i.e. $2\pi \times$ the values given above.) These results are easily generalized to give

$$\rho = \tfrac{1}{2}[1 + \cos\{(g_1 - g_2)\mu_B Bt\} \prod_i \cos^{n_i}(\tfrac{1}{2}a_i t)] \tag{3}$$

where the product covers all the nuclei on both ions in groups of n_i with a values a_i. For nuclei of spin 1 (e.g. deuterons) each cosine factor must be replaced by $\{2\cos(at) + 1\}/3$ because the $m = 0$ component does not affect the energy of the electron.

Equation (3) shows that the singlet probability will oscillate but it also shows that, in effect, it will simply decay to one-half if many types of proton are present, i.e. the oscillations are out of phase with each other. Apart from the $(g_1 - g_2)$ factor (unimportant for hydrocarbon ions), ρ is independent of field, i.e. the effect will saturate once $g\mu_B \gg a$.

T_+ and T_- have different energies at high field; hyperfine interaction etc. cannot convert S and T_0 into these states. Longitudinal spin relaxation (T_1) is relatively slow (microseconds) in these systems. At zero field, all four states become degenerate; the g effect disappears and electrons and nuclei precess about their resultant which can be oriented at random. The classical model is no longer suitable for exact calculations so we turn to wave mechanics. First, we must distinguish between stationary and non-stationary states.

If two identical pendulums are attached to a common support, they do not oscillate independently: if one is set in motion, energy gradually flows into the second pendulum and back again. The system is in a non-stationary state. The stationary states are those in which the motion persists unchanged—both pendulums oscillating with the same amplitude either exactly in phase or exactly out of phase. Because of the coupling through the support, these two motions have slightly different frequencies. The non-stationary state can be regarded as a superposition of the stationary states: the rate of energy transfer between the two pendulums is the beat frequency, i.e. the frequency difference of the stationary states. An excellent exposition of stationary and non-stationary states is given by Feynman *et al.* (1965) who take the inversion of ammonia as an example. In both cases one can think in terms of the frequency domain (spectroscopy, transition between stationary states) and the time domain (non-stationary states, oscillatory behaviour).

These ideas are embodied in the superposition principle—the wave-mechanical treatment of non-stationary behaviour. For the present purpose, this can be written

$$\rho = \sum_{\chi(t)} \sum_{\chi(0)} \left| \sum_{j} \langle S, \chi(t) | \phi_j \rangle \exp(iE_j t/\hbar) \langle \phi_j | S, \chi(0) \rangle \right|^2 \qquad (4)$$

The initial state is a singlet with nuclear wavefunction $\chi(0)$. In equation (4), E_j and ϕ_j represent the energies and wavefunctions (eigenvalues and eigenfunctions) of the stationary states of the system, i.e. one writes the initial state as a sum over the eigenstates, allows each to evolve in time (the complex exponential factor represents oscillations), then recombines them to obtain the final state, from which the singlet probability can be extracted. The matrix elements, $\langle .. | .. \rangle$ represent the amplitudes of the stationary states in the initial and final states. Care is needed to distinguish between the summation of amplitudes (which can interfere) and the summation (outside the brackets) over initial and final nuclear states. If a state is observable in principle, then its probability (amplitude squared) must be summed, not the amplitude. Changes in time occur simply because the system starts in a non-stationary state: if the initial state was pure eigenstate, the time-dependence of the amplitude would disappear when the absolute square was calculated. Before ionization, the molecular eigenstates are singlets and triplets; the hamiltonian is dominated by the exchange interaction. This is suddenly 'switched off' on ionization and new interactions come into play: singlet and triplet states are no longer eigenfunctions.

3. Theory

So the first step is to solve the hamiltonian for each of the radicals. For this purpose, the two radicals can be treated separately and the problem is exactly the same as in electron spin resonance spectroscopy (see e.g. Atherton 1973). The hamiltonian can be written

$$H = g\mu_B B S_z + g_N \mu_{BN} B I_z + \Sigma a_i S I \qquad (5)$$

S, I, S_z, I_z are electron and nuclear angular momentum operators and their z components. The second, nuclear Zeeman, term makes a small contribution at intermediate fields but it cancels out at high fields: it will be ignored in what follows. It is convenient to rewrite (5) as

$$H = g\mu_B B S_z + \Sigma a_i S_z I_z + \Sigma(\tfrac{1}{2}a_i)(S_+ I_- + S_- I_+) \qquad (6)$$

The first two terms give diagonal terms in the hamiltonian matrix, the third gives off-diagonal terms. S_+ etc. are called shift operators because e.g. $S_+\beta = \alpha$, $S_-\alpha = \beta$.

Figure 2 shows the dependence of the eigenvalues on external field for the simple case of an electron interacting with a single proton—the Breit–Rabi diagram. It is worth noting that in some cases (curved lines) the eigenfunction changes with field.

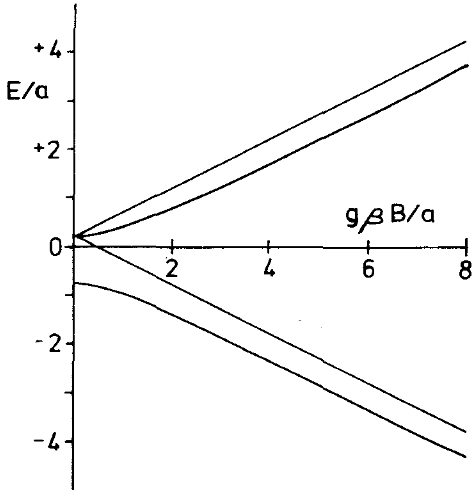

Figure 2. Field-dependence of the energy levels of an electron and a proton.

For convenience, α and β will be used only for electron spin, γ and δ will be used for nuclear spin wavefunctions. At zero field the three degenerate eigenfunctions are $\alpha\gamma$, $2^{-1/2}(\alpha\delta+\beta\gamma)$ and $\beta\delta$, the fourth is $2^{-1/2}(\alpha\delta-\beta\gamma)$. At high field the eigenfunctions are the simple products $\alpha\gamma$, $\alpha\delta$, $\beta\delta$ and $\beta\gamma$.

These results can be used with equation (4) to calculate the spin evolution of an initial singlet for the case of one proton at one centre, none at the other. At high field, equation (2) is obtained (if $g_1=g_2$), while at zero field

$$\rho=\tfrac{1}{8}(5+3\cos at) \tag{7}$$

The oscillation rate is twice as fast as at high field, which reflects the change in the splitting (figure 2). The reduced amplitude of oscillation can be understood in terms of the vector model: the electron and the proton precess about their resultant, so that this electron is never fully (180°) out of phase with the other. In wave-mechanical terms, the result is due to the degeneracy of three levels at zero field: even a small field, which splits these levels, will cause a more extensive oscillation.

Equation (7), giving a larger average value of ρ at zero field compared to high field, is not typical of most systems. Consider next the case of two protons. At high field, it makes no difference whether they are on the same or different centres, but there is a marked difference at zero field. If there is one proton on each centre, then for $\chi(t)=\chi(0)$

$$\rho=(13+7\cos a_1t+7\cos a_2t+5\cos a_1t\cos a_2t)/32 \tag{8}$$

However, there is now the possibility of a double spin flip, e.g. $\chi(0)=\gamma\delta$, $\chi(t)=\delta\gamma$ arising from the S_+I_- terms in the hamiltonian. This gives

$$\rho=(1-\cos a_1t-\cos a_2t+\cos a_1t\cos a_2t)/16 \tag{9}$$

and the overall result, after averaging over the m values, is

$$\rho=(7+3\cos a_1t+3\cos a_2t+3\cos a_1t\cos a_2t)/16 \tag{10}$$

The average value is 7/16, i.e. $<\frac{1}{2}$—a more typical result. In classical terms, the electrons may be pulled in different directions by the protons. In contrast two protons on the same centre give

$$\rho=\tfrac{1}{3}(2+\cos\tfrac{3}{2}at)$$

(The $I=0$ combination gives no spin evolution, hence the increase in the average value.)

These equations can be extended to larger numbers of magnetic nuclei and different I values and to intermediate fields. The resulting equations are complicated and will not be reproduced here: for details see Brocklehurst (1976 a). Except at high fields, analytical solutions are only possible if there is a single type of proton (one value of a) on each centre. This is a serious limitation, because many scintillator molecules chosen for experimental work for other reasons (next section) have three or four different kinds of nuclei. One approach is to make numerical calculations (Werner *et al.* 1977, Lambert 1978, Brocklehurst, unpublished). Few results have been published—probably because of the large amount of computing time required; for example, for *para*-terphenyl, the spin wavefunction of the radical-ion pair has 3·4 million components and the hamiltonian matrices may be as large as 98 × 98. Schulten and Wolynes (1978) (see also Knapp and Schulten 1979, Schulten and Epstein 1979) developed an approximate, 'semi-classical' method: if the total nuclear spin is large, the electron can be regarded as precessing round a fixed vector (like the external field in figure 1, but with random orientations). This is not strictly correct: both vectors precess round their resultant. However, good agreement with the computer calculations was found for large ΣI as would be expected and the errors were small for smaller I values.

An important question has yet to be finally resolved: what is the average value of ρ for molecules of practical interest? At high field the answer is very close to one-half; at zero field one might expect a limiting value of one-quarter in a sufficiently complicated system. However, Lambert was led to suppose that there is a limiting value of one-third and this is the result of Schulten and Wolynes semi-classical approximation. Presumably, the incomplete splitting referred to above is responsible. If the zero-field levels are split by a low field, the average value of ρ should fall initially. Alternatively, if the degeneracy is split by other means, e.g. the anisotropic hyperfine interaction which becomes significant at low temperatures, then an average value of one-quarter is predicted (Brocklehurst 1979 a). The effects of charge transfer are also important in practice; I have discussed the case of a single (solvent to solute) transfer (Brocklehurst 1977 b), while Schulten and his co-workers have used the semi-classical approximation for detailed calculations of the effect of repeated transfer. If the transfer rate is very high, at high field there is no spin evolution: one can think of the differences in precession rate continually changing sign as the electron 'sees' different orientations. This is equivalent to exchange narrowing on E.S.R. The effects at low fields are more complicated.

At long times, spin relaxation will randomize the spins completely giving a singlet : triplet ratio of 1 : 3. For most radicals and radical-ions these times are in the microsecond range. In mobile liquids $T_1 \sim T_2$ but in viscous liquids, $T_1 \gg T_2$, i.e. conversion between T_0 and S states will be much faster than between T_+ or T_- and the others. Since T_1 and T_2 are indistinguishable at zero field, there should be magnetic field effects from this cause—the author's original prediction. Such effects have not been reported in radiolysis experiments. Some radicals relax much more rapidly: an important example is the hydroxyl radical, for which T_1 and T_2 are estimated to be less than one nanosecond (Verma and Fessenden 1976). Hydroxyl and related radicals possess cylindrical symmetry, so that in the gas phase, they have well defined orbital angular momentum, which leads to spin–orbit coupling. Though the symmetry is partly broken down by hydrogen bonding, the interaction is large enough to produce rapid relaxation (Brocklehurst 1979 a).

