Chemically Induced Dynamic Nuclear Polarization. VIII. Spin Dynamics and Diffusion of Radical Pairs

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Abstract: The radical pair theory of CIDNP in high magnetic fields is critically reexamined. A model is developed, in which random walk diffusion of radical pairs is taken into account. Various interactions, which may lead to singlet–triplet mixing in radical pairs, are considered. The nuclear spin dependent probability of geminate recombination is calculated as a product of (i) the probability of geminate reencounters, previously obtained by Noyes, (ii) the probability that the pair is in the electronic singlet state, and (iii) λ, the probability of reaction during singlet encounters. Enhancement factors of the correct order of magnitude are obtained in this way. The theory is similar to a model recently proposed by Adrian; differences arise in the treatment of encounters of free radicals with uncorrelated spins, which is discussed in an Appendix. Furthermore, allowance is made for a nonzero exchange integral. Qualitative predictions of the theory are summarized in two simple rules (eq 52), one for net polarization and another for multiplet effects. A few examples of computer-simulated CIDNP spectra are given.

1. Introduction

The birth of chemically induced dynamic nuclear polarization (CIDNP) was marked by the first reports[2] of emission (E) and enhanced absorption (A) in nmr spectra of reacting systems. Only intensities of the reaction products were anomalous, other characteristics (line frequencies and line width) being normal. Therefore it was obvious that the products were formed with nonequilibrium nuclear spin state populations. First ideas on the mechanism of this effect[2b,d] invoked electron–nuclear cross relaxation in free radicals to explain the enhanced polarization in a way similar to the Overhauser affect. A number of phenomena, however, were inexplicable or even in conflict with these early theories, *viz.*, multiplet effects[2c,d,3,4] (both E and A in the multiplet of a nucleus); dependence on type of reaction[4] (products formed by recombination behaved opposite to transfer-reaction products); dependence on the electronic state multiplicity of the precursor in photochemical reaction;[5,6] observation of polarization,

when the reaction was run in zero magnetic field;[7] the magnitude of the enhancement found to be larger than the Overhauser limit in some cases;[5] polarization found in systems where radical life times were much larger than relaxation times in the radicals.[2c,d,8] Although there is no reason why the originally proposed mechanism should not contribute to the polarization in some favorable cases, this mechanism, however, is usually overshadowed by the more powerful radical-pair mechanism, independently proposed by Closs[5,9] and by Kaptein and Oosterhoff.[10] This recent theory was rather successful, because it could qualitatively account for all published CIDNP spectra, with the possible exception of one or two pathological cases. The essentials of the radical-pair mechanism can be discussed with the aid of Figure 1, showing schematically the energy levels of singlet (S) and triplet (T) states of a radical pair in a magnetic field for separations in the range of a few molecular diameters.

When a pair separates after its birth or after a collision, the S–T energy gap $2J$ (J is the exchange integral) becomes smaller and at distances where degeneracies or neardegeneracies occur the S and T states are mixed by hyperfine (hf) interactions of electrons with nuclei,

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(2) (a) J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch., A*, 22, 1551 (1967); (b) J. Bargon and H. Fischer, *ibid.*, 22, 1556 (1967); (c) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, 89, 5518 (1967); (d) R. G. Lawler, *ibid.*, 89, 5519 (1967).

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(5) (a) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, 91, 4549, 4550 (1969); (b) G. L. Closs, *ibid.*, 91, 4552 (1969); (c) G. L. Closs and A. D. Trifunac, *ibid.*, 91, 4554 (1969).

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(7) (a) H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *J. Amer. Chem. Soc.*, 91, 4928 (1969); (b) M. Lehnig and H. Fischer, *Z. Naturforsch., A*, 24, 1771 (1969).

(8) H. Fischer, *J. Phys. Chem.*, 73, 3834 (1969).

(9) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, 92, 2183, 2186 (1970).

(10) (a) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, 4, 195 (1969); (b) *ibid.*, 4, 214 (1969).
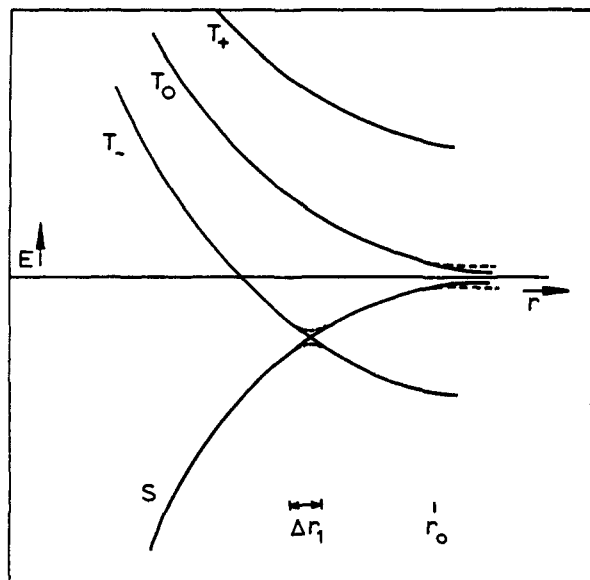
Figure 1. Energies of singlet and triplet states of a radical pair in a magnetic field $vs.$ separation (r). The broken lines are the adiabatic energy levels. The $S-T_-$ mixing region is denoted by Δr_1; $S-T_0$ mixing occurs when $r > r_0$.

provided the time spent in a mixing (or transition) region is sufficiently long. It will be shown in the next section that for the region Δr_1 in high fields (higher than a few thousand Gauss) this time is too short to allow appreciable S–T mixing, so that the system zips essentially unchanged (nonadiabatically) through this region. However, the time spent in the S–T mixing region $r > r_0$ (r_0 roughly given by the condition that J is of the order of the hf parameters) is much larger and S–T transitions may occur. As these transitions are nuclear spin dependent, so is product formation, when this occurs only from the S state. This process has been appropriately called "spin selection."[11,12] The operator for $S-T_0$ mixing is of the form $(S_{z1} - S_{z2})I_z$. As the nuclear spin part (I_z) is diagonal no nuclear spins are "flipped" and no polarization is generated in the sample considered as a whole. Only polarization for *specific products* results from this process. Therefore nuclear polarization in recombination products opposes that of the escaping radicals and hence of transfer-reaction products. It will be clear that the magnitude of the polarization will be closely bound up with the motion of the pair; thus it depends on the dynamics of the "cage" processes. A satisfactory description of the "cage" reaction has been developed by Noyes.[13] He makes the distinction[13b] of primary cage reactions (reactions of a pair of next neighbors, surrounded by a cage of solvent molecules) and secondary recombinations of original partners, after some relative diffusion has occurred. Both processes are frequently lumped together in the name "cage" reactions. The distinction is, however, important for us, because the short time span of primary cage reactions (10^{-11} sec) will not allow nuclear spin-dependent intersystem crossing to

occur and the polarization is due to spin selection in subsequent encounters of the pair. Hence the time scale of CIDNP is limited by that of "geminate" recombination. Accordingly, we shall employ Noyes' approach to the kinetic description of geminate recombination[14] in section 3 and incorporate the dynamics of the spin system, treated in section 2. Thus relative diffusion of radical pairs is explicitly taken into account in our model. In this respect it differs from other kinetic schemes[12,15,16] including our previous simplified treatement,[10b] where the processes of product formation and escape of radical pairs are discussed in terms of time independent rate constants and "mean life times." These rate constants have only a formal meaning but cannot easily be correlated with solvent properties and diffusive behavior of radical pairs.

In section 4 the link is made with the actual CIDNP spectra and it will be shown that all qualitative predictions can be made with but two simple rules, one for net effects (E or A) and one for multiplet effects. If one is concerned with details or if spectra are too complicated, one has to resort to computer simulation techniques, some results of which are discussed in section 5. In this paper we shall be concerned only with the high-field case, where reactions are run in fields of a few thousand gauss or larger. In a following paper[17] this restriction will be removed and the formalism will be extended to include the effects of $S-T_{\pm}$ mixing, which have to be considered in low fields.

2. The Spin Hamiltonian and $S-T_0$ Mixing

Intersystem crossing in a radical pair can be conveniently described in terms of a spin Hamiltonian. Itoh, $et\ al.$,[18] have recently shown how this spin Hamiltonian can be obtained from the total Hamiltonian for cases of near degeneracies of S and T states. The total Hamiltonian can be written

$$H = H_e + H_{LS} + H_{HL} +$$
$$H_{HS} + H_{SS} + H_{SI} + H_{HI} \quad (1)$$

where H_e is the electronic energy term

$$H_e = H_e^a + H_e^b + H_e^{ab} \quad (2)$$

H_e^a and H_e^b describing the radicals a and b and H_e^{ab} their mutual interaction. H_{LS} is the spin-orbit coupling term; H_{HL}, H_{HS}, and H_{HI} denote the interaction of the magnetic field with electronic orbital motion, electron spin, and nuclear spin, respectively; H_{SS} is the electron spin–spin interaction term and H_{SI} the nuclear hyperfine interaction term. Following the pertubation procedure of Itoh, $et\ al.$,[18] the spin Hamiltonian can be obtained containing terms appropriate for the S and T states of the radical pair and terms connecting these states

$$H_{RP} = H_{ex} + H_{ZS} + H_{hf} + H_D + H_{ZI} \quad (3)$$

The various terms will now be discussed.

(14) During the preparation of this paper F. J. Adrian informed us that he also has applied this type of kinetics to the CIDNP problem. In some respects our treatment differs from his: $cf.$ F. J. Adrian, $J.\ Chem.\ Phys.$, **53**, 3374 (1970).

(15) (a) H. Fischer, $Z.\ Naturforsch.,\ A$, **25**, 1957 (1970); (b) M. Lehnig and H. Fischer, $ibid.$, **25**, 1963 (1970).

(16) G. L. Closs and A. D. Trifunac, $J.\ Amer.\ Chem.\ Soc.$, **92**, 7227 (1970).

(17) R. Kaptein and J. A. den Hollander, $ibid.$, **94**, 6269 (1972).

