volved in our treatment. Also, some of the parameters which enter the theory are unknown at present. Yet, this work shows that CIDNP can be fruitfully applied to the study of reactions competing with geminate pair recombinations over a wide range of rate constants ($10^6 < k < 10^{10}$ sec $^{-1}$).

The present extension of the diffusion model accounts for some experimental observations, which could otherwise hardly be explained by radical pair theory. In particular, predictions of CIDNP effects due to long-time spin-correlation effects observed in products, which are formed in extremely low yields, are characteristic of this model.

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Chemically Induced Dynamic Nuclear Polarization. X. On the Magnetic Field Dependence

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Abstract: The radical pair theory of high-field CIDNP is generalized to describe nuclear polarization originating from chemical reactions in magnetic fields of any strength. In low fields mixing of electronic singlet (S) with three triplet states (T_+, T_-, and T_0) of the radical pair has to be considered, whereas in high field only S–T_0 mixing. Starting from pure S or T states the time development of the spin states is described by the Schrödinger equation in which a time-independent Hamiltonian is employed, containing isotropic Zeeman, exchange, and hyperfine interaction terms. It is assumed that the radical pairs undergo random-walk diffusion (giving a $t^{-3/2}$ time dependence for the reencounter probability) and that recombination occurs only from the S state. It is found that low-field CIDNP spectra depend on the probability of reaction during a singlet encounter (λ). Furthermore, S and T precursors (of radical pairs) give rise to opposite polarization in all magnetic fields, whereas recombination and "escape" products give opposite behavior only in high fields and in zero field, but not in low fields. The zero-field problem is treated in an Appendix. Experimental low-field CIDNP spectra recorded on an A-60 spectrometer after photolysis of solutions of propionyl peroxide and of diisopropyl ketone in an auxiliary magnet show good agreement with computer-simulated spectra, when it is assumed that sample transfer to the spectrometer field occurs adiabatically. In particular, the theory can account for the observed oscillations in the polarization *vs.* magnetic field curve.

1. Introduction

The magnetic field dependence of CIDNP has not yet received much attention. In particular, observation of polarization effects in the low-field region (lower than a few thousand gauss) has been reported in only a few studies.[2-4] In most experimental work on CIDNP, reactions are run in the nmr spectrometer probe, *i.e.*, in fields of 14 or 23.5 kG. CIDNP effects have been observed also in nmr spectra after carrying out the reaction in a separate magnet,[2a] in "zero" field,[2b] and in the low field near the spectrometer magnet[3] and furthermore in a spectrometer[4] run at fields below 100 G. Observation of zero-field polarization was actually one of the most obvious pieces of evidence against the originally proposed[5] Overhauser-type mechanism of CIDNP. This mechanism has been replaced by the radical-pair mechanism[6-8] (nuclear spin dependent singlet (S)–triplet (T) mixing in radical pairs). High-field experiments can be explained by considering the mixing of S with T_0 only. This simplification is no longer justified in low magnetic fields, where mixing of S with all three T states has to be considered.

Therefore, a study of low-field CIDNP is of interest, because it can be expected to give more detailed information, *e.g.*, on the behavior (and sign) of the exchange integral *J*, which affects the energy of S and T states of the radical pair. It may also provide a more critical test of the various theoretical models of CIDNP than the high-field experiments.

A first attempt to give a general theory of CIDNP has been made by Glarum.[9] It will appear, however, that his model cannot accommodate all of our experimental results.

In this paper we present an extension of a previously[8] given model of the radical pair mechanism, in which

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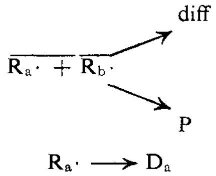
diffusion of radical pairs has been taken into account. Predictions of the theory will be compared with experimental CIDNP spectra in the case of some photochemical reactions, carried out in an auxiliary magnet, after rapid transfer to the spectrometer probe (Varian A-60, $H_0 = 14$ kG); spectra were run before relaxation was completed.

2. General Formalism

2.1. Radical Pair Theory. Radical pair theory is concerned with S–T mixing and its effects on the reaction probabilities of radical pairs. A general reaction scheme is depicted in Scheme I. The radical pair may be formed from a singlet (S) precursor, a triplet (T) precursor, or by encounters of free radicals with uncorrelated spins (F). We have to determine the populations of the nuclear spin states of the recombination product P and of the product D_a (and similarly D_b) formed from radicals, escaped by diffusion (diff).

Scheme I



When the radicals are next-nearest neighbors the mutual interaction between the electron spins (expressed by the exchange interaction J) is very large. When diffusion sets in, J will diminish rapidly with separation. As we have done previously,[7,8] we will describe this by a sudden decrease (at time $t = 0$) of J to a low (constant) value comparable to or smaller than the hyperfine interactions. Singlet–triplet mixing induced by the hyperfine and Zeeman fields acting on the electrons becomes now possible. The time-dependent mixing of states follows from the Schrödinger equation, which now generally leads to a set of more than two coupled equations (mixing of S with T_+, T_0, and T_-). The problem can be solved in three stages. (a) The Hamiltonian matrix for the radical pair in the magnetic field H_r (in which the reaction is carried out) is set up and diagonalized. (b) With the eigenvalues and eigenvectors obtained in stage a, the populations of the product levels are calculated by a procedure similar to the one given in VIII (diffusion model). (c) From the populations calculated in the field H_r the populations of the nuclear states in the spectrometer field H_0 are determined (nuclear states in H_0 may differ from those in H_r).

There are two limiting cases for this last step:[9] (i) the adiabatic case (slow limit) in which populations are transferred according to the correlation diagram connecting low-field with high-field levels and (ii) the nonadiabatic case (fast limit) in which case populations of H_r states may be distributed over several H_0 states. Experiments indicate that in practice the transfer is predominantly adiabatic.

2.2. Stage a. The Hamiltonian Matrix. As we have discussed in VIII, nuclear-spin-dependent S–T mixing occurs probably at separations larger than 6 Å in freely tumbling and diffusing radical pairs. At these separations g factors and hyperfine (hf) coupling constants (A_i) have taken their normal free-radical values. Since intersystem crossing is much slower than the tumbling rate in most solvents, we keep only isotropic terms in the spin Hamiltonian[8] for the radical pair in the field H_r in which it is generated

$$H_{RP} = H^\circ + H' \tag{1}$$

$$H^\circ = g\beta_e\hbar^{-1}H_r(S_{1z} + S_{2z}) - J({}^1/_2 + 2\mathbf{S}_1\cdot\mathbf{S}_2) + {}^1/_2(\mathbf{S}_1 + \mathbf{S}_2)\Big(\sum_j{}^a A_j\mathbf{I}_j + \sum_k{}^b A_k\mathbf{I}_k\Big) \tag{1a}$$

$$H' = {}^1/_2\Delta g\beta_e\hbar^{-1}H_r(S_{1z} - S_{2z}) + {}^1/_2(\mathbf{S}_1 - \mathbf{S}_2)\Big(\sum_j{}^a A_j\mathbf{I}_j - \sum_k{}^b A_k\mathbf{I}_k\Big) \tag{1b}$$

where $g = {}^1/_2(g_a + g_b)$ and $\Delta g = g_a - g_b$ (g factors of radicals a and b); Σ^a and Σ^b run over the nuclei of a and b, respectively; J (exchange integral) and A_j (hyperfine coupling constant) are expressed in radians sec^{-1}. We use a direct product basis of electronic singlet and triplet states $|\sigma\rangle$ and nuclear spin states $|n\rangle : |\sigma n\rangle = |\sigma\rangle|n\rangle$, where σ_1 is the singlet function S and σ_2, σ_3, and σ_4 are the triplet functions T_+, T_0, and T_-; $|n\rangle = |\ldots I_iM_i, I_jM_j, \ldots\rangle$ are the nuclear spin product functions where groups of magnetically equivalent[8] nuclei are coupled together to give resultant spins I_i. In this basis H° is diagonal and singlet–triplet mixing is induced by H'. The Hamiltonian matrix is of the order $4L$, where L is the number of nuclear states

$$L = L_aL_b = \Pi_j{}^a(2I_j + 1)\Pi_k{}^b(2I_k + 1) \tag{2}$$

The diagonal elements of H_{RP} are

$$E_{Sn} = J \quad E_{T_0n} = -J$$

$$E_{T_\pm n} = -J \pm g\beta_e\hbar^{-1}H_r \pm {}^1/_2\sum_l{}^{a,b}A_lM_l \tag{3}$$

The nondiagonal elements are

$$\langle T_0n|H'|Sn\rangle = {}^1/_2\Big[\Delta g\beta_e\hbar^{-1}H_r + \sum_j{}^a A_jM_j - \sum_k{}^b A_kM_k\Big]$$

$$\langle T_\mp m_\pm|H'|Sn\rangle = \pm 8^{-1/2}\xi_iA_i[I_i(I_i + 1) - M_i(M_i \pm 1)]^{1/2}$$

$$\langle T_\mp m_\pm|H'|T_0n\rangle = 8^{-1/2}A_i[I_i(I_i + 1) - M_i(M_i \pm 1)]^{1/2} \tag{4}$$

where $|m_\pm\rangle = |\ldots, I_iM_i \pm 1, I_jM_j, \ldots\rangle$; $\xi_i = +1$ if nucleus i is present in radical a, $\xi_i = -1$ if i is present in radical b. Other matrix elements are zero. The matrix $\mathbf{H}_{RP}$ is diagonalized by the orthogonal transformation

$$\mathbf{T}^{-1}\mathbf{H}_{RP}\mathbf{T} = \boldsymbol{\omega} \tag{5}$$

The columns of $\mathbf{T}$ are the eigenvectors; $\boldsymbol{\omega}$ is a diagonal matrix, the elements of which are the eigenvalues.

