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]

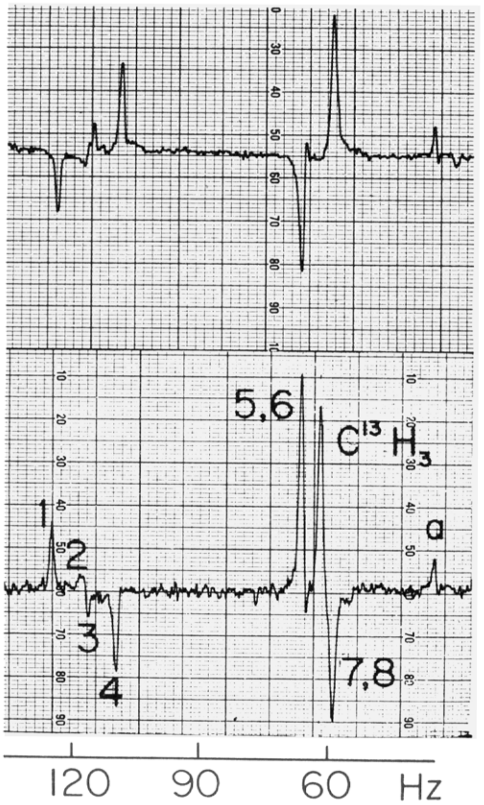

Figure 1. Spin-polarized spectra of 1,1,2-triphenylethane obtained from (a) thermolysis of I in diphenyl ether, shown in upper trace, and (b) photolysis of diphenyldiazomethane in toluene, shown in lower trace. The chemical shift scale is in hertz downfield from the toluene methyl resonance.

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.

of the radical pair. The reactions chosen were the formation of 1,1,2-triphenylethane from diphenylcarbene and toluene, as described in ref 2, and the thermal or photochemical decomposition of the azo compound I. It is generally accepted that acyclic

$$\underset{\mathbf{I}}{(C_6H_5)_2CHN{=}NCH_2C_6H_5} \xrightarrow{h\nu,\ \text{or}\ \Delta} (C_6H_5)_2CHCH_2C_6H_5 + (C_6H_5)_2CHCH(C_6H_5)_2 + C_6H_5CH_2CH_2C_6H_5$$

azo compounds decompose through the singlet state,[7] and there can be little doubt as to the triplet character of the reacting diphenylmethylene. The comparison of the chemistry of the two systems reveals a spin correlation effect because the ratio of unsymmetrical to symmetrical products is higher in the reaction of I (1.5:1) than in the methylene reaction (1:1).

Figure 1 shows the spectra obtained from the two reactions showing the opposite polarizations, in striking confirmation of the considerations outlined above. Analysis of the spectra shows that the triplet reaction produces overpopulation in the nuclear substates with m_{j_z} closest to zero ($\pm{}^1/_2$) and the singlet reaction gives product with overpopulation of substates with m_{j_z} furthest away from 0 ($\pm{}^3/_2$).

It should be pointed out that since the formation of polarized product requires separation of the components of the radical pair, cyclic azo compounds should not give polarized products if decomposed from a singlet state. To deduce the multiplicity of the precursor it is also necessary to know the absolute sign of the nuclear spin coupling constants in the reaction product.

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(7) P. D. Bartlett and P. S. Engels, *J. Am. Chem. Soc.*, **90**, 2960 (1968).

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[2.2]Paracyclophane System Optical Activity. I. Theory[1]

Sir:

Certain chemical systems show optical activity that can be accounted for by the simplest quantum models.[2,3] The experimental study of such synthetically modified systems is important to a better understanding of the origins of the extraordinary molecular spectroscopy associated with optical activity. This communication describes a semiempirical exciton theory that gives straightforward interpretation to observed circular dichroisms of ring-substituted paracyclophanes.[4] There emerges as well a sensitive scheme for defining the sign of Platt's "spectroscopic moments" for benzene ${}^1L_b \leftarrow {}^1A$ transitions[5] and possibly refining the numerical values assigned to them.