(18) K. Itoh, H. Hayashi, and S. Nagakura, $Mol.\ Phys.$, **17**, 561 (1969).

(11) H. R. Ward, paper presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970.

(12) (a) H. R. Ward and R. G. Lawler, $Accounts\ Chem.\ Res.$, **5**, 18 (1972); (b) R. G. Lawler, $ibid.$, **5**, 25 (1972).

(13) (a) R. M. Noyes, $J.\ Chem.\ Phys.$, **22**, 1349 (1954); (b) $J.\ Amer.\ Chem.\ Soc.$, **77**, 2042 (1955); (c) $ibid.$, **78**, 5486 (1956); (d) $Progr.\ React.\ Kinet.$, **1**, 129 (1961).

2.1. The Exchange Term. The action of H_e^{ab} together with the Pauli exclusion principle gives rise to an energy difference between S and T states, ΔE_{ST}. In valence bond (VB) theory the energy expression is

$$E_{S/T} = 2E_0 + (C \pm J)/(1 \pm S_{ab}{}^2) \qquad (4)$$

where E_0 is the energy of the two fragments without interaction; C, J, and S_{ab} are Coulomb, exchange, and overlap integrals. As the VB theory gives a very good approximation to the electronic energy at large separations and as the condition $S_{ab}{}^2 \ll 1$ is also satisfied at large r, we may identify $\Delta E_{ST} = 2J$ for our purposes.[19] The Dirac exchange operator

$$H_{ex} = -J(^1/_2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2) \qquad (5)$$

in the spin Hamiltonian will reproduce this energy difference ($\mathbf{S}_1$ and $\mathbf{S}_2$ are electron spin operators). The exchange integral is

$$J = \langle \Psi_a(1)\Psi_b(2)|H_e^{ab}|\Psi_b(1)\Psi_a(2)\rangle \qquad (6)$$

where Ψ_a and Ψ_b are the orbitals carrying the unpaired electrons. It is enlightening to consider the expression for J in the case of two H atoms

$$J_{H_2} = e^2 S_{ab}{}^2/r_{ab} - 2S_{ab}\langle\Psi_a(1)|e^2/r_{b1}|\Psi_b(1)\rangle +$$
$$\langle\Psi_a(1)\Psi_b(2)|e^2/r_{12}|\Psi_b(1)\Psi_a(2)\rangle \quad (7)$$

In this case the second term prevails, making J negative' which places the S state below the T state. J decreases exponentially with distance,[22] giving the behavior sketched in Figure 1. For radicals in general a similar expression will hold. If there is a π-electron radical present, which is usually the case, there will be orientations for which $S_{ab} = 0$ and J is positive. This is confirmed by recent calculations.[23] So J will then depend both on separation and orientation. For freely tumbling and diffusing radicals this means that J fluctuates (correlation time of reorientation $\tau_c = 10^{-11}$–10^{-10} sec) within an exponential envelope. In addition, there may be contributions from indirect exchange mechanisms *via* intervening solvent molecules. Calculations indicate that $|J|$ becomes of the order of the hf coupling constants at about 6 Å for H-atom 1s orbitals[22] and about 10 Å for 2p and 2s orbitals.[23] Experiments show that r_0 may be even smaller. Hirota and Weissman[24] found a neglible J at separations of 5–6 Å in ion pairs. A value $r_0 = 6$ Å is quoted by Ferruti, *et al.*[25] For nitroxide biradicals and from the work of Itoh, *et al.*,[18] a value of 7 Å can be deduced. So it seems reasonable to assume that J drops to a value comparable

to the hf constants after only a few diffusive displacements.

We have previously[10] approximated the time dependence of J by a step function, changing J suddenly at $t = 0$ from a very large to a low (constant) value and we shall do the same here. It has the great advantage of making the effective Hamiltonian time independent. We considered only S–T_0 mixing. These simplifications are justified if (i) we can neglect S–$T_\pm$ transitions; (ii) the time necessary to reach a separation $r = r_0$ is short compared to the time spent in the S–T_0 mixing region $r > r_0$; (iii) the residual fluctuations of J around a mean value are small. If we anticipate that the transition probabilities for short times[26] are of the order $a^2 t^2$, where $a = |\langle\Psi_S|H_{RP}|\Psi_T\rangle| \sim 10^8$ radians/sec, and that the thermal equilibrium polarization is about 10^{-5}, we see that we need times $t > 10^{-10}$ sec to give appreciable enhancements. This is longer than the time needed for a few displacements (a few times 10^{-11} sec) and the time spent in Δr_1, which is even shorter. So conditions i and ii seem to be satisfied. We do not really know very much about J for $r > r_0$ so it is simplest to assume that iii will hold also. Glarum[27] has worked out the problem with an exponential model for J and $r(t) = vt$. It seems that this overestimates somewhat the S–$T_\pm$ transition probabilities, for which there are no experimental indications in high fields. In view of the neglect of fluctuations in J and the simplified description of the motion of the pair, we are of the opinion that this model[27] does not necessarily provide a better description than the present diffusion model.

2.2. The Zeeman Terms. The combined effects of H_{LS} and H_{HL} give rise[18,28] to a term linear in the field H_0 and $\mathbf{S}_1$, $\mathbf{S}_2$

$$H_{ZS} = \beta_e \mathbf{H}_0 \cdot \mathbf{g}_a \cdot \mathbf{S}_1 + \beta_e \mathbf{H}_0 \cdot \mathbf{g}_b \cdot \mathbf{S}_2 \qquad (8)$$

The anisotropy of the g tensors, $\mathbf{g}_a$ and $\mathbf{g}_b$, is averaged out by the tumbling motion of the radicals, which is usually faster ($\tau_c \sim 10^{-11}$–10^{-10} sec) than intersystem crossing. We may therefore neglect the anisotropic terms

$$H_{ZS} = \beta_e H_0(g_a S_{1z} + g_b S_{2z}) \qquad (9)$$

Although the nuclear Zeeman term $H_{ZI} = \Sigma_i g_N \beta_N \cdot I_{zi} H_0$ is comparable to the hf terms in high fields, it may be ignored, because it simply shifts the zero of energy, if only S–T_0 mixing is considered. Of course it is also unimportant in low fields.

2.3. The Hyperfine Terms. The term H_{SI} in (1), averaged over the space part of the wave function, leads to the hf term describing the interaction of electrons with nuclei I_j

$$H_{hf} = \mathbf{S}_1 \cdot \sum_j{}^a A_j I_j + \mathbf{S}_2 \cdot \sum_k{}^b A_k I_k \qquad (10)$$

The sum Σ^a runs over the nuclei of radical a. A_j are the isotropic hf coupling constants; we have again neglected the anisotropic contributions. Equation 10 is valid when the density of Ψ_a at the nuclei of b is neg-

(19) The VB theory describes the process of homolytic dissociation quite well, because it takes account of electron correlation. In MO theory also exchange integrals appear (difference between *excited* S and T configurations). However, MO theory without extensive configuration interaction gives a very unreliable description at large separations[20] so that arguments derived from MO theory[21] are not suitable to deduce the sign of J; also because we are interested in S and T states of the *ground-state* electronic configuration of the radical pair. The nature of the excited state of the precursor (*e.g.*, in photochemical reactions) does not seem to be relevant except for its multiplicity.

(20) C. A. Coulson, "Valence," Oxford University Press, London, 1961, p 156.

(21) H. Fischer, *Chem. Phys. Lett.*, **4**, 611 (1970).

(22) C. Herring and M. Flicker, *Phys. Rev.*, **134**, A362 (1964).

(23) J. N. Murrell and J. J. C. Teixeira-Dias, *Mol. Phys.*, **19**, 521 (1970).

(24) H. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **86**, 2538 (1964).

(25) P. Ferruti, D. Gill, M. P. Klein, H. H. Wang, G. Entine, and M. Calvin, *ibid.*, **92**, 3704 (1970).

(26) The Landau–Zener formula (*cf.* E. E. Nikitin in "Chemische Elementarprozesse," H. Hartmann, Ed., Springer-Verlag, West Berlin, 1968, pp 43–77) which gives time-proportional transition probabilities is unreliable for short times or high velocities: *cf.* D. R. Bates, *Proc. Roy. Soc. Ser. A*, **257**, 22 (1960).

(27) S. H. Glarum, personal communication.

(28) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapter 9.

ligible, which certainly is the case at separations $r > r_0$.

2.4. Other Terms. The electron dipolar coupling term $H_D = S_1 \cdot D \cdot S_2$ is obtained by integrating H_{SS} over the space part of the wave function. It is important to note that H_D cannot induce S–T transitions (it mixes only T states). The tensor D is completely anisotropic. In our case its main effects will be to modulate the energy of the T states; reorientation of the interradical vector may not be fast enough to average this out to zero. However, the uncertainty in J will be larger than the effects of H_D, so we may as well disregard this term.

Other interactions that might mix S and T states are effects of spin-orbit coupling that have not yet been included in (8) and of spin-rotation interactions, which act during reorientation of a radical. Because they are zero on the average and have extremely short correlation times $(10^{-14}–10^{-15}$ sec),[29] spin-rotation interactions will not be very important. Spin-orbit coupling is considered in Appendix A, where it is shown that it is probably not important at $r > r_0$, although it may play a role at shorter distances. This is important because no cross terms with terms included in eq 3 will appear in our results, in this way assuring that g factor differences and hf parameters can be obtained with some confidence from CIDNP spectra.

We are left with the effective spin Hamiltonian of the radical pair, which can be written in the form

$$H_{RP} = H^0 + H' \tag{11}$$

$$H^0 = \tfrac{1}{2}(g_a + g_b)\beta_e \hbar^{-1} H_0(S_{1z} + S_{2z}) - J(\tfrac{1}{2} +$$
$$2S_1 \cdot S_2) + \tfrac{1}{2}(S_1 + S_2)(\textstyle\sum_j{}^a A_j I_j + \sum_k{}^b A_k I_k) \tag{11a}$$

$$H' = \tfrac{1}{2}(g_a - g_b)\beta_e \hbar^{-1} H_0(S_{1z} - S_{2z}) +$$
$$\tfrac{1}{2}(S_1 - S_2)(\textstyle\sum_j{}^a A_j I_j - \sum_k{}^b A_k I_k) \tag{11b}$$

Angular frequency units are used (10^8 radians/sec ~ 6 G $\sim 6 \times 10^{-4}$ cm^{-1}). H^0 is diagonal in a basis of S and T functions and H' nondiagonal.