2.3. Stage b. The Populations in H_r. Let us first consider the populations of recombination product P, or equivalently the fraction of pairs with a certain nuclear spin state, that recombines. We make again the fundamental assumption that only pairs in the singlet state can recombine. The time development of each radical pair state is given by the Schrödinger equation, written in the form

$$i\dot{\mathbf{C}}(t) = \mathbf{H}_{RP}\mathbf{C}(t) \tag{6}$$

$\mathbf{C}(t)$ is a matrix of order $4L$, the columns of which represent the states of the pair at time t. The elements are the coefficients of the wave functions expanded in our basis. Written in this form eq 6 represents a collection of $4L$ differential equations corresponding to the possible initial conditions, which will be specified by a suitable choice of $\mathbf{C}(0)$. The solution of eq 6, subject to initial conditions, is

$$\mathbf{C}(t) = e^{-i\mathbf{H}_{\mathrm{RP}}t}\mathbf{C}(0) = \mathbf{T}e^{-i\omega t}\mathbf{T}^{-1}\mathbf{C}(0) \qquad (7)$$

To obtain this result, we have used eq 5 and a well-known property of exponential operators.[10] For $\mathbf{C}(0)$ we take a direct product

$$\mathbf{C}(0) = \mathbf{E} \otimes \mathbf{S}^{\mathrm{A}} \qquad (8)$$

where $\mathbf{E}$ is the unit matrix of order 4 representing the pure singlet and triplet states as starting states. $\mathbf{S}^{\mathrm{A}}$ is an orthogonal matrix of order L, which diagonalizes the nuclear spin Hamiltonian of the precursor

$$(\mathbf{S}^{\mathrm{A}})^{-1}\mathbf{H}^{\mathrm{A}}\mathbf{S}^{\mathrm{A}} = \Omega^{\mathrm{A}} \qquad (9)$$

In this way mixing of nuclear spin states in the precursor is accounted for in the initial conditions. However, it will be shown presently that any mixing of nuclear spins in the precursor is irrelevant, so that we might have taken the unit matrix instead of $\mathbf{S}^{\mathrm{A}}$ as well. As far as the electron spins are concerned, the four initial states S, T_+, T_0, and T_- are included in eq 8 and we have to select the states pertinent to a specific problem (S, T, or F precursor) later on. Keeping in mind that our first goal is to find the populations of the nuclear spin states in the reaction field H_{r}, we define an eigenvector matrix $\mathbf{S}^{\mathrm{P}}$ for the recombination product P with nuclear spin Hamiltonian H^{P} in the field H_{r}, similarly to eq 9

$$(\mathbf{S}^{\mathrm{P}})^{-1}\mathbf{H}^{\mathrm{P}}\mathbf{S}^{\mathrm{P}} = \Omega^{\mathrm{P}} \qquad (10)$$

and a matrix $\mathbf{Q}^{\mathrm{P}}$ representing P in $4L$ dimensional space.

$$\mathbf{Q}^{\mathrm{P}} = \mathbf{E}_{\mathrm{S}} \otimes \mathbf{S}^{\mathrm{P}} \text{ with } \mathbf{E}_{\mathrm{S}} = \begin{bmatrix} 1 & & & \\ & 0 & & \\ & & 0 & \\ & & & 0 \end{bmatrix} \qquad (11)$$

This expresses the assumption mentioned above that recombination occurs exclusively from the S state. The S states of the pair $|\nu\rangle = |1\nu'\rangle$ (ν' designates a nuclear state and 1 the electronic S state), corresponding to those of P, are represented by the column vectors $\mathbf{Q}_\nu{}^{\mathrm{P}}$ of $\mathbf{Q}^{\mathrm{P}}$. The populations of $|\nu'\rangle$ are determined with the help of the projections of the radical pair states, described by $\mathbf{C}(t)$, on the states $|1\nu'\rangle$

$$\mathbf{F}_\nu(t) = \tilde{\mathbf{C}}(t)\mathbf{Q}_\nu{}^{\mathrm{P}} \qquad (12)$$

where $\tilde{\mathbf{C}}(t)$ is the transpose of $\mathbf{C}(t)$. The elements of the vector $\mathbf{F}_\nu(t)$ are contributions of all possible initial states. A population function $P^g{}_\nu(t)$ of the state $|1\nu'\rangle$, *i.e.*, the probability of finding the pair in the state $|1\nu'\rangle$ (g denoting the type of precursor), is now given by

$$P^g{}_\nu(t) = \sum_r G_{rr}|F_{r\nu}|^2 = \tilde{\mathbf{F}}_\nu(t)\mathbf{G}\mathbf{F}_\nu{}^*(t) \qquad (13)$$

$\tilde{\mathbf{F}}_\nu(t)$ is a row vector and $\mathbf{F}_\nu{}^*(t)$ the complex conjugate. The diagonal matrix $\mathbf{G}$ weights initial electronic states of a given multiplicity according to the manner in which the pair is formed, *e.g.*, from S or T precursors or by random encounters of free uncorrelated radicals (F). All nuclear states will be given equal weights. $\mathbf{G}$ can then be written

$$\mathbf{G} = \mathbf{E}_g \otimes \mathbf{I} \qquad (14)$$

where $\mathbf{I}$ is the unit matrix of order L; $\mathbf{E}_g$ (g = S, T, or F) takes the form (*cf.* VIII)[8]

$$\mathbf{E}_{\mathrm{S}} = \begin{bmatrix} 1 & & & \\ & 0 & & \\ & & 0 & \\ & & & 0 \end{bmatrix} \quad \mathbf{E}_{\mathrm{T}} = {}^1\!/_3\begin{bmatrix} 0 & & & \\ & 1 & & \\ & & 1 & \\ & & & 1 \end{bmatrix}$$
$$\mathbf{E}_{\mathrm{F}} = {}^1\!/_4\begin{bmatrix} 1-\lambda & & & \\ & 1 & & \\ & & 1 & \\ & & & 1 \end{bmatrix} \qquad (15)$$

λ is a steric factor being the probability of reaction during a singlet encounter. For $\mathbf{E}_{\mathrm{F}}$ in the case of free-radical encounters, it is assumed that a fraction $^1\!/_4\lambda$ leads immediately to product during the first encounter. This fraction is disregarded for the moment, since it does not give rise to nuclear polarization. However, it is included later on in the final result (eq 29).

We have neglected Boltzmann differences and other possible population differences among the precursor T states, which, however, could have been easily incorporated in $\mathbf{E}_{\mathrm{T}}$ and $\mathbf{E}_{\mathrm{F}}$. The function $P^g{}_\nu(t)$ obtained in this way plays a role similar to $|C_{\mathrm{S}\nu}(t)|^2$ in VIII (eq 58). It can be written in the form

$$P^g{}_\nu(t) = \tilde{\mathbf{Q}}_\nu{}^{\mathrm{P}}\mathbf{C}(t)\mathbf{G}\mathbf{C}^\dagger(t)\mathbf{Q}_\nu{}^{\mathrm{P}} \qquad (16)$$

If eq 7 for $\mathbf{C}(t)$ is substituted in eq 16, the following matrix product appears in the center

$$\mathbf{C}(0)\mathbf{G}\tilde{\mathbf{C}}(0) = \mathbf{E} \otimes \mathbf{S}^{\mathrm{A}}\cdot\mathbf{E}_g \otimes \mathbf{I}\cdot\mathbf{E} \otimes (\mathbf{S}^{\mathrm{A}})^{-1} =$$
$$\mathbf{E} \otimes \mathbf{S}^{\mathrm{A}}\cdot\mathbf{E}_g \otimes (\mathbf{S}^{\mathrm{A}})^{-1} = \mathbf{E}_g \otimes \mathbf{I} = \mathbf{G} \qquad (17)$$

which shows that mixing of nuclear spin states in the precursor does not affect the results whatsoever, a result that has been used in VIII. Thus, we obtain for the population function

$$P^g{}_\nu(t) = \tilde{\mathbf{Q}}_\nu{}^{\mathrm{P}}\mathbf{T}e^{-i\omega t}\mathbf{T}^{-1}\mathbf{G}\mathbf{T}e^{i\omega t}\mathbf{T}^{-1}\mathbf{Q}_\nu{}^{\mathrm{P}} \qquad (18)$$

To evaluate this expression further we introduce two matrices $\mathbf{V}^{\mathrm{P}}$ and $\mathbf{W}^g$ defined by

$$V^{\mathrm{P}}{}_{\nu l} = \sum_n Q_{n\nu}{}^{\mathrm{P}}T_{nl} \qquad (19)$$

$$W^g{}_{lj} = \sum_r T_{rl}G_{rr}T_{rj} \qquad (20)$$

Equation 18 can then be written

$$P^g{}_\nu(t) = \sum_{l,j} V^{\mathrm{P}}{}_{\nu l}V^{\mathrm{P}}{}_{\nu j}W^g{}_{lj}e^{i(\omega_j - \omega_l)t} \qquad (21)$$

Note that this expression still pertains to the radical pair, although the label ν already reflects the anticipated recombination product. For the formation of this product the pair has to be in the singlet state (probability given by eq 21) and, furthermore, there has to be a reencounter. Thus, in order to obtain the populations $P^g{}_{\nu'}$ of the nuclear states of the product $|\nu'\rangle$, we have to multiply $P^g{}_\nu(t)$ by λ and by the probability

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[10] *Cf.* P. L. Corio, "Structure of High-Resolution Nmr Spectra," Academic Press, New York, N. Y., 1966, p 480.

of a reencounter $f(t) = mt^{-3/2}$, valid after a few diffusion steps,[11] and to integrate (*cf.* VIII), giving

$$P^{g}{}_{\nu'} = \int_0^\infty \lambda P^{g}{}_{\nu}(t)f(t)dt = \lambda\sum_{l,j} V^{P}{}_{\nu l}V^{P}{}_{\nu j}W^{g}{}_{lj}(p - m\sqrt{2\pi\omega_{jl}}) \quad (22)$$

where $p = \int_0^\infty f(t)dt$; $m \sim 10^{-6}\ \mathrm{sec}^{-1/2}$; $\omega_{jl} = |\omega_j - \omega_l|$.

