an encounter of duration t_0 is

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

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 $\Psi_{0\text{S}}$ and $\Psi_{0\text{T}}$ can be described as follows

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

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

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 $U = U_{\text{RP}}(t,t_0)$, describing S–T mixing in the radical pair. In terms of the evolution operator the coefficients of eq 16 are

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

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

where we have suppressed the label n. The fraction that gives product during the first encounter is

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

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

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

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

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 $C_{\text{S}}(0)$, $C_{\text{T}}(0)$, and γ. Averaging also over all possible values of $|C_{\text{S}}(0)|^2$ and $|C_{\text{T}}(0)|^2$ and using the identity $(1 + \eta^2)^{-1} = 1 - \lambda$ (from B6) we obtain

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

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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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]

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

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[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).

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

here to reactions carried out in high magnetic fields, since this simplifies the problem of S–T mixing considerably (only S–T_0 mixing is involved at high fields). Furthermore, there are no experimental data available on competitive reactions in low fields.

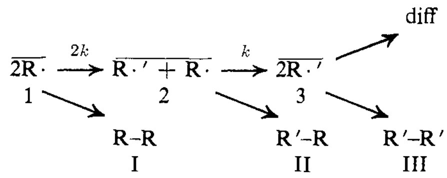
We shall consider radical transformations, such as fragmentations (*e.g.*, decarboxylation of acyloxy radicals), rearrangements (*e.g.*, cyclopropylcarbinyl → butenyl), and fast scavenging by transfer reactions.

When one of the radicals of a pair undergoes a transformation, a new pair is formed, which continues the random walk and has a certain chance of recombination as well. Because of the very short time needed for the actual process of the transformation (10^{-13}–10^{-12} sec) spin correlation of the pair will not be destroyed during this process; it could only be destroyed by magnetic interactions which have a much longer time scale. Thus, if a pair is in the singlet (S) state just before the reaction of one of its members, the new pair will also start as a S pair. This is important, because it implies that CIDNP effects can be expected for products of the secondary pair and of other subsequent pairs with a common precursor. A detailed discussion of this is given in section 2. The special case of stereospecificity and CIDNP during homolytic rearrangements, where "reaction" is reorientation of a fragment, is treated separately (section 3). A few experimental examples are discussed in section 4.

2. Theory

2.1. Competitive Reactions. We consider the general reaction sequence of Scheme I, where k is the unimolecular rate constant for the reaction R· → R·′. The bar indicates pairs with correlated spins ("cage" in the extended sense). Radical pairs will be denoted P_1, P_2, P_3 and products by P_I, P_{II}, P_{III}. We will examine what the conditions are under which polarization occurs in these products.

Scheme I



Some general observations can already be made. For extremely fast reactions (large value of k) it will be as if pair 3 is formed almost instantaneously and yields of products I and II will be small. In contrast, for slow reactions (small k) yields of II and III will be small. The nuclear polarization for these products will follow a similar pattern. However, since CIDNP involves S–T mixing, which usually has a longer time scale than that associated with the bulk of geminate recombination, the optimum for polarization will be shifted toward longer times (or smaller values of k) as compared to that for the product yields. Necessary conditions for product formation from a certain pair are (i) that the pair exists, (ii) that there is a reencounter, and (iii) that the pair is in the singlet state. If no recombination occurred, the probability that the pair, born at $t = 0$, is present as pair 1, 2, or 3 at time t is

$$P_1(t) = e^{-2kt} \tag{1a}$$

$$P_2(t) = 2(1 - e^{-kt})e^{-kt} \tag{1b}$$

$$P_3(t) = (1 - e^{-kt})^2 \tag{1c}$$

and of course we have $P_1(t) + P_2(t) + P_3(t) = 1$. The probability of a first reencounter at time t after separation at $t = 0$ is[3]

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

where m depends mainly on the frequency of diffusive displacements ($\nu \sim 10^{11}$ sec^{-1}) and has a value of about 10^{-6} sec$^{1/2}$; p (Noyes: β)[3] is the total probability of at least one reencounter, $p = \int_0^\infty \mathrm{f}(t)\mathrm{d}t$, $0.5 < p < 1$. After a few diffusion steps f(t) approaches $mt^{-3/2}$, which is a slowly decreasing function of time.

Furthermore, our model for S–T mixing in radical pairs[2a,4,5] leads to the following expressions for the probability of the pair with nuclear state n being in the S state

$$|C_{S_n}{}^{S}(t)|^2 = 1 - (a_n/\omega)^2 \sin^2 \omega t \tag{3a}$$

$$|C_{S_n}{}^{T}(t)|^2 = (a_n/\omega)^2 \sin^2 \omega t \tag{3b}$$

where the superscripts denote the precursor multiplicities; a_n is the S–T_0 mixing matrix element, and $\omega = (J^2 + a_n{}^2)^{1/2}$, with the exchange integral J (for ω we suppress the label n, which labels the nuclear spin states).

If probabilities for both S–T_0 mixing and product formation are small, we may treat these processes and the competing reaction independently. The probability of recombination at time t is then a product of the probabilities (1), (2), (3), and λ the chance of reaction during a singlet encounter.

This factor λ (Noyes: α) can be thought of as a steric factor, which takes into account the fact that singlet encounters will not lead to reaction, when a favorable relative orientation is not attained during the encounter. For small radicals λ will be close to unity, while for larger radicals it may be smaller. The cases of S and T precursors are now treated respectively.

2.2. S Precursor. In this case the fraction of pairs with nuclear state n, present as pair 1 in the S state, will be

$$P_{1S_n}(t) = |C_{1S_n}{}^{S}(t)|^2e^{-2kt} \tag{4}$$

where $C_{1S_n}{}^{S}(t)$ is given by eq 3a with the matrix element a_n calculated with the magnetic parameters of pair 1 (a_{1n}).

