

Electron spin polarization studies of the dynamics of geminate free radical reactions

Robert W. Eveson and Keith A. McLauchlan

Chemistry Department, New Chemistry Laboratory, University of Oxford, UK

The probability that pairs of radicals which are created together in a photolysis flash subsequently react during the geminate phase of a reaction is obtained as a function of the viscosity of the solution, from electron spin polarization studies.

When free radicals are produced in solution they are invariably created in pairs. Since small free radicals react with very low activation energies it might be thought that they recombine immediately and no radicals would escape this early, "geminate", period. That they do results from two factors. Firstly the breaking of chemical bonds occurs with release of energy so that the radicals separate. Secondly electron spin orientation is conserved on bond breaking and the radicals produced constitute a "spin correlated radical pair" which possesses the spin multiplicity of their molecular precursor. In photochemical reactions this is very often a triplet state so that the spin selection rule for chemical reaction prevents reaction of the triplet-correlated pair occurring even if the radicals encounter. But as the radicals separate state mixing induces mixed Singlet-Triplet (S-T) character in the pair so that if they re-encounter later reaction occurs with a probability directly proportional to the S character.

This process, or its inverse that tends to diminish the reactivity of singlet-born radical pairs, underlies all radical combination reactions including those which happen in conventional photochemistry. It is also the source of electron and nuclear polarization in chemical reactions involving radicals, of the effects of magnetic fields on these reactions, and of magnetic isotope effects. Central to all these problems is the fraction of radical pairs created which survive annihilation by reaction within the geminate pair.

This can be determined in principle directly from studies of the electron spin polarization that is observed in the radicals produced from triplet precursors and which escape geminate recombination.

Origins of electron spin polarization in reactions

Almost invariably the electron spin resonance spectra of radicals produced by flash photolysis and observed during the first microsecond of their existence exhibit electron spin polarization. That is, the intensities (and often phases) of the lines do not correspond to an ensemble which is in thermal equilibrium with its surroundings. Processes which occur within this period therefore create non-Boltzmann spin distributions which persist until equilibrium is attained via spin relaxation. In most of those cases in which the radicals are created by reaction of the excited triplet state of a molecule two independent mechanisms contribute to the polarization.

The Triplet mechanism (TM) has its origins in the inter-system crossing process between the singlet and triplet states in the precursor molecule in which the triplet sub-levels that are non-degenerate in the molecule as a result of electron-electron dipolar couplings are populated at different rates, leading to a spin polarized triplet state. Within the magnetic field of an ESR spectrometer these levels correlate with the Zeeman states to yield triplets polarized in the laboratory frame of reference. Their subsequent dissociation or reaction produces an observable spin-polarized radical system. The characteristic effect on the observed spectra is that the absolute intensities of the lines differ from those at equilibrium but the relative intensities are determined by hyperfine state degeneracies, as in equilibrated radicals. For the system reported below the TM yields absorptive polarization.

The TM is evident immediately after the radicals are created and is a characteristic of the whole ensemble.

The RPM is analogous in its origin to the mechanism of radical reaction described above. Radicals are always created in pairs, and with conservation of spin multiplicity: At the instant of creation a triplet molecule dissociates, or reacts to form a triplet-correlated radical pair. As the radicals separate the initially pure triplet state evolves under the influence of the spin Hamiltonian and if the radicals later re-encounter within the geminate cage the exchange interaction leads to the production of Radical Pair Mechanism (RPM) polarization. It is not a true polarization in that the overall relative populations of the electron spin states is unaffected. Rather spin population becomes re-distributed amongst the hyperfine states and the overall spectrum displays some of its intensity in absorption (A) and an equal amount in emission (E), yielding an E/A pattern with increasing magnetic field from neutral radicals produced from a triplet reaction. But the absolute sizes of the signals from the two radicals are normally different, and there are strong distortions in the intensities of the hyperfine lines. It has long been known how to calculate these from a knowledge of the Hamiltonian and a simple diffusion model.¹⁾

But not all radicals created together in the geminate cage subsequently re-encounter and generate RPM polarization, which therefore arises only in a sub-ensemble, in contrast to the TM. It follows that the magnitude of the RPM relative to the TM reflects the size of that sub-ensemble, and in a system of un-reactive radicals such a measurement would yield

the absolute probability of radicals re-encountering during the geminate period following their instantaneous formation. In practice, however, the very process of state mixing which is a requisite for RPM polarization is exactly that needed for reaction, and the experiment actually yields the size of the subensemble which re-encounters but survives to be observable.

