believe that the observations are best explained by postulating the matrix reaction between Li and N_2 to form LiN_2. It must be noted that this reaction is much slower and less energetically favorable than the Li and O_2 reaction.[5,6] The $N_2Li_2N_2$ species is most likely made by the union of two LiN_2 molecules produced in adjacent matrix sites.

The LiN_2 and $N_2Li_2N_2$ species postulated here are of chemical interest as reduced N_2 species. N–N stretching fundamentals reported for N_2 complexes[1] fall near 2000 cm^{-1}. The N–N modes observed here at 1800 and 1535 cm^{-1} are clearly lower than any N_2 complexes discussed in recent reviews.[1-3] Hence, the lithium–nitrogen species contain N_2 which is *more reduced* than in the usual N_2 complex compounds. Close agreement

between the N–N modes of N_2^- and LiN_2 suggests that the species LiN_2 is $Li^+N_2^-$; the valence electron of lithium becomes antibonding in the N_2 molecular orbital scheme and the vibrational frequency is decreased from the free N_2 value (2331 cm^{-1}). The bonding in N_2LiN_2 leading to a still lower N–N frequency is not so readily explained.

Chemically Induced Dynamic Nuclear Polarization. General Solution of the CKO Model. Applicability to Reactions Run in Low Magnetic Fields[1]

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Abstract: CIDNP is currently attributed to the dynamic behavior of associated radical pairs. In an approximation intended for reactions carried out in high magnetic fields, the CKO model has been used by several workers. For reactions carried out in fields of a few to a few hundred gauss, no clearly justifiable approximate solution of the CKO model is available. Moreover, some of the other approaches to the theory of CIDNP, based on perturbation treatments, fail to provide methods of calculating polarization arising from low-field reactions. For the CKO model, and (in principle) for related diffusion models, this difficulty is overcome by solving the equations describing the model without approximation. The general solution for the CKO model has been programmed for a digital computer in series with other calculations which simulate the polarized nmr spectra of the reaction products. For high-field reactions, the calculations agree with those based on the high-field approximate CKO model. Sample calculations for low-field reactions are presented. For a one-proton radical pair, the intersystem crossings leading to product polarization are examined. The relative contributions from $T_\pm \rightarrow S$ and $T_0 \rightarrow S$ crossings are strongly dependent on the reaction magnetic field, and they vary in a surprising manner. The consequences of these variations are considered in the light of the mechanism and kinetics of reactions of alkyl halides with sodium naphthalene, for which the $T_0 \rightarrow S$ contribution to product polarization is entirely suppressed. The predictions of the theory agree with the experimentally observed polarization patterns, but an effective value of J, the radical pair electronic singlet–triplet splitting parameter, different from zero must be assumed. The field dependence of low-field polarization may provide a useful test of radical pair models and parameters.

W
hile the earliest CIDNP experiments involved reactions run in magnetic fields of thousands of gauss,[3,4] it was soon discovered that the phenomenon persists for reactions run in lower fields, even in zero field.[5,6] In fact, at least one group of reactions has been discovered for which CIDNP can be detected

only if they are run in low, nonzero magnetic fields, a few to a few hundred gauss.[7-9]

The high-field phenomena have been successfully accounted for, in nearly every detail, by the radical pair theory of CIDNP[10a,11] which seems to have displaced the earlier Overhauser-analog theory.[12,13] Cal-

(1) Portions of this work were presented at the Southeast-Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970, paper ORGN 415, and at the 162nd National American Chemical Society Meeting, Washington, D. C., Sept 1971, paper ORGN 77.

(2) National Institutes of Health Postdoctoral Fellow, 1970–1971.

(3) See H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969), and works cited therein.

(4) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

(5) H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *ibid.*, **91**, 4928 (1969).

(6) M. Lehnig and H. Fischer, *Z. Naturforsch., A*, **24**, 1771 (1969).