The (fractional) population of level n of product I is

$$P_{In} = \int_0^\infty \lambda_I P_{1S_n}(t)\mathrm{f}(t)\mathrm{d}t$$

Evaluating this integral (Laplace transform) with eq 2, 3, and 4 we obtain

$$P_{In} = \lambda_I(y_I - q_{1n}) \tag{5}$$

where

$$y_I = pe^{-(2m/p)(2\pi k)^{1/2}} \tag{6}$$

and

$$q_{1n} = m\pi^{1/2}(a_{1n}/\omega)^2F(k) \tag{7}$$

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

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

with

$$F(k) = \{k + (k^2 + \omega^2)^{1/2}\}^{1/2} - (2k)^{1/2} \quad (8)$$

Limiting expressions for q_{1n} are for $k \gg \omega$

$$q_{1n} = {}^1/_2 m\pi^{1/2}a^2{}_{1n}(2k)^{-3/2} \quad (9a)$$

and for $k \ll \omega$

$$q_{1n} = m\pi^{1/2}a^2{}_{1n}\omega^{-3/2}\{1 - (2k/\omega)^{1/2}\} \quad (9b)$$

The latter (eq 9b) approaches x_n (eq 22, part VIII) for small k, as it should.

Neglecting product formation for the moment we can write for $P_{2n}(t)$, the probability for pairs with nuclear state n being present as pair 2

$$\frac{\mathrm{d}}{\mathrm{d}t}P_{2n}(t) = 2kP_{1n}(t) - kP_{2n}(t) = 2k|C_{1\mathrm{S}_n}{}^{\mathrm{S}}(t)|^2e^{-2kt} - kP_{2n}(t) \quad (10)$$

where we have set $P_{1n}(t) \cong P_{1\mathrm{S}_n}(t)$, excluding from consideration pairs 1 in the T_0 state. This amounts to effectively neglecting any transitions back to the S state, once a pair has arrived in the T_0 state, which is allowed for small transition probabilities. Furthermore, it is reasonable to assume that $|C^{\mathrm{S}}{}_{1\mathrm{S}_n}(t)|^2$ reaches a stationary value before $P_{2n}(t)$ does, so we replace it by its average value

$$\overline{|C_{1\mathrm{S}_n}{}^{\mathrm{S}}(t)|^2} = 2k\int_0^\infty |C_{1\mathrm{S}_n}{}^{\mathrm{S}}(t)|^2e^{-2kt}\mathrm{d}t = 1 - \frac{a^2{}_{1n}}{2(k^2 + \omega^2)} = 1 - \hat{x}_{1n} \quad (11)$$

Integrating (10) and correcting for product formation ($P_{\mathrm{I}n}(t)$ similarly is replaced by its stationary value $P_{\mathrm{I}n}$ for long times) we obtain

$$P_{2n}(t) = (1 - P_{\mathrm{I}n})(1 - \hat{x}_{1n})2(1 - e^{-kt})e^{-kt} \quad (12)$$

and for product II

$$P_{\mathrm{II}n} = \int_0^\infty \lambda_{\mathrm{II}}|C_{2\mathrm{S}_n}{}^{\mathrm{S}}(t)|^2P_{2n}(t)\mathrm{f}'(t)\mathrm{d}t \quad (13)$$

Now the S–T_0 mixing coefficients have to be calculated with the magnetic parameters pertaining to pair 2.

Here we cannot use the function f(t) of eq 2, which is the reencounter probability of a pair, *just separated from an encounter*. To determine the function f′(t) we make use of a procedure of Braun, *et al.*[6] The total encounter probability of a pair formed at a distance $r(t_1)$ at time t_1 is $p\rho 1.13/r(t_1)$, where $r(t_1)$ is given by[7] $r(t_1) = (\nu\sigma^2t_1)^{1/2}$. ($\rho$ is the encounter diameter, and σ and ν are the mean diffusion step length and frequency, respectively.) The function f′(t) is the encounter probability at $t > t_1$; hence

$$\int_{t_1}^\infty \mathrm{f}'(t)\mathrm{d}t = p\rho 1.13/\nu^{1/2}\sigma t_1{}^{1/2} \quad (14)$$

and by differentiating (14)

$$\mathrm{f}'(t) = (p\rho/2\nu^{1/2}\sigma)t^{-3/2} = m't^{-3/2} \quad (15)$$

When the radicals in pairs 1 and 2 have similar sizes m and m' are expected to have a similar magnitude. We can now integrate (13) with (15), obtaining the result

$$P_{\mathrm{II}n} = \lambda_{\mathrm{II}}(1 - P_{\mathrm{I}n})(1 - \hat{x}_{1n})\{y_{\mathrm{II}} - q_{2n}\} \quad (16)$$

where

$$y_{\mathrm{II}} = 2p\{e^{-(2m'/p)(\pi k)^{1/2}} - e^{-(2m'/p)(2\pi k)^{1/2}}\} \quad (17)$$

and

$$q_{2n} = m'\pi^{1/2}(a_{2n}/\omega)^2\{F({}^1/_2k) - F(k)\} \quad (18)$$

with $F(k)$ given by eq 8. It has been assumed that f′(t) approaches f(t) in the limit of very large k, hence the appearance of p in eq 17. However, in the region $k < 10^{10}$ sec^{-1}, eq 17 becomes independent of p.

For the calculation of $P_{\mathrm{III}n}$ we make similar approximations and for the sake of simplicity we assume that m' (*cf.* eq 15) is the same for pairs 2 and 3. Using the average value of $|C_{2\mathrm{S}_n}{}^{\mathrm{S}}(t)|^2$

$$\overline{|C_{2\mathrm{S}_n}{}^{\mathrm{S}}(t)|^2} = k\int_0^\infty |C_{2\mathrm{S}_n}{}^{\mathrm{S}}(t)|^2 2e^{-kt}(1 - e^{-kt})\mathrm{d}t = 1 - a^2{}_{2n}\{4/(k^2 + 4\omega^2) - 1/[2(k^2 + \omega^2)]\} = 1 - \hat{x}_{2n} \quad (19)$$

we arrive at

$$P_{3n}(t) = (1 - P_{\mathrm{I}n})(1 - P_{\mathrm{II}n}) \times (1 - \hat{x}_{1n})(1 - \hat{x}_{2n})(1 - e^{-kt})^2 \quad (20)$$

and the population of product III becomes

$$P_{\mathrm{III}n} = \int_0^\infty \lambda_{\mathrm{III}}|C_{3\mathrm{S}_n}{}^{\mathrm{S}}(t)|^2P_{3n}(t)\mathrm{f}'(t)\mathrm{d}t = \lambda_{\mathrm{III}}(1 - P_{\mathrm{I}n})(1 - P_{\mathrm{II}n}) \times (1 - \hat{x}_{1n})(1 - \hat{x}_{2n})\{y_{\mathrm{III}} - q_{3n}\} \quad (21)$$

where

$$y_{\mathrm{III}} = p\{1 - 2e^{-(2m'/p)(\pi k)^{1/2}} + e^{-(2m'/p)(2\pi k)^{1/2}}\} \quad (22)$$

and

$$q_{3n} = m'\pi^{1/2}(a_{3n}/\omega)^2\{\omega^{1/2} - 2F({}^1/_2k) + F(k)\} \quad (23)$$