S Precursor. Equation 20 with 14 and 15 becomes in the case of a S precursor

$$W^{S}{}_{lj} = \sum_{r'} T_{1r'.l}T_{1r'.j} \quad (23)$$

The double index $1r'$ labels electron and nuclear functions, respectively (r' runs over all nuclear states). This gives for the populations

$$P^{S}{}_{\nu'} = \lambda\Big(p - m\sum_{r'}\sum_{l,j} T_{1r'.l}T_{1r'.j}V^{P}{}_{\nu l}V^{P}{}_{\nu j}\sqrt{2\pi\omega_{jl}}\Big) \quad (24)$$

The fraction λp would be the "cage effect" in the absence of S–T mixing and the remainder of this expression gives rise to nuclear polarization through its dependence on ν and hence on the nuclear states.

T Precursor. In the case of T precursor one has

$$W^{T}{}_{lj} = {}^{1}/_{3}\sum_{e=2}^{4}\sum_{r'} T_{er'.l}T_{er'.j} \quad (25)$$

giving

$$P^{T}{}_{\nu'} = \frac{\lambda m}{3(1-p)}\sum_{e=2}^{4}\sum_{r'}\sum_{l,j} T_{cr'.l}T_{er'.j} \times V^{P}{}_{\nu l}V^{P}{}_{\nu j}\sqrt{2\pi\omega_{jl}} \quad (26)$$

where e runs over the T states and where we have corrected for multiple reencounters (factor $(1 - p)^{-1}$, *cf.* VIII). Combining eq 24 and eq 26, we obtain the result $P^{S}{}_{\nu'} + 3(1 - p)P^{T}{}_{\nu'} = \lambda p$, or for a transition $\nu' \rightarrow \mu'$

$$P^{S}{}_{\nu'} - P^{S}{}_{\mu'} = -3(1 - p)(P^{T}{}_{\nu'} - P^{T}{}_{\mu'}) \quad (27)$$

showing that S and T precursors give opposite polarizations, just as in the high-field case.

F Precursor. Proceeding as before we have from eq 20, 14, and 15

$$W^{F}{}_{lj} = {}^{1}/_{4}\Big(\delta_{lj} - \lambda\sum_{r'} T_{1r'.l}T_{1r'.j}\Big) \quad (28)$$

which gives for F-case populations

$$P^{F}{}_{\nu'} = {}^{1}/_{4}\lambda\Big[1 + c^{-1}\Big\{p(1 - \lambda) + \lambda m\sum_{r'}\sum_{l,j} T_{1r'.l}T_{1r'.j}V^{P}{}_{\nu l}V^{P}{}_{\nu j}\sqrt{2\pi\omega_{lj}}\Big\}\Big] \quad (29)$$

A fraction ${}^{1}/_{4}\lambda$ of unpolarized product formed during the first encounter has been included in eq 29; a factor $c = 1 - p\{1 - {}^{1}/_{2}\lambda(1 - \lambda)\}$ accounts for the effect of multiple reencounters of pairs that fail to react during the first reencounter (*cf.* VIII). Comparison of eq 29 with eq 24 shows that F-type polarization is opposite to that from S precursors (hence similar to T-type polarization) for all magnetic fields.

D Products. Polarization in products from radicals that escape from the "cage" by diffusion (D products) can be treated similarly. Generally it is not simply related to P-product polarization as in the high-field case, where P and D products behave oppositely. In the case of D products we have to count contributions from pairs in all four electronic states, not only from the S state as in case of P products. Therefore, the matrices $\mathbf{Q}^{D}$ and $\mathbf{V}^{D}$ (analogous to eq 11 and 19) are defined in this case

$$\mathbf{Q}^{D} = \mathbf{E} \otimes \mathbf{S}^{D} \quad (30)$$

$$V^{D}{}_{\nu l} = \sum_{n} Q^{D}{}_{n\nu}T_{nl} \quad (31)$$

where $\mathbf{E}$ is again the unit matrix of order 4; $\mathbf{S}^{D} = \mathbf{S}^{D_a} \otimes \mathbf{S}^{D_b}$, $\mathbf{S}^{D_a}$ being the eigenvector matrix (of order L_a) of the product of fragment a: $(\mathbf{S}^{D_a})^{-1}\mathbf{H}^{D_a}\mathbf{S}^{D_a} = \mathbf{\Omega}^{D_a}$. The same analysis as given above leads to a quantity

$$R^{g}{}_{f\nu'}(t) = \sum_{l,j} V^{D}{}_{f\nu'.l}V^{D}{}_{f\nu'.j}W^{g}{}_{lj}e^{i(\omega_j - \omega_l)t} \quad (32)$$

which is analogous to $P^{g}{}_{\nu}(t)$. We have written $f\nu'$ for ν (f labels electronic states and ν' the nuclear state of interest). The populations $D^{g}{}_{\nu'}$ are obtained as follows (*cf.* footnote 23)

$$D^{g}{}_{\nu'} = \int_0^\infty dt\Big[R^{g}{}_{1\nu'}(t)f(t)(1 - \lambda) + \sum_{f=2}^{4} R^{g}{}_{f\nu'}f(t)\Big] = \sum_{f=1}^{4}\sum_{l,j} V^{D}{}_{f\nu'.l}V^{D}{}_{f\nu',j}W^{g}{}_{l.j}(p - m\sqrt{2\pi\omega_{lj}}) - P^{g}{}_{\nu'} \quad (33)$$

The factor $(1 - \lambda)$ takes into account the depletion of singlet pairs due to recombination. $P^{g}{}_{\nu'}$ is given by eq 22 (but with $\mathbf{S}^{D}$ instead of $\mathbf{S}^{P}$). Substituting eq 23 and 25 for S and T cases, respectively, we arrive at the following results.

S precursor

$$D^{S}{}_{\nu'} = p - m\sum_{f}\sum_{r'}\sum_{l,j} T_{1r'.l}T_{1r'.j} \times V^{D}{}_{f\nu',l}V^{D}{}_{f\nu'.j}\sqrt{2\pi\omega_{lj}} - P^{S}{}_{\nu'} \quad (34)$$

T precursor

$$D^{T}{}_{\nu'} = p - \frac{m}{3(1-p)}\sum_{f}\sum_{e=2}^{4}\sum_{r'}\sum_{l,j} T_{er'.l}T_{er.'j} \times V^{D}{}_{f\nu'.l}V^{D}{}_{f\nu',j}\sqrt{2\pi\omega_{lj}} - P^{T}{}_{\nu'} \quad (35)$$

It can be easily verified that eq 34 and 35 represent polarization of opposite character also in this case. It is also to be noted that $P^{S}{}_{\nu'}$ and $P^{T}{}_{\nu'}$ depend on λ, while the second terms in eq 34 and 35 do not. Therefore, it is possible to estimate λ from relative line intensities in the low-field CIDNP spectrum of a D product. If $\lambda = 0$ there is still polarization in low fields, whereas in high fields there is not. The populations of fragment a can be obtained from $D^{g}{}_{\nu'}$ through $D^{g}{}_{\nu'_a} = \Sigma_{\nu'_b}D^{g}{}_{\nu'}$, where the summation extends over the nuclear states of fragment b.

Enhancement factors can be calculated from the populations $P^{g}{}_{\nu'}$ and $D^{g}{}_{\nu'}$, by the procedures of VIII. A computer program (Fortran IV) has been written, based on the formalism presented in this section.

2.4. Stage c. The Populations in H_0.

Now we have to see what happens when the sample polarized in the field H_r is transferred to the spectrometer field H_0. Generally one will try to carry out this transfer as fast as possible, because one has to record the spectrum (or

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(11) R. M. Noyes, *J. Amer. Chem. Soc.*, 78, 5486 (1956).

part of it) before the nuclear spins have relaxed. There are two problems associated with the rapidity of the transfer. The first, which regards the axis of quantization, can be discussed in the case of a one-proton system. The directions of H_r, H_0, and of intermediate fields need not be the same. However, the magnetization follows the instantaneous field direction, if the following condition is met.[12]

$$\mathrm{d}H/\mathrm{d}t \ll \gamma H^2 \tag{36}$$

Thus the transfer is "adiabatic" in this sense, roughly, if the transfer time is longer than the reciprocal of the precession frequency, $\tau = (\gamma H)^{-1}$ sec. For protons $\gamma = 2.7 \times 10^4$ radians/sec G; hence, for a field of only 1 G this time $\tau = 3.7 \times 10^{-5}$ sec, so that the adiabatic condition will always prevail in practice.[13] Accordingly we have found the spectra to be independent of the direction of H_r relative to H_0.

The second problem arises because of the fact that the eigenstates of coupled nuclei in H_r may differ from those in H_0. As mentioned above we may ask again whether the transfer occurs adiabatically or not (adiabatic in the sense of the system remaining in the same eigenstate). For two groups of protons i,j, with coupling constant J_{ij} (in Hz) and chemical shift difference $\delta_i - \delta_j$ (in ppm), the states are determined by the ratio $2\pi J_{ij}/\gamma H(\delta_i - \delta_j)10^{-6}$.

For $J_{ij} = 7$ Hz and $\delta_i - \delta_j = 2$ ppm the states change appreciably in the region $H = 200$–5000 G. The matrix element responsible for the mixing of nuclear states is $^1/_2J_{ij}$. The system behaves adiabatically during transfer if the time spent in the critical region (200–5000 G) is longer than $\tau' = (^1/_2J_{ij}2\pi)^{-1}$ sec, which is $^1/_{22}$ sec in our example. This is short enough to expect adiabatic behavior, which, indeed, has been observed experimentally (*vide infra*). For small coupling constants, however, there may occur deviations from this adiabatic behavior. In order to determine the spectrum in H_0 after adiabatic transfer we have to identify the population of a state in H_0 with the calculated population of the same eigenstate in H_r. In other words we have to know the correlation diagram, connecting high-field with low-field levels. In the case of A_nB nmr spectra, where the highest order of submatrices is 2, this correlation is easily found. However, in more complex spectra, this presents a computational problem, since in the usual matrix diagonalization procedures the correlation is lost. We solved the problem by calculating a large number (k) of spectra, starting in H_r and multiplying the field each time by a factor $x = \exp[k^{-1} \ln (H_0/H_r)]$, ending up in $H_0 = H_rx^k$. In this way the correlation is found and thus the high field populations. For a complex spectrum like the propene spectrum of Figure 6, the number of steps required was $k = 300$ when $H_r = 0.5$ G. For still higher values of k the CIDNP spectrum did not change appreciably.