2.5. S–T$_0$ Mixing. For the description of time-dependent mixing of S and T$_0$ states we shall use a direct product basis of electronic S and T functions, $S = 2^{-1/2}(\alpha_1\beta_2 - \beta_1\alpha_2)$; $T_0 = 2^{-1/2}(\alpha_1\beta_2 + \beta_1\alpha_2)$, and nuclear spin product functions χ_n. A nuclear state n is characterized by a collection of nuclear spin quantum numbers: $n = (\ldots M_j, M_k \ldots)$. We shall make use of magnetic equivalence factoring, the conditions being in our case: (i) the nuclei must be magnetically equivalent in the reaction product in the usual sense of having the same chemical shifts and the same coupling constants to other nuclei and (ii) they must have the same hf coupling constant and reside in the same radical. These nuclei are first coupled (e.g., in case of two equivalent nuclei we make symmetric and antisymmetric combinations) and summations over j and k run over all composite nuclei. As in III[10b] the wave function is expanded as

$$\phi_n(t) = \{C_{Sn}(t)S + C_{Tn}(t)T_0\}\chi_n \tag{12}$$

The time dependence is given by $i\partial\phi/\partial t = H_{RP}\phi$. This leads to two coupled equations; solving these with

initial conditions $C_S(0)$ and $C_T(0)$ we find

$$C_{Sn}(t) = C_S(0)\{\cos \omega t -$$
$$(iJ/\omega) \sin \omega t\} - C_T(0)a_n \sin \omega t \tag{13}$$

where $\omega = (J^2 + a_n{}^2)^{1/2}$ and

$$a_n = \langle S\chi_n | H' | T_0\chi_n \rangle =$$
$$\tfrac{1}{2}\{\Delta g \beta_e \hbar^{-1} H_0 + \textstyle\sum_j{}^a A_j M_j - \sum_k{}^b A_k M_k\} \tag{14}$$

with $\Delta g = g_a - g_b$. The probability of finding the pair in the singlet state is

$$|C_{Sn}(t)|^2 = |C_S(0)|^2 +$$
$$\{|C_T(0)|^2 - |C_S(0)|^2\}(a_n/\omega)^2 \sin^2 \omega t \tag{15}$$

which gives for the special case of a singlet precursor with $C_S(0) = 1$, $C_T(0) = 0$

$$|C_{Sn}{}^S(t)|^2 = 1 - (a_n/\omega)^2 \sin^2 \omega t \tag{16a}$$

and for a triplet precursor

$$|C_{Sn}{}^T(t)|^2 = (a_n/\omega)^2 \sin^2 \omega t \tag{16b}$$

It may be argued that our initial conditions imply that the functions χ_n are eigenfunctions of the precursor, which may not generally be correct. In a following paper[17] we will give the general proof that mixing of the χ_n in the precursor does not affect the results whatsoever; therefore we may as well start with the χ_n.

A further condition for the validity of our treatment is that the radicals keep their phase relationship during the diffusive excursions, except for the effect of H'. This condition seems to be satisfied because spin–spin relaxation in radicals, which might destroy the spin correlation, is several orders of magnitude slower $(T_1 \sim 10^{-5}–10^{-6}$ sec) than the process of geminate recombination. In the following it will be assumed that recombination occurs only from the singlet state, so its probability is proportional to $|C_{Sn}(t)|^2$. This basic assumption of radical pair theory is certainly justified, when the triplet state is repulsive as in the case of the coupling of two H atoms or alkyl radicals. Apparently it holds also for most disproportionation reactions, because the resulting CIDNP spectra can be treated on an equal footing. There are, however, reactions known where products are formed in a triplet state, notably in radiolysis,[30] where fragments dissociate and recombine with large excess energy and in certain reactions of peroxy radicals where triplet state ketones are formed, as evidenced by chemiluminiscence.[30,31]

We have previously[10] averaged eq 16 over a distribution of lifetimes τ of the pair and obtained for the probability of product formation

$$P_n{}^S \propto 1 - 2a_n{}^2\tau^2/(1 + 4\omega^2\tau^2) \tag{17a}$$

$$P_n{}^T \propto 2a_n{}^2\tau^2/(1 + 4\omega^2\tau^2) \tag{17b}$$

These formulas may still be useful in the case of biradicals[32] and other cases where the fragments disappear by first-order kinetics. For freely diffusing radical pairs, however, the recombination reaction cannot strictly be described with first-order rate constants and we will now examine this process in more detail.

(29) P. W. Atkins and D. Kivelson, *J. Chem. Phys.*, **44**, 169 (1966).

(30) For a recent review see J. K. Thomas, *Annu. Rev. Phys. Chem.*, **21**, 17 (1970).
(31) R. F. Vassil'ev, *Makromol. Chem.*, **126**, 231 (1969).
(32) R. Kaptein, M. Fráter-Schröder, and L. J. Oosterhoff, *Chem. Phys. Lett.*, **12**, 16 (1971).

3. Diffusion and Recombination of Radical Pairs

At large separations the motion of the pair can be treated classically and is governed by stochastic processes. Using the theory of random flights,[33] Noyes[13c] showed that the probability of the first reencounter between t and $t + dt$ for a pair, separating from an encounter at $t = 0$, is $f(t) \, dt$ where

$$f(t) = mt^{-3/2}e^{-\pi m^2/p^2 t} \quad (18)$$

p (Noyes:β) is the total probability of at least one reencounter: $p = \int_0^\infty f(t) \, dt$. For long times $f(t) \sim mt^{-3/2}$. The exponential factor ensures that $f(t)$ drops to zero for $t = 0$; the exact behavior at short times, however, is not very important. Both p and m can be expressed in the basic quantities ρ (the encounter diameter), σ (the root mean square displacement for relative diffusive motion), and ν (the frequency of relative diffusive displacements)

$$p \sim 1 - (^1/_2 + 3\rho/2\sigma)^{-1} \quad (19)$$

$$m = 1.036(1 - p)^2(\rho/\sigma)^2/\nu^{1/2} \quad (20)$$

For small radicals in ordinary solvents ν will be about 10^{11} sec^{-1}; σ will be equal to ρ or may be smaller, giving $0.5 \leq p < 1$ and $m \sim 10^{-6}$ sec$^{1/2}$ (the ratio ρ/σ does not affect m very much).

Let λ be the probability for recombination during a singlet encounter; then for small S–T transition probabilities, the chance of product formation during a first reencounter at time t is $\lambda |C_{Sn}(t)|^2 f(t)$. Radicals of a pair that fails to react during the first reencounter start again their random walk and have a new chance of meeting each other. Setting $\lambda_n(t) = \lambda |C_{Sn}(t)|^2$, the probability for recombination in the interval $(t, t + dt)$ becomes $P_n(t) \, dt$ with

$$P_n(t) = \lambda_n(t)f(t) + \int_0^t dt_1 \lambda_n(t - t_1) \times$$
$$\{1 - \lambda_n(t_1)\} f(t - t_1)f(t_1) +$$
$$\int_0^t dt_2 \lambda_n(t - t_2)f(t - t_2) \int_0^{t_2} dt_1 \{1 - \lambda_n(t_2 - t_1)\} \times$$
$$\{1 - \lambda_n(t_1)\} f(t_2 - t_1)f(t_1) + \ldots \quad (21)$$

where t_1, t_2, … are times of the first, second, … unsuccessful encounters. We shall discuss approximations to this rather unwieldy expression for the cases of S, T, and F precursors (F: pairs formed by encounters of free radicals with uncorrelated spins).

3.1. S Precursor. For small radicals both λ and $|C_{Sn}^S(t)|^2$ will be close to unity so that we may neglect all but the first term in eq 21. The total fraction of pairs, with nuclear state n that recombines, becomes $P_n^S = \int_0^\infty \lambda |C_{Sn}^S(t)|^2 f(t) \, dt$. This integral can be evaluated with (16a) and (18) giving

$$P_n^S = \lambda(p - m\pi^{1/2}a_n^2\omega^{-3/2}) = \lambda(p - x_n) \quad (22)$$

defining x_n. We have neglected terms of order $(m^4 \cdot a_n^2 p^{-3})$, which are several orders of magnitude smaller than x_n. For an estimate of the polarization enhancement we use $m = 10^{-6}$ sec$^{1/2}$, $a_n = 2 \times 10^8$ radians/sec, $J = 6 \times 10^8$ radians/sec, giving $x_n \sim 4 \times 10^{-3}$. If

(33) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943).

$p = \frac{1}{2}$ and the thermal polarization $(g_N \beta_N H_0/kT)$ is 10^{-5}, we find a respectable enhancement of about 800, which is of the order of the largest value that has been found experimentally.

3.2. T Precursor. As $|C_{Sn}^T(t)|^2$ (eq 16b) remains very small we have to consider the effect of the other terms in (21). The largest contributions come from unreactive encounters at times t_1, t_2, … close to zero. Counting only those contributions, we get for long times (*cf.* ref 13c)

$$P_n^T(t) = {}^1/_3\lambda |C_{Sn}^T(t)|^2 f(t)(1 + p + p^2 + p^3 + \ldots) =$$
$$[\lambda/3(1 - p)]|C_{Sn}^T(t)|^2 f(t) \quad (23)$$

The factor $^1/_3$ has been included, because only one of the T states is active. The fractional population of product level n becomes

$$P_n^T = \int_0^\infty P_n^T(t) \, dt = [\lambda/3(1 - p)]x_n \quad (24)$$

where x_n (defined in eq 22) enters with a positive sign. From eq 22 and 24 we find that $P_n^S - P_m^S = -3(1 - p) \cdot (P_n^T - P_m^T)$, so that the polarization is opposite to that of the S case. If we had put $J = 0$ we would have found $P_n^T \propto \sqrt{|a_n|}$, a result obtained by Adrian.[14] However, relative line intensities calculated with this form are rather bad in most cases and we get usually much better results when intermediate values of J are used.