Summarizing the results for the S case, eq 5, 16, and 21, and neglecting products of small quantities, we get

$$P^{\mathrm{S}}{}_{\mathrm{I}n} = \lambda_{\mathrm{I}}\{y_{\mathrm{I}} - q_{1n}\} \quad (24a)$$

$$P^{\mathrm{S}}{}_{\mathrm{II}n} = \lambda_{\mathrm{II}}(1 - P_{\mathrm{I}})\{y_{\mathrm{II}}(1 - \hat{x}_{1n}) - q_{2n}\} \quad (24b)$$

$$P^{\mathrm{S}}{}_{\mathrm{III}n} = \lambda_{\mathrm{III}}(1 - P_{\mathrm{I}})(1 - P_{\mathrm{II}}) \times \{y_{\mathrm{III}}(1 - \hat{x}_{1n} - \hat{x}_{2n}) - q_{3n}\} \quad (24c)$$

where P_{I} and P_{II} are the nuclear spin independent parts[8] of $P_{\mathrm{I}n}$ and $P_{\mathrm{II}n}$. A notable result is the fact that polarization in products II and III is a sum of contributions from all preceding pairs. This might be called a "memory effect," because the effect of S–T transitions in a specific pair is stored and appears later as polarization in the recombination products of other pairs. Of course this effect arises only if the same nuclei are present in the pairs. There are experimental examples of this effect, as will be discussed in section 4.

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

(7) A. Einstein, *Z. Elektrochem.*, **14**, 235 (1908).

(8) The "escape" polarization arising from the factor $(1 - P_{\mathrm{I}n})$ is only a fraction of the (opposite) polarization due to the factor $(1 - \hat{x}_{1n})$. Therefore, as to the polarization of P_{II}, the radicals of pair 2 cannot simply be considered as "escaped" from recombination in pair 1.

2.3. T Precursor. We make the same approximations as for the S case; only the first reencounter is considered. Then

$$P_{\mathrm{I}n} = \int_0^\infty {}^1/_3\lambda_{\mathrm{I}}|C_{1\mathrm{S}n}{}^{\mathrm{T}}(t)|^2 e^{-2kt}\mathrm{f}(t)\mathrm{d}t = {}^1/_3\lambda_{\mathrm{I}}q_{1n} \quad (25)$$

where we have used (3b) and q_{1n} is defined by eq 7. Again assuming that transitions back to triplet are not important and noting that $\overline{|C_{1\mathrm{S}n}{}^{\mathrm{T}}(t)|^2} = \hat{x}_{1n}$ (*cf.* eq 11) we have, similarly to eq 12

$$P_{2n}(t) = (1 - \hat{x}_{1n})2(1 - e^{-kt})e^{-kt} \quad (26)$$

The singlet fraction of pairs 2 is

$$P_{2\mathrm{S}n}(t) = {}^1/_3\{|C_{2\mathrm{S}n}{}^{\mathrm{T}}(t)|^2(1 - \hat{x}_{1n}) + (1 - P_{\mathrm{I}n})\hat{x}_{1n}\}2(1 - e^{-kt})e^{-kt} \quad (27)$$

where we have separately included the fraction that has crossed over from T_0 to S in pair 1.

The factor $^1/_3$ arises, because only one-third of the triplets (the T_0 state) gives rise to S–T mixing in high fields. In the same notation as used in eq 24 we have

$$P_{\mathrm{II}n} = \int_0^\infty \lambda_{\mathrm{II}}P_{2\mathrm{S}n}(t)\mathrm{f}'(t)\mathrm{d}t = {}^1/_3\lambda_{\mathrm{II}}\{q_{2n}(1 - \hat{x}_{1n}) + (1 - P_{\mathrm{I}n})\hat{x}_{1n}y_{\mathrm{II}}\} \quad (28)$$

Similarly

$$P_{3n}(t) = (1 - \hat{x}_{1n})(1 - \hat{x}_{2n})(1 - e^{-kt})^2 \quad (29)$$

$$P_{3\mathrm{S}n}(t) = {}^1/_3[|C_{3\mathrm{S}n}{}^{\mathrm{T}}(t)|^2(1 - \hat{x}_{1n})(1 - \hat{x}_{2n}) + (1 - P_{\mathrm{II}n})\{(1 - P_{\mathrm{I}n})\hat{x}_{1n} + \hat{x}_{2n}\}](1 - e^{-kt})^2 \quad (30)$$

$$P_{\mathrm{III}n} = {}^1/_3\lambda_{\mathrm{III}}[q_{3n}(1 - \hat{x}_{1n})(1 - \hat{x}_{2n}) + y_{\mathrm{III}}(1 - P_{\mathrm{II}n})\{(1 - P_{\mathrm{I}n})\hat{x}_{1n} + \hat{x}_{2n}\}] \quad (31)$$

Neglecting products of small quantities the results for the T case (25), (28), and (31) become

$$P^{\mathrm{T}}{}_{\mathrm{I}n} = {}^1/_3\lambda_{\mathrm{I}}q_{1n} \quad (32a)$$

$$P^{\mathrm{T}}{}_{\mathrm{II}n} = {}^1/_3\lambda_{\mathrm{II}}\{q_{2n} + y_{\mathrm{II}}\hat{x}_{1n}\} \quad (32b)$$

$$P^{\mathrm{T}}{}_{\mathrm{III}n} = {}^1/_3\lambda_{\mathrm{III}}\{q_{3n} + y_{\mathrm{III}}(\hat{x}_{1n} + \hat{x}_{2n})\} \quad (32c)$$

Again we have as a result that to a good approximation the polarization is a sum of contributions of all preceding pairs.

