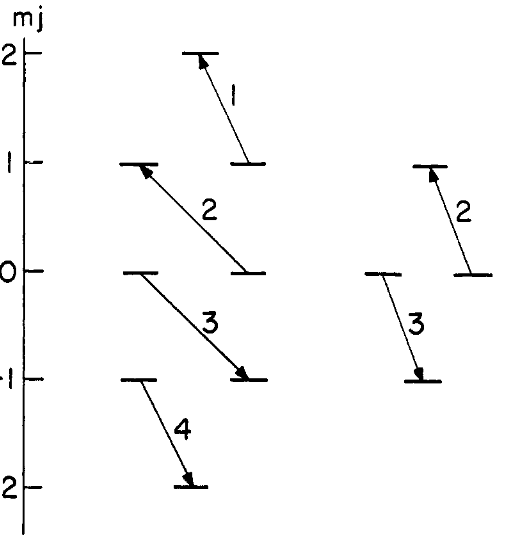

Figure 3. Transition diagram of A_3B system of polarized IIb.

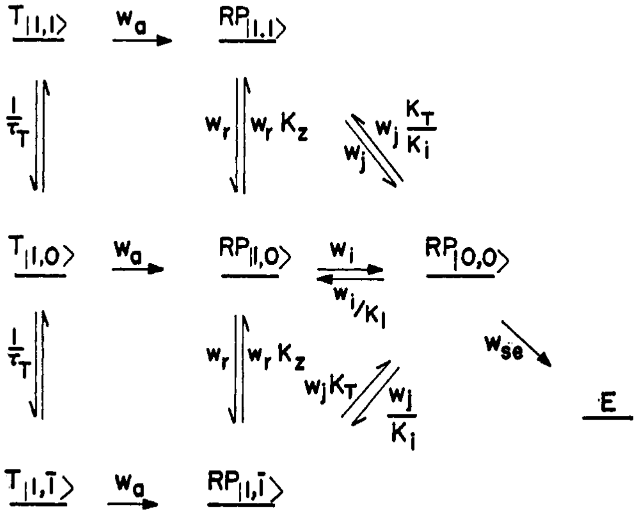

Figure 1. Reaction diagram with electron Zeeman states consisting of a triplet molecule (T), a radical pair (RP), and the radical combination product E.

value for a pure dipolar coupling. In contrast, the entropy polarization can theoretically reach magnitudes of $>10^4$.

As in the preceding communication, the spectra reported in the reaction with ethylbenzene cannot be explained by the previously advanced schemes. Also, a quantitative calculation of the electron relaxation time, T_{1_e}, by previously described methods,[4] of benzophenone triplet state shows that the relaxation rate, $1/T_{1_e}$ (10^8 sec^{-1}), is much larger than the known rates of hydrogen abstraction. This again leads to the formation of the radicals in thermal equilibrium before hydrogen abstraction has taken place. This, together with the magnitude of the polarization, emphasizes the need for a new theory on chemically induced dynamic nuclear spin polarization.

These results demonstrate unequivocally that the products II are formed from a paramagnetic precursor, in agreement with the conclusions derived previously from chemical studies.[3] They also point to the potential value of dynamic polarization in mechanistic photochemistry.

(4) Footnote 11 in ref 2.

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A Mechanism Explaining Nuclear Spin Polarizations in Radical Combination Reactions[1]

Sir:

The preceding communications describe the observation of large nuclear spin polarizations caused by photochemical reactions involving radical combinations.[2] This communication presents a mechanism capable of explaining the observed spectra.

The reactions described have in common that the first paramagnetic species generated is a triplet molecule (T) containing none of the hydrogens causing the polarized spectra. Also, because of very fast electron spin relaxation, $1/\tau_T$, the Zeeman states, $T_{|1,1\rangle}$, $T_{|1,0\rangle}$, and $T_{|1,\bar{1}\rangle}$, of the triplet molecule (T) are in thermoequilibrium before reaction. Rapid molecular rotation and a strong magnetic field (H_0) effectively decouple the spin from the molecular frame and assure quantization of the spin with reference to H_0. The probabilities of hydrogen abstraction (w_a) are assumed to be equal for each Zeeman state yielding a radical pair (RP) whose triplet Zeeman states are being populated according to the equilibrium population (Figure 1). The singlet state, $RP_{|0,0\rangle}$, will be populated by either "intersystem crossing" with probabilities w_j, w_i, and w_jK_z [$K_z = \exp(-g\beta H_0/kT)$], or by separation of the components of the radical pair occurring with probability w_d from each state and recombination of the free radicals with the appropriate spin wave function. Irreversible depopulation of $RP_{|0,0\rangle}$ occurs by product formation with probability w_{se}.