4. Experiments with magnetic fields

The first experimental studies were carried out in 1973 by the Radiation Chemistry group at the Laboratories of Atomic Energy of Canada Ltd. at Pinawa, Manitoba. Pulse radiolysis was used to study squalane solutions of a number of aromatic hydrocarbons. To avoid deflection by the field, the electron beam was passed through a hole in one of the magnet poles; even so, careful alignment was necessary to avoid small deflections which gave spurious results. When these problems were overcome, two important results were obtained: (i) the fluorescence yield was enhanced by the field and this effect increased with time after the pulse; (ii) the rise in fluorescence was matched by a fall in triplet yield showing a similar field dependence (Brocklehurst *et al.* 1974, Sargent *et al.* 1977, Dixon *et al.* 1977 b). Triplet states formed during the pulse have long lifetimes so that the field-dependent changes after the pulse were relatively small and not easily measured. Later work has concentrated on fluorescence measurements: the use of scintillator molecules such as *para*-terphenyl which have fluorescence lifetimes $\leqslant 1$ ns makes it possible to follow the ion-recombination process more precisely. Therefore, the early study of triplets is important because it demonstrated that the field reduces the singlet–triplet conversion in the ion pair as predicted.

The Pinawa group moved on to a much simpler experiment, measuring the effect of magnetic field on the fluorescence produced by γ-rays without time resolution. Positive results were obtained for a variety of hydrocarbon solvents and solutes (Sargent *et al.* 1975, Dixon *et al.* 1975, 1977 a, b; Dixon and Lopata 1979). They made detailed studies of the field dependence showing that the effect tended to saturate above 0·1 T: this shows that hyperfine interaction is the predominant cause of the spin evolution; the difference in g values has little or no effect as one would expect from the few measurements available (Segal *et al.* 1965). The extent of the enhancement varied considerably with solvent from 20% in squalane where the viscosity slows the recombination, so increasing the proportion of ion pairs in which the correlation can decay, to 3% in benzene where the bulk of the fluorescence follows energy transfer rather than charge transfer. A striking effect of deuteration was found in agreement with prediction. As figure 3 shows, the curves for naphthalene-h_8 and naphthalene-d_8 cross over. At high fields the deuterated compound gives a smaller effect because the time evolution is slower—a values for deuterium are smaller, about one-sixth of the proton values. The ion pair singlet and triplet states are degenerate at zero field but they are not single states but groups of levels corresponding to the different nuclear orientations relative to the electron spins (figure 1). The effect of the field is to separate these groups (T_+, T_- from S, T_0) so preventing oscillation between them; the magnitude of the field must be comparable with the a values to produce an effect. Therefore, a smaller field suffices in the case of the deuterated compounds. As can be seen, fields less than 1 mT produce a detectable effect.

Meanwhile, I turned to single-photon counting techniques to make more precise measurements on the time-dependence of fluorescence produced by beta particles (Brocklehurst 1976 b). This method was originally developed for studying scintillation pulse shapes (Bollinger and Thomas 1961) but has found widespread application to fluorescence decay measurements when used with nanosecond flashlamps and lasers

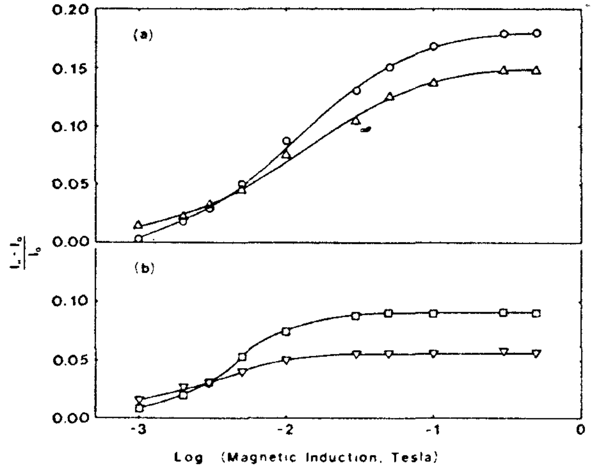

Figure 3. Increase in fluorescence intensity as a function of applied magnetic field. (*a*) 10^{-2} mol dm^{-3} naphthalene (○) and naphthalene-d_8 (△) in squalane. (*b*) 10^{-2} mol dm^{-3} naphthalene (□) and naphthalene-d_8 (▽) in cyclohexane. Reprinted by permission of North-Holland Physics Publishing (Dixon *et al.* 1977a).

(Demas 1983). The original pulse radiolysis work used pulses with 50 or 15 ns width; beta particles are absorbed in about a picosecond, so that time resolution depends only on the instrument response function ($\sim$0·7 ns) and the excited state lifetime. Most important, a dynamic range of 10^3 is easily achieved; it is necessary to balance counting time (some hours) against the background due to the random emission from the beta-source; the time-to-amplitude converter may be 'started' by one scintillation pulse and 'stopped' by a photon from another.

The scintillation consists of a sharp pulse followed by a long tail: some typical results are shown in figure 4. *Para*-terphenyl is not very soluble; it was chosen for its short fluorescence lifetime. Because of the sharp fall in intensity after the peak, a decay time of even a few nanoseconds would distort the curves considerably. From these data, fluorescence enhancement ratios can be calculated (see figure 5). After an initial oscillation the ratio remains constant—for microseconds in the case of squalane, which gives a longer tail than the more mobile alkanes studied. Most solvents give very similar results except that cyclohexane, methylcyclohexane and the decalins give lower limiting values than n-hexane, iso-octane and squalane. Also the former group show a more rapid rise in the field-dependence at low fields (Brocklehurst 1977a). The implications of these results will be discussed later.

Figure 5 also shows the results of theoretical calculations with the following hyperfine coupling constants (mT) (number of protons in brackets): 0·300(2), 0·197(4), for the cation, 0·3314(2), 0·2075(4) for the anion. The anion values are experimental: there are two smaller *a* values, 0·0976(4) and 0·052(4). The cation values have not been reported apparently: the values used were estimated from those of related compounds (Landolt–Bornstein 1980).

Theoretical and experimental curves show common features—the damped oscillation, the nearly constant value at long times: the time-scale of the increase in fluorescence is accurately predicted. These results and the effect of solute deuteration

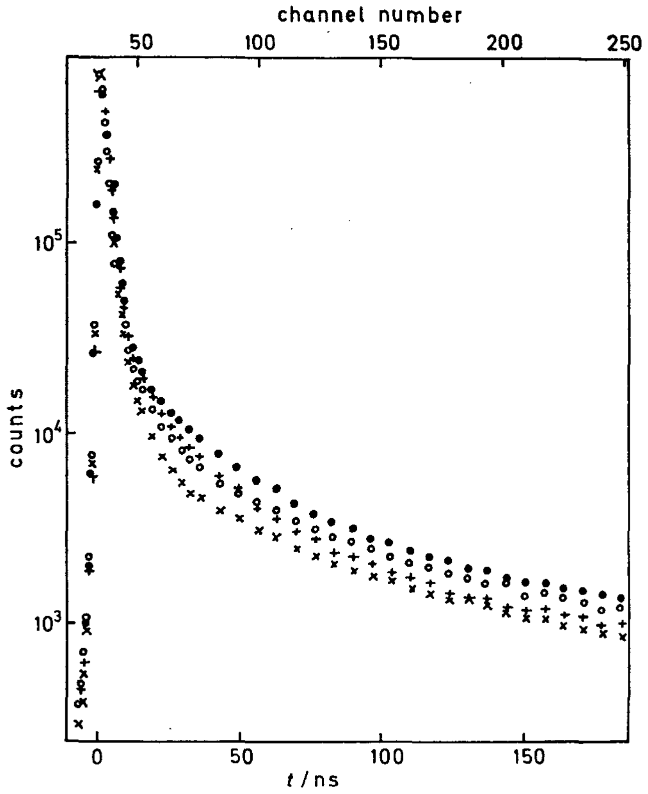

Figure 4. Scintillation pulse shapes for *para*-terphenyl, 0·005 mol dm^{-3} in mixed *cis*- and *trans*-decalins. ○ ×, $C_{18}H_{14}$; ● +, $C_{18}D_{14}$; × +, zero field; ○ ●, 0·16T. Reprinted by permission of the Royal Society of Chemistry (Brocklehurst 1977a).

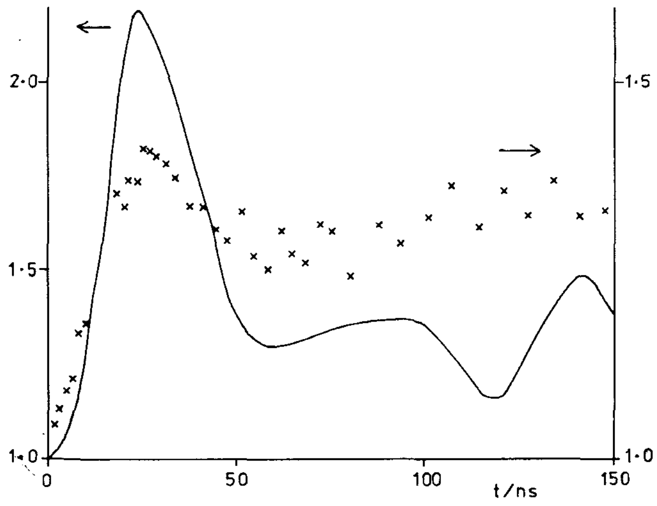

Figure 5. Ratio of fluorescence intensities, 0·16 T to zero field, as a function of time after the scintillation peak for 0·001 molar *p*-terphenyl in cyclohexane, ×. Full line is a theoretical calculation (see text).

(Brocklehurst 1976 b, 1977 a) strongly support the theoretical interpretation. If all the protons could be included in the calculations, the limiting enhancement would increase towards 1·5; presumably the height of the first peak would be reduced somewhat and the oscillations at >100 ns would be smoothed out. One would like to see more extensive calculations and measurements on simpler systems (e.g. partly deuterated solutes).

Single-photon counting measurements have also been carried out by Voltz (Strasbourg) and Molin (Novosibirsk) and their co-workers. Klein and Voltz (1976, 1977) used solutions of scintillators such as diphenyloxazole; these molecules have short fluorescence lifetimes and are also much more soluble than para-terphenyl; on the other hand, no E.S.R. data are available for the ions, not even the negative ion. They observed time-dependent magnetic field effects and, at low fields, a concentration-dependent decay which they ascribe to spin relaxation resulting from electron transfer among the solute molecules.