(7) These are reactions of some alkyl halides with sodium naphthalene in DME. Included are 1,4-diiodobutane, 1,4-dibromobutane, 1,4-dichlorobutane,[8] isopropyl chloride,[9] and *n*-propyl chloride.

(8) J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *J. Amer. Chem. Soc.*, **92**, 5761 (1970).

(9) J. F. Garst, F. E. Barton, II, and J. I. Morris, *ibid.*, **93**, 4310 (1971).

(10) (a) G. L. Closs, *ibid.*, **91**, 4552 (1969); (b) G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183 (1970).

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

(12) J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch., A*, **22**, 1551 (1967); J. Bargon and H. Fischer, *ibid., A*, **22**, 1556 (1967).

culations are relatively easy for reactions run in high magnetic fields. In such cases, mixing of spin functions containing the electronic triplets $\phi_{T\pm}$ ($m_s = \pm 1$) with those containing ϕ_S (electronic singlet) and ϕ_{T_0} (triplet, $m_s = 0$) can be neglected because the relevant Zeeman energy gaps are so large.[10,11]

Calculations for reactions run in low fields are less straightforward. For example, Fischer and Lehnig recently reported quantitative polarization data for reaction fields ranging from 0 to 20,000 G.[14a] They fitted some of their data with calculations based on a radical pair model which permitted high-field and zero-field calculations, but not those for reactions carried out in nonzero fields below several hundred gauss.

In connection with CIDNP generated in reactions of alkyl halides with sodium naphthalene in low magnetic fields, we earlier presented the results of calculations which included ϕ_{T_+} and ϕ_{T_-}, as well as ϕ_S, but which neglected ϕ_{T_0}. These calculations reproduced the gross aspects of our data satisfactorily, but because there is no justification for neglecting T_0 functions, we also performed calculations in which all mixing among T_+, T_-, T_0, and S functions was included. It was found that the general calculations did not entirely agree with the approximate calculations involving only $T_{\pm}$–S mixing.[8] It was clear that successful calculations of the same type were possible for *any* reaction magnetic field only if all $T_{\pm}$–T_0–S mixings were simultaneously included.

We have since extended the method of performing the general calculations, and we describe the details here of a procedure which provides a means of predicting polarized nmr spectra of products of reactions run in any magnetic field. As a framework, we have used the CKO radical pair model,[14b] first described by Kaptein and Oosterhoff,[11] whose formalism was later adapted by Closs.[10b] We do not particularly endorse this model, which lacks detail in its mechanical radical pair description. It seems likely that it will be displaced by some version of a "diffusion" model like that suggested by Adrian.[15] However, it is not the purpose here to attempt to discriminate among such models. In fact, calculations using the CKO model differ from those using Adrian's model only in the method of averaging the spin character of the radical pairs over the times during which they are eligible to react. The methods of calculation we describe are adaptable to any method of such averaging, and the nature of the results we wish to illustrate should be rather insensitive to the particular method chosen.

The CKO Model. In the CKO model, loosely coupled associated radical pairs are considered to be created instantaneously, each with an initial spin function reflecting that of its precursor. The wave functions of the radical pairs created in this fashion are, in general, time dependent, their evolution being governed by the

effective Hamiltonian (eq 1) and by the time-dependent Schrödinger equation. It is usually considered that

$$\mathcal{3C} = \beta H(g_1 S_{z1} + g_2 S_{z2}) - J(^{1}/_{2} + 2S_1 \cdot S_2) + \sum_m (A_{m1} I_m \cdot S_1 + A_{m2} I_{m2} \cdot S_2) \quad (1)$$

a particular proton has a nonzero hyperfine coupling constant A_{m1} or A_{m2} with only one electron, the one belonging to the radical in which the proton resides.

Because it is considered that only electronic singlet radical pairs can collapse to a singlet product, and because the time development of a radical pair wave function affects both its electronic and its nuclear spin characters, collapse to a product may be more probable for radical pairs formed with some initial nuclear spin states than for those formed with others. It follows that the collapse product may be preferentially populated in some nuclear spin states relative to others.