2.4. Enhancement Factors and Product Yields. An illustration of expressions 24 for the case of a S precursor will now be given. If the extent of S–T_0 mixing is small, the product yields may be equated with the nuclear spin independent parts of eq 24

$$P_{\mathrm{I}} = \lambda_{\mathrm{I}}y_{\mathrm{I}} \quad (33a)$$

$$P_{\mathrm{II}} = \lambda_{\mathrm{II}}(1 - P_{\mathrm{I}})y_{\mathrm{II}} \quad (33b)$$

$$P_{\mathrm{III}} = \lambda_{\mathrm{III}}(1 - P_{\mathrm{I}})(1 - P_{\mathrm{II}})y_{\mathrm{III}} \quad (33c)$$

where y_{I}, y_{II}, and y_{III} are given by eq 6, 17, and 22. In Figure 1 these yields (in per cent) are plotted as a function of k, for the case where $p = {}^1/_2$, $m' = m = 10^{-6}$ sec$^{1/2}$ and $\lambda_{\mathrm{I}} = \lambda_{\mathrm{II}} = \lambda_{\mathrm{III}} = 1$. The maximum yield is 50% due to our choice of $\lambda p = 0.5$. The behavior is as expected: for small k only product I is formed in appreciable yield and in the region of very large k, only product III. P_{II} goes through a maximum at about $k = 2 \times 10^{10}$ sec^{-1}. In the region of small k we have $y_{\mathrm{II}} = 1.64m'(\pi k)^{1/2}$ and $y_{\mathrm{III}} = 1.17m'(\pi k)^{1/2}$, and hence both P_{II} and P_{III} exhibit a $k^{1/2}$ dependence[3c] in this region.

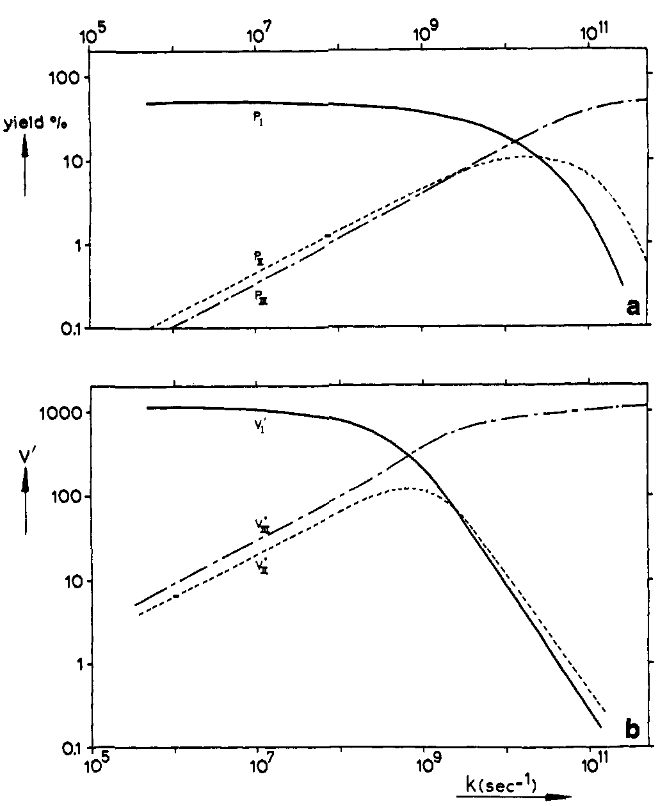

Figure 1. Plot of the yields P_{I}, P_{II}, P_{III} (in per cent) (a) and enhancement factors V_{I}', V_{II}', V_{III}' (b) *vs.* k. The parameters used in the calculations were the same for all three radical pairs. For their values, see the text. No "memory effect" has been taken into account, which corresponds to situations where polarization is due only to pairs from which the product is formed directly.

The enhancement factors (*cf.* VIII)

$$V'_i = (P_{in} - P_{im})(kT/g_{\mathrm{N}}\beta_{\mathrm{N}}H_0) \quad (34)$$

where i = I, II, or III, have been calculated for a one-proton case (S precursor). V' is used, because this is a better measure of the observability of the effects than the enhancement factor V based on the amount of product formed.[9] Besides, V' for different products of the same precursor is proportional to the relative CIDNP intensities of these products corrected for nuclear relaxation. The results are plotted in Figure 1. In order to facilitate comparison, the magnetic parameters have been given the same values for the three radical pairs: $A_{\mathrm{H}} = 4.4 \times 10^8$ radians/sec, $|J| = 5 \times 10^8$ radians/sec, $\Delta g = -6.5 \times 10^{-3}$, $kT/g_{\mathrm{N}}\beta_{\mathrm{N}}H_0 = 10^5$. These values have bearing on the alkyl/trichloromethyl radical pair, which is discussed in section 4. Inspection of Figure 1b is revealing. It can be seen that the general behavior of V' is similar to that of the product yields. However, the curves are shifted toward lower values of k. For instance, the maximum of V'_{II} occurs at about $k = 8 \times 10^8$ sec^{-1}, a factor 25 lower than for the maximum of P_{II}. In the high k region, V' goes as $k^{-3/2}$, but for low values of k a $k^{1/2}$ behavior similar to P_{II} is predicted. This result is characteristic for the diffusion model. A consequence is that the polariza-

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(9) To obtain the enhancement factor V, related to the thermal equilibrium intensity of the product (*cf.* VIII), one has to divide V' by the yield, which may be very small, giving very large values of V even when the signal would be too small to be detectable.

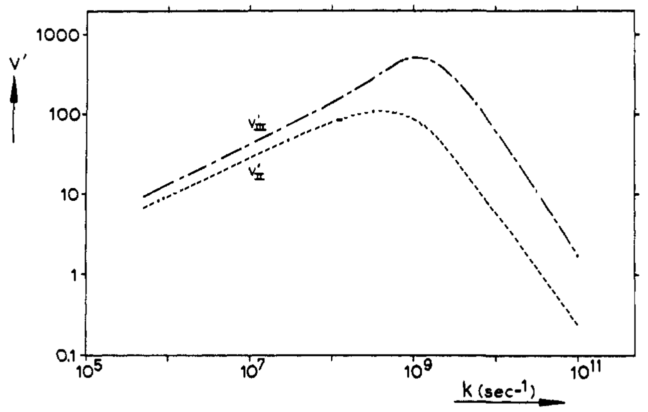


Figure 2. Plot of $|V_{\mathrm{II}}'|$ and $|V_{\mathrm{III}}'|$ *vs.* k for the case that polarization arises only from pair 2 (memory effect).

tion for products II and III drops off much slower for low values of k than other models would predict.