We consider now the possibility of obtaining nuclear spin polarization from the processes characterized by w_j, w_i, and w_jK_z. For this we assume a radical pair having one proton bonded to each component. The spin-dependent part of the Hamiltonian for a stationary four-spin system can be written as in eq 1, where S, I,

$$\mathcal{H} = (\gamma_e/2\pi)H_0\cdot(S_1 + S_2) + (\gamma_n/2\pi)H_0\cdot(I_1 + I_2) + \mathcal{H}_d + \mathcal{H}_{sc} \quad (1)$$

γ_e, and γ_n are the electron and nuclear spin operators (each of $^1/_2$) and the electron and nuclear magnetogyric ratios, respectively. The first two terms represent the electron and nuclear Zeeman splitting while the next term ($\mathcal{H}_d$) is the sum of all dipolar interactions. The last term includes all scalar interactions and can be written explicitly as eq 2, where A_{jk} is the electron–

$$\mathcal{H}_{sc} = \sum_{j=1}^{2}\sum_{k=1}^{2} A_{jk}(S_j\cdot I_k) + J_{ee}S_1\cdot S_2 + J_{nn}I_1\cdot I_1 \quad (2)$$

nuclear and J_{nn} the nuclear–nuclear spin coupling constant and J_{ee} is the electron–electron scalar exchange coupling constant.[3] Because of its small size the term

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(1) Supported in part by National Science Foundation Grant GP-7043X.

(2) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **91**, 4549, 4550 (1969).

(3) All coupling constants are in hertz.

with J_{nn} will be neglected. As has been pointed out before,[4] three distinctly different cases exist if J_{ee} is varied. In *case 1*, $|J_{ee}| \gg |A_{jk}| > 0$, each nucleus is coupled to *both* electrons equally well ($A_{11} = A_{12}$; $A_{22} = A_{21}$) and the radical pair has well-defined triplet and single manifolds with no off-diagonal elements between them except those provided by spin–orbit coupling. *Case 2*, $|J_{ee}| \sim |A_{jk}| > 0$, signifies a relatively small exchange coupling ($\sim 10^6$ to 10^7 Hz) where A_{11} and A_{12} (or A_{22} and A_{21}) become distinguishable. Off-diagonal elements of $\mathcal{H}_{sc}$ of the form $\pm {}^1/_4(A_{11} + A_{22} - A_{12} - A_{21})$ no longer vanish and will connect "singlet" and "triplet" first-order states of identical F_z, as shown in Figure 2, where $F_z = m_{s_z} + m_{j_z}$. This leads to a second-order energy shift of the connected states and to singlet–triplet mixing by $\mathcal{H}_{sc}$ without spin-orbit coupling. Finally, *case 3*, $J_{ee} = 0$, $|A_{jk}| > 0$, describes two independent doublet states. In a radical pair the magnitude of J_{ee}, which also equals the "singlet–triplet" splitting, is a function of the mutual orientation and the separation of the two components. Previous work on radical-anion pairs[5] shows that J_{ee} can become smaller than typical values of A_{jk} (10^7 Hz) with separation of the components equal to or smaller than their molecular diameter