This gives rise to unusual nmr spectra. One can compute the predicted nmr signal enhancements (before relaxation) if he knows the occupation numbers n_k of all the product nuclear eigenstates ϕ_k. If V_{12} is the signal enhancement of an allowed nmr transition and ϕ_1 is the nuclear eigenstate of lower energy

$$V_{12} = \frac{n_1 - n_2}{n_1^0 - n_2^0} - 1 = \frac{(4.89)(10^6)(T/H_0)(2^p)(n_1 - n_2)}{\sum_k n_k} - 1 \quad (2)$$

where T is the temperature of the sample in the nmr probe, H_0 is the spectrometer magnetic field, and p is the number of protons in the product whose spectrum is being examined.

The effective Hamiltonian above has become usual for calculations of this type, but the formal treatment outlined here is independent of the choice of terms which are neglected or included. In this Hamiltonian J governs valence interactions between the radicals of a pair leading to electronic singlet–triplet splitting of magnitude $2J$, the singlet being of lower energy if $J < 0$. In CKO model calculations, J is fixed at some effective value; thus the Hamiltonian is time independent. The time development arises because the radical pairs are regarded as suddenly created in a process which greatly alters J, so that the precursor eigenfunctions are not eigenfunctions of the loosely coupled radical pairs. In a realistic view of radical pairs, J would vary as the two radicals are jostled about by solvent molecules. In a CKO treatment, it must be considered that the constant J employed represents some kind of average over such variations.

Behavior of an Ensemble of Radical Pairs. In a real system, not one but many radical pairs react, giving products of radical pair collapse or permanently separated radicals. Our problem is to compute the populations n_k of nuclear spin eigenstates ϕ_k of the various products.

Imagine an ensemble of N radical pairs. For a product formed from this ensemble

$$n_k = N\gamma_k \quad (3)$$

where γ_k is the probability that a randomly chosen radical pair of the ensemble will give rise to the chosen product in nuclear eigenstate ϕ_k.

(13) R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5519 (1967).

(14) (a) H. Fischer, paper presented at the American Chemical Society Division of Physical Chemistry Symposium on Electron Spin Resonance, The University of Georgia, Athens, Ga., Dec 1970; H. Fischer and M. Lehnig, unpublished manuscript, 1970, and private communication, 1971. (b) All versions of the radical pair theory of CIDNP, relying on different detailed models, invoke nonadiabatic radical pair behavior. They do not differ in fundamental concepts from one another or from the original ideas of Closs[10a] and of Kaptein and Oosterhoff.[11]

(15) F. J. Adrian, *J. Chem. Phys.*, **53**, 3374 (1970); **54**, 3912, 3918 (1971).

The density matrix whose elements are $\gamma_{k',k}$, expressed in the basis $\{\phi_k\}$, has diagonal elements $\gamma_{k,k} = \gamma_k$ with precisely the desired property, provided that the corresponding density matrices for all the products arising from this ensemble of radical pairs are mutually normalized so that the sum of their traces is unity. Accordingly, we address the problem of computing such density matrices.

We begin with the density matrix $\mathbf{P}(t)$ for an ensemble of suddenly created, noninteracting radical pairs. $\mathbf{P}(0)$ describes the ensemble with each radical pair in its initial state.[16] Because the radical pairs are suddenly created, their initial states are not radical pair eigenstates, and $\mathbf{P}(t)$ must undergo time development.