Relation to observed spectra

In any properly run ESR spectrum there is a direct relationship between the observed signal and the radical concentration, for example for stable radicals,

$$S = c \cdot P_{eq}[R],$$

where c is an apparatus constant. For polarized radicals P_{eq} must be replaced by the appropriate polarization factor. But as described above the whole ensemble contributes to the contribution to the signal dependent upon the TM, S_{TM} , whereas only a sub-ensemble $f[R]$ contributes to that dependent upon the RPM, S_{RPM} . Since the two polarization mechanisms are independent, the overall observed signal can be written

$$S = S_{TM} + S_{RPM} = c \cdot [R] \{P_{TM} + f \cdot P_{RPM}\}.$$

That is the signal is the sum of two independent contributions. If these are measured, and if P_{TM} and P_{RPM} are known, it follows that the fraction of radicals that re-encounters in the geminate cage and survive re-encounter can be investigated.

Unfortunately it is difficult to measure the polarizations, and nor is it possible to calculate them with sufficient accuracy using existing theory through lack of knowledge of the magnitudes of the parameters involved, and an alternative strategem is applied. This depends upon the fact that the viscosity dependence of the two forms of polarization is known from theory so that the variation of f with viscosity (η) can be obtained with reference to a chosen standard (here the polarizations in methanol).

Experimental and spectral analysis

The above analysis is valid in comparisons between various liquids only if $[R]$ (strictly at radical creation) is invariant. Thus spectra were obtained at constant optical density using a micro-processor controlled constant average intensity from an XeCl laser, and averaged over many flashes. The molecule chosen for experimental study was $\text{CH}_2\text{OHCOCH}_2\text{OH}$ since its relaxation characteristics have been previously investigated in our laboratory,²⁾ allowing straightforward simulation of spectra (Fig. 1). Furthermore it dissociates directly through its excited triplet state to form radicals and it was at first thought that this unimolecular process would be sufficiently fast that relaxation within the polarised triplet would be negligible, with all the polarization in the triplet molecule carried to the radicals in any solvent. In this case, P_{TM} would be constant from one solution to another and S_{TM} could be used as an internal standard for assessing the RPM contribution (but see below).

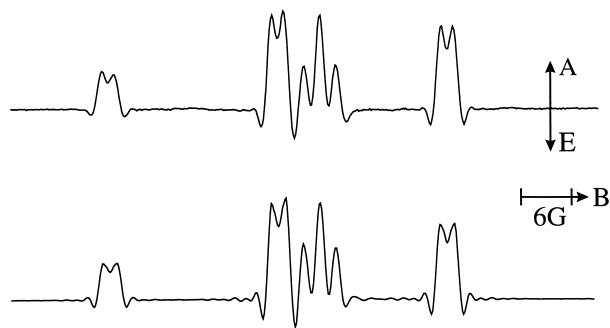
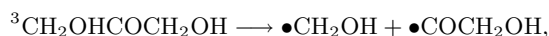


Fig. 1. The spectrum observed 0.20–0.32 μs after the photolytic flash, and its simulation. The triplet of doublets results from the $\bullet\text{CH}_2\text{OH}$ radical, and the triplet from the $\bullet\text{COCH}_2\text{OH}$ one. The relaxation times used in the simulations (with $T_1 = T_2$) were 0.51 and 0.30 μs respectively and all features of the observed spectra including the Torrey oscillations are reproduced.

The two radicals produced on bond breaking in the reaction,



have very different relaxation times and it is convenient to obtain the information needed using the spectrum of the slower relaxing hydroxymethyl radical alone. This was done by calculating the relative intensities of the lines using TM and RPM theory, and obtaining expressions for the total intensities using the approach outlined above. After some manipulation this yields, for example,

$$\frac{P_{TM}(LF)}{P_{RPM}(LF)} = \frac{f(1 + 0.775r)}{(r - 1)},$$

where LF refers to the low-field line and r is the ratio of the intensities of the high and low field lines, measured experimentally. As explained above, the value of the left hand side and the fraction f_η in any solvent, can be related to the corresponding values in methanol, using the established viscosity dependence of the polarizations.

From standard RPM theory,

$$P_{RPM} \propto \eta^{1/2},$$

and it was expected, under the assumption on P_{TM} made above, that the contribution from RPM polarization would increase significantly as the viscosity was increased. This, particularly, since instinct would also be that the fraction of radicals that encounter within the geminate cage should increase with viscosity.