In a radical pair in solution in which the components move relative to each other from a geometry corresponding to case 1 to a geometry described by case 2 and then back to case 1, the perturbing Hamiltonian becomes time dependent, $\mathcal{H}_{sc}(t)$, leading to transitions between states connected by off-diagonal elements which are "turned on and off" as a function of the fluctuating geometry. If this fluctuation is expressed as a correlation function similar to the one for chemical exchange,[6] $A(t)A^*(t + \tau) = A^2 \exp(-\tau/\tau_f)$, where $1/\tau_f \mathrm{d}t$ is the probability of the radical pair completing such a cycle in the time element dt, one can obtain the transition probability between states n_r and n_s from eq 3, which integrates for the radical pair to

$$w \approx \frac{1}{t\hbar^2}\left|\int \langle n_s|\mathcal{H}(t')|n_r\rangle \exp\left(-i\frac{\Delta E}{\hbar}t'\right)\mathrm{d}t'\right|^2 \qquad (3)$$

give (4) when $A_{11} \gg A_{12}$ for the geometry corresponding to case 2

$$w = {}^1/_2(A_{11} + A_{22})^2 \frac{\tau_f}{1 + (\Delta E/\hbar)^2\tau_f^2} \qquad (4)$$

The term $(\Delta E/\hbar)^2$ is equal to $J_{ee}^2 + ({}^1/_2A_{11} + {}^1/_2A_{22})^2$ for transition w_0 ($\Delta m_{s_z} = 0$; $\Delta m_{j_z} = 0$) and to $[J_{ee} + \omega_e + \omega_I - {}^1/_2(A_{11} + A_{22})]^2$ for transition w_0' ($\Delta m_{s_z} = \pm 1$; $\Delta m_{j_z} = \mp 1$), where ω_e and ω_I are the electron and nuclear angular precession frequencies. Since $J_{ee} \leq A_{jk} \ll \omega_e$, it follows that $w_0 \gg w_0'$, thus rendering the w_0' processes negligible. With a typical value of A_{jk} for benzylic radicals of 3×10^7 Hz and τ_f ranging from 10^{-7} to 10^{-8},[7] w_0 becomes of the orders 10^8 to 10^7 sec^{-1}.

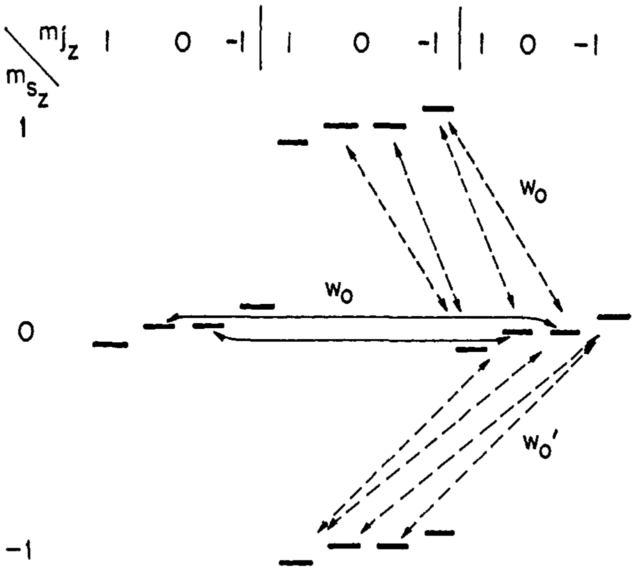

Figure 2. Schematic diagram of Zeeman states and connections by off-diagonal matrix elements $\pm {}^1/_4(A_{11} + A_{22} - A_{12} - A_{21})$, in a weakly coupled radical pair with two protons (for clarity the elements connecting the states on the left with states of $m_{s_z} = \pm 1$ are omitted).

A detailed consideration of $\mathcal{H}_d(t)$, using the same correlation time, shows a comparable contribution to w_0. These hyperfine-coupling-induced transition probabilities compete with processes giving unpolarized product *via* separation of the components of RP and diffusion, w_d ($\sim 10^9$ to 10^{10} sec^{-1}), and electron transitions not involving nuclear spins (w_{er}). The observed values of the polarization require that $w_0/(w_d + w_{er} + w_0) \simeq 10^{-2}$, in agreement with the above estimates.

For a radical pair produced from a triplet state this mechanism leads to a higher steady-state population of nuclear states with $m_{j_z} = 0$ than those with $m_{j_z} = \pm 1$ in RP$_{(0,0)}$ and consequently also in E.

A comparison of this effect with the Overhauser effect is illuminating. In Overhauser experiments the total z component of the nuclear spin expectation values is displaced from the equilibrium. The process described here corresponds to a transverse effect in which the x,y components of the two spin sets interchange under the driving force of the required electron spin pairing in the product E. The term *transverse Overhauser effect* is suggested to describe this phenomenon.