The time-dependent magnetic field effect and magnetic isotope effect provide strong evidence for the theory set out above. However, if the decay of correlation is a coherent process, one would like to see oscillatory behaviour ('quantum beats'). This is not easy because the scintillators which are convenient in other respects (short lifetime in particular) usually contain several kinds of protons, so that the overlapping oscillations lead to an apparently smooth decay. Equation (3) demonstrates this; at zero field the situation is worse because, for example, four protons can be grouped to give $I=2, 1, 0$ leading to oscillations with frequencies of $2\frac{1}{2}a$ and $1\frac{1}{2}a$ (and zero) with weights in the ratio 1 : 3 : 2. Klein and Voltz claim to see an oscillation when using an oxadiazole. This is probably a result of the spin statistics: if the strongest coupling is to the nitrogen atoms, then two nitrogens give $I=2, 1, 0$ in the ratio 1, 1, 1 (cf. four protons, above). A much better defined oscillation has been observed recently by Anisimov *et al.* (1983) using solutions of perdeutero-terphenyl (electron scavenger, chosen for its small hyperfine interaction) and tetramethylethylene (positive ion scavenger, TME): some results are shown in figure 6. TME has of course only one type of proton and so gives a simple oscillation. The high-field oscillation frequency was in excellent agreement with that calculated from the a values determined in other ways. The amplitude of the oscillation is small—probably the result of varying times of charge transfer from solute to solvent.

Klein and Voltz (1977) found that alpha particles gave a smaller effect than betas—as one would expect because of the overlap of spurs in the track, leading to cross-recombination of ions with uncorrelated spins. They also found that freezing the solvent reduced the extent of the effect, a result confirmed by Brocklehurst and Wood (unpublished results): in a glass, solute cation neutralization by solvated electrons is at least comparable with electron transfer from the deeper traps of the solute anion (Brocklehurst 1974). As equations (3), (10) and (11) show, decay of spin correlation at one centre only leads to a reduced field effect or even one in the reverse direction. (Trapped electrons are only weakly coupled to solvent nuclei (Kevan 1974).)

Following a claim (Lapersonne-Meyer 1980) that solids irradiated with beta particles show two decays, ascribed to single and multiple ion pairs (see below), the author (with R. Wood), attempted unsuccessfully to differentiate these species by their magnetic field effects. The experiment is not easy because the fast decay is very close to the instrument response function. Also, the beta source could not be placed as close to the sample as at room temperature: deflection of the particles by the field does not affect the scintillation pulse shape of course, but it does alter the observed intensity of

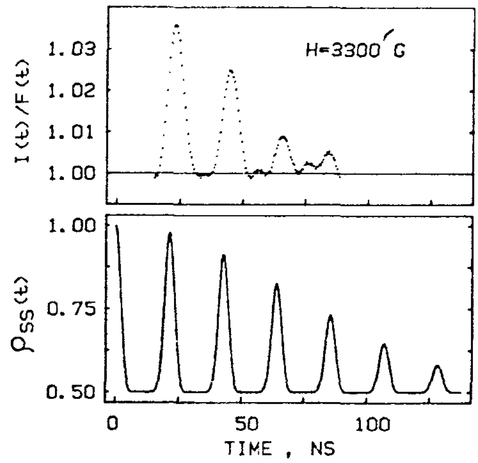

Figure 6. Top: the experimental curve of quantum beats in the recombination of (tetramethylethylene)$^+$/(*para*-terphenyl-d_{14})$^-$ pairs in *trans*-decalin, determined as the ratio of $I(t)$ to the smoothed function $F(t)$ which initiates the pair-lifetime distribution before collisions. Bottom: the calculated curve of singlet-state population, $\rho_{ss}(t)$. Both top and bottom curves are for high magnetic fields. Reprinted by permission of North-Holland Physics Publishing (Anisimov *et al.* 1983).

Cerenkov radiation which is emitted at a specific angle to the particle's path and forms the bulk of the radiation from these solids. Decay over a few nanoseconds gives little net signal above the instrument response function. Similar studies (Brocklehurst and Kroh, unpublished) with glassy ethers and aqueous glasses and with ice also showed very rapid luminescence decays and small field effects: there appeared to be a correlation with the production of 'infrared' (shallowly trapped) electrons (Buxton *et al.* 1976, 1977) but quantitative deconvolution was not possible.

5. Spectroscopic studies of radical ions

In principle, values of hyperfine coupling constants could be obtained from the magnetic field effect, though precise values can only be determined if oscillations are observed. A rough measure of the mean *a* value is provided by the field required to enhance the total fluorescence to one-half of the saturation value. A puzzling feature of the early results was the relatively large value obtained when positive charge resided in the solvent for a significant time. I 'missed the boat' here: early E.S.R. studies had suggested that coupling to protons in alkane radical cations was very weak, but much larger values (~5 mT) have since been observed (Symons 1980, Shida *et al.* 1981, Toriyama *et al.* 1981, Wang and Williams 1981).

A much more powerful technique is to use microwaves to change the electron spin state of the ion pair. The experiment is carried out in a strong magnetic field, of course: conversion between singlet and triplet states is forbidden, but irradiation at the appropriate frequency converts T_0 into T_+ and T_-; fewer pairs can then oscillate back to singlet and the fluorescence yield is reduced.

Anisimov *et al.* (1979, 1980) reported the first such experiments using naphthalene in squalane excited by a positron source: the sensitivity obtained is remarkable—a steady-state concentration of twenty ion pairs in the sample could be detected. Since then a number of spectra of hydrocarbon and fluorocarbon ions have been reported (see references in Molin *et al.* 1984). Smirnov *et al.* (1985) have developed the theory of this form of optically detected magnetic resonance and discussed the likely role of spin relaxation. Cation and anion spectra overlap of course but they can be separated by deuteration. A typical spectrum is shown in figure 7.

Solvent radical-cations (holes) have been detected in benzene and *p*-xylene solutions. When *p*-xylene is added to benzene (containing small amounts of para-terphenyl), a structured spectrum ascribed to the *p*-xylene cation is seen; this collapses to a single line when the xylene concentration is increased as a result of charge transfer (exchange narrowing) (Molin *et al.* 1984): however, the rate of the process could be shown to be comparable with that of molecular diffusion. In the alkanes, no mobile holes were detected; in cyclohexane and decalin, in which fast hole transport is believed to occur (below), structured spectra were seen (Melekhov *et al.* 1984) but these disappeared on careful purification: they were shown to be due to olefins present as impurities initially or produced by irradiation. The mobility of solvated electrons in alkenes is very high; they would normally recombine or attach to a solute too quickly to be detected. However, they can be slowed by solvation and spectra of electrons solvated by water or methanol in alkane solvents have been obtained (Molin *et al.* 1984).

Smith and Trifunac (1981 a, b) at the Argonne laboratory have introduced a more sophisticated technique using pulsed irradiation followed by a microwave pulse (30–500 ns); fluorescence detection was also gated and delay times between the electron and microwave pulses and before detection could be varied. While the total fluorescence decays smoothly after the electron pulse, the effect of the microwaves was observed to increase with time at first because of the need for interconversion of T_0 and S. As expected, this process was slowed by deuteration of the solute (biphenyl, anthracene). Increasing dose led to more rapid fluorescence decays, probably because of overlap of different electron tracks leading to random recombination. Spectra of, for example, the radical-cations of aliphatic amines (Lefkowitz and Trifunac 1984) have

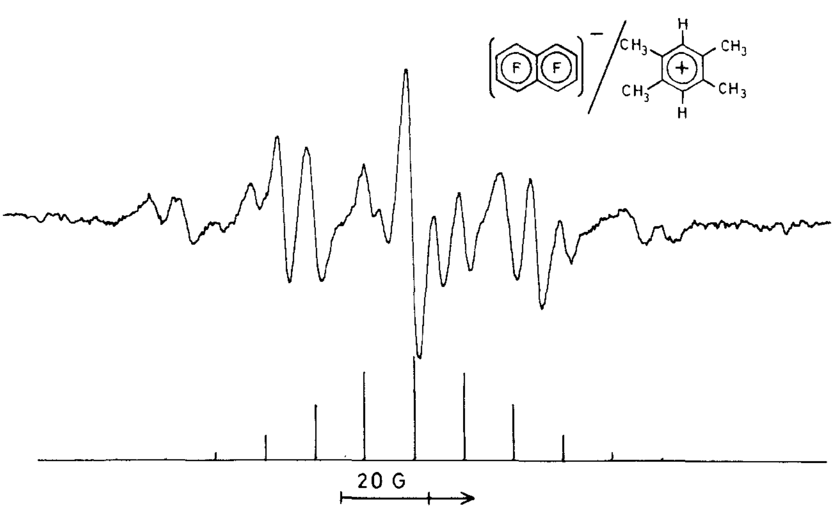

Figure 7. O.d.e.s.r. spectrum for $1{\cdot}4\times10^{-3}\,\mathrm{mol\,dm^{-3}}$ durene and $1{\cdot}5\times10^{-3}\,\mathrm{mol\,dm^{-3}}$ perfluoronaphthalene in squalane under X-ray irradiation at 290 K. The stick diagram shows lines belonging to durene cations; other lines belong to perfluoronaphthalene anions. Reprinted by permission of the Royal Society of Chemistry (Molin *et al.* 1984).

been recorded; changes in time of the relative intensities of solvent and solute peaks were detected: this should prove very valuable for mechanistic studies. However, good frequency resolution and good time resolution are not compatible because of the uncertainty principle and experimental spectra taken under various conditions demonstrate this.

6. Implications for radiation chemistry

It is generally accepted that in hydrocarbons most of the excited states are formed by ion recombination and that in alkanes, a significant proportion of the electrons travel far enough (~5–10 nm) before thermalization that positive and negative charges can be scavenged before recombination leading to solute excitation. (See, for example, papers presented at the Tokyo conference on Fast Processes in Radiation Chemistry by Ausloos *et al.*, Choi *et al.*, Luthjens *et al.*, Tagawa *et al.* 1983). The magnetic field work, especially the observation of oscillations and the solute isotope effect and the spectroscopic studies are in agreement with this view. In aromatic solvents, the thermalization range is less so that most recombination occurs in the solvent and scintillation from additives is due to energy transfer. However, the observation of small magnetic field effects (Brocklehurst 1976 b, Dixon *et al.* 1977 a) show that some charge scavenging takes place.

If spin evolution at low fields eventually leads to the limiting value of one-quarter singlet character in the ion pairs, then one expects a limiting enhancement factor of two at long times. In practice the largest observed values are about 1·45 (Brocklehurst 1976 a, Klein and Voltz 1977, Sargent *et al.* 1977). Several explanations are plausible: the yields of excited states might depend on other factors e.g. Franck–Condon factors (Brocklehurst 1976 a)—but this seems unlikely as the density of states should be high enough for either singlets or triplets to be formed easily given the energy available (Brocklehurst 1973); also, more variation between solutes would be expected.