Taking a value of $k = 5 \times 10^8$ sec^{-1}, the yield of product I has decreased from 50 to 40%, whereas V'_I has dropped from 1200 to 400. A conclusion is that times of 10^{-8}–10^{-9} sec contribute appreciably to the polarization of geminate recombination products.

2.5. Memory Effect. As an example of this effect we have calculated the enhancement factors V'_{II} and V'_{III} for a one-proton case, where polarization in both products II and III is due only to pair 2. This situation is thought to occur in the decomposition of acetyl peroxide,[10] where emission in both methyl acetate and ethane arises probably from S–T_0 mixing in the methyl/acetoxy radical pair. If pairs 1 and 3 cannot contribute to the polarization, we have

$$P_{\mathrm{II}n} = \lambda_{\mathrm{II}}(1 - P_\mathrm{I})\{y_{\mathrm{II}} - q_{2n}\} \tag{35a}$$

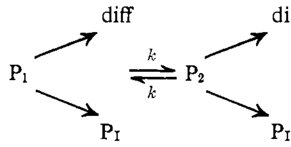
$$P_{\mathrm{III}n} = \lambda_{\mathrm{III}}(1 - P_\mathrm{I})(1 - P_{\mathrm{II}})(1 - \bar{x}_{2n})y_{\mathrm{III}} \tag{35b}$$

In Figure 2, $|V'_{\mathrm{II}}|$ and $|V'_{\mathrm{III}}|$, defined as in eq 34 with 35, are plotted *vs.* k. The values $A_\mathrm{H} = -4.0 \times 10^8$ radians/sec and $\Delta g = -3.2 \times 10^{-3}$, pertaining to the methyl/acetoxy pair,[10b] have been used in the calculations. This choice results in a negative polarization.[11] Values of the other parameters are the same as those used in Figure 1. Notably, $|V'_{\mathrm{III}}|$ is everywhere larger than $|V'_{\mathrm{II}}|$, in the fast reaction region ($10^9 < k < 10^{10}$ sec^{-1}) a factor 6–10 larger. Thus, in the case of rapid reactions it may even occur that polarization from pair 2 is visible only in products of pair 3.

3. Stereospecific Homolytic Rearrangements

A few rearrangements of optically active compounds have been reported,[12,13] where a high degree of retention of configuration was observed and the homolytic nature of the process was established by the observation of CIDNP. It might appear as if these observations are in conflict with the present diffusion model, which, however, is not the case. The process of racemization competing with recombination is depicted in Scheme II. P_1 and P_2 are radical pairs that differ only in their relative orientation (*l* and *d* pairs) and similarly the products P_I and P_{II} (*l* and *d* products), P_I being the product with retention of configuration. The rate of racemization k is related to the tumbling frequency of the fragments. If no product formation occurred we would have

Scheme II



$$P_1(t) = {}^1/_2(1 + e^{-2kt}) \tag{36a}$$

$$P_2(t) = {}^1/_2(1 - e^{-2kt}) \tag{36b}$$

3.1. S Precursor. For $k > \omega$ populations of the products are now given by

$$P_{\mathrm{I/II}n} = \int_0^\infty \lambda|C_{\mathrm{S}n}{}^\mathrm{S}(t)|^2\,{}^1/_2(1 \pm e^{-2kt})\mathrm{f}(t)\mathrm{d}t = {}^1/_2\lambda[p\{1 \pm e^{-(2m/p)(2\pi k)^{1/2}}\} - m\pi^{1/2}a_n{}^2\{\omega^{-3/2} \pm {}^1/_2(2k)^{-3/2}\}] \tag{37}$$

Hence polarization occurs in both products, irrespective of the exact value of k. Interesting quantities are the sum and difference

$$P_{\mathrm{I}n} + P_{\mathrm{II}n} = \lambda\{p - m\pi^{1/2}a_n{}^2\omega^{-3/2}\} \tag{38}$$

$$P_{\mathrm{I}n} - P_{\mathrm{II}n} = \lambda\{pe^{-(2m/p)(2\pi k)^{1/2}} - {}^1/_2 m\pi^{1/2}a_n{}^2(2k)^{-3/2}\} \tag{39}$$

and the fraction of retention

$$(P_\mathrm{I} - P_{\mathrm{II}})/(P_\mathrm{I} + P_{\mathrm{II}}) = e^{-(2m/p)(2\pi k)^{1/2}} \tag{40}$$

Only the sum (38) has been observed so far;[12,13] it is equal to the normal S case (eq 22, part VIII). For solvents of ordinary viscosity k will be not much smaller than 10^{10} sec^{-1}. If we put $k = 10^{10}$ sec^{-1}, we find 40–60% retention for $^1/_2 < p < 1$. In fact this percentage could be even higher, because of "primary" cage recombination in the sense of Noyes, which we have not properly accounted for (*cf.* ref 3b). From (39) the difference of polarization of P_I and P_{II} is expected to be very small. Observation of $P_{\mathrm{I}n} - P_{\mathrm{II}n}$ requires that the nmr signals of P_I and P_{II} do not coincide. Separate signals can be observed when there is more than one asymmetric center present in the molecules[14] or when an optically active solvent is used. Observation of difference polarization could provide a stringent test on the theory presented here.