3.3. F Precursor. The case of uncorrelated free-radical encounters is not so straightforward as the S and T cases. During their first encounter a fraction $\lambda |C_S(0)|^2$ of pairs with $M_S = 0$ combines and the remainder has a chance of meeting again, thereby giving polarization, because these pairs have more T than S character. Adrian's treatment amounts to multiplying the escaping fraction $1 - \lambda |C_S(0)|^2$ by $|C_{Sn}(t)|^2$ given in eq 15 and averaging the result over a distribution of all possible values of $|C_S(0)|^2$ and $|C_T(0)|^2$. We believe that this is not correct. We give a different procedure, the justification of which is given in Appendix B.

The product formed at the first encounter of a pair with uncorrelated spins is not polarized, because the effect of any S → T (or lower → upper level) transitions that may have occurred before is canceled by an equal number of T → S (or upper → lower level) transitions. As half of the first encounter pairs will have $M_S = 0$, the fraction that combines is $^1/_2\lambda\langle|C_S(0)|^2\rangle = ^1/_4\lambda$, because the singlet fraction $|C_S(0)|^2$ is a random number between 0 and 1, so its mean value is $^1/_2$. The recombination probability at the next encounter is $^1/_2 \lambda \langle|C_{Sn}^F(t)|^2\rangle f(t)$ where

$$\langle|C_{Sn}^F(t)|^2\rangle = ^1/_2\{(1 - \lambda)|C_{Sn}^S(t)|^2 + |C_{Sn}^T(t)|^2\} \quad (25)$$

Equation 25 is derived in Appendix B; $|C_{Sn}^S(t)|^2$ and $|C_{Sn}^T(t)|^2$ are given by eq 16. As an interpretation of (25) one might say that after a collision *the pairs separate behaving partly as singlets and partly as triplets*. Taking into account subsequent encounters with t_1, t_2, … ~ 0, we obtain from (21), similarly to the T case

$$P_n^F(t) = \frac{^1/_2\lambda}{1 - p\{1 - ^1/_2\lambda(1 - \lambda)\}}\langle|C_{Sn}^F(t)|^2\rangle f(t) \quad (26)$$

and

$$P_n{}^F = \frac{1}{4}\lambda + \int_0^\infty P_n{}^F(t)\, dt =$$

$$\frac{1}{4}\lambda\left[1 + \frac{1}{1 - p\{1 - \frac{1}{2}\lambda(1 - \lambda)\}}\{p(1 - \lambda) + \lambda x_n\}\right] \tag{27}$$

where we have included the initially formed product. For $\lambda = 1$, eq 27 takes the simple form

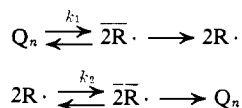$$P_n{}^F = \frac{1}{4} + \frac{1}{4}(1 - p)^{-1}x_n \tag{28}$$

It is seen that the polarization per molecule of product formed is smaller than for a T precursor, but, in contrast to results of other treatments,[12,14] it may become *larger* than for an S precursor. Qualitatively the polarization is similar to the T case; this is in accord with intuitive predictions by Gerhart and Ostermann[34] and by Closs[9] and with experimental results.[9,15b]

A remark on the viscosity dependence of the polarization seems to be in order. The quantity p can be estimated by various models,[13c] leading to expressions similar to eq 19. All models will agree that p becomes larger (closer to unity) when the viscosity increases, because σ (the diffusion step) decreases. This has been confirmed experimentally in studies on the cage effect.[35] The quantity m (eq 20) will not be very much affected by viscosity. Consequently, our model predicts that for an S precursor CIDNP intensities will not change very much by changing viscosity (whereas cage recombination yields may increase). However, polarization in the F and T case is predicted to become larger in more viscous solvents, due to the additional factor depending on p (in the T case $(1 - p)^{-1}$).

In the remainder of this section the special case of thermal equilibrium is discussed in the light of the diffusion model. Reactions competing with geminate recombination are treated in a subsequent paper.[36]

3.4. Thermal Equilibrium. When a dimer (Q) is in thermal equilibrium with its radical monomers, there can be no enhanced polarization according to general thermodynamic principles. Hence polarization originating from geminate recombinations (S case) must be exactly canceled by that of free-radical encounters (F case). We have the situation depicted in Scheme I.

Scheme I

$$Q_n \underset{}{\overset{k_1}{\rightleftharpoons}} \overline{2R \cdot} \longrightarrow 2R \cdot$$

$$2R \cdot \underset{}{\overset{k_2}{\rightleftharpoons}} \overline{2R \cdot} \longrightarrow Q_n$$

We shall neglect Boltzmann differences and consider the case where the lifetime of the radicals is much longer than their relaxation times, so we can neglect polarization in the free radicals. The rate of formation of encounter pairs r_2 is then independent of n. We can write the steady-state condition for the populations of Q

$$dQ_n/dt = -k_1(1 - P_n{}^S)Q_n - (Q_n - Q_n{}^0)T_1{}^{-1} + P_n{}^F r_2 = 0$$

$$Q_n = \frac{Q_n{}^0 + P_n{}^F r_2 T_1}{(1 - P_n{}^S)k_1 T_1 + 1} \tag{29}$$

(34) F. Gerhart and G. Ostermann, *Tetrahedron Lett.*, 4705 (1969).
(35) *Cf.* O. Dobis, J. M. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 278 (1968).
(36) R. Kaptein, *ibid.*, **94**, 6262 (1972).

$Q_n{}^0 = Q^0$ is the equilibrium population of the levels of Q and T_1 is a relaxation time. We consider the case where $\lambda = 1$, because eq 22 is strictly valid only for this case, so $P_n{}^S = p - x_n$ and $P_n{}^F$ is given by eq 28. The steady-state assumption imposes a further condition on Q^0

$$k_1(1 - p)Q^0 = \frac{1}{4}r_2 \tag{30}$$

Substituting (22), (28), and (30) in (29) we have the result

$$Q_n = \frac{r_2}{4(1 - p)k_1}\frac{\{1 + (1 - p + x_n)k_1 T_1\}}{\{1 + (1 - p + x_n)k_1 T_1\}} = Q^0 \tag{31}$$

and indeed there is no polarization. Thus our model reproduces the expectations made on general thermodynamic grounds for this case. Note that this result (31) would not have been obtained if other forms for $P_n{}^F$ had been used.[14]

4. CIDNP Intensities and Enhancement Factors

All relevant quantities can now be obtained from the P_n, the fractional population of recombination product level n, calculated in the preceding section. Recombination products (P) and products of radicals that escape the "cage" by diffusion (D products) are treated respectively (see Scheme II).

Scheme II
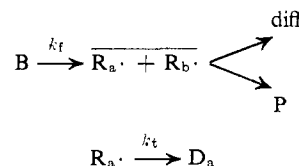
We shall first consider first-order spectra, where the functions χ_n are correct eigenfunctions for the product and afterward see how second-order effects can be handled.

4.1. Recombination and Disproportionations Products (P). Usually the nmr signal of a quasi-steady-state concentration of polarized product is measured. The intensity *vs.* time curve goes through a maximum; it is built up in a time corresponding to the relaxation time of the product, $T_1{}^P$ (photochemical reactions), or to the sample warming-up time (thermal reactions) if this time is longer than $T_1{}^P$; it falls off due to consumption of initiator. The intensity I_{mn} is proportional to the population difference of levels m and n, $I_{mn} \propto N_m - N_n$. The steady-state condition for this difference is

$$\frac{d}{dt}(N_m - N_n) = r_f(P_m - P_n) -$$

$$\frac{\{(N_m - N_n) - (N_m{}^0 - N_n{}^0)\}}{T_{1mn}{}^P} = 0 \tag{32}$$

$$(N_m - N_n) - (N_m{}^0 - N_n{}^0) = r_f T_{1mn}{}^P(P_m - P_n) \tag{33}$$

r_f is the rate of radical-pair formation and $T_{1mn}{}^P$ is the nuclear relaxation time of line mn of P (usually in the range 2-20 sec). The population difference at thermal equilibrium of the accumulated product at time t' is

$$N_m{}^0 - N_n{}^0 = \frac{\sum_n P_n}{L}\frac{g_N\beta_N H_0}{kT}\int_0^{t'} r_f(t)\, dt \tag{34}$$

where $L = \Pi_i(2I_i + 1)$, the total number of levels of P.

From (33) and (34) we obtain for the intensity enhancement at the maximum of the curve (at time t')

$$\frac{I_{mn} - I_{mn}^0}{I_{mn}^0} = V_{mn}T_{1mn}^{\mathrm{P}}f \qquad (35)$$

I_{mn}^0 is the intensity after quenching of the reaction; $f = r_f(t')/\int_0^{t'} r_f(t)\,dt$; V_{mn} is the theoretical enhancement factor per molecule P formed, first introduced by Closs[5,37,38]

$$V_{mn} = \frac{(P_m - P_n)}{\sum_n P_n}\frac{LkT}{g_N\beta_N H_0} \qquad (36)$$

with P_n given in eq 22 and 24. For the S case $\sum_n P_n = L\lambda p$ for $x_n \ll p$; hence

$$V_{mn}^{\mathrm{S}} = \frac{-(x_m - x_n)}{p}\cdot\frac{kT}{g_N\beta_N H_0} \qquad (37)$$

For the T case

$$V_{mn}^{\mathrm{T}} = \frac{(x_m - x_n)}{\sum_n x_n}\cdot\frac{kT}{g_N\beta_N H_0} \qquad (38)$$

As $\sum_n x_n$ is of the same order as $(x_m - x_n)$ enormous enhancement factors (10^4–10^5) result from this definition. This is, however, rather meaningless, when there are contributions from intersystem crossing via other pathways. This difficulty could be avoided by defining an enhancement factor per radical pair formed

$$V_{mn}' = (P_m - P_n)kT/g_N\beta_N H_0 \qquad (39)$$

which could be related to the loss of precursor signal intensity, $I_{mn}(B_0) - I_{mn}(B_{t'})$

$$\frac{I_{mn} - I_{mn}^0}{I_{mn}(B_0) - I_{mn}(B_{t'})} = V_{mn}'T_{1mn}^{\mathrm{P}}f \qquad (40)$$

Unfortunately, $I(B_0) - I(B_{t'})$ is often more difficult to obtain experimentally than I^0, the intensity of a newly formed product.