Theoretical calculations (above) suggest that the limiting value at zero field should be one-third rather than one-half, giving a limiting enhancement of 1·5. However, these calculations refer to spin evolution on two centres only. In alkanes electron scavenging is much faster than spin evolution, but positive charge scavenging is relatively slow, e.g. a diffusion-controlled process in a millimolar solution will take an average time of 100 ns. The ion pair will exist for significant times as $RH^{\dot{+}} + M^{\dot{-}}$ and as $M^{\dot{+}} + M^{\dot{-}}$ (RH represents the solvent, M the solute). If both these times are long compared to the oscillation period ($\sim a^{-1}$), then one can estimate that the limiting value will be 5/18 giving an enhancement of 1·8 (Brocklehurst 1977 b). This solvent involvement in the spin evolution is demonstrated by the variation in half-value fields with solvent in the steady-state work (Dixon *et al.* 1975, 1977 a, Dixon and Lopata 1979). In these measurements, cyclohexane always gives the lowest value, while in time-resolved measurements its limiting value is only ~1·3 (Brocklehurst 1977 a): methylcyclohexane and the decalins also give low values. These results are consistent with the fast hole transport in these solvents which had already been observed in scavenging studies and pulse radiolysis measurements (Rzad *et al.* 1969, Zador *et al.* 1973).

These results led me (Brocklehurst 1977 a, c) to propose that the low limiting values were due to the *initial* production of some ion pairs in triplet states, by cross recombination in spurs, etc. If the initial singlet : triplet ratio was 1 : 3, there would be no magnetic field effect because spin evolution would take place equally in both directions. From the results one can calculate initial singlet : triplet ratios of ~1·85 which are the same within experimental error for squalane and cyclohexane (using limiting values of the enhancement of 1·8 and 1·5 respectively).

This proposal was met by the criticism that, if correct, it should be possible to observe triplet solute molecules by pulse radiolysis at very short times; several searches have failed to find them (Beck and Thomas 1972, Salmon and Selby 1977, Kroh and Mayer 1977, Jonah and Sauer 1982, Trifunac 1984). Trifunac *et al.* (1985) have also argued that the 'fast cation' observed in cyclohexane is not the radical cation, $C_6H_{12}^{+}$, but may be either $C_6H_{11}^{+}$ or $C_6H_{13}^{+}$. These problems are as yet unresolved; they are discussed further below.

7. Spurs

Yields of ions in the gas phase are easy to measure: G-values (yields per 100 eV) are typically about 4. In liquids, only a small proportion of the ions can be separated by applied fields: total yields are not known but may be greater than in the gas phase. In aqueous solutions (Hunt 1976), G-values of $\gtrsim 4$ are found for solvated electrons after 30 ps; addition of very high concentrations of scavengers provides evidence for 'dry electrons' which would otherwise recombine before solvation. Their yield is very uncertain; estimates of the total ionization yield vary between 4·5 and 6·5. In hydrocarbons, detectable ion yields are somewhat smaller, but the total yield must be comparable with that in water.

Again, the distribution of spur sizes in the gas phase is known from cloud chamber measurements (Ore and Larsen 1964), but there is no experimental information about liquids; one has to use estimates derived from theoretical studies of track structure. Mozumder and Magee (1966) classify energy loss processes into spurs ($\leqslant 100$ eV, 67% of the energy), blobs (100–500 eV; 11%) and short tracks (500–5000 eV; 22%). Single ion pairs constitute only 24·5% of the total ion pairs in spurs and blobs, 35% are found in two-pair spurs, 15% in three-pair spurs etc.

Magee (1960) pointed out that spurs should be overall singlet (because of the high velocity of the primary electron) and that recombination with different partners within a spur should lead to triplet products. Magee and Huang (1972) discussed this in more detail and also considered molecular triplet excitation by low energy electrons; cross-sections for this process are large just above threshold and, of course, the electron exchange involved must leave a triplet ion pair.

Estimates of the efficiency of this process are not easy to make but presumably it will be enhanced by a large energy gap between the lowest states of the singlet and triplet manifolds; i.e. it should be most probable in aromatic liquids. Brocklehurst (1976 b) observed a fluorescence enhancement of 1·09 in benzene solutions at long times (i.e. after the energy transfer process is complete); if the interpretation given above is correct, this corresponds to a triplet fraction of 67% (cf. 35% for cyclohexane and squalane). However, too much weight should not be attached to one isolated measurement.

For the triplet yield P_T in spurs, Magee and Huang (1972) quote

$$P_T = \frac{3}{4}\left(1 - \frac{1}{2n-1}\right) \tag{12}$$

where n is the number of ion pairs. This formula was derived from a branching diagram which gives the total number of singlet states arising from $2n$ spin-one-half particles.

For example, two ion pairs can give an overall singlet state in two ways: one is made up of two singlets, the other of two triplets with opposed angular momenta. Magee and Huang (1974) argue that these two possibilities are equally probable, but Higashimura *et al.* (1972) and the author (Brocklehurst and Higashimura 1974) concluded that the initial state would consist of two singlet ion pairs which would recombine directly or, equally probably, could recombine with the other partner with 75% triplet probability as there would be no spin correlation except that either both pairs are singlet or both are triplet. For two-pair spurs this gives 3/8 triplet or generally

$$P_T = \frac{3}{4}\left(1 - \frac{1}{n}\right) \tag{13}$$

This view appears to be more consistent with the retention of spin correlation which gives rise to the field effect. Equation (12) gives the correct result for neutral species which can recombine in more ways: two ions of the same sign do not react. (For further discussion see Brocklehurst 1979 a, 1982.)

Combination of equation (13) with Mozumber and Magee's spur size distribution gives a variety of values for the effective triplet fraction: 37% for blobs and spurs, 46% overall if short tracks are taken to give 75% triplets. However if it is assumed that in for instance a two-pair spur one electron must necessarily recombine very quickly because of the coulomb forces (and that no ion pairs survive long from the short tracks) the result is 22%. Within considerable uncertainty, the experimental estimate of 35% for squalane and cyclohexane is consistent with these calculations.

However, the problem remains: if triplet pairs are formed initially, then solute triplets should be observed at short times. Trifunac (1984) finds no experimental evidence for spur processes with more than one ion pair. Scavenging of ions in alkanes can be interpreted adequately in terms of single ion pairs (Hummel 1974). On the other hand, there is clear-cut evidence for multiple-pair spurs in the gas phase. Radiolysis product yield studies provide ample evidence for reactions in larger spurs. Notably, aqueous solutions give significant non-scavengeable yields of hydrogen ($G = 0{\cdot}45$) and hydrogen peroxide ($G = 0{\cdot}7$); these can only result from cross-reactions in the spur. In addition, there must be a considerable amount of recombination of dry and solvated electrons: G for the latter drops from 4·0 to 2·7 as the spurs diffuse (Hunt 1976); H_2 formation accounts for 0·9 of the 1·3 lost. Before discussing the fate of triplet ion pairs, it will be convenient to look at one system in more detail.

8. Radiolysis of cyclohexane

The following mechanism has been adapted from Ausloos *et al.* (1983). RH_2 represents cyclohexane, M an aromatic hydrocarbon ion scavenger (N. B. Ausloos used toluene which does not scavenge electrons):

$$RH_2 \rightsquigarrow RH_2^*,\ RH_{2+} + e^- \tag{14}$$

$$RH_2^{+\cdot} + M \rightarrow RH_2 + M^{+\cdot} \tag{15}$$

$$e^- + M \rightarrow M^{-\cdot} \tag{16}$$

$$RH_2^{+\cdot} + e^- \rightarrow RH_2^* \tag{17}$$

$$RH_2^{+\cdot} + M M^{+\cdot} + (RH_2^* + M) \tag{18}$$

$$(RH_2^* + M) \rightarrow (RH_2 + M^*) \tag{19}$$

$$M^{+} + M^{-} \rightarrow M^{*} + M \qquad (20)$$

$$^{1}RH_2^{*} \rightarrow R + H_2 \qquad (21)$$

$$^{1}RH_2^{*} \rightarrow {}^{1}RH_2' \qquad (22)$$

$$^{3}RH_2^{*} \rightarrow RH^{\cdot} + H^{\cdot} \qquad (23)$$

$$H^{\cdot} + RH_2 \rightarrow H_2 + RH^{\cdot} \qquad (24)$$

$$2RH^{\cdot} \rightarrow (RH)_2 \qquad (25)$$

$$2RH^{\cdot} \rightarrow RH_2 + R \qquad (26)$$

$^1RH_2'$ represents the equilibrated first excited singlet which is stable to dissociation and can be scavenged, e.g. by toluene. Ausloos's vacuum ultraviolet photolysis studies show that singlets with excess energy decompose to give more H_2 than H atoms in the energy range available. After discussing measurements of the yields of $^1RH_2'$, H_2, R_2 (i.e. bicyclohexyl) and R (cyclohexene), Ausloos points out the difficulty of explaining the large yields of H_2 and radicals. Either one has to suppose that higher excited singlets give large yields of radicals and hydrogen atoms or one has to postulate that triplet ion pairs and (23) play a major role. The former appears unlikely; reaction (17) with thermalized electrons does not release enough energy. The latter is plausible: $RH^{\cdot} + H^{\cdot}$ correlate only with the singlet ground state and a triplet repulsive excited state; excited singlets may predissociate into triplets but they correlate directly only with higher-energy products ($R + H_2$, $R + 2H$?).

In the presence of an electron scavenger (naphthalene, biphenyl etc.) in dilute solution, (18) is much more important than (20) at short times (Infelta and Rzad 1973, Sauer and Jonah 1980); it is usually supposed that (18) leads to excited solute, but the process is here written as a two-stage reaction (18) and (19). (The brackets indicate the close proximity of RH_2^* and M.) The recombination can be described as an electron tunnelling process (Brocklehurst 1973) and this makes it possible to estimate that (18) will take place when the molecular separation is about 2 nm. Also one may argue that the least-bound electron in M^- will tunnel because of the steep dependence of tunnelling rate on barrier height, that is, that (18) will be preferred to direct formation of M^*. However, this conclusion is by no means certain (Brocklehurst 1979 b) and more theoretical work is needed. If RH_2^* is a bound singlet state then energy transfer, (19), will certainly follow: however, if it is a triplet then energy transfer will be much slower at this distance; if the triplet is repulsive, then (23) will surely compete with (19) so that no triplet M^* will result.

In this search for triplet states at short times (50 ps), Jonah and Sauer (1982) used very high scavenger concentrations (0·1 molar) for which (20) is predominant even on the picosecond time-scale. In seeking a consistent explanation for the discrepancy between the magnetic field work and the pulse radiolysis studies, one must bear in mind the difference in time-scale: the former measurements (of the limiting enhancement) are made on ion pairs that were initially well separated and recombined only after ~ 100 ns. The pulse radiolysis work probes the spur directly: however, excited states formed in the spurs are subject to quenching by radicals. Consider for instance a two-pair spur which recombines as two triplets; if one electron is scavenged to form M^- then the other will recombine first giving $RH^{\cdot}$ and H which can then quench the nearby M^* when it is formed shortly afterwards: on a longer time-scale the radicals will have diffused away. I am carrying out model calculations in the hope of clarifying this point.