A longitudinal chemical Overhauser effect can also be superimposed on the transverse effect and is the only one observable in the reaction of benzophenone with toluene.[2] It probably arises from the individual free radicals whose electron spin states are in thermoequilibrium when they are formed. Since the product E requires electron pairing, a net fraction of the molecules has to undergo an electron transition from the low-energy to the high-energy Zeeman level, thus providing a mechanism for nuclear polarization. This is essentially the reverse of the previously suggested mechanisms.[8] The proposed mechanism can also

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(4) D. C. Reitz and S. I. Weissman, *J. Chem. Phys.*, **33**, 700 (1960).
(5) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2538 (1964).
(6) I. Solomon and N. Bloembergen, *J. Chem. Phys.*, **25**, 261 (1956).
(7) The magnitude of $1/\tau_f$ must be considerably smaller than w_d because most component pairs will not reunite after they have reached a geometry corresponding to case 2 or case 3.

(8) R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5519 (1967).

account for spin polarizations in radical disproportionation reactions.[9]

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[9] R. Kaptein (private communication) has informed us that he has followed up a previous suggestion[10] and has developed a theory very similar to the one presented here. His treatment, to be published shortly, differs from ours in that it does not involve perturbation methods.

[10] R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968).

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Chemically Induced Nuclear Spin Polarization as a Tool for Determination of Spin Multiplicities of Radical-Pair Precursors[1]

Sir:

The preceding communications describe large nuclear spin polarizations in radical combination reactions in which the radical pairs are generated from triplet-state molecules *via* hydrogen abstraction from the solvent.[2,3] In these systems the manifold of states of the radical pair (RP) is populated in its triplet branch while product formation occurs from the singlet branch. The crossover from one multiplicity to the other has been proposed to cause nuclear spin polarization.[4]

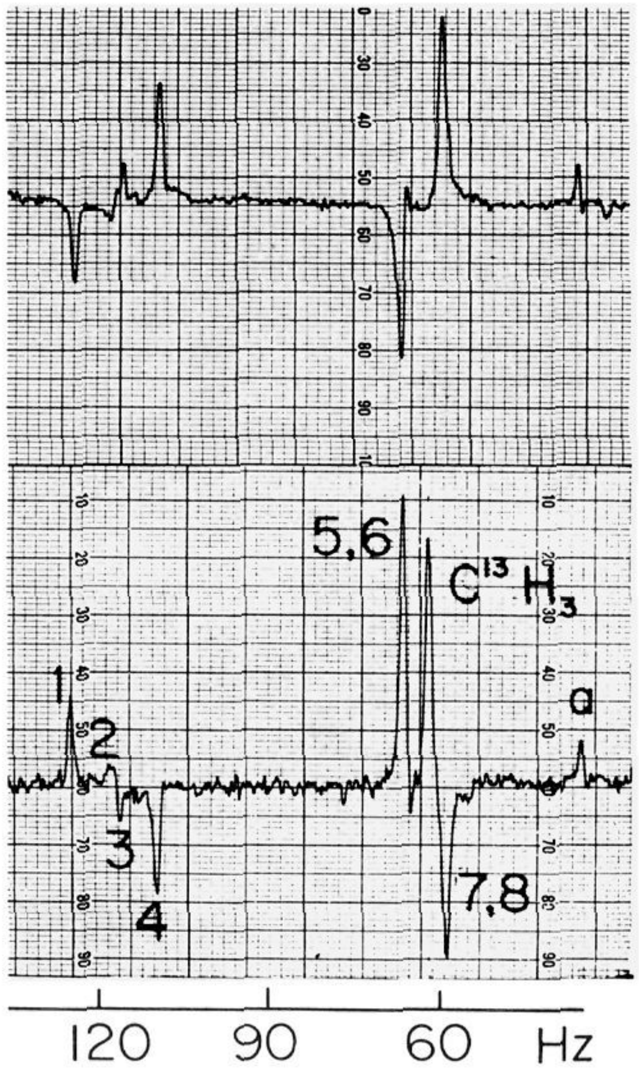

Figure 1. Spin-polarized spectra of 1,1,2-triphenylethane obtained from (a) thermolysis of I in diphenyl ether, shown in upper trace, and (b) photolysis of diphenyldiazomethane in toluene, shown in lower trace. The chemical shift scale is in hertz downfield from the toluene methyl resonance.