It appears that this is a generally useful and effective procedure. It also seems time consuming. However, for the propene problem, which took 45 min on an IBM 360-50 computer, the major part was taken by the diagonalization of the radical pair Hamiltonian matrix.

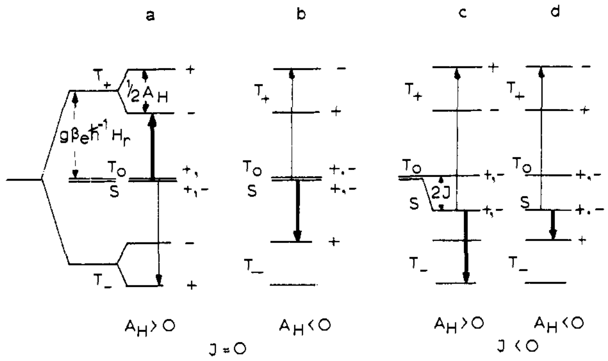

Figure 1. Energy levels of a one-proton radical pair in a magnetic field H_r. Nuclear states are designated by + and −. S–$T_\pm$ transitions are indicated; the heavier arrows represent larger transition probabilities. A_H is the hyperfine coupling constant; J is the exchange integral.

3. Qualitative Features and Predictions of the Theory

3.1. Effects of S–$T_\pm$ Mixing. The expressions for the populations $P^q_{\nu'}$ and $D^q_{\nu'}$ derived in section 2.3 do not particularly excel in transparency. It may be asked if simpler procedures would not give similar results; these would have the additional advantage of giving more insight into the problem. For instance, a perturbation treatment has been used by Glarum,[9] who considered mixing of only two levels at a time. We will examine what can be learned from simpler arguments and compare predictions with those of the general formalism presented above.

The effects of S–$T_\pm$ transitions will be discussed in the case of a one-proton radical pair, starting in the S state. If the nuclear states are denoted by $|+\rangle$ and $|-\rangle$, the "selection rules" (*cf.* eq 4) lead to the following allowed transitions from the S level: $|S+\rangle \rightarrow |T_0+\rangle$, $|S-\rangle \rightarrow |T_0-\rangle$, $|S+\rangle \rightarrow |T_+-\rangle$, and $|S-\rangle \rightarrow |T_-+\rangle$. The S–$T_0$ transitions alone would not give appreciable polarization in very low fields (below about 100 G), because the Δg term is very small (transition probabilities are about the same for $|+\rangle$ and $|-\rangle$ states). Thus polarization in this field region must arise from differences in S–T_+ and S–T_- transitions. These are depicted in the energy level scheme of Figure 1.

The degeneracy of the T states is lifted by the Zeeman term; each of the T_+ and T_- levels is further split by the hf interaction. According to perturbation theory an "adiabatic transition" $i \rightarrow j$ would have a probability

$$P_{ij} = f|H'_{ij}|^2/(E_i - E_j)^2 \tag{37}$$

where f is a dynamical factor and E_i and E_j are the zero-order energies. For S → $T_\pm$ transitions only the values of $(E_i - E_j)$ differ. Smaller energy differences give rise to larger transition probabilities, indicated by the heavy arrows in Figure 1. In the case that $J = 0$ and $A_H > 0$ (Figure 1a), the predominance of $|S+\rangle \rightarrow |T_+-\rangle$ transitions would lead to emission (E) in both recombination and "escape" products, since the $|-\rangle$ state (upper state in the product) is preferentially populated. When $A_H < 0$, however, $|S-\rangle \rightarrow$

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(12) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, Chapter II.

(13) One might think of arranging the directions of H_r and H_0 exactly opposite to each other, so that a negatively polarized sample in H_r would show enhanced absorption in H_0. However, when the transfer time is 1 sec, the transverse components of the magnetic field would have to be less than 0.037 mG during transfer. This conditions would not appear to be easily satisfied in practice.

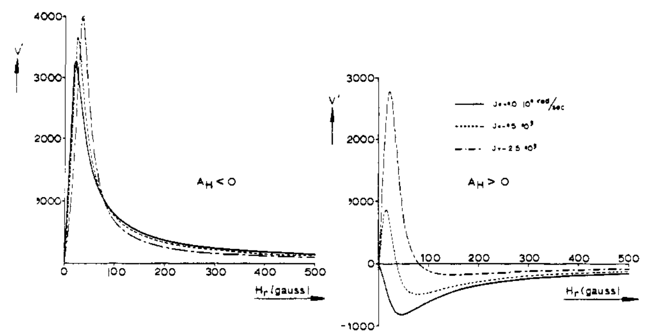


Figure 2. Polarization *vs.* magnetic field (H_r) calculated for a one-proton radical pair with $A_H = -4.4 \times 10^8$ radians/sec (left) and $A_H = +4.4 \times 10^8$ radians/sec (right). Values for the exchange integral (J) are indicated in the figure.

$|T-+\rangle$ transitions are more probable, giving enhanced absorption (A). In case of a negative J (Figure 1c and d), S and T_0 states are no longer degenerate and both positive and negative A_H would give A (at least when $|J| > {}^1/_4|A|$). Thus we see that the sign of the polarization does not depend on the magnitude of J when $A_H < 0$ but is critically dependent on $|J|$ when $A_H > 0$. For positive J the argument is reversed: positive A_H would give E, whereas for a negative A_H, A or E could occur, depending on the magnitude of J.

On the basis of this simplified treatment one would expect that these polarization effects due to S–$T_\pm$ mixing would go through a maximum, when the field is increased, and die out at large fields. However, computer calculations, based on the formalism of section 2, show that matters are more complicated, at least in the case of positive A_H. In Figure 2 the results of some calculations for the one-proton case are presented. The curves represent the magnetic field dependence of the enhancement factor V' for different negative values of J where

$$V' = (P^S{}_{\nu'} - P^S{}_{\mu'})(kT/g_N\beta_N H_0) \tag{38}$$

and $|\nu'\rangle = |+\rangle$, $|\mu'\rangle = |-\rangle$. $P^S{}_{\nu'}$ is given by eq 24. The factor $kT/g_N\beta_N H_0$ has been set equal to 10^5. It can be seen that when $A_H < 0$ (Figure 2a), the behavior is "normal;" only the magnitude of V' is affected by $|J|$. However, when $A_H > 0$, V' changes sign for certain values of J. We have actually observed this peculiar behavior (even a double change of sign, due to a Δg effect); an example is discussed in section 4 (*cf.* Figure 7). Apparently it arises from an interference effect, due to the simultaneous mixing of S, T_0, and T_+ (or T_-) states. Garst, *et al.*,[3] have mentioned calculations of these types of oscillations. Although they do not give details, their calculations are probably similar to ours, except for a different averaging procedure.

As far as we can see, this behavior would not follow from first-order perturbation treatments,[9] allowing for mixing of only two states at a time; it seems necessary to go to second-order perturbation theory or to solve a set of coupled equations, as we have done.

Summarizing some characteristics of low-field S–$T_\pm$ polarization for a single group of nuclei. 1. S precursors give polarization opposite to that of T and F precursors. 2. D products behave similar to P products. 3. In the case of a S precursor, if $J < 0$ (expected to be most common), negative A_H gives A; positive A_H may give A or E depending on $|J|$ and on the field. The field dependence may show a change of sign in the latter case. 4. If $J > 0$ rule 3 is reversed: positive A_H gives E; negative A_H gives field and J dependent behavior.

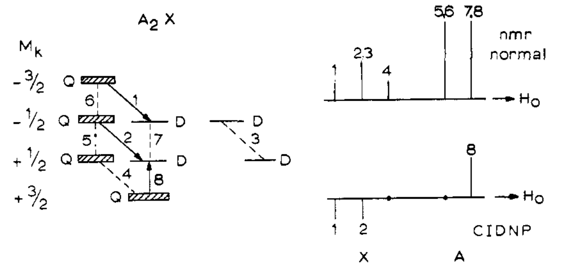


Figure 3. Energy levels and nmr spectra (normal and zero-field CIDNP) for an A_2X case, with $J_{AX} > 0$. Correlation with the zero-field levels is indicated by Q (quartet) and D (doublet). Numbers indicate assignment of transitions.

3.2. The Zero-Field Case. In zero magnetic field there can be no polarization for a single nucleus, because there is no preferred direction of quantization. Polarization can only arise when at least two coupled nuclei are present, due to unequal population of the zero-field levels of the product. These levels are characterized by the quantum numbers K and M_K, because nuclear states are eigenstates of K^2 and K_Z (**K** is the total nuclear spin operator, $\mathbf{K} = \Sigma_i \mathbf{I}_i$). It will be shown in the Appendix that each K manifold is uniformly populated, *i.e.*, populations are independent of M_K. When only two coupled groups of equivalent nuclei (say n_i of type i and n_j of type j) are present in the product and sample transfer to H_0 occurs adiabatically, this leads to the so-called "$n - 1$ multiplets;" nuclei i (appearing downfield in the spectrum, say) normally exhibiting a multiplet of $n_j + 1$ lines (for spin $^1/_2$ nuclei) will now give rise to a multiplet of n_j lines, the high-field line being absent, similarly for the nuclei j (appearing upfield): a multiplet of n_i lines (instead of $n_i + 1$), the low-field line being absent. The polarizations are E for the downfield group and A for the upfield group or *vice versa* (see below). This phenomenon has first been noticed by Glarum,[9] who treated the case of two nuclear spins by explicit calculation. A more general proof (based on our formalism) of the equality of populations within the K manifolds, giving rise to the "$n - 1$ multiplets," will be given in the Appendix.