9. L.E.T. effects

Linear energy transfer (l.e.t.) is the rate of energy loss of the primary charged particle along the line of the track: it is proportional to z^2/v^2 where z is the charge, v the velocity of the particle. So, heavy particles have much greater l.e.t. than electrons; instead of isolated spurs, they give dense tracks of ions, excited states and radicals. Product yields in water decrease with l.e.t. because of increasing efficiency of back reactions in the tracks: fewer radicals escape to attack solute molecules. Radiolysis of alkanes is not very dependent upon l.e.t., but liquid aromatics which are extremely stable at low l.e.t.—they have even been used as reactor coolants—show a sharp increase in decomposition with the track density especially around 100 eV nm^{-1}. This effect has been studied over many years (e.g. Gaumann and Schuler 1961, Burns and Reed 1963, Boyd and Connor 1964, Burns and Marsh 1968, LaVerne and Schuler 1982) but the mechanism is still uncertain. Voltz (1969) noted that the fluorescence yield falls in the same region: this suggests that interaction of two excited singlet molecules might be involved, but singlet–singlet annihilation in crystals merely leads to ionization (Jarnagin 1971) so it may be that some precursor of the excited states is involved. LaVerne and Schuler concluded that the processes 'must be very efficient but also involve species with a very short intrinsic lifetime'.

Aromatic hydrocarbons are normally stable because their most easily excited states involve only the π-electrons. To break bonds presumably one needs to excite the σ-electrons and, following the arguments above, excite σ-σ^* triplet states. Such states have not been detected spectroscopically: their vertical excitation energies must be large probably slightly higher than the corresponding states in alkanes at ~7–8 eV. Interestingly, the presence of the latter can be detected by the decomposition of alkanes sensitized by higher triplets of aromatic solutes produced by two-photon absorption (see e.g. Brocklehurst *et al.* 1966, Bagdasar'yan *et al.* 1972).

As the l.e.t. increases, spur overlap will lead to more triplet pairings of radical anions and electrons: the energy release on recombination of thermalized pairs will be insufficient to populate the σ-σ^* states, but dry electron recombination will also increase with track density. The excited states produced may well re-ionize but, again, at high excitation densities in the tracks, there is likely to be repeated conversion between ions, Rydberg states and valence states. To confirm this mechanism will not be easy but it may be possible to make use of isotope effects. In the gas phase, deuterated compounds ionize more efficiently when excited above the ionization potential because dissociation is slower than in hydrogen compounds (Jesse 1967, Person and Nicole 1968). In the present case, dissociation of the triplet σ-σ^* states must compete with re-ionization and internal conversion. A search for deuteration effects on the fluorescence yield would be worth while.

10. Electron exchange in spurs

In this section and the next, the discussion will be confined to two-pair spurs, partly because even two pairs can lead to considerable complexity, partly because spin correlation must be less important in large spurs in which essentially random reactions occur. In any case, two-pair spurs contain 30–35% of the ion pairs.

Many spurs will initially consist of two singlet pairs (type (i)). For convenience, the radicals are numbered 1–4: the 12 and 34 pairs then are singlet, the other pairings are random (one-quarter singlet, three-quarter triplet). Some spurs (type (ii)) are initially two triplets (this can arise e.g. if one pair results from a molecular triplet produced by electron exchange excitation): rearrangement of the wavefunction shows that if 12 and

34 are triplet, then the other pairings are not random but three-quarter singlet, one-quarter triplet. Now, suppose that in a type (i) spur, radicals 1 and 4 meet: radical ions will react but neutral radicals (or a radical plus a solvated electron) will react only if the pair wavefunction is singlet. In three-quarters of the encounters, no reaction occurs: the 14 pair and the 23 pairs must now both be triplet, that is, the encounter converts type (i) to type (ii) in 75% of the cases. This can be demonstrated by writing out the wavefunction—

$$\psi(1234)=\tfrac{1}{2}(\alpha\beta\alpha\beta-\alpha\beta\beta\alpha-\beta\alpha\alpha\beta+\beta\alpha\beta\alpha) \tag{27}$$

$$\psi(1423)=\tfrac{1}{2}(\alpha\beta\beta\alpha-\alpha\alpha\beta\beta-\beta\beta\alpha\alpha+\beta\alpha\alpha\beta) \tag{28}$$

$$\begin{aligned}&=-\tfrac{1}{4}(\alpha\beta\alpha\beta-\alpha\beta\beta\alpha-\beta\alpha\alpha\beta+\beta\alpha\beta\alpha)\\&\quad+\tfrac{1}{4}(\alpha\beta\alpha\beta+\alpha\beta\beta\alpha+\beta\alpha\alpha\beta+\beta\alpha\beta\alpha)-\tfrac{1}{2}(\alpha\alpha\beta\beta+\beta\beta\alpha\alpha)\end{aligned} \tag{29}$$

Removal of the SS term in (29) leaves

$$\psi(1423)=\tfrac{1}{2}(T_0T_0-T_+T_--T_-T_+) \tag{30}$$

Rearranging this gives

$$\psi(1234)=\tfrac{1}{4}(\alpha\alpha\beta\beta+\alpha\beta\alpha\beta+\beta\alpha\beta\alpha+\beta\beta\alpha\alpha)-\tfrac{1}{2}(\alpha\beta\beta\alpha+\beta\alpha\alpha\beta) \tag{31}$$

$$\begin{aligned}&=\tfrac{1}{4}(\alpha\alpha\beta\beta+\beta\beta\alpha\alpha)-\tfrac{1}{8}(\alpha\beta\alpha\beta+\alpha\beta\beta\alpha+\beta\alpha\alpha\beta+\beta\alpha\beta\alpha)\\&\quad+\tfrac{3}{8}(\alpha\beta\alpha\beta-\alpha\beta\beta\alpha-\beta\alpha\alpha\beta+\beta\alpha\beta\alpha)\\&=\tfrac{1}{4}(T_+T_-+T_-T_+-T_0T_0)+\tfrac{3}{4}SS\end{aligned} \tag{32}$$

Squaring the amplitudes gives probabilities of one-sixteenth for each of the three triplet components and nine-sixteenths for the singlets. The same is true for the 13 and 24 pairings. This apparently strange effect is due to electron exchange; exchange in the 14 encounter redistributes singlet and triplet character between the 1234 and 1324 pairings. If the encounter is a more distant one, so that no reaction can occur, exchange can still take place. In this case, it is an oscillatory process, but if the encounter is close enough for many oscillations to occur, ($Jt \gg 2\pi$), then the average result is the same (Brocklehurst 1982).

Another example is relevant to the earlier discussion of hydrocarbon radiolysis. Suppose that 12 is a triplet radical pair, $RH^{\cdot}+H$, 34 is a triplet ion pair, $M^{+}+M^{-}$ (or $RH_2^{+}+M^{-}$). A 13 encounter could result in electron transfer to give $M(RH_2)+RH^{+}$: presumably this process is feasible only for a singlet pair. Neutralization of RH^{+} by M^{-} will finally leave an $RH^{\cdot}+H^{\cdot}$ pair which is necessarily singlet, i.e. it can react back more readily. This behaviour is shown by 75% of the spurs: in the other 25% the 13 encounter is triplet; there is no reaction but exchange occurs leaving both 12 and 34 pairs with 75% triplet, 25% singlet character. In a larger spur, the $RH^{\cdot}$ spin will be randomly oriented in effect: if the 13 encounter is singlet, transfer occurs leaving the M^{-} spin uncorrelated; 34 singlet and 13 triplet leads to a final 3 : 1 singlet : triplet ratio, while 34 and 13 both triplet gives a 1 : 11 ratio! If 34 is initially random, there is of course no net effect.

These exchange processes do not directly produce magnetic field effects. There is no direct evidence of their occurrence in spurs and they may be difficult to detect because of the complexity of spur dynamics and inadequate information about spatial distributions. However, it seems appropriate to incorporate spin considerations into computer models of spurs and the author has made a first attempt at this (Brocklehurst

1984 a). There have been numerous computer simulations of spur behaviour, usually for aqueous solutions (see below); see e.g. Schwarz (1969) and the recent papers of Burns *et al.* (1984) and Trumbore *et al.* (1984). The usual approach is to work with average concentrations and to calculate reaction rates in the context of diffusive expansion of the spur: this is not appropriate for spin effects because one must keep track of the evolution of the wavefunction of each electron and nucleus. I have written programs to do this and combined them with a Monte Carlo calculation of encounter probabilities in a two-pair spur. Extension to a three-pair spur is feasible but beyond that approximate methods will be necessary.

11. Coherent decay and spin relaxation in spurs

In a mobile liquid, spurs expand by diffusion over some tens of nanoseconds. For most radicals, coherent decay will not be very extensive over this period, certainly not over the first 10 ns. The notable exception to this statement is the hydrogen atom for which $a = 1{\cdot}42$ GHz. The formation of H_2 is of particular interest: spin selection will not lead to CIDNP (except in HD) because the transitions are forbidden for two identical atoms. Instead, there may be changes in the ratio of *ortho* to *para*-hydrogen (Brocklehurst 1982). Despite the extensive studies of *ortho–para* conversion, there are no reports of differential production of the two forms, except in the gas phase where a different explanation must apply.

The random encounter of two hydrogen atoms should lead to field and isotope effects arising from re-encounters of those pairs that met originally as triplets. This is likely to be a small fraction of the total since the initially singlet pairs (one-quarter) will react without spin selection. Without the amplification of the polarization that occurs in CIDNP, the effects will be difficult to detect. However, the distinctive field and isotope dependence (Brocklehurst 1982, 1984 b) should be useful. The same applies to encounters of hydrogen atoms in spurs: the computer calculations predict very small effects for type (i) spurs. In this case 14 and 23 encounters introduce some singlet character into the 24 (H + H) wavefunction so that the direction of the field effect is the opposite of the random case. Large effects are likely only if there is a significant proportion of type (ii) spurs, in which there is an intial 3 : 1 singlet : triplet ratio for the H + H pair.

The radiolysis of aqueous solutions is the most important part of radiation chemistry because of the connection with the biological effects of radiation. The primary products are hydroxyl radicals and solvated electrons: the latter convert rapidly into hydrogen atoms in acid solutions. However, any correlation effects are lost very rapidly because of the exceptionally fast relaxation of the hydroxyl radical (Brocklehurst 1979 a). It is noteworthy that the recombination of OH with H is faster than either the reaction of OH with OH or H with H (see Brocklehurst (1984 b) for references). This suggests that OH can relax even during encounters so that its reactions can occur in every encounter whereas the reaction of two hydrogen atoms cannot (Verma and Fessenden 1973).