3.2. T Precursor. The results for the T case are

$$P_{\mathrm{I/II}n} = \int_0^\infty \frac{\lambda}{3(1-p)}|C_{\mathrm{S}n}{}^\mathrm{T}(t)|^2\,{}^1/_2(1 \pm e^{-kt})\mathrm{f}(t)\mathrm{d}t = \frac{\lambda}{6(1-p)}m\pi^{1/2}a^2{}_n\{\omega^{-3/2} \pm {}^1/_2(2k)^{-3/2}\} \tag{41}$$

$$P_{\mathrm{I}n} - P_{\mathrm{II}n} = \frac{\lambda}{6(1-p)}m\pi^{1/2}a^2{}_n(2k)^{-3/2} \tag{42}$$

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(10) (a) R. Kaptein, *Chem. Phys. Lett.*, 2, 261 (1968); (b) R. Kaptein, J. Brokken-Zijp, and F. J. J. de Kanter, *J. Amer. Chem. Soc.*, 94, 6280 (1972).

(11) The sign of net polarization and the "phase" of multiplet effects can be readily obtained from the rules for high field CIDNP: *cf.* R. Kaptein, *Chem. Commun.*, 732 (1971), and ref 2a.

(12) U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Lett.*, 3415 (1969).

(13) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970).

(14) This experiment was suggested by Professor J. E. Baldwin, personal communication.

$$P_{\mathrm{I}n} + P_{\mathrm{II}n} = \frac{\lambda}{3(1-p)} m\pi^{1/2}a^2{}_n\omega^{-3/2} \qquad (43)$$

$$(P_{\mathrm{I}} - P_{\mathrm{II}})/(P_{\mathrm{I}} + P_{\mathrm{II}}) = 2^{-5/2}(\omega/k)^{-3/2} \qquad (44)$$

Both retention (44) and difference polarization (42) will be very small for $k > 10^{10}$ sec^{-1}, whereas the sum (43) is identical with eq 24 (VIII). If short distance spin-orbit coupling would contribute to the intersystem crossing, there could be some retention.

4. Discussion of Experimental Examples

4.1. Radical Scavenging. We have previously reported[15] on the decomposition of isobutyryl peroxide (IBP) in the presence of CCl_3Br, which acts as a scavenger for isopropyl radicals, Chloroform, a product of the secondary isopropyl/trichloromethyl radical pair, exhibits a change of sign of the polarization, going from E to A, when the concentration of CCl_3Br is increased. The sign change occurred at 0.11 *M* CCl_3Br. This phenomenon was interpreted[15] in terms of a competition between S-precursor polarization of spin-correlated pairs and (opposite) F-type polarization (due to free-radical encounters of uncorrelated isopropyl and $CCl_3\cdot$ radicals).

The reactions are those of Scheme I, with $R\cdot$ = isopropyl, $R\cdot'$ = $CCl_3\cdot$ and $k = k_{tr}[CCl_3Br]$. The value of k_{tr} for the transfer reaction $R\cdot + CCl_3Br \rightarrow RBr + CCl_3\cdot$ is not known. For a similar radical ($CCl_3CH_2CHOCOCH_3$), Melville, *et al.*,[16] have found $k_{tr} = 2 \times 10^4$ l./mol sec (for a reaction temperature 80°). If our interpretation is correct, k_{tr} must be higher in our case. One can estimate a lower limit of k_{tr} from the theory presented here.

The signal intensities (*I*) are related to the enhancement factor V' (eq 34) as follows (*cf.* eq 42, VIII)

$$I = V'I(B_{t'})k_fT_1 \qquad (45)$$

where $I(B_{t'})$ is the intensity of a transition between the same nuclear states in the precursor at time t', when the maximum polarization occurs; k_f is the rate constant for the formation of pairs, and T_1 is the nuclear relaxation time. In our case $k_f = 4.5 \times 10^{-3}$ sec^{-1} (ref 17) and T_1 = 50 sec for chloroform. Thus, for instance, if $V' = 2$, the CIDNP intensity would be about half the intensity of the peroxide signal (normalized to one proton). This would be well observable. From Figure 1b, it can be inferred that in the range $k \sim 5 \times 10^5$–5×10^6 sec^{-1}, one could still have observable *A* effects for chloroform (V_{II}). This implies $k_{tr} \sim 5 \times 10^6$–$5 \times 10^7$ l./mol sec, in the CCl_3Br concentration range of 0.1 *M*. If we put (somewhat arbitrarily) $\lambda_{\mathrm{I}} = \lambda_{\mathrm{II}} = {}^1/_2$ and $k = 10^6$ sec^{-1}, we find $V'_{\mathrm{II}} = 4.6$, while the yield would be only about 0.1%, which would be properly called a "trace."

To see whether F-type polarization can compete at 0.1 *M* CCl_3Br, we first estimate the steady-state concentration of $CCl_3\cdot$ radicals. The peroxide concentration is 0.2 *M*. Thus the rate of formation of isopropyl radicals $r_f = 9 \times 10^{-4}$ mol/. sec. Assuming that $^3/_4$ of the radicals eventually becomes $CCl_3\cdot$ and that these radicals disappear predominantly by bimolecular coupling, $2CCl_3\cdot \rightarrow C_2Cl_6$ (k_1) with a rate constant $k_1 = 0.5 \times 10^8$ l./mol sec[16], we find from the steady-state condition $[CCl_3]\cdot = 3.7 \times 10^{-6}$ mol/l. If the rate constant for the reaction

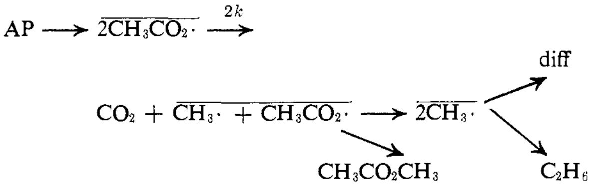
$$R\cdot + CCl_3\cdot \xrightarrow{k_2} \text{products} \qquad (46)$$

is taken to be $k_2 = 2 \times 10^9$ l./mol sec (*cf.* ref 16), the rate of disappearance of isopropyl radicals by reaction 46 would be $k_2[CCl_3\cdot] = 7.4 \times 10^3$ sec^{-1}, or a factor 135 slower than that of the transfer reaction ($k = 10^6$ sec^{-1}). However, F-type polarization for this reaction could well be a factor 135 larger than V'_{II} ($V'_{\mathrm{F}} = -620$ is not unreasonable), thus canceling the effect of the singlet-correlated pairs.