In this communication we wish to present evidence that nuclear spin polarization can also occur when the manifold of states of the radical pair is populated in and depopulated from the singlet branch. Using the same symbols as in ref 4, this situation corresponds to entering the system at $\mathrm{RP}_{|0,0\rangle}$ and leaving it from the same state to form E. The triplet branch of RP will be populated by diffusion and recombination of the components of RP with the appropriate spin wave function and by direct crossover within the radical pair. As has been shown in ref 4, in a radical pair with two protons[5] a hyperfine-coupling-induced transition probability (w_0) exists between singlet and triplet branches of RP connecting states with $m_{s_z} = 0, m_{j_z} = 0$, corresponding to a transverse-spin-component exchange between electrons and nuclei. Therefore nuclear substates of $\mathrm{RP}_{|0,0\rangle}$ with $m_{j_z} = 0$ should cross over to the triplet branch somewhat faster than states with $m_{j_z} = \pm 1$. Since the triplet state of RP is a nonbonding state and does not lie on the reaction coordinate, the population of its manifold is kinetically equivalent to the separation of the components of RP into free radicals. Therefore w_0 may be viewed as an additional probability of the nuclear substates of RP with $m_{j_z} = 0$ to separate into doublet states.[6]

Conversely w_0 provides also an additional probability of radical combination to form a new radical pair from the free-radical components. Therefore no change in populations is expected when the two components of RP are identical. However, if the radical pair consists of two different components, only approximately 50% of the radicals which have been formed by separation of RP will recombine. The other 50% combine to form the two symmetrical products. This will give a change in the steady-state populations of the nuclear substates of $\mathrm{RP}_{|0,0\rangle}$ and consequently in E, which is expressed in eq 1 as a function of the individual rate

$$N(m_{j_z} = \pm 1)/N(m_{j_z} = 0) = \frac{C + w_0 w_{\mathrm{se}}/X}{C + w_0 w_{\mathrm{se}} Y} \qquad (1)$$

constants, with $C = [(w_{\mathrm{se}}/X) + (w_{\mathrm{d}} Y)](w_{\mathrm{d}} + w_{\mathrm{se}}) + w_0 Y w_{\mathrm{d}}$, where w_{se} and w_{d} are the probabilities of product formation and separation into free radicals, respectively, X is the total fraction of unsymmetrical product, and Y is the fraction of unsymmetrical product formed from the free-radical recombination. Since both X and Y are smaller than 1, it follows that $N(m_{j_z} = \pm 1)/N(m_{j_z} = 0) > 1$. The spin-polarized product should therefore be depleted in nuclear substates with $m_{j_z} = 0$, which is opposite to the case in which the radical pair was generated from a triplet precursor.

To test this hypothesis we have compared spin polarizations obtained in two reactions giving the same products but differing in the multiplicity of the precursor

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[1] Work supported in part by National Science Foundation Grant GP-7043X.

[2] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **91**, 4549 (1969).

[3] G. L. Closs and L. E. Closs, *ibid.*, **91**, 4550 (1969).

[4] G. L. Closs, *ibid.*, **91**, 4552 (1969).

[5] The considerations in ref 4 can easily be expanded to more than two nuclear spins. It can be shown that transition probabilities will be greatest for states with m_{j_z} closest to 0.

[6] On a molecular level this phenomenon may be understood if one imagines the two components of RP to have separated to the point where $J_{\mathrm{ee}} \sim A_{jk}$, where J_{ee} is the scalar electron exchange coupling and A_{jk} is the hyperfine coupling constant. Under those conditions for molecules with $m_{j_z} = 0$ there is substantial hyperfine-coupling-induced singlet–triplet mixing. If the molecule returns to smaller separation the probabilities are equal that it finds itself in either the singlet or the triplet state. The triplet state does not lead to product and will therefore separate again. Molecules with nuclear substates $m_{j_z} = \pm 1$, however, will have to diffuse further apart before singlet and triplet are mixed, thus having effectively a slower rate of separation.