Because of this rapid relaxation, spin effects are not likely to be important in aqueous solutions unless there is a significant number of type (ii) spurs. The correlation, exchange and spin evolution effects are more likely to be important in organic liquids or at low temperatures where the hydroxyl radical relaxation time must increase. Mixed solvents (e.g. aqueous alcohols) may be suitable because hydroxyl reacts very rapidly to form water and a new radical; the behaviour of pure alcohols will depend on the rate of conversion of the RCH_2O radical, which probably relaxes rapidly, to the

RCHOH radical which does not. Concentrated aqueous salt solutions have low freezing points or do not solidify until they become glasses: in any case, the required temperature reduction may be small; the relaxation process involves breaking or weakening the hydrogen bonds to the radical, so restoring the cylindrical symmetry which leads to spin–orbit coupling.

12. Related phenomena: field effects on chemical reactions

Research on magnetic field effects and on chemically-induced dynamic polarization up to 1980 has been comprehensively reviewed by Salikhov *et al.* (1984). The Novosibirsk group has made a considerable number of experimental and theoretical contributions to the subject, including the first clearcut observation of a field effect on a chemical reaction (Sagdeev *et al.* 1973). Pentafluorobenzyl chloride reacts with n-butyl lithium in n-hexane by electron transfer to give a singlet radical pair: an applied field reduces the singlet–triplet conversion and increases the yield of recombination in the solvent cage by 50% at the expense of the products of radicals that escape the cage; the effect saturates at 0·1 T—a characteristic of the hyperfine effect.

The attempts that were made in several laboratories to follow this up were unsuccessful for some years: the lifetime of encounters in mobile liquids is very short compared to the spin evolution so field effects on yields are generally small, even in cases where CIDNP is readily detectable. The reaction above is a favourable case because n-butyl-lithium forms oligomers in an alkane solvent: presumably the radicals remain complexed for some time. Later, several cases of field effects were reported; e.g. Sakaguchi *et al.* (1980) studied the decomposition of dibenzoyl peroxide: the effect changes sign with increasing field showing that both a and Δg mechanisms are present.

One way of extending the encounter lifetime is to use micellar solutions: this was first studied by Turro and Kraeutler (1978). Since then a considerable number of papers has appeared describing yield measurements and flash photolysis observations on intermediate radicals (Turro and Kraeutler 1980, Turro 1983). Dibenzyl ketone was studied in detail: it shows a $^{13}C/^{12}C$ isotope effect: in non-micellar solutions, careful choice of solvent viscosity gives zero field differences up to 7%—not much more than expected from the mass difference—but in micellar solutions the difference is 40%. Turro *et al.* (1980) found a striking and potentially useful effect of field on emulsion polymerization: the molecular weight of polystyrene could be increased fivefold by fields of 0·1 T. Nagakura, Hayashi and their co-workers have made experimental and theoretical studies of micellar processes: in addition to hyperfine and Zeeman effects they have also found evidence of spin relaxation and the 'triplet mechanism': intersystem crossing leads to a singlet–triplet component which can result in polarization if reaction with the solvent is fast enough (see e.g. Sakaguchi *et al.* 1984; Hayashi and Nagakura 1984).

In the irradiated alkanes, the 'cage' is a large one provided by the coulombic attraction between the ions: the same applies to a lesser extent to photoionization of donor–acceptor pairs in polar solvents (Schulten *et al.* 1976, Werner *et al.* 1977, Michel-Beyerle *et al.* 1976, 1979). In systems such as alcoholic solutions of pyrene and aniline derivatives, the excited singlet is not accessible because of ion solvation; recombination into the ground state is slow because of the large energy gap, so the excited pyrene triplet is the preferred product. Some ions escape and recombine at random—no field effect expected—but many undergo rapid recombination after spin evolution in the radical-ion pair. Detailed calculations of the hyperfine effect (Werner *et al.* 1977, Schulten and Wolynes 1978) give good agreement with experiment. Exchange interaction plays an important role in the spin-evolution of close radical pairs: recently Weller *et al.* (1984) have studied this quantitatively using the field effect on donor–acceptor pairs linked by an alkane chain.

Closely related are the studies of photosynthetic centres. Normally, several rapid electron transfers lead to very efficient charge separation but this can be stopped by reducing or removing the quinone acceptor. Recombination into the chlorophyll triplet state can then take place and magnetic field effects were discovered in 1977 (Hoff *et al.* 1977, Blankenship *et al.* 1977). Since then, field and polarization effects have been studied in several laboratories in the hope of obtaining information about the spatial relationships of the chlorophyll dimer and the electron acceptors in photosynthetic centres (Blankenship 1981, Boxer *et al.* 1982, Norris *et al.* 1982).

13. Spin correlation and spin resonance

The radical pair mechanism is essentially common to the magnetic field effects described above and to CIDNP and CIDEP though the latter can also arise from the 'triplet mechanism' mentioned above. Also closely related are time-resolved spin resonance studies which are essential to the observation of CIDEP. The amount of work on CIDEP, and especially on CIDNP, has increased dramatically in the last fifteen years: no attempt will be made to review it here. (See e.g. Lawler and Ward 1973, Lepley and Closs 1973, Muus *et al.* 1977, Salikhov *et al.* 1984.)

Fessenden and Trifunac and their colleagues have continued to develop e.s.r. techniques allied to pulse radiolysis for radiation-chemical studies. Verma and Fessenden (1973, 1976) used conventional e.s.r. detection with a time resolution of 0·3 μs to demonstrate that spin orientation is preserved in a number of electron transfer and radical abstraction reactions. Of course, the theory of the magnetic field effects depends on this: coulombic interactions in electron–molecule collisions and reactions do not alter the spin orientation. Initial polarization can be detected—in the sense that solvated electrons etc. are produced with equal numbers of α and β spins; that is, there is no signal until some relaxation occurs. Rather surprisingly, however, spur processes in the first few tens of nanoseconds do not appear to produce detectable effects on the e.s.r. time-scale. The role of spurs has been questioned recently by Trifunac (1984).

Techniques for time-resolved e.s.r. have been reviewed by Trifunac and Lawler (1982); these authors have added pulse techniques (electron spin-echo and free induction decays) to the conventional methods. There is increasing interest in 'reaction yield detected magnetic resonance spectroscopy' in which observation of the attenuation of the microwaves is replaced by the modulation of some product yield by microwave absorption by the transient radicals. An interesting new technique involves N.M.R. studies of the products (Trifunac and Evanochko 1980). The use of fluorescence emission described above is another example and the formation of triplet states can be monitored by light absorption. These new techniques have advantages in sensitivity and in time resolution. For instance, Wasiliewski *et al.* (1983) have been able to detect the primary radical pair in reduced photosynthetic centres which has a lifetime of only 15 ns.

Finally, mention must be made of an ingenious *nuclear* resonance experiment involving hydrogen atoms in the gas phase. Consider the collision of hydrogen atoms in a strong magnetic field at an extremely low temperature, $kT \ll g\mu_B B$. Only the two lowest levels in figure 1 are populated. For $g\mu_B B \gg a$, the wavefunctions are $\beta\gamma$ and $\beta\delta$: reaction cannot occur because the electron spins are parallel. However, this is not quite true: while $\beta\delta$ is a pure state, unless the field is infinite, $\beta\gamma$ contains a small admixture of

$\alpha\delta$, so this state can react. The rate of reaction increases if r.f. irradiation is used to convert $\beta\delta$ to $\beta\gamma$. This experiment has been carried out successfully by Yurke *et al.* (1983).

14. Muonium chemistry

Positive muons have a mass 207 times that of the electron and a lifetime of 2·2 μs. When pions decay, fast muons are formed with an initial spin polarization; they themselves decay into positrons which are emitted preferentially along the direction of the muon spin. If the muons are stopped in matter in a longitudinal field, the observed polarization depends greatly on the target material; more information can be obtained using a transverse field because the muons precess around the field at different rates depending on their chemical state. One can distinguish diamagnetic muons (e.g. MuOH in water), muonium atoms (Mu, a light isotope of hydrogen), and muonic radicals. The muon has a spin of one-half, with a larger magnetic moment than the proton leading to a hyperfine coupling constant in muonium of 4·463 GHz (cf. 1·420 for H).

The study of these exotic atoms has several interesting aspects. Many rate constants for muonium reactions have been measured and compared with those of hydrogen atoms; muonic radicals were first observed in 1978, but already a considerable number of muonium spin resonance studies have been made. (The parallel is with e.s.r.; chemical shift measurements distinguishing different types of diamagnetic muons are not feasible.) A strong connection with radiation chemistry is provided by the problem of the 'missing fraction': in different materials the observable (oscillating) fraction varies greatly—it also depends on the applied field; the remainder is probably depolarized in rapid reactions (or electron exchange processes) in the first few nanoseconds. This problem has given rise to a great deal of controversy—partly because little is yet known of the final stages of thermalization of the muon. A fast muon produces a track like any other particle; as it slows down, electron attachment may give neutral muonium which travels on some distance beyond the end of the track; alternatively, the charged muon may produce a terminal spur.

For reviews of this subject, see Walker (1983) and Webster (1983). Recent papers by Miyake *et al.* (1983), Percival (1984) and Roduner *et al.* (1984) are useful sources of references.

15. Triplet–triplet annihilation and triplet quenching

Radical pair processes are dominated by the hyperfine interaction in most cases: when two triplets meet, the zero-field splitting ('fine structure') is important. In crystalline anthracene, for example, triplet excitons annihilate each other leading to excited singlets: the resulting fluorescence shows magnetic field effects which are quite different from the hyperfine effect (Merrifield 1968, Sokolik and Frankevich 1974, Avakian 1974). At high field, the electron spins are constrained to precess around the field: two triplets meeting give singlet, triplet and quintet combinations; only the first can react. At zero field, the electron spins are oriented along the molecular axes by the spin–spin interaction which mixes singlet and quintet states, i.e. the latter may convert to a singlet product.

Triplet–triplet annihilation in solution gives both monomer and excimer fluorescence. It has been found that the two fluorescences behave differently in a magnetic field; temperature and viscosity were varied and a theorectial model developed, showing that the different orientations of the triplets lead to different products (Spichtig *et al.* 1976, Lendi *et al.* 1976, 1977). Triplet states can be generated by light absorption but also by recombination of radical-ions produced by electrolysis; triplet annihilation then leads to electrochemiluminescence. Again magnetic field effects are observed—first in 1969, a momentous year for magnetic field effects! (For details, see Faulkner and Bard (1969) and Faulkner *et al.* (1972).) The main field effect appears to be due to quenching of the triplets by the doublet radical ions rather than triplet–triplet annihilation. Atkins and Evans (1975) have given a theoretical description of both processes. Triplet–radical interaction can lead to energy transfer as well as quenching; Naqvi *et al.* (1977) have observed field effects on energy transfer from benzophenone to the related ketyl radical.

Anthracene crystals, bombarded with fast particles, show magnetic field effects on both ion recombination and triplet–triplet annihilation (Fuchs *et al.* 1983). One may expect to see triplet–triplet annihilation in tracks in liquids too—a potentially useful tool for l.e.t. studies—but no reports have appeared.