The secular determinant of first-order degenerate perturbation theory[6] for a pair of substituted benzene molecules (A and B) will assume diagonal form with the excited state wave functions

$$\Psi_i^+ = 2^{-1/2}[A_0B_i + A_iB_0] \qquad (1)$$

and

$$\Psi_i^- = 2^{-1/2}[A_0B_i - A_iB_0]$$

where, for instance, A_0 and A_i are isolated molecule wave functions for molecule A in the ground state ${}^1A$ and excited state ${}^1L_b$, respectively. The perturbation matrix elements are based on the *inter*benzene nuclei and electron electrostatic potential terms, H'. *Inter*benzene overlap and thus also *inter*benzene electron exchange are neglected. Additional higher order terms will mix in higher states under the perturbation. Unequal weighting of A_0B_i and A_iB_0 in Ψ_i^+ and Ψ_i^- obtains insofar as the interaction of excited A and ground state B differs slightly from that of excited B and ground state A. This will be the case to some degree since A and B represent phenyl rings which bear different substituents.

The wave functions of eq 1 give first-order perturbation energies for the states

$$E_\pm^{(1)} = (A_iB_0|H'|A_iB_0) \bullet (A_iB_0|H'|A_0B_i) \qquad (2)$$

relative to the separated (noninteracting) members of the pair. The nondegenerate ground state has a wave function $\Psi_0 = A_0B_0$ at the corresponding level of approximation with a first-order perturbation energy $(A_0B_0|H'|A_0B_0)^6$ relative to separated members of the pair both in the ground state.

The electric dipole operator $\vec{m} = \vec{m}(\text{A}) + \vec{m}(\text{B})$ gives the familiar "in phase" and "out of phase" transition moments of substituted benzenes such that the dipole strengths from the ground state to the states with degeneracy now lifted according to eq 2 are

$$D_{0,\pm} = |\vec{m}_{0,\pm}|^2 = {}^1/_2|\vec{m}(\text{A})_{0i} \pm m(\text{B})_{0i}|^2 \qquad (3)$$

The magnetic dipole operator may be defined with respect to an arbitrary origin[7]

$$\mu = \frac{e}{2mc}\{[\vec{R}(\text{A}) \times \vec{p}(\text{A})] + \vec{l}(\text{A}) + [\vec{R}(\text{B}) \times \vec{p}(\text{B})] + \vec{l}(\text{B})\} \qquad (4)$$

where $R(\text{A})$ and $\vec{R}(\text{B})$ are vectors to the centers of gravity of the benzenes, $\vec{p}(\text{A})$ and $\vec{p}(\text{B})$ are linear momenta, and $\vec{l}(\text{A})$ and $\vec{l}(\text{B})$ are angular momentum operators referred to the respective benzene centers of gravity. Most conveniently, one may choose the arbitrary origin to be midway between the benzene centers of gravity, such that $\vec{R}(\text{A}) = \vec{R}(\text{B})$.

Neglecting small terms,[8] it follows that the rotatory

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(1) This work supported by Public Health Service Grant GM 11644.

(2) (a) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940); A. Moscowitz, *Advan. Chem. Phys.* **4**, 67 (1962); (b) O. E. Weigang, Jr., and E. H. Höhn, *J. Amer. Chem. Soc.*, **88**, 3673 (1966).

(3) J. Tinoco, Jr., and R. W. Woody, *J. Chem. Phys.* **40**, 160 (1964).

(4) D. J. Cram and N. C. Allinger, *J. Amer. Chem. Soc.* **77**, 6289 (1955); D. J. Cram and L. A. Singer, *ibid.*, **85**, 1078 (1963).

(5) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951); J. Petruska, *ibid.*, **34**, 1111, 1120 (1961).

(6) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley & Sons., Inc., New York, N. Y., 1948.

(7) The origin independence of rotatory strength in this model is assured. It persists even through the first order of perturbation of wave functions if only dynamic coupling terms are considered. See the appendix: E. G. Hohn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).

(8) The neglected terms like $\vec{m}(\text{A})_{0i} \cdot \vec{\mu}_{i0}(\text{A})$ are zero for optically inactive benzene "monomers." But even at a level where one monomer is considered active from alkyl group substituents, these terms are demonstrably small for the ${}^1L_b \leftarrow {}^1A$ (${}^1B_{2u} \leftarrow {}^1A_{1g}$) related transitions of benzene. The relevant experiment and theoretical reasons have been discussed by Moscowitz, *et al.*[9] The terms $\vec{m}_{0i}(\text{A}) \cdot \vec{\mu}_{i0}(\text{B})$ can be expected to be small for the same reasons in the case of parallel-plane benzene systems.

(9) A. Moscowitz, A. Rosenberg, and A. E. Hansen, *J. Amer. Chem. Soc.*, **87**, 1813 (1965).