This effect is illustrated in Figure 3, where the energy levels are depicted for a hypothetical A_2X nmr spectrum (with $J_{AX} > 0$) of a recombination product

$$\overline{R(H_A)_2H_X\cdot + R'\cdot}^{\,S} \longrightarrow R(H_A)_2H_X\text{-}R' \tag{39}$$

(S precursor, reaction in zero field). For three nuclear spins the zero-field states are a quartet, Q ($K = {}^3/_2$) and two doublets, D ($K = {}^1/_2$); the levels in Figure 3 are labeled with Q and D according to their origin from these coupled states (adiabatic transfer is assumed). Population differences indicated in Figure 3 are those expected for the case where $A_A > 0$ and $A_X < 0$, a situation occurring, *e.g.*, for β and α protons in alkyl radicals. From the assignments of transitions it can be seen that the reason for the absence of the inner lines in the CIDNP spectrum is that these lines belong to

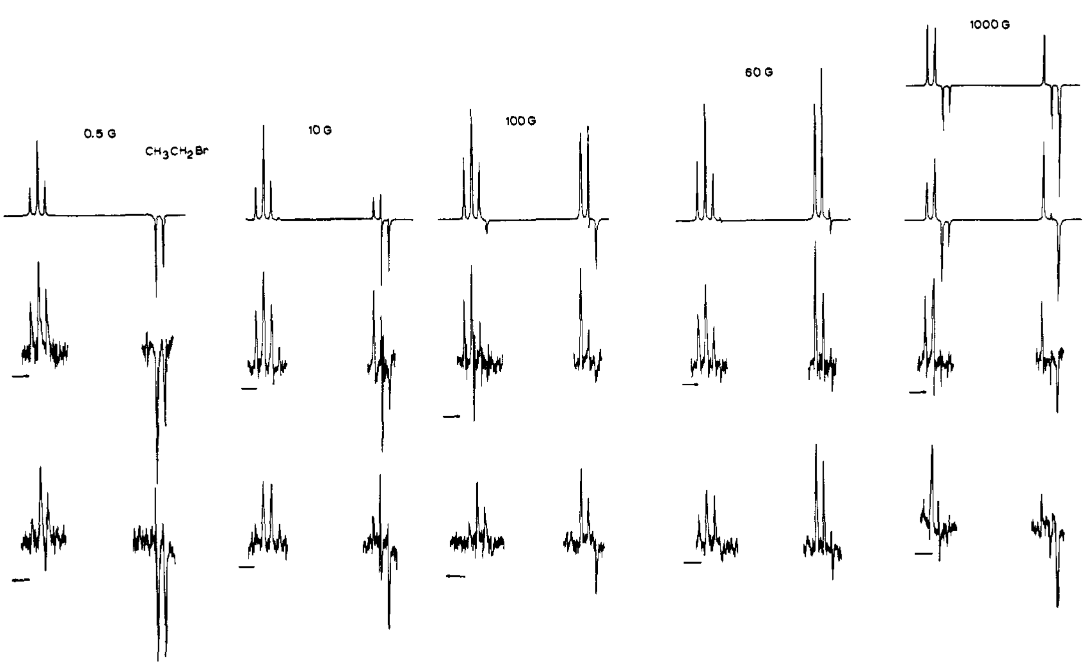


Figure 4. 60-Mc spectra of ethyl bromide formed during photolysis of 0.4 *M* propionyl peroxide in CCl_4 in the presence of 0.5 *M* CCl_3Br. Irradiation was carried out in a separate magnet, in fields H_r as indicated in the figure. Scans in both directions are presented (see arrows). Computer simulations for escape from the pair $CH_3CH_2\cdot/R\cdot'$ with $A(CH_2) = -22G$, $A(CH_3) = 27$ G, $J = -5 \times 10^8$ radians/sec, $\lambda = 0.75$ are shown on top. For the 1000-G top spectrum an extra nucleus $I = {}^5/_2$, $A = 25$ G, has been added to $R\cdot'$.

transitions between equally populated states, originating from states with the same *K* multiplicity. Furthermore, it can be seen that emission and absorption effects balance, this being a general property of zero-field spectra.

It should be noted that the inner lines always are absent; when J_{AX} is negative, both the correlation with the zero-field levels and the assignment of transitions in the level diagram change in such a way that again the inner lines vanish and one would have emission for the X group and absorption for the A group.

For predictions as to the sign of the effects (*E* for nuclei *i* and *A* for *j* or *vice versa*) one may again use the rule which was derived in VIII for multiplet effects[14]

$$\Gamma_{me} = \mu\epsilon A_i A_j J_{ij}\sigma_{ij}\begin{cases}+E/A\\-A/E\end{cases} \qquad (40)$$

where the symbols have the same meaning as in VIII; J_{ij} is the nuclear coupling constant

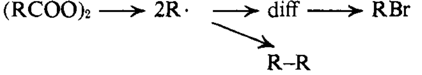
$$\mu\begin{cases}+\text{ T and F precursor}\\-\text{ S precursor}\end{cases} \qquad \epsilon\begin{cases}+\text{ recombination product}\\-\text{ “escape” product}\end{cases}$$

$$\sigma_{ij}\begin{cases}+\text{ nuclei } i \text{ and } j \text{ in the same radical}\\-\text{ nuclei } i \text{ and } j \text{ in different radicals}\end{cases}$$

E/*A* has to be interpreted now as *E* for the nuclei appearing downfield in the spectrum and *A* for the upfield group. In the example of Figure 2, discussed above, one would have $\Gamma_{me} = - + + - + + = +$, *E*/*A*. Thus, for this reaction (39) run in a high field, one would expect *E*/*A* multiplets, whereas in zero-field it would give *E* and *A* "*n* − 1 multiplets" for I_X and I_A, respectively. The zero-field effects discussed here remain visible to some extent, when reactions are run in low fields, but are superimposed with effects due to differences S–T₊ and S–T₋ mixing, as discussed in section 3.1.

4. Experimental Examples

4.1. Photolysis of Propionyl Peroxide. A solution of about 0.4 *M* propionyl peroxide (PPO) and 0.5 *M* CCl_3Br in CCl_4 was irradiated in a separate magnet during 60 sec and rapidly transferred to the probe of an A-60 spectrometer. The reactions are as follows



$$(RCOO)_2 \xrightarrow{h\nu} \overline{2R\cdot}^{\,S} \longrightarrow \text{diff} \xrightarrow{CCl_3Br} RBr \qquad (41)$$
$$\overline{2R\cdot}^{\,S} \longrightarrow R\text{–}R$$

where $R\cdot = CH_3CH_2\cdot$. Pair formation occurs from a S state. In high-field (14,000 G) *A*/*E* multiplets are observed for the escape product ethyl bromide (RBr) (CH_2 2.45, CH_3 0.90 ppm). Figure 4 shows a series of experiments in different fields H_r. The spectra of CH_2 and CH_3 groups of ethyl bromide were recorded in separate experiments; scans in both directions (for fresh samples) are presented in Figure 4. The effect of nuclear relaxation can be observed clearly from the difference between middle and lower traces. When $H_r = 0.5$ G a spectrum results, which is almost that expected for the zero-field case: "*n* − 1 multiplets" (the quartet has become a triplet, the triplet appears as a doublet). The "phase" is such as predicted by rule (40) for an escape product from a S precursor. We have $A(CH_2) = -22$ G, $A(CH_3) = +27$ G, $J_{ij} = +6.4$ Hz. Thus $\Gamma_{me} = - - + - + + = -$, *A*/*E*, and hence *A* for the low-field CH_2 group and *E* for the high-field CH_3 group.

Proceeding to higher fields H_r a striking difference in behavior of the methylene and methyl groups is observed: whereas the CH_2 spectrum did not alter very much, the CH_3 spectrum changed drastically, first acquiring *A* character and ending up as *A*/*E* multiplets

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[14] (a) R. Kaptein, *Chem. Commun.*, 732 (1971); (b) Ph.D. Thesis, Leiden, 1971.

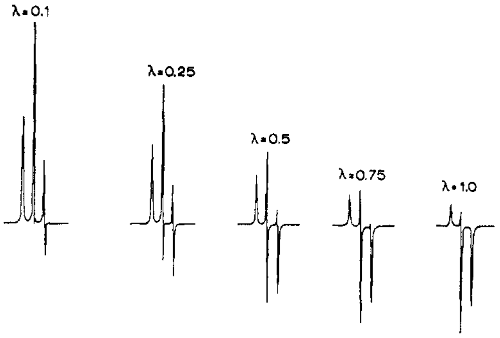


Figure 5. Simulated spectra of the CH_3 group of ethyl bromide, formed in a field of 10 G, for various values of λ.

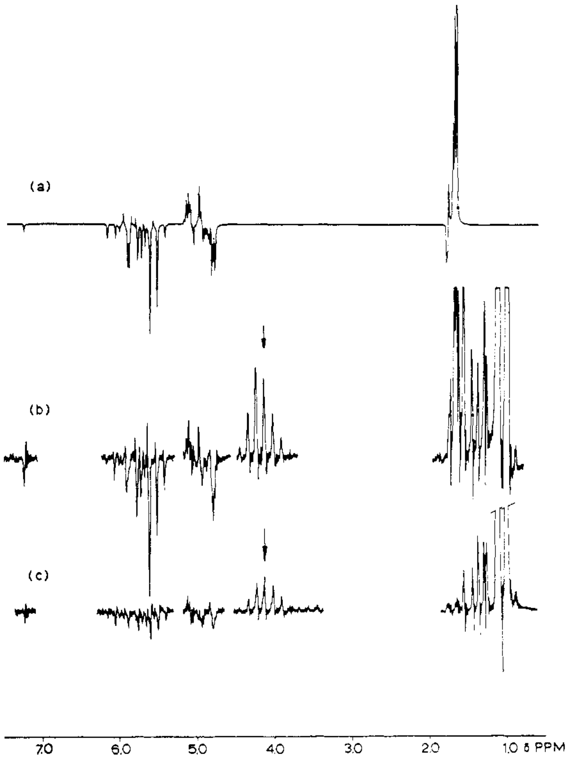


Figure 6. 60-Mc spectrum taken in parts after irradiation of diisopropyl ketone in CCl_4 in a field H_r = 100 G (b). Second scans of the same samples, taken just after those of (b) are shown in (c). The arrows indicate the center line of the methine septet of isopropyl chloride. A computer simulation of the propene and $CHCl_3$ spectrum is shown on top (a) (see text).