16. Concluding remarks

'Magnetic field effects on chemical reactions have long been a romping ground for charlatans' (Atkins 1976). They are now more respectable, but the amount of published work is small, especially when compared with the number of papers on CIDNP and CIDEP. One must ask if studying field effects on yields has any advantage. Certainly, if the aim is to detect the involvement of neutral radical pairs in a reaction mechanism, then CIDNP is easier and more sensitive. However, it depends on a difference in the reactions of singlet and triplet pairs: when both singlet and triplet channels are open, no polarization will arise. More generally, magnetic field studies have advantages of time-scale (though time-resolved e.s.r. is catching up); one can use optical detection of fluorescence and light absorption down to one nanosecond and below. Quantitative interpretation of CIDNP is difficult because assumptions must be made about the diffusion processes (and about the distance dependence of J) before integrating over time. In the case of flash photolysis and pulse radiolysis studies of triplet state absorption and of fluorescence, one can 'see' the wavefunction of the radical pair evolve and measure the rate of the recombination process at the same time. Most of the work reported to date has been in the nanosecond region; the aromatic radical-ions involved have relatively small a values (~ 10 MHz). However, larger ones are available, e.g. alkane radical cations (100–200 MHz) and fluorocarbon radical anions (~ 500 MHz). Illustrative calculations have been made for $C_4F_8^{\cdot -}$ (Brocklehurst 1983).

Spin conservation and intersystem crossing in photophysical processes are well understood (Matsen and Klein 1969). *Their role in chemical reactions is less clear.* Tentatively, one may suggest that spin will be conserved when both singlet and triplet products are accessible: no differential energy barrier, high densities of product states. If only one channel is open, there will be competition between intersystem crossing in some form and separation of the reactants; the timescale of the encounter is a vital parameter. One must remember that spin changes can occur during reactions; predissociation often involves a change of multiplicity so the same must be possible for the reverse process. Ferguson (1983) failed to find any spin limitations on the rate of a number of charge-transfer reactions in the gas phase.

Studies described here of magnetic field and magnetic isotope effects have clearly established the role of spin conservation in radical-ion recombination, but they have been limited to excited state formation. There have been no reports of field effects on radiation chemical yields as yet; a search would certainly be justified as changes of up to

20% should be found in favourable cases. One can think of the field as a kind of scavenger which diverts reaction from one channel to another. Interpretation of the results should be simpler than with chemical scavengers which can interfere with the mechanism at several points. The role of multiple-pair spurs remains controversial; while they must be formed initially they may decay rapidly into a single (singlet) ion pair; more work is needed because spin effects may well play a major part in the chemistry in the spurs.

References

ADRIAN, F. J., 1972, *J. chem. Phys.*, **57**, 5107.
ANISIMOV, O. A., BIZYAEV, V. L., LUKSEN, N. N., GRIGORYANTS, V. M., and MOLIN, YU.N., 1983, *Chem. Phys. Lett.*, **101**, 131.
ANISIMOV, O. A., GRIGORYANTS, V. M., MOLCHANOV, V. K., and MOLIN, YU. M., 1979, *Chem. Phys. Lett.*, **66**, 265.
ANISIMOV, O. A., GRIGORYANTS, V. M., and MOLIN, YU. M., 1980, *Chem. Phys. Lett.*, **74**, 15.
ATHERTON, N. M., 1973, *Electron Spin Resonance* (Chichester: Ellis Horwood).
ATKINS, P. W., 1976, *Chemy Britain*, **12**, 214.
ATKINS, P. W., and EVANS, G. T., 1975, *Mol. Phys.*, **29**, 921.
ATKINS, P. W., and LAMBERT, T. P., 1975, *A. Rep. chem. Soc.*, **72a**, 67.
AUSLOOS, P., REBBERT, R. E., SCHWARZ, F. P., and LIAS, S. G., 1983, *Radiat. Phys. Chem.*, **21**, 27.
AVAKIAN, P., 1974, *Pure appl. Chem.*, **37**, 1.
BAGDASAR'YAN, KH. S., KIRJUKHIN, YU. I., and SINITSINA, Z. A., 1972, *J. Photochem.*, **1**, 225.
BARGON, J., FISCHER, H., and JOHNSON, U., 1967, *Z. Naturf.* (a), **22**, 1551.
BECK, G., and THOMAS, J. K., 1972, *Chem. phys. Lett.*, **16**, 318.
BLANKENSHIP, R. E., 1981, *Acc. chem. Res.*, **14**, 163.
BLANKENSHIP, R. E., SCHAAFSMA, T. J., and PARSON, W. W., 1977, *Biochim. biophys. Acta*, **461**, 297.
BOLLINGER, L. M., and THOMAS, G. E., 1961, *Rev. scient. Instrum.*, **32**, 1044.
BOXER, S. G., CHIDSEY, C. E. D., and ROELOFS, M. G., 1982, *J. Am. chem. Soc.*, **104**, 2674.
BOYD, A. W., and CONNOR, H. W. J., 1964, *Can. J. chem.*, **42**, 1418.
BROCKLEHURST, B., 1969, *Nature*, **221**, 921.
BROCKLEHURST, B., 1973, *Chem. Phys.*, **2**, 6.
BROCKLEHURST, B., 1974, *Int. J. Radiat. phys. Chem.*, **6**, 483.
BROCKLEHURST, B., 1976 a, *J. chem. Soc., Faraday Trans.* II, **72**, 1869.
BROCKLEHURST, B., 1976 b, *Chem. Phys. Lett.*, **44**, 245.
BROCKLEHURST, B., 1977 a, *Faraday Discuss. Chem. Soc.*, **63**, 96.
BROCKLEHURST, B., 1977 b, *Faraday Discuss. Chem. Soc.*, **63**, 191.
BROCKLEHURST, B., 1977 c, *Nature*, **265**, 613.
BROCKLEHURST, B., 1979 a, *J. chem. Soc., Faraday Trans.* II, 75, 123.
BROCKLEHURST, B., 1979 b, *J. phys. Chem.*, **83**, 536.
BROCKLEHURST, B., 1982, *J. chem. Soc., Faraday Trans.* II, **78**, 751, 1791.
BROCKLEHURST, B., 1983, *Radiat. Phys. Chem.*, **21**, 57.
BROCKLEHURST, B., 1984 a, *Faraday Discuss. chem. Soc.*, 78, 303.
BROCKLEHURST, B., 1984 b, *Radiat. Phys. Chem.*, **23**, 187.
BROCKLEHURST, B., DIXON, R. S., GARDY, E. M., LOPATA, V. J., QUINN, M. J., SINGH, A., and SARGENT, F. P., 1974, *Chem. Phys. Lett.*, **28**, 361.
BROCKLEHURST, B., GIBBONS, W. A., LANG, F. T., PORTER, G., and SAVADATTI, M. I., 1966, *Trans. Faraday Soc.*, **62**, 1793.
BROCKLEHURST, B., and HIGASHIMURA, T., 1974, *J. phys. Chem.*, **78**, 309.
BUCHACHENKO, A. L., 1984, *Prog. Reaction Kinetics*, **13**, 164.
BURNS, W. G., SIMS, H. E., and GOODALL, J. B., 1984, *Radiat. Phys. Chem.*, **23**, 143.
BURNS, W. G., and MARSH, W. R., 1968, *Trans. Faraday Soc.*, **64**, 2375.
BURNS, W. G., and REED, C. R. V., 1963, *Trans. Faraday Soc.*, **59**, 101.
BUXTON, G. V., GILLIS, H. A., and KLASSEN, N. V., 1976, *Can. J. Chem.*, **54**, 367.
BUXTON, G. V., GILLIS, H. A., and KLASSEN, N. V., 1977, *Can. J. Chem.*, **55**, 2385.
CHOI, H. T., WU, K. C., and LIPSSKY, S., 1983, *Radiat. Phys. Chem.*, **21**, 95.
CLARIDGE, R. E. C., and FISCHER, H., 1983, *J. phys. Chem.*, **87**, 1960.
CLOSS, G. L., 1969, *J. Am. chem. Soc.*, **91**, 4552.

Demas, J. N., 1983, *Excited State Lifetime Measurements* (New York: Academic Press).

Dixon, R. S., Gardy, E. M., Lopata, V. J., and Sargent, F. P., 1975, *Chem. Phys. Lett.*, **30,** 463.

Dixon, R. S., and Lopata, V. J., 1979, *Can. J. Chem.*, **57,** 3023.

Dixon, R. S., Sargent, F. P., Lopata, V. J., and Gardy, E. M., 1977 a, *Chem. Phys. Lett.*, **47,** 108.

Dixon, R. S., Sargent, F. P., Lopata, V. J., Gardy, E. M., and Brocklehurst, B., 1977 b, *Can. J. Chem.*, **55,** 2093.

Engel, P. S., and Bartlett, P. D., 1970, *J. Am. chem. Soc.*, **92,** 5883.

Faulkner, L. R., and Bard, A. J., 1969, *J. Am. chem. Soc.*, **91,** 209.

Faulkner, L. R., Tachikawa, H., and Bard, A. J., 1972, *J. Am. chem. Soc.*, **94,** 691.

Ferguson, E. E., 1983, *Chem. Phys. Lett.*, **99,** 89.

Fessenden, R. W., and Schuler, R. H., 1963, *J. chem. Phys.*, **39,** 2147.

Feynman, R. P., Leighton, R. B., and Sands, M., 1965, *The Feynman Lectures on Physics*, Vol. 3 (Reading, Mass.; Addison-Wesley), Chap. 8.

Fox, J. R., and Hammond, G. S., 1964, *J. Am. chem. Soc.*, **86,** 1918, 4031.

Fuchs, C., Klein, J., and Voltz, R., 1983, *Radiat. Phys. Chem.*, **21,** 67.

Gaumann, T., and Schuler, R. H., 1961, *J. phys. Chem.*, **65,** 703.

Hayashi, H., and Nagakura, S., 1984, *Bull chem. Soc. Japan*, **57,** 322.

Higashimura, T., Hirayama, K., and Katsuura, K., 1972, *Ann. Rep. Res. Reactor Inst., Kyoto Univ.*, **5,** 11.

Hoff, A. J., Rademaker, H., van Grondelle, R., and Duysens, L. M. N., 1977, *Biochim. biophys. Acta*, **460,** 547.

Hummel, A., 1974, *Advances in Radiation Chemistry*, Vol. 4, edited by M. Burton and J. L. Magee (New York: Wiley), p. 1.

Hunt, J. W., 1976, *Advances in Radiation Chemistry*, Vol. 5., edited by M. Burton and J. L. Magee (New York: Wiley), p. 185.

Infelta, P. P., and Rzad, S. J., 1973, *J. chem. Phys.*, **58,** 3775.

Jarnagin, R. C., 1971, *Acc. chem. Res.*, **4,** 420.

Jesse, W. P., 1967, *J. chem. Phys.*, **46,** 4981.