In photochemical reactions, r_f is frequently independent of the precursor concentration and the CIDNP signal is constant over an extended time range. In that case $\int_0^{t'} r_f(t)\,dt = r_f t'$ and $f = 1/t'$; furthermore if $I_{mn} \gg I_{mn}^0$, the relation of V_{mn} with experimental quantities is particularly simple

$$V_{mn} = I_{mn}/I_{mn}^0\cdot t'/T_{1mn}^{\mathrm{P}} \qquad (41)$$

where T_{mn}^0 is measured at $t' \gg T_{1mn}^{\mathrm{P}}$. This form has been used recently by Lehnig and Fischer.[15b] For thermal reactions (S case) one may use $f = k_f B_{t'}/(B_0 - B_{t'})$, B_0 and $B_{t'}$ being the precursor concentrations at $t = 0$ and $t = t'$. Equation 40 then takes the simple form

$$V_{mn}' = \frac{I_{mn}}{I_{mn}(B_{t'})T_{1mn}^{\mathrm{P}}k_f} \qquad (42)$$

relating V' with the intensity of a precursor transition at time t'. This expression (42) can be conveniently

(37) Closs[5] actually used $V_{mn} = (P_m - P_n)/(P_m + P_n)\langle I_z\rangle_0$, which does not seem to be properly normalized. For the S case both definitions amount to the same.

(38) The enhancement factor V_{max}, introduced by Fischer,[2a,b] is $V_{max} = (I_{mn} - I_{mn}^0)/I_{mn}^0$. Previously[4,10b] we have used this definition.

used in thermal reactions. For the F case r_f is a function of $k_f B_{t'}$, radical concentrations, and the rate constants for diffusion-controlled encounters.

In eq 32 we have assigned a relaxation time T_{1mn}^{P} to every line mn in the spectrum of P. This is a simplification because relaxation cannot generally be described with a single time constant for a transition mn; one should actually solve the coupled relaxation equations, which present a formidable problem in complex spectra (cf. ref 39). Instead one often makes the further simplification of setting $T_{1mn}^{\mathrm{P}} = T_1^{\mathrm{P}}$ where T_1^{P} is an "average" relaxation time, and indeed this procedure can be a serious source of errors, when calculated relative intensities are compared with experimental ones. As is discussed elsewhere[17] this problem is most serious when both net effects and multiplet effects are present and it renders the precise determination of g values difficult.

4.2. Escape Products (D). We mentioned that radicals escaping from geminate recombination carry a polarization opposite to that of P. Frequently this polarization is transferred to products of radical-transfer reactions, but it may also appear in combination products,[16] if it is not overshadowed by F-type polarization. We treat the case where the subsequent reaction can be described with a first-order rate constant k_t (cf. Scheme II). The steady-state condition for the populations of radical a escaping the "cage" is

$$\frac{d}{dt}(R_{ma} - R_{na}) = r_f\{(1 - P_{ma}) - (1 - P_{na})\} -$$
$$(R_{ma} - R_{na})\{(T_{1mn}^{\mathrm{R}})^{-1} + k_t + k_c\} = 0 \quad (43)$$

with T_{1mn}^{R}, the relaxation time for transition mn in the radical, k_c describing all other path by which the radical may disappear and

$$P_{ma} = \sum_{k,M_k}^{\mathrm{b}} P_m \qquad (44)$$

where the summation runs over all nuclear states of radical b. Similarly for product D

$$\frac{d}{dt}(D_{ma} - D_{na}) = k_t(R_{ma} - R_{na}) -$$
$$\{(D_{ma} - D_{na}) - (D_{ma}^0 - D_{na}^0)\}/T_{1mn}^{\mathrm{D}} = 0$$
$$(D_{ma} - D_{na}) - (D_{ma}^0 - D_{na}^0) =$$
$$\frac{(P_{ma} - P_{na})r_f k_t T_{1mn}^{\mathrm{D}}}{(T_{1mn}^{\mathrm{R}})^{-1} + k_t + k_c} \quad (45)$$

where $(D_{ma}^0 - D_{na}^0)$ is given by

$$D_{ma}^0 - D_{na}^0 =$$
$$\sum_n \frac{(1 - P_n)}{L_a}\cdot\frac{g_N\beta_N H_0}{kT}\cdot\frac{k_t}{k_t + k_c}\int_0^{t'} r_f(t)\,dt \quad (46)$$

Thus we have for the intensity enhancement of D

$$\frac{I_{mn} - I_{mn}^0}{I_{mn}^0} = V_{mn}^{\mathrm{D}}T_{1mn}^{\mathrm{D}}\frac{(k_t + k_c)}{(1/T_{1mn}^{\mathrm{R}} + k_t + k_c)}f \quad (47)$$

with

$$V_{mn}^{\mathrm{D}} = -\frac{(P_{ma} - P_{na})}{\sum_n(1 - P_n)}\frac{L_a kT}{g_N\beta_N H_0} \qquad (48)$$

(39) R. Freeman, S. Wittenkoek, and R. R. Ernst, J. Chem. Phys., 52, 1529 (1970).
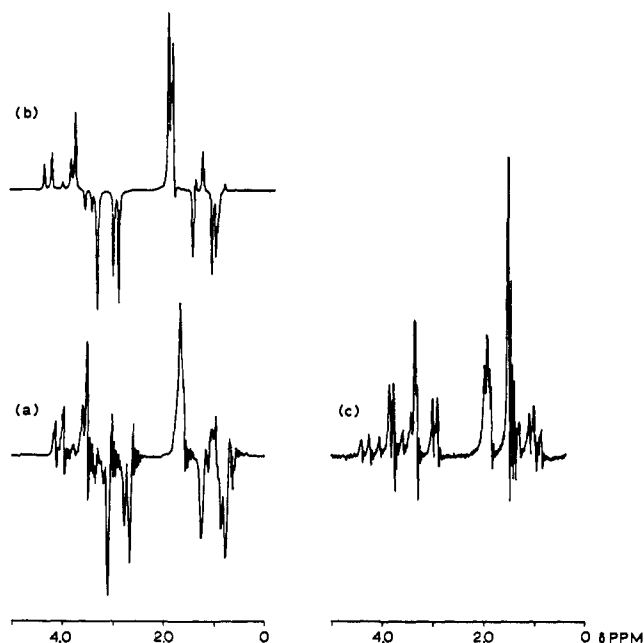
Figure 2. (a) 15.1-Mc nmr spectrum obtained during thermal decomposition of propionyl peroxide in hexachloroacetone; (b) computer simulated spectrum of ethyl chloride; and (c) normal 15.1-Mc spectrum of ethyl chloride. Because of computer limitations the simulated spectrum has been calculated for escape from the pair $CH_3CH_2 \cdot / R \cdot$, where $R \cdot$ is a dummy radical with the same g value as that of the ethyl radical.

By substituting (44) with (22), (24), or (27) formulas for the S, T, and F cases are obtained. Comparing eq 48 with 36, it is seen that D polarization has the opposite sign as to the states of fragment a.

In addition to nuclear relaxation in D, the intensities (47) depend further on relaxation in the radical, which tends to decrease the polarization in the simple treatment given here. Again the relaxation problem is more complex[40] and as noted in II[10a] there may also be effects due to electron polarization, which might even increase nuclear polarization *via* cross relaxation. However, there are not many experimental indications as to the importance of these effects, and it is surprising that eq 47 with the further assumption of equal relaxation times for different transitions, $T_{1mn}{}^D = T_1{}^D$ and $T_{1mn}{}^R = T_1{}^R$, often reproduces relative intensities rather well (*cf.* Figure 2).

Formulas equivalent to (47) have recently been used[15b,16,41] to estimate the magnitude of $T_1{}^R$ from CIDNP experiments. Values in the range $10^{-4}–10^{-3}$ sec were found, somewhat larger than commonly obtained in esr experiments. The reason may well be that $T_1{}^R$ is strongly field dependent, because the correlation times are of the order of $\omega_S{}^{-1}$ ($\omega_S = g \cdot \beta_e H_0 \hbar^{-1} = 6 \times 10^{10}$ radians/sec for $H_0 = 3300$ G), so that $T_1{}^R$ increases in the higher nmr fields.

4.3. Structure of CIDNP Spectra. When $J^2 \gg a_n{}^2$ intensities (33) and enhancement factors (36) are proportional to $a_m{}^2 - a_n{}^2$. We examine this case because it reveals some features which remain valid in the more general case. If we look at the spectrum of nucleus i of fragment a and consider a transition from

(40) *Cf.* J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).
(41) G. L. Closs and D. R. Paulson, *J. Amer. Chem. Soc.*, **92**, 7229 (1970).

$m = (\ldots M_i, M_j, M_k \ldots)$ to $n = (\ldots M_i - 1, M_j, M_k, \ldots)$ we obtain from (14)

$$I_{mn} \propto (a_m{}^2 - a_n{}^2) = \frac{1}{2}A_i[\Delta g\beta_e H_0\hbar^{-1} + \sum_{j \neq i}{}^a A_jM_j - \sum_k{}^b A_kM_k + A_i(M_i - \frac{1}{2})] \quad (49)$$

Except for the last term this expression has also been given by others.[27,15,12] It is instructive to consider the effect of the various terms of (49). The first term gives rise to a net effect, E or A, depending on the sign of ΔgA_i (note that $\Delta g = g_a - g_b$, so that this effect is opposite for nuclei of fragments a and b). As long as $J^2 \gg a_n{}^2$ for all a_n, eq 49 predicts that I_{mn} increases linearly with the field H_0 (V_{mn} independent of H_0). However, when J^2 is comparable to or smaller than $a_n{}^2$, the theory predicts a decrease of I_{mn} for higher fields (*cf.* ref 2). Thus there will be a maximum[42] in the curve I_{mn} *vs.* H_0.