Results

Figure 2 shows spectra obtained in solvents of widely differing viscosity and simple inspection shows that the relative contributions of TM and RPM signals do not vary greatly, against prediction. It is apparent that either conventional RPM theory is wrong or that our assumption concerning the TM is. This contribution was therefore extracted directly using an analysis analogous to that given above on spectra obtained at constant $[R]$ in the various solutions, with the



Fig. 2. Spectra observed a) in ethanol solution with $\eta = 0.997$ mPa s and b) in propan-1,2-diol solution with $\eta = 30.28$ mPa s. The fraction of radicals re-encountering would be expected to be higher in the high viscosity solution but even if it was unchanged the RPM contribution would be expected to grow by a factor of 5.5 relative to the TM one. This clearly is not the case, showing that the P_{TM} varies substantially with change of viscosity.

absolute sizes of the signals now measured. It was found that P_{TM} varied quite strongly with viscosity, increasing by a factor of 3.7 between methanol (0.997 mPa s) and propan-1,2,-diol (30.28 mPa s). This demonstrates that relaxation in the triplet competes with its unimolecular decay (both occur at rates of $\sim 10^9$ s $^{-1}$). It is expected to depend on viscosity through its dependence on the rotational correlation time, but the extent of the variation is greater than expected using accepted theory.³⁾

Knowledge of the TM contribution in each solution relative to that in methanol now enables the ratio of the TM and RPM contributions in each to be deduced, and the values of f_η obtained. Again, simple theory would predict that the fraction re-encountering would increase as $\eta^{1/2}$ but the values obtained (see Table 1) show the values of f_η measured to vary little with viscosity, and actually to fall as the viscosity is increased. We stress that these two fractions differ in their definition: The latter is that fraction which contributes to the observed spectrum.

Table 1. Typical errors in the ratio are ± 0.13 .

Solvent	Viscosity/mPa s	$f(\eta)/f_{\text{methanol}}$
Methanol	0.554	1.00
Ethanol	0.997	1.45
Propan-2-ol	2.01	1.20
50% Ethanol, 50% ethan-1,2-diol	4.60	0.93
Ethan-1,2-diol	11.55	0.97
40% Ethan-1,2-diol, 60% Propan-1,2-diol	20.20	0.92
Propan-1,2-diol	30.28	0.89

The answer lies therefore in reaction. As mentioned above, the conditions for producing reaction in a triplet-born pair is exactly that it should attain singlet character before an effective re-encounter can occur. The probability of reaction is directly proportional to this character, which is equally needed for the production of RPM polarization. In consequence the very thing (increase in viscosity) which appears that it should increase S_{RPM} also increases the probability of reaction within the geminate cage and decreases the observed radical concentration. The implication is that the experiment does not measure the re-encounter probability in the geminate period of the reaction, but rather measures the fraction of those radicals created in a photolytic flash which survives re-encounter during the geminate period and can be observed (or to initiate polymerisation etc.). A simple analysis involves writing the probability of reaction within the geminate cage as⁴⁾

$$P_R = \lambda \int_0^\infty P_s(t) \cdot P_E(t) dt,$$

where λ is a parameter to take care of the fact that not all radicals which encounter to form singlet pairs react, $P_s(t)$ is the probability that the pair is in the S state at time t , and $P_E(t)dt$ is the probability of an encounter occurring in the interval t to $t + dt$. The latter is given to sufficient accuracy by the Noyes equation whilst the former is calculated using standard state mixing theory. This leads to the result

$$\frac{f_\eta}{f_{\text{methanol}}} = \frac{(1 - \beta\eta^{1/2})}{(1 - \beta\eta_{\text{methanol}}^{1/2})},$$

where β is a constant which depends upon the size of the radicals and on the mixing coefficients in the precise pair. Fitting to the experimental results yields a value of $0.842N^{-1/2}$ ms $^{-1/2}$ for our system, and a reasonable value of 0.35 nm for the molecular diameter. It further implies that in methanol 98% of the radicals produced survive geminate reaction, whilst in propan-1,2-diol only 85% do.⁵⁾ This is exactly the information needed to understand the radical processes outlined in the introduction.

It is interesting that in the lowest viscosity solvents the fraction of radicals observed to have survived reaction in the geminate cage does seem to reflect an increased re-encounter probability within the cage, without proportionately increased reactivity.

References

- 1) L. Monchik and F. J. Adrian: J. Chem. Phys. **68**, 4376 (1978).
- 2) K. A. McLauchlan and M. T. Yeung: Mol. Phys. **89**, 1423 (1996).
- 3) P. W. Atkins and G. T. Evans: Mol. Phys. **27**, 1633 (1974).
- 4) R. Kaptein: J. Am. Chem. Soc. **94**, 6251 (1970).
- 5) R. W. Eveson and K. A. McLauchlan: Mol. Phys. **96**, 133 (1999).