Jonah, C. D., and Sauer, M. C., 1982, *Chem. Phys. Lett.*, **90,** 402.

Kaptein, R., and Oosterhoff, L. J., 1969, *Chem. Phys. Lett.*, **4,** 214.

Kevan, L., 1974, *Advances in Radiation Chemistry*, Vol. 4, edited by M. Burton and J. L. Magee (New York: Wiley), p. 181.

Klein, J., and Voltz, R., 1976, *Phys. Rev. Lett.*, **36,** 214.

Klein, J., and Voltz, R., 1977, *Can. J. Chem.*, **55,** 2102.

Knapp, E. W., and Schulten, K., 1979, *J. chem. Phys.*, **71,** 1878.

Kroh, J., and Mayer, J., 1977, *Faraday Discuss. chem. Soc.*, **63,** 191.

Lambert, T. P., 1978, D. Phil. thesis, Oxford University.

Landolt-Bornstein, 1980, *Numerical Data and Functional Relationships*, Vol. 9, Part d, *Magnetic Properties of Free Radicals*, edited by H. Fischer and K.-H. Hellwege (Berlin: Springer-Verlag).

Lapersonne-Meyer, C., 1980, *Radiat. Phys. Chem.*, **15,** 371.

LaVerne, J. A., and Schuler, R. H., 1982, *J. phys. Chem.*, **86,** 2282.

Lawler, R. G., and Evans, G. T., 1971, *Ind. Chem. Belg.*, **36,** 1087.

Lawler, R. G., and Ward, H. R., 1973, *Determination at Organic Structures by Physical Methods*, Vol. 5, edited by F. C. Nachod and J. J. Zuckerman (New York: Academic Press), p. 99.

Lefkowitz, S. M., and Trifunac, A. D., 1984, *J. phys. Chem.*, **88,** 77.

Lendi, K. Gerber, P., and Labhart, H., 1976, *Chem. Phys.*, **18,** 449.

Lendi, K., Gerber, P., and Labhart, H., 1977, *Chem. Phys.*, **20,** 145.

Lepley, A. R., and Closs, G. L., (eds.), 1973, *Chemically Induced Dynamic Nuclear Polarisation* (New York: Wiley-Interscience).

Luthjens, L. H., Codee, H. D. K., de Leng, H. C., Hummell, A., and Beck, G., 1983, *Radiat. Phys. Chem.*, **21,** 21.

Lyon, R. K., 1964, *J. Am. chem. Soc.*, **86,** 1907.

Magee, J. L., 1960, *Comparative Effects of Radiation*, edited by M. Burton, J. S. Kirby-Smith and J. L. Magee (New York: Wiley), p. 130.

Magee, J. L., and Huang, J.-T. J., 1972, *J. phys. Chem.*, **76,** 3801.

Magee, J. L., and Huang, J.-T. J., 1974, *J. phys. Chem.*, **78,** 310.

Matsen and Klein, 1969, *Advances in Photochemistry*, Vol. 7., edited by J. N. Pitts, G. S. Hammond and W. A. Noyes, Jr. (New York: Wiley Interscience), p. 1.

Melekhov, V. I., Anisimov, O. A., Saik, V. O., and Molin, Yu. N., 1984, *Chem. Phys. Lett.*, **112,** 106.

Merrifield, R. E., 1968, *Acc. chem. Res.*, **1,** 129.

Michel-Beyerle, M. E., Haberkorn, R. Bube, W., Steffens, E., Schroder, H., Neusser, H. J., Schlag, E. W., and Seidlitz, H., 1976, *Chem. Phys.*, **17,** 139.

Michel-Beyerle, M. E., Kruger, H. W., Haberkorn, R., and Seidlitz, H., 1979, *Chem. Phys.*, **42,** 441.

Miyake, Y., Tabata, Y., Ito, Y., Ng, B. W., Stadlbauer, J. M., and Walker, D. C., 1983, *Chem. Phys. Lett.*, **101,** 372.

Molin, Yu. N., Anisimov, O. A., Melekhov, V. I., and Smirnov, S. N., 1984, *Faraday Discuss. chem. Soc.*, **78,** 289.

Mozumder, A., and Magee, J. L., 1966, *Radiat. Res.*, **28,** 203, 215.

Muus, L. T., Atkins, P. W., McLauchlan, K. A., and Pedersen, J. B., (eds.) 1977, *Chemically Induced Magnetic Polarisation* (Dordrecht: D. Reidel).

Naqvi, K. R., Staerk, H., and Gillbro, T., 1977, *Chem. Phys. Lett.*, **49,** 610.

Norris, J. R., Bowman, M. K., Budil, D. E., Tang, J., Wraight, C. A., and Closs, G. L., 1982, *Proc. natn. Acad. Sci., U.S.A.*, **79,** 5532.

Noyes, R. M., 1965, *J. Am. chem. Soc.*, **86,** 4529.

Ore, A., and Larsen, A., 1964, *Radiat. Res.*, **21,** 331.

Percival, P. W., Brodovitch, J. C., and Newman, K. E., 1984, *Faraday Discuss. chem. Soc.*, **78,** 315.

Person, J. C., and Nicole, P. P., 1968, *J. chem. Phys.*, **49,** 5421.

Roduner, E., Brinkman, G. A., and Louwrier, P. W. F., 1984, *Chem. Phys.*, **88,** 143.

Rzad, S. J., Schuler, R. H., and Hummel, A., 1969, *J. chem. Phys.*, **51,** 1369.

Sagdeev, R. Z., Molin, Yu. N., Salikhov, K. M., Leshina, T. V., Kamkha, M. A., and Shein, S. M., 1973, *Org. Magn. Resonance*, **5,** 603.

Sakaguchi, Y., Hayashi, H., and Nagakura, S., 1980, *Bull chem. Soc. Japan*, **53,** 39.

Salikhov, K. M., Molin, Yu. M., Sagdeev, R. Z., and Buchachenko, A. L., 1984, *Spin Polarisation and Magnetic Effects in Radical Reactions* (Amsterdam: Elsevier).

Salmon, G. A., and Selby, K., 1977, *Faraday Discuss. chem. Soc.*, **63,** 189.

Sargent, F. P., Brocklehurst, B., Dixon, R. S., Gardy, E. M., Lopata, V. J., and Singh, A., 1977, *J. phys. Chem.*, **81,** 815.

Sauer, M. C., and Jonah, C. D., 1980, *J. phys. Chem.*, **84,** 2539.

Schulten, K., and Epstein, I. R., 1979, *J. chem. Phys.*, **71,** 309.

Schulten, K., Staerk, H., Weller, A., Werner, H. J., and Nickel, B., 1976, *Z. Phys. Chem.*, (*Frankfurt*), **101,** 371.

Schulten, K., and Wolynes, P. G., 1978, *J. chem. Phys.*, **68,** 3292.

Schwarz, H. A., 1969, *J. phys. Chem.*, **73,** 1928.

Segal, B. G., Kaplan, M., and Fraenkel, G. K., 1965, *J. chem. Phys.*, **43,** 41911.

Shida, T., Kubodera, H., and Egawa, Y., 1981, *Chem. Phys. Lett.*, **79,** 179.

Smirnov, S. N., Rogov, V. A., Shustov, A. S., Sheberstov., S. V., Panfilovitch, N. V., Anisimov, O. A., and Molin, Yu. N., 1985, *Chem. Phys.*, **92,** 381.

Smith, J. P., and Trifunac, A. D., 1981 a, *Chem. Phys. Lett.*, **83,** 195.

Smith, J. P., and Trifunac, A. D., 1981 b, *J. phys. Chem.*, **85,** 1645.

Sokolik, I. A., and Frankevich, Y. L., 1974, *Soviet Physics 'Uspekhi'*, **16,** 687.

Spichtig, J., Bulska, H., and Labhart, 1976, *Chem. Phys.*, **15,** 279.

Symons, M. C. R., 1980, *Chem. Phys. Lett.*, **69,** 198.

Tagawa, S., Washio, M., Kobayashi, H., Katsumura, Y., and Tabata, Y., 1983, *Radiat. Phys. Chem.*, **21,** 45.

Toriyama, K., Nunome, K., and Iwasaki, M., 1981, *J. phys. Chem.*, **85,** 2149.

Trifunac, A. D., 1984, *Faraday Discuss. chem. Soc.*, **78,** 337, 338.

Trifunac, A. D., and Evanochko, W. T., 1980, *J. Am. chem. Soc.*, 102, 4598.

Trifunac, A. D., and Lawler, R. G., 1982, *Magnetic Resonance Rev.*, **7,** 147.

Trifunac, A. D., Sauer, M. C., and Jonah, C. D., 1985, *Chem. Phys. Lett.*, **113,** 316.

Trifunac, A. D., and Smith, J. P., 1980, *Chem. Phys. Lett.*, **73,** 94.

Trumbore, C. N., Youngblade, W., and Short, D. R., 1984, *J. phys. Chem.*, **88,** 5057.

Turro, N. J., 1983, *Proc. natn. Acad. Sci., U.S.A.*, **80,** 609.

Turro, N. J., Chow, M.-F., Chung, C.-J., and Tung, C.-H., 1980, *J. Am. chem. Soc.*, **102,** 7391.

Turro, N. J., and Kraeutler, B., 1978, *J. Am. chem. Soc.*, **100,** 7432.

Turro, N. J., and Kraeutler, B., 1980, *Acc. chem. Res.*, **13,** 369.

Verma, N. C., and Fessenden, R. W., 1973, *J. chem. Phys.*, **58,** 2489, 2501.

Verma, N. C., and Fessenden, R. W., 1976, *J. chem. Phys.*, **65,** 2139.

Voltz, R., 1969, *Actions Chimique et Biologique des Radiations*, Vol. 13, edited by M. Haissinsky (Paris: Masson).

Walker, D. C., 1983, *Muon and Muonium Chemistry* (Cambridge: Cambridge University Press).

Wang, J. T., and Williams, Ff., 1981, *Chem. Phys. Lett.*, **82,** 177.

Ward, H. R., and Lawler, R. G., 1967, *J. Am. chem. Soc.*, **89,** 5518.

Wasiliewski, M. R., Bock, C. H., Bowman, M. K., and Norris, J. R., 1983, *J. Am. chem. Soc.*, **105,** 2903.

Webster, B. C., 1983, *Chemy Britain*, **19,** 110.

Weller, A., Staerk, H., and Treichel, R., 1984, *Faraday Discuss. chem. Soc.*, **78,** 271.

Werner, H.-J., Schulten, Z., and Schulten, K., 1977, *J. chem. Phys.*, **67,** 646.

Yurke, B., Denker, J. S., Johnson, B. R., Bigelow, N., Levy, L. P., Lee, D. M., and Freed, J. H., 1983, *Phys. Rev. Lett.*, **50,** 1137.

Zador, E., Warman, J. M., and Hummel, A., 1973, *Chem. Phys. Lett.*, **22,** 480.