The calculations presented here are demonstrative rather than precise. They seem to indicate, however, that CIDNP effects can be observed from radical pairs that retain their spin-correlation for rather long times, up to the microsecond region. This is anyhow about the limit for the validity of this treatment, since for longer lifetimes the correlation is spoiled by transverse relaxation processes.

It is probable that observation of *A* for pentachloroacetone formed during decomposition of a cyclohexadienone peroxide[10a] (giving a pair of *tert*-butyl radicals) in hexachloroacetone (HCA) similarly results from rather long-lived radical pairs.

4.2. Fragmentation. An example of this type of transformation is provided by the decarboxylation of acetoxy radicals, formed during decomposition of acetyl peroxide[10] (AP)



$$\begin{tikzcd} AP \arrow[r] & \overline{2CH_3CO_2\cdot} \arrow[r, "2k"] & {} & & \\ & & & & \text{diff} \\ & CO_2 + \overline{CH_3\cdot + CH_3CO_2\cdot} \arrow[r] \arrow[dr] & \overline{2CH_3\cdot} \arrow[urr] \arrow[drr] & & \\ & & CH_3CO_2CH_3 & & C_2H_6 \end{tikzcd} \qquad (47)$$

Emission for both methyl acetate (OCH_3) and ethane was reported previously.[10a] We have experimental indications that both *E* effects are due to S–T_0 transitions in the methyl/acetoxy radical pair (memory effect). The value of *k* has been estimated[6,18] to be in the range 10^9–10^{10} sec^{-1}. The ratio $V'_{\mathrm{II}}/V'_{\mathrm{III}}$ was found to be 0.26, in fair agreement with the values 0.17–0.10 derived from Figure 2 for this range. When the experimental value of $P_{\mathrm{II}} = 0.32$ is used, the theoretical ratios become 0.27–0.13. The theory correctly predicts larger enhancements for III than for II, in spite of the fact that the latter product is directly formed from the pair, in which polarization is generated.

In our opinion, the emission effects of ethane, toluene, and methyl benzoate, observed during the decomposition of benzoyl peroxide (BPO) in the presence of methyl iodide,[19,20] have a similar origin and are probably an extreme case of the memory effect for the fourth

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(15) R. Kaptein, F. W. Verheus, and L. J. Oosterhoff, *Chem. Commun.*, 877 (1971).

(16) H. W. Melville, J. C. Robb, and R. C. Tutton, *Discuss. Faraday Soc.*, **14**, 150 (1953).

(17) J. Smid and M. Szwarc, *J. Chem. Phys.*, **29**, 432 (1958).

(18) M. Szwarc in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience, New York, N. Y., 1962, p 153.

(19) S. V. Rykov, A. L. Buchachenko, and A. V. Kessenich, *Spectrosc. Lett.*, 3, 55 (1970).

(20) (a) H. R. Ward, *Accounts Chem. Res.*, **5**, 18 (1972). (b) As no benzoic acid is formed in the presence of water, iodine abstraction by benzoyloxy radicals probably does not occur: H. R. Ward, personal communication.

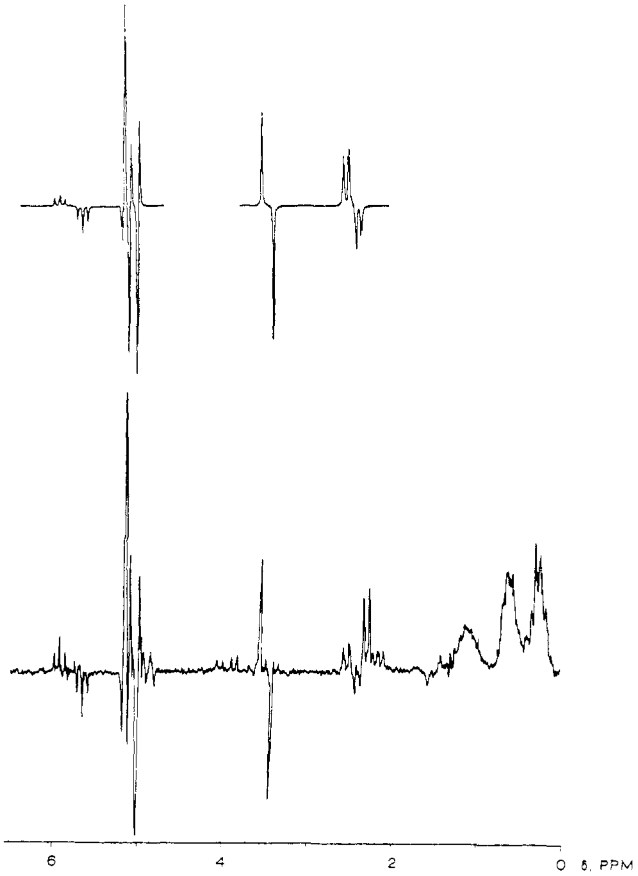
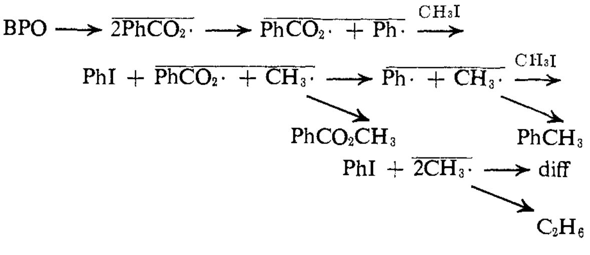