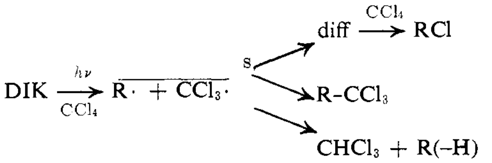
at the higher fields. This reflects the different signs of the hf coupling constants as discussed in section 3.1.

Computer calculations, based on the theory given in section 2, have been carried out for this case. As the complete problem exceeded the capabilities of our computer, we treated the problems as escape from the truncated pair $CH_3CH_2\cdot/R'\cdot$ where $R'\cdot$ is a dummy radical without nuclei ($\Delta g = 0$). This was satisfactory in the low-field range but caused some deviations at intermediate fields (*vide infra*). The transfer of the sample to the probe was assumed to occur adiabatically. The values of J and λ were varied. The best results were obtained for $\lambda = 0.75$ and $J = -5 \times 10^8$ radians/sec. This value of J is consistent with the high-field spectra of ethyl chloride (*cf.* VIII and XII[14b]). The final series of simulations (Figure 4), which should be compared with an average of scans in both directions, shows an astonishing agreement with experiment. Only the 1000-G spectrum, calculated in this way (second from top), showed more or less serious deviations, which, in our opinion, are due to the neglect of the additional nuclei in the pair. By adding an extra nucleus with spin $^5/_2$ and with A = 25 G, to the dummy radical $R'\cdot$ (the maximum that the computer could handle), the simulation improved significantly (top spectrum, 1000 G): more A character for the quartet and more E for the triplet. This influence of nuclei, which does not contribute to the nmr spectrum of the product under consideration, is not observed in high-field spectra. It is probably due to shifting of certain $T_\pm$ levels with respect to the S level, enhancing the S–$T_\pm$ transition probabilities to some extent.

Since we are dealing with an escape product, the value of the steric factor λ affects the relative intensities in the CIDNP spectrum (*cf.* section 2.3). This can be seen in Figure 5, where some calculations are presented for the ethyl bromide CH_3 group, for reaction in a field H_r = 10 G. The best value $\lambda = 0.75$ was obtained by comparing simulations for other fields as well.

4.2. Photolysis of Diisopropyl Ketone in CCl_4. The photoreaction of diisopropyl ketone (DIK) in CCl_4 has been discussed in VII[15] and a 60-Mc CIDNP spectrum has been presented there. The reaction probably involves complex formation of excited S state ketone with CCl_4. High-field CIDNP effects could be accounted for by assuming formation and subsequent reactions of isopropyl/trichloromethyl radical pairs

(S pairs)



$$\mathrm{DIK} \xrightarrow[CCl_4]{h\nu} \overline{R\cdot + CCl_3\cdot} \overset{S}{\rightarrow} \begin{cases} \mathrm{diff} \xrightarrow{CCl_4} \mathrm{RCl} \\ \mathrm{R\text{-}CCl_3} \\ \mathrm{CHCl_3 + R(\text{–}H)} \end{cases} \qquad (42)$$

where $R\cdot = (CH_3)_2\dot{C}H$ and R(–H) is propene. Figure 6b shows a 60-Mc spectrum taken in parts after 90-sec irradiation of a solution of DIK in CCl_4 in a field H_r = 100 G. The traces of Figure 6c are run just after those of 6b (of the same sample) and show the effect of relaxation. They represent still large polarizations, as the signals vanish almost completely, except for the parent compound (δ 1.04 ppm).

Enhancements are observed for chloroform (δ 7.27 ppm), propene (CH 5.73, CH_2 4.92, CH_3 1.72 ppm), isopropyl chloride (CH 4.13, CH_3 1.54 ppm) and trichloroisobutane (CH_3 1.30 ppm). Polarization of the first three products will now be discussed.

Chloroform. The field dependence of the chloroform signal (E in Figure 6) exhibited a very peculiar behavior; it changed sign two times, as shown in Figure 7. The points represent experiments, conducted under as nearly as possible identical conditions. The curve represents computer calculations for the polarization of $CHCl_3$ formed by reaction 42, with $J = -1.0 \times 10^8$ radians/sec, $g_{i\text{-Pr}} = 2.0026$, $g_{CCl_3\cdot} = 2.0091$ (*cf.* ref 16), and hf parameters for the isopropyl radical $A(CH_3) = +4.4 \times 10^8$ radians/sec, $A(CH) = -3.9 \times 10^8$ radians/sec. The curve was scaled to fit more or less to the experimental

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(15) J. A. den Hollander, R. Kaptein, and P. A. T. M. Brand, *Chem. Phys. Lett.*, 10, 430 (1971).

(16) A. Hudson and H. A. Hussain, *Mol. Phys.*, 16, 199 (1969).

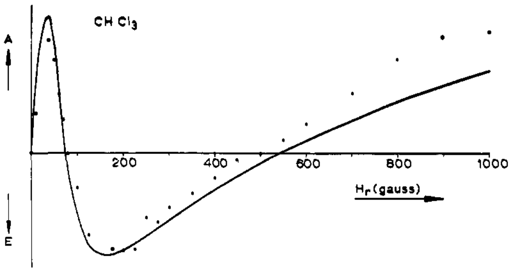

Figure 7. Polarization of $CHCl_3$ (formed during irradiation of DIK in CCl_4) *vs.* magnetic field. The curve represents computer calculations ($J = -1.0 \times 10^8$ radians/sec) and has been scaled to the experimental points.

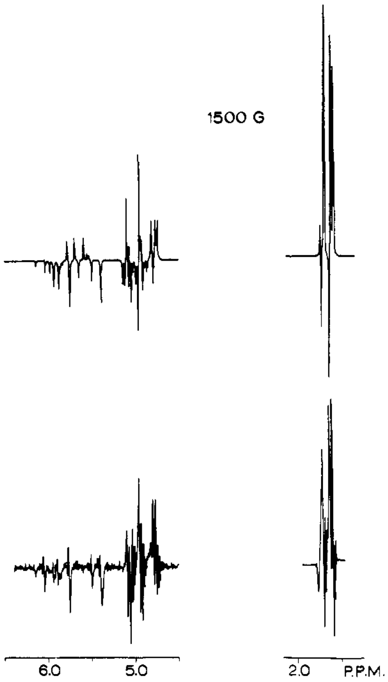

Figure 8. 60-Mc spectrum of propene, formed in a field H_r = 1500 G (in the photoreaction of DIK in CCl_4). A computer simulation is shown on top.

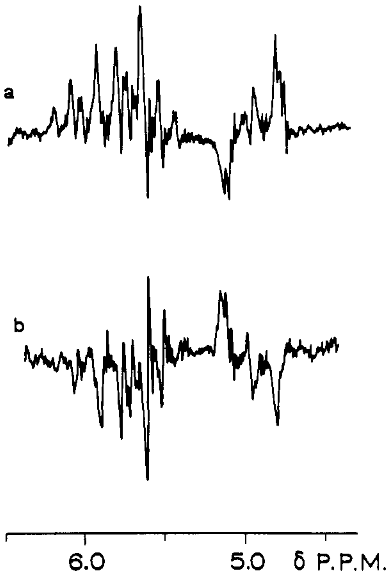

Figure 9. Spectrum of the vinyl region of propene, formed during photolysis of DIK in $CF_2Cl-CFCl_2$ (a) and in CCl_4 (b). Both reactions were run in a field of 10 G.

points. The first crossing at 80 G depended strongly upon the value of J used in the calculation (*cf.* Figure 2 for $A_H > 0$); the second crossing, however, found experimentally at 490 G, did not (unless very large values of J were used). The rising of the curve at higher fields is due to a Δg effect. The field, at which the second crossing occurs, depends therefore on Δg, but also on the number of protons present in the radical pair, so that it was necessary to make the calculations for the complete isopropyl/$CCl_3\cdot$ pair. For a one-proton pair with $\Delta g = 0.0065$ the theory predicts a crossing at about 200 G. This dependence of protons which do not contribute to the nmr transition (of $CHCl_3$) was also observed in the case of ethyl bromide in the previous section and was verified experimentally.

When pinacolone (methyl *tert*-butyl ketone) in CCl_4 is irradiated a similar reaction occurs (formation of the pair *tert*-butyl/$CCl_3\cdot$) and the observed second crossing point of the $CHCl_3$ polarization curve is shifted to 550 G, as there are now nine protons present instead of seven.

The agreement with experiment, observed in Figure 7, would have been even better if a slightly higher value for Δg had been used. It shows most clearly that a nonzero J is needed in our model, at least in this case, to account for the A effect in the region 0–80 G (*cf.* Figures 2 and 7).

Propene. The problem of propene formed from the isopropyl/$CCl_3\cdot$ pair was about the limit that could be handled by our computer. It comprises a nine-spin problem, with magnetic equivalence only for one methyl group (*cf.* VIII). In order to simulate the adiabatic transfer of the sample, a large number of steps (300) was needed. The simulation of propene and $CHCl_3$, formed in a 100-G field, shows a very good agreement with experiment (Figure 6). The same parameters as in the case of $CHCl_3$ have been used. The E line for the CH_3 group at 1.70 ppm is not present in the experimental spectrum. However, if one is very fast, it can be observed, but it vanishes rapidly by relaxation. The spectrum did not change very much, when reaction was carried out in lower fields.