The second term gives the multiplet effect; it depends on the sign of $A_iA_jM_j$ and, in a multiplet of nucleus i coupled to j, the lines are labeled according to $M_j = I_j, -I_j + 1, \ldots, +I_j$. The "phase" of the multiplet effect (E/A or A/E) depends further on the absolute sign[43] of the coupling constant J_{ij}, because this determines whether lines with positive M_j appear low or high field in the multiplet of i.

The third term gives a multiplet effect of opposite phase for coupling of i to a nucleus of radical b. As to the field dependence of multiplet effects, I_{mn} is independent of H_0 and $V_{mn} \propto (H_0)^{-1}$.

The last term is of no importance in pure first-order spectra, because transitions with $M_i > \frac{1}{2}$ and $M_i < \frac{1}{2}$ are degenerate and the effects cancel. However, in spectra exhibiting second-order effects (which is common in case of proton nmr) polarization due to this term appears. For instance, consider the A lines in A_nB spectra. If $I_B = \frac{1}{2}$ and $n > 1$ several transitions contribute to the A "doublet" and the degeneracy of these transitions is always lifted in such a way[44] that transitions with $M_i > \frac{1}{2}$ appear inside and with $M_i < \frac{1}{2}$ outside the "doublet" or *vice versa* depending on the sign of J_{AB}. Thus the lines of the doublet acquire, *e.g.*, A/E and E/A character, irrespective as to whether nucleus B was present in the pair or not. This might be called a "second order" multiplet effect, which may be superimposed on a "first order" multiplet effect. Examples hereof are given below (*cf.* Figures 3 and 4).

For D products we find, carrying out the summation of eq 44

$$P_{ma} - P_{na} = -\frac{\lambda m \pi^{1/2}}{\omega^{3/2}} \frac{1}{2} A_i\{\Delta g\beta_e H_0\hbar^{-1} + \sum_{j \neq i}{}^a A_jM_j + A_i(M_i - \frac{1}{2})\}L_b \quad (50)$$

(42) This has actually been observed for benzene formed during decomposition of benzoyl peroxide (H. Fischer and M. Lehnig, personal communication).
(43) Whereas normal nmr spectra are unaffected by a simultaneous change in sign of all J_{ij}, the CIDNP spectrum in the case of a pure multiplet effect ($\Delta g = 0$) is completely reversed. The proof is easily given by an extension of the proof given by Corio for normal spectra (ref 44, p 167), by noting that the populations $N_m \propto a_m{}^2$ in this case are invariant to a change in sign of all M_i, M_j, because $a_m{}^2$ is a bilinear form in M_iM_j.
(44) P. L. Corio, "Structure of High-Resolution Nmr Spectra," Academic Press, New York, N. Y., 1966, p 208.
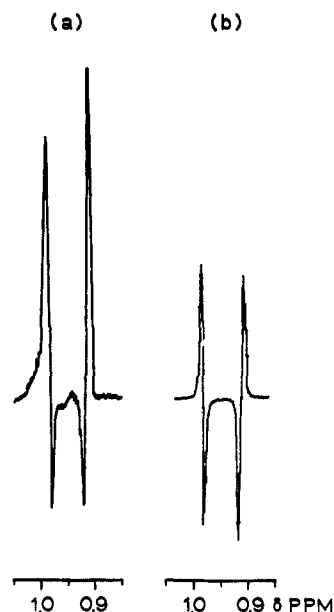
(a) **(b)**

1.0 0.9 1.0 0.9 δ PPM

Figure 3. (a) 100-Mc nmr spectrum obtained during thermal decomposition of azobisisobutyronitrile in thiophenol and (b) computer-simulated spectrum of 2-cyanopropane.

and as $\Sigma_n(1 - P_n) \sim L(1 - \lambda p)$ and $L = L_a L_b$ we have for the S case

$$V_{mn}{}^{D} = -\frac{\lambda}{(1 - \lambda p)}\frac{m\pi^{1/2}}{\omega^{3/2}}\frac{kT}{g_N\beta_N H_0}\,{}^{1}/_{2}A_i\{\Delta g\beta_e H_0 \hbar^{-1} +$$
$$\sum_{j\neq i}{}^{a}A_j M_j + A_i(M_i - {}^{1}/_{2})\}\quad (51)$$

Thus D_a product polarization is not effected by the presence of nuclei in radical b. Incidentally eq 51 shows that if there is no recombination ($\lambda = 0$) the D product is not polarized.

We may now give a summary of the predictions of radical-pair theory for high-field CIDNP spectra. 1. S precursor polarization is opposite to polarization of T and F precursors. 2. D product polarization is opposite to polarization in P products. Spectra of fragment D_a are independent of the presence of nuclei in radical b. 3. Net effect $\propto \Delta g A_i$. Sign is different for nuclei of fragments a and b. 4. Multiplet effect $\propto A_i{}^{a}A_j{}^{a}$ or $\propto A_i{}^{a}A_k{}^{b}$. The sign depends further on the sign of J_{ij} and J_{ik}. 5. "Second-order" multiplet effects may appear in spectra of magnetically equivalent nuclei, even when coupled to a nucleus not present in the radical pair. The sign depends on the sign of J_{ij} but not on the sign of A_i.

4.4. Simple Rules. The first four results can be taken together in two rules containing all sign reversals. Qualitative features of CIDNP spectra can be described with the signs of two quantities, Γ_{ne} for net effects and Γ_{me} for multiplet effects

$$\Gamma_{ne} = \mu\epsilon\Delta g A_i \quad \begin{cases} +, A \\ -, E \end{cases} \quad (52a)$$

$$\Gamma_{me} = \mu\epsilon A_i A_l J_{il}\sigma_{il} \quad \begin{cases} +, E/A \\ -, A/E \end{cases} \quad (52b)$$

where it is to be understood that the spectrum of nucleus i of fragment a is considered. μ, ϵ, and σ_{il} are labels indicating precursor multiplicity, P or D product, and presence of i and l in the same or different radicals

(a) **(b)**
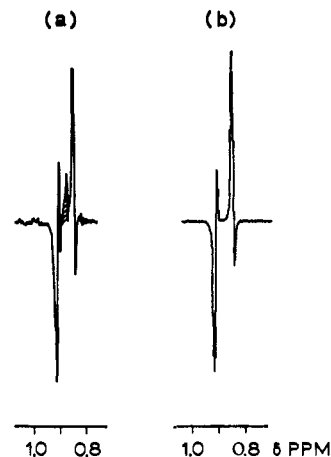
1.0 0.8 1.0 0.8 δ PPM

Figure 4. (a) High-field part of the 100-Mc nmr spectrum of isobutane formed from disproportionation of *tert*-butyl radicals. The shaded signal is due to the precursor; (b) computer simulation.

$$\mu \begin{cases} + \text{ for T and F precursor} \\ - \text{ for S precursor} \end{cases}$$

$$\epsilon \begin{cases} + \text{ for P products (recombination)} \\ - \text{ for D products (escape)} \end{cases}$$

$$\sigma_{il} \begin{cases} + \text{ when } i \text{ and } l \text{ reside in the same radical} \\ - \text{ when } i \text{ and } l \text{ reside in different radicals} \end{cases}$$

It is a striking fact that in almost all cases, where reaction conditions are unambiguous, CIDNP spectra can be qualitatively explained by the two simple rules (52). We have found them quite useful for instant determination of precursor multiplicities, signs of hf parameters, etc., from the spectra. The use of these rules will be illustrated with two examples.

(i) Methyl acetate formed during thermal decomposition of acetyl peroxide was reported[4] to show emission for the methoxy group: $\overline{CH_3\cdot + CH_3CO_2\cdot} \longrightarrow CH_3CO_2CH_3*$. In the methyl (a)–acetoxy (b) radical pair, the acetoxy radical undoubtedly has the larger g value, due to the presence of the oxygen atoms, so Δg is negative. A_i is also negative in the methyl radical and we are looking at a recombination product from a singlet precursor, so $\Gamma_{ne} = - + - - = -$, hence E. For the D product, methyl chloride, we have all minus signs, hence A.

(ii) From the decomposition of a cyclohexadienone peroxide[4] two *tert*-butyl radicals are formed which disproportionate to give isobutane and isobutene, both showing E/A multiplet effects. For the *tert*-butyl

$$2C(CH_3)_3\cdot \longrightarrow HC(CH_3)_3 + H_2C=C(CH_3)_2 \quad (53)$$
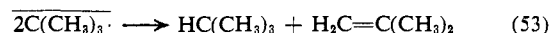
radical A is positive. In isobutane J_{il} is positive and the methine H is abstracted from the other radical so we have $\Gamma_{me} = - + + + + - = +$, E/A. For isobutene J_{il} is negative[45] and the splitting is due to protons of the same fragment, giving $\Gamma_{me} = - + + + + - + = +$, hence also E/A (but for different reasons).

When a small multiplet effect is superimposed on a large net effect, rule 52b may break down, because the apparent multiplet effect may be reversed. In that case and in the case of strongly coupled spectra it is better to employ computer simulation techniques.

(45) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nmr Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, Chapter 10.