Figure 3. 100-Mc nmr spectrum obtained during decomposition of cyclopropylacetyl peroxide in hexachloroacetone at 80°. The simulated spectrum of 4-chloro-1-butene shown on top is a superposition of spectra calculated with the hyperfine parameters of the cyclopropylcarbinyl radical and with those of the 3-butenyl radical in the ratio 8:1. The hyperfine coupling constants[22] of the cyclopropylcarbinyl radical are $A_\alpha = -20.7$ G, $A_\beta = +2.55$ G (sign determined from this CIDNP spectrum; α and β protons become vinyl protons, δ 5–6 ppm, in the product), $A_\gamma = 2.98$ (anti) and 2.01 G (syn). The hyperfine parameters of the 3-butenyl radical are $A_\alpha = -22.2$ G and $A_\beta = +28.5$ G.[22]

or fifth subsequent pair



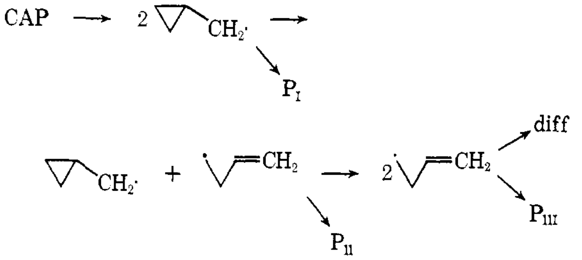
$$\mathrm{BPO} \longrightarrow \overline{2\mathrm{PhCO_2}\cdot} \longrightarrow \overline{\mathrm{PhCO_2}\cdot + \mathrm{Ph}\cdot} \xrightarrow{\mathrm{CH_3I}} \mathrm{PhI} + \overline{\mathrm{PhCO_2}\cdot + \mathrm{CH_3}\cdot} \longrightarrow \overline{\mathrm{Ph}\cdot + \mathrm{CH_3}\cdot} \xrightarrow{\mathrm{CH_3I}} \mathrm{PhI} + \overline{2\mathrm{CH_3}\cdot} \longrightarrow \mathrm{diff}$$

(48)

where $PhCO_2\cdot$ and $Ph\cdot$ are the benzoyloxy and phenyl radicals and polarization is due to the benzoyloxy/methyl radical pair.

Furthermore, observations[21] of ^{13}C polarization during thermolysis of BPO in cyclohexanone (*E* for benzene and CO_2, *A* for biphenyl, and *A* for the three C atoms of the CC(=O)OC moiety of phenyl benzoate) are also in accordance with a reaction scheme like (47), the polarization originating in this case from the phenyl/benzoyloxy radical pair. The observed effects show that the hyperfine coupling constants are positive for the 1-C atom of the phenyl radical (which is expected for a σ radical) and negative for both the carboxyl and neighboring ring C atoms of the benzoyloxy radical, which is not unreasonable for an allyl-type radical.

4.3. Rearrangements of Radicals. The cyclopropylcarbinyl radical is known[22] to rearrange to give the 3-butenyl radical. We have studied the decomposition of cyclopropylacetyl peroxide (CAP) in HCA at 80° (see Figure 3). The reactions are



(49)

P_I, P_{II}, and P_{III} represent coupling and disproportionation products, the CIDNP spectrum of which is not clear. However the "escape" product, 4-chloro-1-butene, resulting from transfer reaction with the solvent shows a strongly polarized spectrum (multiplet effects for all protons), which could well be accounted for by computer simulation. The polarization was partly determined by the cyclopropylcarbinyl radical (from pairs 1 and 2) and partly by the butenyl radical (pairs 2 and 3) in the ratio 8:1. From this ratio, the rate constant *k* for the rearrangement can be estimated, when a number of assumptions is made. To this end we define for the escape polarization (*cf.* eq 24)

$$D_{1n} = \lambda_I q_{1n} + (1 - P_I)\hat{x}_{1n} \times \{\lambda_{II} y_{II} + \lambda_{III}(1 - P_{II}) y_{III}\} \quad (50a)$$

$$D_{2n} = \lambda_{II}(1 - P_I) q_{2n} + \lambda_{III}(1 - P_I)(1 - P_{II}) y_{III} \hat{x}_{2n} \quad (50b)$$

$$D_{3n} = \lambda_{III}(1 - P_I)(1 - P_{II}) q_{3n} \quad (50c)$$

and for the contributions from the cyclopropylcarbinyl and the butenyl radical, respectively

$$D_{an} = 2D_{1n} + D_{2n} \quad (51a)$$

$$D_{bn} = D_{2n} + 2D_{3n} \quad (51b)$$

from which we obtain the enhancement factors

$$V'_a = (D_{an} - D_{am})(kT/g_N \beta_N H_0) \quad (52a)$$

$$V'_b = (D_{bn} - D_{bm})(kT/g_N \beta_N H_0) \quad (52b)$$

V'_a gives the polarization of the vinyl group and V'_b that of the methylene groups in 4-chloro-1-butene. Assuming $\lambda_I = \lambda_{II} = \lambda_{III} = 1$, $p = 0.5$, $m = m' = 10^{-6}$ sec$^{1/2}$, $|J| = 5 \times 10^8$ radians/sec, and, using known hyperfine parameters,[22] we calculate a ratio $V'_a/V'_b = 8$, for $k = 3 \times 10^7$ sec^{-1}, in good agreement with the value 10^8 sec^{-1} estimated by others.[22b] If the lifetime of the butenyl radical would be comparable to or longer than the spin-lattice relaxation time of this radical, the value $k = 3 \times 10^7$ sec^{-1} would be a lower limit, since *b*-type polarization would be more affected by relaxation than *a*-type.

4.4. Conclusions. From the foregoing discussion it will be clear that there are many approximations in-

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(21) E. Lipmaa, T. Pehk, A. L. Buchachenko, and S. V. Rykov, *Chem. Phys. Lett.*, **5**, 521 (1970).

(22) (a) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, **91**, 1877 (1969); (b) R. A. Sheldon and J. K. Kochi, *ibid.*, **92**, 4395 (1970).

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.

Acknowledgment. The author thanks Professor L. J. Oosterhoff for his continuous encouragement. Stimulating discussions with Professors H. R. Ward and J. E. Baldwin and with Dr. R. A. van Santen and Dr. J. A. den Hollander are gratefully acknowledged.

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

(3) (a) J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *ibid.*, **92**, 5761 (1970); (b) J. F. Garst and R. H. Cox, *ibid.*, **92**, 6389 (1970).

(4) S. V. Rykov, A. L. Buchachenko, and V. I. Baldin, *Zh. Strukt. Khim.*, **10**, 928 (1969).

(5) J. Bargon and H. Fischer, *Z. Naturforsch., A*, **22**, 1556 (1967).

(6) (a) G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); (b) G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183 (1970).

(7) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

(8) Part VIII: R. Kaptein, *J. Amer. Chem. Soc.*, **94**, 6251 (1972).

(9) (a) S. H. Glarum, paper presented at the 159th National Meeting of the American Chemical Society, Houston, Feb 1970; (b) S. H. Glarum, personal communication.