The propene spectrum resulting from reaction in a field of 1500 G and a computer simulation are shown in Figure 8. There are some deviations; *e.g.*, the A lines, predicted for the methine proton at 5.70 ppm, seem to be missing. The general behavior of the propene spectrum, however, was reasonably well reproduced over the whole field range.

The prediction of the general theory that S pairs behave opposite to T and F pairs, in low fields as well as in high fields, is borne out by the spectra presented in Figure 9. In both cases reactions were run in a field H_r = 10 G. Spectrum b shows the vinyl region of propene formed from the isopropyl/$CCl_3\cdot$ radical pair during photolysis of DIK in CCl_4 (S case) and is similar to Figure 6.

Spectrum a was obtained after photolysis of DIK in the freon $CF_2Cl-CFCl_2$, in which case propene is formed mainly from the pair of two isopropyl radicals (F or T case, *cf.* VII). The spectra a and b are almost exactly each other's mirror image. They show, incidentally, that the nature of the other radical in the pair is not important in the very low-field range.

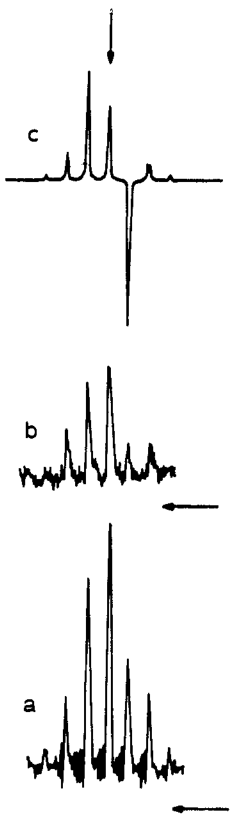

Figure 10. Spectrum of the methine proton (δ 4.13 ppm) of isopropyl chloride, resulting from photolysis of DIK in CCl_4, in a field H_r = 1000 G of a separate magnet (a) and in the fringing field (1000 G) of the spectrometer magnet (b). A computer simulation is shown on top (c).

Isopropyl Chloride. The methine proton shows a "$n - 1$ multiplet" (sextet) in very low fields, which is still visible at 100 G in Figure 6b. From the lower trace in this figure (6c) it can be seen that relaxation toward thermal equilibrium is not uniform but is faster for the low-field lines of the septet (this multiplet disappears eventually). This skew relaxation seems to be particularly troublesome for this compound. Tentative calculations[17] indicated that it is possible that E lines of the septet are inverted due to nuclear dipole relaxation. Our failure to simulate correctly the high-field spectra has been blamed on this effect (*cf.* VII).[15] It seems to be even stronger in low fields.[18] An experimental indication for this can be observed in Figure 10, which shows the isopropyl chloride septet as it arises from reaction in a 1000-G field of a separate magnet (a), the same when reaction is run in the fringing field H_r = 1000 G of the A-60 magnet (b), and a rather unusual simulation with one E line as calculated for this field (c). The difference between a and b must be due to relaxation during the time the sample dwells in the earth's field (about 1 sec). Although spectrum b still does not show E, the trend is in the right direction.

The spectra calculated for the methyl doublet of isopropyl chloride show also deviations from experiment (Figure 11), most seriously for the 100-G case. Values of λ close to unity gave the best results.

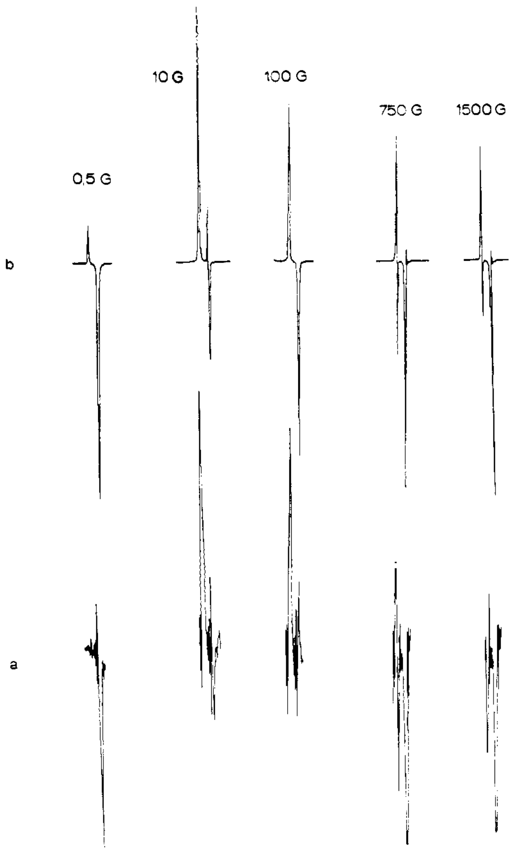

Figure 11. Spectra of the isopropyl chloride methyl doublet after irradiation of DIK in CCl_4 in various fields as indicated in the figure. Experimental (a) and simulated (b) spectra are shown.

4.3. Other Work. Ward, *et al.*,[2b] have reported polarization in isopropyl iodide, present during decomposition of benzoyl peroxide in the earth's field. The observed pattern, an E sextet for the methine proton and an E/A doublet (E smaller than A) for the methyl group, is in accordance with escape from an F pair of isopropyl radicals (2R·) and subsequent thermoneutral iodine atom transfer.

$$\begin{tikzcd} \overline{2\mathrm{R}\cdot}^{\,\mathrm{F}} \arrow[r] \arrow[dr] & \text{diff} & \mathrm{R}\cdot^{*} + \mathrm{RI} \arrow[r] & \mathrm{R^{*}I} + \mathrm{R}\cdot \\ & \mathrm{R{-}R} & & \end{tikzcd} \qquad (43)$$

In zero-field E and A "$n - 1$ multiplets" are expected; $\Gamma_{\mathrm{me}} = + - + - + + = +$, E/A. The presence of the E line in the methyl doublet is reproduced by a computer simulation taking H_r = 0.5 G and $0.5 < \lambda < 1.0$. It is probably not caused by deviations from a adiabatic behavior during transfer.

Another system reported in this paper[2b] involves the formation of 1-chloro-1-phenylpropane in the reaction of α,α-dichlorotoluene with ethyllithium

$$\mathrm{PhCCl_2H + CH_3CH_2Li} \longrightarrow$$

$$\begin{tikzcd} & \text{diff} \\ \mathrm{LiCl} + \overline{\mathrm{PhCClH}\cdot + \mathrm{CH_3CH_2}\cdot}^{\,\mathrm{S}} \arrow[ur] \arrow[dr] & \\ & \mathrm{PhCClHCH_2CH_3} \end{tikzcd} \qquad (44)$$

The 1 proton showed an E triplet, both when the reaction was run in the earth's field and in "zero field."[19]

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(17) A more detailed study of this relaxation problem is in progress.

(18) In case of reaction in zero-field intramolecular dipole relaxation does not alter the populations in zero field, because transitions between different K manifolds are forbidden and levels within a given K manifold have already equal populations.

(19) In this experiment the earth's field was shielded such that the residual field was in the milligauss range: H. R. Ward and R. G. Lawler, personal communication.

We have simulated this system with $H_r = 0$ and with $H_r = 0.5$ G and in both cases an *E* triplet, with lines of about equal intensities, was obtained for the methine proton. Apparently the inner lines of multiplets vanish in zero field only when but two groups of equivalent nuclei are present in the product. We note that the population of the zero-field levels still occurs uniformly within the *K* manifolds; however, this does not lead to "$n - 1$ multiplets" when more than two groups are present.

Fischer and Lehnig[20] have studied the field dependence of the benzene line during decomposition of benzoyl peroxide. The *E* effect in high fields changed to *A* at lower fields. This behavior would require a negative *J* in our model.

5. Conclusions

The diffusion model of CIDNP, extended to include mixing of S with all three T states of the radical pair, is capable of accounting for polarization in products formed in low as well as in high magnetic fields. It seems necessary to retain a nonzero effective exchange integral in this model. The magnitude of *J* was found to be consistent with values which gave the best fit for high-field spectrum simulations in the case of the ethyl radical pair (*cf.* VIII and XII).[14b] A nonzero *J* is also necessary to reproduce the peculiar oscillations of the polarization *vs.* magnetic field curve in the case of chloroform formed in the photoreaction of diisopropyl ketone in CCl_4 (Figure 7).

Little or no information on the actual behavior of *J* in diffusing radical pairs in available from other sources. Adrian[21] has set $J = 0$. This value or at least values much lower than the hf parameters seemes to give good results for high-field spectrum simulations in cases where benzyl or diphenyl methyl type radicals are involved.[21b,22] The difference with the alkyl radical systems, which we have been concerned with, may reflect the larger electron delocalization in the aromatic radicals, which, if anything, would be expected to decrease $|J|$ for a given interradical separation. It may be noted that our averaging procedure selects those pairs which have a shorter than average separation. This is obvious in the case of recombination products because there we are concerned with pairs that eventually react. It is, however, also true for escape products in our treatment.[23]

It is interesting that the chemically significant parameter λ can be obtained from the low-field CIDNP spectra. Our results for small radicals show that λ is close to unity. For larger radicals one might expect smaller values for λ, since it becomes less probable that the orientation, favorable for reaction, is attained during an encounter.

Furthermore, it appears from the low-field spectra that adiabatic behavior during sample transfer between magnets is closely obeyed, in the case that nmr coupling constants are of the order 6–7 Hz. For coupling constants of about 1 Hz, however, departures may occur and this may partly be the cause of some of the differences between the experimental and simulated spectra of propene (Figures 6 and 8).[24,25]

Acknowledgment. We thank Dr. S. H. Glarum and Professors H. Fischer, G. L. Closs, F. J. Adrian, H. R. Ward, and R. G. Lawler for communicating results prior to publication. We are indebted to Mr. P. C. M. van Rossum, G. A. van Albada, and F. W. Verheus for experimental assistance.