4.5. Second-Order Spectra and Computer Simulation. When chemical shift differences are not much larger than the coupling constants J_{ij}, second-order effects appear in nmr spectra. The functions χ_n are then not eigenfunctions of the nuclear Hamiltonian of the product

$$H_P = \sum_i h_i I_{iz} + \sum_{i<j} J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j \qquad (54)$$

where h_i are chemical shifts relative to a reference signal. To describe the spectrum the eigenvalues $\Omega_\nu{}^P$ of H_P are obtained by the transformation

$$\mathbf{S}^{-1} H_P \mathbf{S} = \Omega^P (\Omega^P \text{ diagonal}) \qquad (55)$$

The eigenfunctions are

$$\chi_\nu = \sum_n S_{n\nu} \chi_n \qquad (56)$$

Line frequencies are given by $\Omega_\mu{}^P - \Omega_\nu{}^P$ and relative intensities by[46]

$$I_{\mu\nu} \propto |\langle \chi_\mu | \sum_i \gamma_i I_{xi} | \chi_\nu \rangle|^2 (P_\mu - P_\nu) \qquad (57)$$

The populations P_ν of the mixed states are calculated from the projections of $\phi_n(t)$ (eq 12) on the state χ_ν

$$|C_{S\nu}(t)|^2 = \sum_n |\langle S\chi_\nu | \phi_n(t) \rangle|^2 = \sum_n S_{n\nu}{}^2 |C_{Sn}(t)|^2 \qquad (58)$$
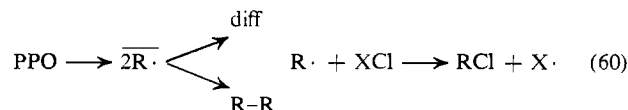
where the last step follows from (56) and the orthogonality of the χ_n. Along the lines of sections 3 this leads to

$$P_\mu - P_\nu = \sum_n (S_{n\mu}{}^2 - S_{n\nu}{}^2) P_n \qquad (59)$$

with P_n given by (22), (24), or (27) for S, T, and F cases. A nmr spectrum simulation program was modified[47] by incorporating (57) with (59) for relative CIDNP intensities. A few examples of computer simulations are shown below.

5. Examples

5.1. Ethyl Chloride at 15.1 Mc. The 100-Mc CIDNP spectrum of the thermal decomposition of propionyl peroxide (PPO) in hexachloroacetone has been given in I.[4] The spectrum shows A/E and E/A multiplet effects for ethyl chloride and butane, respectively, and is in accord with the formation of two ethyl radicals (R·) giving the reactions

$$\text{PPO} \longrightarrow \overline{2\text{R}\cdot} \overset{\text{diff}}{\underset{\text{R-R}}{\diagup\diagdown}} \quad \text{R}\cdot + \text{XCl} \longrightarrow \text{RCl} + \text{X}\cdot \qquad (60)$$
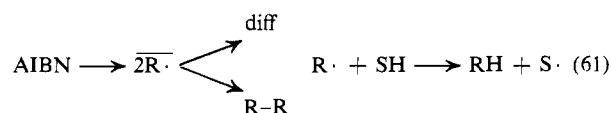
The 15.1-Mc spectrum (Varian DA-60, $H_0 = 3550$ G) is shown in Figure 2a together with a computer simulation (Figure 2b) and the normal 15-Mc spectrum of ethyl chloride (Figure 2c). Due to its greater solubility at the temperature of the reaction (110°), ethyl chloride appeared much stronger in the 100-Mc spectrum than butane; this is even more pronounced at 15.1 Mc because of cancellation of opposite polarization effects in nearly degenerate butane lines, so the spectrum of Figure 2a is almost completely that of ethyl chloride. The enhancement factor is 2500 ± 1000 (difficult to estimate for gases). It is about a factor 7 larger than at 100 Mc as expected for multiplet effects. The hf coupling constants of the ethyl radical are[48] $A(\text{CH}_3) = 26.9$ G, $A(\text{CH}_2) = -22.4$ G. For the simulated spectrum the best fit was obtained with $|J| = 6 \times 10^8$ radians/sec, but higher values did not change the spectrum dramatically. Values of $|J| < 10^8$ radians/sec gave worse results. Differences in relaxation times were not taken into account. The agreement with experiment is satisfactory, the largest deviations occurring in the region around 1 ppm, where butane may contribute (Figure 2a). The following can be inferred from the good agreement. (i) $S-T_\pm$ transitions do not contribute to the polarization. This was observed in several other systems run at 15 Mc as well. So these transitions are certainly unimportant in the higher field (14 and 23.5 kG), where CIDNP spectra are usually recorded. (ii) Relaxation effects in the radical are probably not important. (iii) Relaxation in the product also does not affect relative intensities in this case. Lines involving transitions between isolated levels, such as the strong line at 1.47 ppm, are expected to have a longer T_1 than others. This line, however, has completely vanished in a pure multiplet spectrum, because it has $M_j = 0$. If the mean time for escape of gaseous products from the sample is shorter than $T_1{}^D$, there would also be little dependence on relaxation.

5.2. 2-Cyanopropane. The 100-Mc spectrum (Varian HA-100 spectrometer) shown in Figure 3a is obtained during thermal decomposition of azobisisobutyronitrile (AIBN) in thiophenol (SH). The reactions are

$$\text{AIBN} \longrightarrow \overline{2\text{R}\cdot} \overset{\text{diff}}{\underset{\text{R-R}}{\diagup\diagdown}} \quad \text{R}\cdot + \text{SH} \longrightarrow \text{RH} + \text{S}\cdot \qquad (61)$$

where $\text{R}\cdot = (\text{CH}_3)_2\dot{\text{C}}\text{CN}$, $A(\text{CH}_3) = 20.3$ G,[49] and RH is 2-cyanopropane, normally giving a somewhat broadened doublet for the methyl groups at 0.95 ppm.

According to simple first-order arguments one would not expect polarization at all, because the splitting of the equivalent methyl groups is due to a proton not present in the pair. So we have a case of a pure second-order multiplet effect of the type discussed in section 4.3, caused by the term $A_i{}^2(M_i - 1/2)$ in eq 49. The "phase" is such as expected for an A_6B spectrum of a D product with positive J_{AB}, as can be seen from the computer simulation (Figure 3b). The experimental spectrum seems to have A character, but this is due to underlying unpolarized product, the enhancements being not very large in this case. The abstracted proton did not show polarization. Neither this nor other cases provide indications of polarization resulting from a transfer reaction itself.[34] Emission of chloroform ascribed to such a process[38,50] is better explained by a radical disproportionation reaction (F case) of $\text{CCl}_3\cdot$ with alkyl radicals.

5.3. Isobutane. In part I[4] we studied a reaction involving a pair of *tert*-butyl radicals, $A(\text{CH}_3) = 22.7$

(46) P. L. Corio, ref 44, p 164.

(47) We thank Dr. C. W. Haigh for a listing of LAME, a program employing magnetic equivalence factoring. We are indebted to Mr. J. A. den Hollander for making the modification.

(48) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(49) S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969).

(50) A. L. Buchachenko, S. V. Rykov, and A. V. Kessenick, *Zh. Fiz. Khim.*, **44**, 876 (1970).

G,[48] reaction 53. The 100-Mc spectrum of the iso-butane methyl groups is presented in Figure 4a.

Superimposed on the E/A doublet is a second-order multiplet effect, not to be confused with wiggles. The sign is opposite to that of Figure 3, because isobutane is a P product. The simulated spectrum of Figure 4b reproduces both of these effects. It may be noted that for the problem of two tert-butyl radicals (20 spins!) the use of magnetic equivalence factoring is imperative.

Conclusions

Radical pair theory can account for the coarse structure of CIDNP spectra, as well as for details of complex spectra. In the cases, which we have studied, the high-field spectra are not very sensitive to the dynamic model used for the description of the diffusion process. The spectra could be accommodated by both the diffusion model and the exponential averaging model.[10] However, in other cases,[51] which seem to require smaller values of the effective exchange integral J, the differences are more pronounced and the diffusion model gives a better description of relative line intensities.

Another discriminative feature of this model is the fact that relatively long-lived radical pairs are predicted to contribute to the polarization. As will be reported shortly,[36] studies of the time scale by means of competitive reactions of radical pairs also afford evidence in favor of the diffusion model.

Acknowledgment. The author is very grateful to Professor L. J. Oosterhoff for his valuable advice and for his continuous interest in this work. He wishes to thank Professors H. R. Ward, R. G. Lawler, G. L. Closs, H. Fischer, F. J. Adrian, and Dr. S. H. Glarum for making available results in advance of publication. Helpful conversations with Professors H. R. Ward and H. Fischer and numerous stimulating discussions with Mr. J. A. den Hollander and Dr. R. A. van Santen are gratefully acknowledged. The author is indebted to Mr. F. J. J. de Kanter for assistance with the computer simulations and to the Netherlands Organization for the Advancement of Pure Research (ZWO) for financial support.

Appendix A

Spin–Orbit Coupling in Radical Pairs. Spin–orbit interactions are responsible for intersystem crossing in molecules in excited states.[52,53] If they were equally important in radical pairs they could seriously detract from the effects of the hf interactions. The spin–orbit coupling Hamiltonian may be written

$$H_{\mathrm{LS}} = \sum_i \zeta_i \mathbf{L}_i \cdot \mathbf{S}_i \qquad (A1)$$

$\mathbf{L}_i$ is the orbital angular momentum operator for electron i and ζ_i is a constant, depending on the nucleus, in the field of which the electron is moving. Other contributions to H_{LS} are usually negligible.[52,53] We are looking for matrix elements H_{ST} connecting S and T states of the radical pair in the ground-state electronic

(51) G. L. Closs, personal communication.
(52) (a) H. F. Hameka and L. J. Oosterhoff, Mol. Phys., 1, 358 (1958); (b) H. F. Hameka in "The Triplet State," A. Zahlan, Ed., Cambridge University Press, New York, N. Y., 1967, p 2.
(53) (a) J. H. Van der Waals and M. S. De Groot, ref 52b, p 101; (b) W. S. Veeman and J. H. van der Waals, Mol. Phys., 18, 63 (1970).

configuration. Up to second order[18]

$$H_{\mathrm{ST}} = \langle \Psi_{0\mathrm{S}} | H | \Psi_{0\mathrm{T}} \rangle - \sum_j{}' \frac{\langle \Psi_{0\mathrm{S}} | H | \Psi_j \rangle \langle \Psi_j | H | \Psi_{0\mathrm{T}} \rangle}{E_j - E_0} \qquad (A2)$$

where $\Psi_{0\mathrm{S}}$ and $\Psi_{0\mathrm{T}}$ are ground-state singlet and triplet wave functions (space and spin) and H is the full Hamiltonian of eq 1. There are no first-order contributions of H_{LS} because this term mixes the ground state only with excited configurations. In second order the combined effects of H_{LS} and H_{HL} lead to deviations of the g values from the free electron value (Δg term), which have already been considered. Furthermore we have to worry about terms involving H_{LS} and H_{e} (eq 2) because these may become relatively large

$$H_{\mathrm{ST}} = - \sum_j{}' \frac{\langle \Psi_{0\mathrm{S}} | H_{\mathrm{LS}} | \Psi_{j\mathrm{T}} \rangle \langle \Psi_{j\mathrm{T}} | H_{\mathrm{e}} | \Psi_{0\mathrm{T}} \rangle}{E_j - E_0} \qquad (A3)$$

Consider a pair of radicals a and b with localized electrons. The angular momentum operators $L_{ui}{}^{\mathrm{a}}$ ($u = x, y, z$ at center a) are axial vectors that are antisymmetric with respect to reflection in a plane that contains the axis u. Hence $L_{ui}{}^{\mathrm{a}}$ mixes only symmetric (σ) with antisymmetric (α) states (local space symmetry at a). We need only consider one-center contributions of $L_{ui}{}^{\mathrm{a}}$; if the wave functions are labeled according to their spacial symmetry by $x_\mathrm{a} x_\mathrm{b}$ ($x_\mathrm{a} = \sigma$ or α), nonvanishing matrix elements of H_{LS} are

$$\langle \Psi_{0\mathrm{S}}(\sigma_\mathrm{a} x_\mathrm{b}) | L_{ui}{}^{\mathrm{a}} S_i | \Psi_{j\mathrm{T}}(\alpha_\mathrm{a} x_\mathrm{b}) \rangle \qquad (A4)$$

and similar expressions for center b. The operator H_e, however, is symmetric. Therefore, when its matrix element

$$\langle \Psi_{j\mathrm{T}}(\alpha_\mathrm{a} x_\mathrm{b}) | H_\mathrm{e} | \Psi_{0\mathrm{T}}(\sigma_\mathrm{a} x_\mathrm{b}) \rangle \qquad (A5)$$

is expanded in integrals over atomic orbitals, all one-center contributions vanish by symmetry and there are only contributions from two-center integrals involving orbitals of both a and b for relative orientations such that x_b is nonsymmetric.

The order of magnitude of H_{ST} in (A1) is $\zeta(\Delta E)^{-1} K_{\mathrm{ab}} \sim 10^{-3} K_{\mathrm{ab}}$ where K_{ab} is an electron repulsion integral, which is exponentially dependent on distance, similarly to the exchange integral J. Thus we conclude that at distances $r > r_0$, where J has become very small, S–T mixing by spin–orbit coupling of the type discussed here will be negligible. At short distances it might become relatively more important.

Appendix B

Free-Radical Encounters. We wish to examine the process of product-forming encounters of free radicals with initially uncorrelated spins. We make use of evolution operators $U(t,t_0)$ to describe the time evolution of wave functions.[54]

$$\Psi(t) = U(t,t_0)\Psi(t_0) \qquad (B1)$$

Considering only $M_\mathrm{S} = 0$ encounters (others are inreactive) we start with

$$\Psi(0) = C_\mathrm{S}(0)\Psi_{0\mathrm{S}} + C_\mathrm{T}(0)\Psi_{0\mathrm{T}} \qquad (B2)$$

where $\Psi_{0\mathrm{S}}$ and $\Psi_{0\mathrm{T}}$ are the same as in Appendix A (space and spin functions). The wave function after

(54) A. Messiah, "Quantum Mechanics," Vol. 1, North Holland Publishing Co., Amsterdam, 1967, p 310.

an encounter of duration t_0 is

$$\Psi(t_0) \;=\; U_{enc}(t_0)\Psi(0) \;=\; e^{-i\int_0^{t_0} H_{enc}(t)\,dt}\,\Psi(0) \quad \text{(B3)}$$

where H_{enc} represents the Hamiltonian during the encounter, describing the process of product formation by energy transfer to surrounding solvent molecules, which we do not consider explicitly. When product formation occurs only from the singlet state, the action of U_{enc} on Ψ_{0S} and Ψ_{0T} can be described as follows

$$U_{enc}(t_0)\Psi_{0S} \;=\; e^{-i\alpha}(1 + \eta^2)^{-1/2}[\Psi_{0S} + \eta\Psi_{PS}] \quad \text{(B4a)}$$

$$U_{enc}(t_0)\Psi_{0T} \;=\; e^{-i\beta}\Psi_{0T} \quad \text{(B4b)}$$

where Ψ_{PS} represents a lower vibrational state of the product and α and β are phase angles. After the encounter $\Psi(t)$ is given by (B1) with $U = U_{RP}(t,t_0)$, describing S–T mixing in the radical pair. In terms of the evolution operator the coefficients of eq 16 are

$$C_S{}^S(t) \;=\; \langle \Psi_{0S}| U_{RP}(t,t_0)|\Psi_{0S}\rangle \quad \text{(B5a)}$$

$$C_S{}^T(t) \;=\; \langle \Psi_{0S}| U_{RP}(t,t_0)|\Psi_{0T}\rangle \quad \text{(B5b)}$$

where we have suppressed the label n. The fraction

that gives product during the first encounter is

$$|\langle \Psi_{PS}|\Psi(t_0)\rangle|^2 \;=\; \frac{\eta^2}{1 + \eta^2}|C_S(0)|^2 \;=\; \lambda|C_S(0)|^2 \quad \text{(B6)}$$

where we have used the orthogonality $\langle \Psi_{PS}|\Psi_{0S}\rangle = 0$. Using (B1–5) the quantity of interest, $|C_S{}^F(t)|^2$, can be obtained

$$C_S{}^F(t) = \langle \Psi_{0S}|\Psi(t)\rangle = e^{-i\alpha}(1 + \eta^2)^{-1/2} \times$$
$$C_S(0)C_S{}^S(t) + e^{-i\beta}C_T(0)C_S{}^T(t) \quad \text{(B7)}$$

$$|C_S{}^F(t)|^2 = (1 + \eta^2)^{-1}|C_S(0)|^2|C_S{}^S(t)|^2 +$$
$$|C_T(0)|^2|C_S{}^T(t)|^2 +$$
$$e^{i\gamma}(1 + \eta^2)^{-1/2}C_S{}^*(0)C_S{}^S(t)^*C_T(0)C_S{}^T(t) + cc \quad \text{(B8)}$$

where $\gamma = \alpha - \beta$ and cc denotes complex conjugate. The last two terms of (B8) vanish when this expression is averaged over the random phases of $C_S(0)$, $C_T(0)$, and γ. Averaging also over all possible values of $|C_S(0)|^2$ and $|C_T(0)|^2$ and using the identity $(1 + \eta^2)^{-1} = 1 - \lambda$ (from B6) we obtain

$$\langle |C_S{}^F(t)|^2\rangle = \tfrac{1}{2}[(1 - \lambda)|C_S{}^S(t)|^2 + |C_S{}^T(t)|^2] \quad \text{(B9)}$$

This expression has been used in section 3.

Chemically Induced Dynamic Nuclear Polarization. IX. Reactions Competitive with Geminate Recombination of Radical Pairs

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Contribution from the Department of Theoretical Organic Chemistry, University of Leiden, Leiden, The Netherlands. Received July 22, 1971

Abstract: A previously developed theory of CIDNP in high magnetic fields is extended to describe cases where rapid reactions occur by which radical pairs are transformed into other pairs. Since the newly formed pairs remain spin-correlated and have a chance of reencounter during their random walk diffusion, nuclear polarization can occur for products of these radical pairs and of pairs formed by subsequent reactions. It is shown that polarization in products of a certain pair may originate from S–T$_0$ mixing in preceding pairs (memory effect). It is found that both product yields and polarization for products of secondary pairs depend on $\sqrt{k}$ in the region of small k (k is the first-order rate constant for the reaction). This result is typical for the diffusion model. Calculations indicate that secondary pairs formed after relatively long times (up to 10^{-6} sec) could still give rise to observable CIDNP effects in favorable cases. Experimental examples of the reactions discussed here are radical scavenging reactions (transfer reaction of isopropyl radicals with bromotrichloromethane), fragmentations (decarboxylation of acetoxy radicals), and rearrangements (cyclopropylcarbinyl → butenyl). It appears that CIDNP can be used to study fast radical reactions over a wide range of rate constants (10^6–10^{10} sec^{-1}), although at present uncertainties in the determination of k are rather large.

1. Introduction

Potentially CIDNP is an extremely useful tool for the study of fast reactions that compete with geminate recombination of radical pairs. It is the purpose of this paper to give a discussion of polarization effects in the case of competitive reactions, by an extension of a diffusion model for CIDNP given previously in VIII.[2]

(1) Address correspondence to Shell Research Laboratories, Amsterdam, The Netherlands.
(2) (a) Part VIII: R. Kaptein, *J. Amer. Chem. Soc.*, 94, 6251 (1972); (b) *cf.* also, F. J. Adrian, *J. Chem. Phys.*, 53, 3374 (1970); 54, 3912 (1971).

This model is based on singlet (S)–triplet (T) mixing in radical pairs, induced by magnetic (Zeeman and hyperfine) interactions, and its effect on the geminate recombination probabilities of radical pairs. *Via* the hyperfine interactions with the electron spins, nuclear spins have a handle on the electronic multiplicity of the pairs. Apart from electronic and possibly steric effects during reencounters, geminate recombination obviously depends also on the reencounter probability of the pairs, which we have treated[2] in terms of a random-walk diffusion model.[3] We will limit ourselves

(3) (a) R. M. Noyes, *ibid.*, 22, 1349 (1954); (b) *J. Amer. Chem. Soc.*, 77, 2042 (1955); (c) *ibid.*, 78, 5486 (1956).