Appendix

Populations of Zero-Field Levels. The Hamiltonian for a radical pair in zero field becomes (*cf.* eq 1)

$$H_{\mathrm{RP}} = -J(^1/_2 + \mathbf{S}_1\cdot\mathbf{S}_2) + \mathbf{S}_1\cdot\sum_j{}^a A_j\mathbf{I}_j + \mathbf{S}_2\cdot\sum_k{}^b A_k\mathbf{I}_k \quad \text{(A1)}$$

A total spin operator can be defined as $\mathbf{F} = \mathbf{S} + \mathbf{K}$, where $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ and $\mathbf{K} = \Sigma_i\mathbf{I}_i$ (**K** is the total nuclear spin operator). The nuclear Hamiltonian for the reaction product is simply

$$H^{\mathrm{P}} = \sum_{i>j} J_{ij}\mathbf{I}_i\cdot\mathbf{I}_j \quad \text{(A2)}$$

which is diagonal in the *K* representation[29] because $[H^{\mathrm{P}}, K^2] = 0$ and $[H^{\mathrm{P}}, K_z] = 0$. Therefore, the nuclear states of the product are eigenstates of K^2 and K_z and will be denoted by $|KM_K\rangle$. We wish to show that our model predicts that the populations of these nuclear states do not depend on M_K, which should be the case, since in zero field the system is rotationally invariant.

The zero-field CIDNP problem can be treated most conveniently in a basis $|SM_SKM_K\rangle$. Using this basis

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(20) H. Fischer and M. Lehnig, personal communication.

(21) (a) F. J. Adrian, *J. Chem. Phys.*, **53**, 3374 (1970); (b) *ibid.*, **54**, 3912 (1971).

(22) G. L. Closs, personal communication.

(23) We use the same distribution function f(*t*) as has been used in the case of P products. We have considered other functions as well, *e.g.*, $\exp[-kt]$, where *k* is a rate constant for disappearance of the radicals. However, it can be verified that this does not lead to S–$T_\pm$ polarization, when $k < \omega$, which normally will be the case. Therefore, in our opinion, polarization in escape products is due to those pairs which have undergone at least one unreactive reencounter and originates from S–T transitions during the time between birth and reencounters. For this reason the function f(*t*) appears in eq 33.

(24) After submission of this paper we have performed more extended computer calculations on the field-dependent CIDNP problem, taking into account all nuclear spins present in the pairs. In the case of the photolysis of diisopropyl ketone in CCl_4 it appears that the observed oscillation in the field dependence of the chloroform polarization can be reproduced using for the exchange integral $J = 0$, provided that all protons and, remarkably, *all chlorine nuclei* $A(^{35}Cl) = 6.3$ G, $A(^{37}Cl) = 5.2$ G[16] present in the isopropyl/trichloromethyl radical pair are included in the calculation. Similarly, high-field simulations give good results with $J = 0$, when all nuclear spins are taken into account. Thus, in the diffusion model with $J = 0$ it seems to be essential for a quantitative fit to consider all nuclei coupled to the "unpaired" electrons of the radical pair, even those that do not normally affect the nmr spectrum of the product in any way. Hence, our conclusion regarding the magnitude of *J* has to be modified, since it appears that the more complete calculations can account for the experimental data using $J = 0$, which is more consistent with the general idea of the diffusion model.[21] This would eliminate one of the ambiguous parameters in the theory. We are indebted to Professor G. L. Closs for helpful suggestions regarding this matter.

(25) Since this work was completed three papers have appeared which have bearing on the low-field CIDNP problem.[26–28] Bargon and Charlton[26] observed zero-field polarization in reactions of deuterated benzoyl peroxides. Their spectra can be accounted for by the rule (40) for zero-field multiplets. Adrian's[27] low-field theory considers mixing of S with T_- separately, whereas simultaneous coupling of the four electronic states seems essential to account for the observed oscillations in the field dependence of the polarization. Garst and coworkers[28] have treated the field dependence of CIDNP in a way that is very similar to the theory presented here, apart from a different averaging procedure. We thank Dr. Garst for sending us a copy of his manuscript.

(26) J. L. Charlton and J. Bargon, *Chem. Phys. Lett.*, 8, 442 (1971).

(27) F. J. Adrian, *ibid.*, 10, 70 (1971).

(28) J. I. Morris, R. C. Morrison, D. W. Smith, and J. F. Garst, *J. Amer. Chem. Soc.*, **94**, 2406 (1972).

(29) *Cf.* ref 10, p 177.

the formalism of section 2 can be applied. Since H_{RP} commutes with F^2 and with the components of **F**

$$[H_{RP},F^2] = 0 \quad [H_{RP},\mathbf{F}] = 0 \qquad (A3)$$

the eigenstates of the radical pair can be characterized by F and M (M is the eigenvalue of F_z); the elements of the eigenvector matrix **T** (eq 5) are essentially Clebsch–Gordon coefficients. The matrix $\mathbf{Q}^P$ appearing in eq 11 becomes $\mathbf{Q}^P = \mathbf{E}_S \otimes \mathbf{I}$ (**I** is the unit matrix of order L) and therefore eq 18 now reads

$$V^P{}_{\nu l} = T_{1\nu',l} \qquad (A4)$$

As a result, we have for the population of state $|1\nu'\rangle = |00KM_K\rangle$ in the case of a S precursor (*cf.* eq 24)

$$P^S{}_{\nu'} = \lambda(p - m\sum_{r'}\sum_{l,j} T_{1r',l}T_{1r',j}T_{1\nu',l}T_{1\nu',j} \times \sqrt{2\pi\omega_{lj}}) \qquad (A5)$$

the Clebsch–Gordon coefficient $T_{1\nu',l} = \langle 00KM_K|FM\rangle$ has nonzero values for $M = M_K$, $F = K$, which restricts the sum over l and j to states with the same K and M_K. However, the coefficients $\langle 00KM_K|KM_K\rangle$ are all equal to unity[30] and therefore do not depend on M_K. Furthermore, ω_{jl} can be written

$$\omega_{jl} = |\omega_j - \omega_l| = |(H_{RP})_{jFM} - (H_{RP})_{lF'M'}| = |(H_{RP})_{jKM_K} - (H_{RP})_{lKM_K}| \qquad (A6)$$

By using the fact that H_{RP} commutes with the components of **F** (eq A3) it is easy to show[31] that the diagonal matrix elements $(H_{RP})_{jKM_K}$ are independent of M_K. Thus the populations $P^S{}_{\nu'}$ do not depend on M_K either and are all equal within a K manifold. Since we have shown that the polarization from S and T precursors is opposite (eq 27), the same will hold in the case of a T precursor.

[30] A. Messiah, "Quantum Mechanics," Vol. II, North-Holland Publishing Co., Amsterdam, 1961, p 1058.

[31] *Cf.* ref 30, p 569.

Chemically Induced Dynamic Nuclear Polarization. XI. Thermal Decomposition of Acetyl Peroxide

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Abstract: A CIDNP study has been made of the thermal decomposition of acetyl peroxide and of carbon-13 and deuterium-substituted analogs. Proton, carbon-13, and deuterium CIDNP spectra have been recorded and are compared with computer simulations. The spectra can be accommodated with formation of acetoxy radicals, which decarboxylate rapidly to give methyl radicals. Net polarization in the geminate recombination products, methyl acetate and ethane, is probably due to singlet–triplet (T_0) transitions in the methyl–acetoxy radical pair (memory effect). In the case of the substituted acetyl peroxides, most of the ethane polarization arises from the methyl radical pairs. Applying a quantitative theory developed previously (part IX) for the case of reactions that compete with geminate recombination, it is found that (i) the absolute magnitude of the polarization enhancement, (ii) the ratio of the polarizations of methyl acetate and ethane, and (iii) the ratio of contributions from methyl–methyl and methyl–acetoxy radical pairs are compatible with a rate constant for the decarboxylation of the acetoxy radical in the range 2–3 × 10^9 sec^{-1}.

1. Introduction

The decomposition of acetyl peroxide (AP) is one of the most extensively investigated homolytic reactions. We have therefore choosen to study this reaction with nmr[2] in order to test current theories of CIDNP and to see whether nuclear polarization can help to answer some of the remaining questions concerning the reaction mechanism.

In most solvents the thermal decomposition of AP, $CH_3C(=O)OOC(=O)CH_3$, follows first-order kinetics with a rate constant very similar to a number of other acyl peroxides.[3] This has been taken as evidence[4] for the fact that the primary step is formation of a pair of acetoxy radicals by simple O–O bond scission; this is substantiated by a study of oxygen and deuterium isotope effects.[5] Szwarc and coworkers[4] suggested that methyl acetate and ethane were formed by a "cage" reaction, following decarboxylation of the very unstable acetoxy radical. This was inferred from their observation that these products were always formed in solution but not in the gas phase. ^{18}O scrambling found in both peroxide[5a] and methyl acetate[5a,6] from specifically labeled AP supports the intermediacy of short-lived acetoxy radicals. Cage recombination of acetoxy radicals may be responsible for the observed viscosity dependence of the overall decomposition rate.[7] Recent

[1] Address correspondence to Shell Research Laboratories, Amsterdam, the Netherlands.

[2] (a) Presented in part at the CIDNP symposium of the American Chemical Society meeting in Houston, Texas, Feb 1970. (b) A preliminary account for this work was given in part I: R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968).

[3] R. C. P. Cubbon, *Progr. React. Kinet.*, **5**, 29 (1970).

[4] (a) M. Szwarz in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience, New York, N. Y., 1962, p 153; (b) A. Rembaum and M. Szwarc, *J. Amer. Chem. Soc.*, **77**, 3486 (1955); (c) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961).

[5] (a) J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967); (b) T. Koenig and R. Cruthoff, *ibid.*, **91**, 2562 (1969).

[6] T. Kashiwagi, S. Kozuka, and S. Oae, *Tetrahedron*, **26**, 3619 (1970).

[7] W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).