We label the basis functions $\phi_{Xi} = \phi_X\phi_i$ as follows: $X (= T_+, T_0, T_-,$ or $S)$ refers to one of the electronic spin functions, while i indexes the nuclear spin functions. The $\{\phi_i\}$ will, in general, be different from the $\{\phi_k\}$. Throughout this paper, we reserve the subscripts $i, j,$ and k to designate quantities related to bases $\{\phi_i\}$, $\{\phi_j\}$, and $\{\phi_k\}$, where $\{\phi_k\}$ are product nuclear eigenfunctions, $\{\phi_j\}$ are radical pair precursor nuclear eigenfunctions, and $\{\phi_i\}$ are arbitrarily chosen nuclear basis functions. The $\{\phi_i\}$ are selected from considerations of computational ease and efficiency.

In

$$\mathbf{P}(t) = \sum_X\sum_{X'}\sum_i\sum_{i'}P_{X'i',Xi}(t)\,\phi^*_{X'i'}\phi_{Xi} \qquad (4)$$

$\mathbf{P}(t)$ is the density matrix in the basis $\{\sigma\}$, which are the coordinates of the spin functions ϕ_{Xi}. The $P_{X'i',Xi}(t)$ are the elements of the related density matrix in the basis $\{\phi_{Xi}\}$.

Solutions to the equation of motion of the density matrix are of the form

$$\mathbf{P}(t) = \sum_r\sum_s B_{rs}e^{-i(E_s-E_r)t}\Phi_r{}^*\Phi_s \qquad (5)$$

where the $\{B_{rs}\}$ are constants reflecting the initial condition of the radical pair ensemble and the $\{\Phi_r\}$ and $\{E_r\}$ are solutions of the time-independent equation

$$H\Phi_r = R_r\Phi_r \qquad (6)$$

In terms of the basis $\{\phi_{Xi}\}$

$$\Phi_r = \sum_X\sum_i U_{Xi,r}\phi_{Xi} \qquad (7)$$

Substitution into (5) gives

$$\mathbf{P}(t) =$$
$$\sum_X\sum_{X'}\sum_i\sum_{i'}\left(\sum_r\sum_s U_{X'i',r}U_{Xi,s}B_{rs}e^{-i(E_s-E_r)t}\right)\phi^*_{X'i'}\phi_{Xi} \qquad (8)$$

from which the quantities in large parentheses are identified by comparison with eq 4.

$$P_{X'i',Xi}(t) = \sum_r\sum_s U_{X'i',r}U_{Xi,s}B_{rs}e^{-i(E_s-E_r)t} \qquad (9)$$

The constants B_{rs} are found by setting $t = 0$ in eq 9.

$$B_{rs} = \sum_X\sum_{X'}\sum_i\sum_{i'}U_{X'i',r}U_{Xi,s}P_{X'i',Xi}(0) \qquad (10)$$

We will later consider the assignment of values to the matrix elements $P_{X'i',Xi}(0)$.

We now have the radical pair ensemble density matrix as a function of time. Up to this point, the development we have given could be incorporated into treatments of radical pair models related to the CKO model, but involving different detailed mechanical radical pair descriptions and different methods of ensemble averaging. In the CKO model, the radical pairs are considered to vanish according to a first-order rate law, the mean radical pair lifetime being τ. When a radical pair vanishes, it produces either a product of radical pair collapse or a pair of permanently separated radicals. Since the probabilities of these kinds of events are related to the spin characters of the radical pairs at the moments of their destruction, we require the time-independent density matix $\mathbf{P}$, which describes the ensemble of radical pairs, each considered at its moment of destruction.

$$\mathbf{P} = (1/\tau)\int_0^\infty \mathbf{P}(t)e^{-t/\tau}dt \qquad (11)$$

This gives

$$P_{X'i',Xi} = \sum_r\sum_s\frac{U_{X'i',r}U_{Xi,s}B_{rs}}{1 + \tau^2(E_s - E_r)^2} \qquad (12)$$

It is the electronic spin characters of radical pairs at the moments of their destruction which play roles in determining their fates. It is considered that the nuclear spin characters remain intact in the product, be they collapse products or permanently separated radicals. Therefore it is convenient to consider appropriate density matrix blocks and to reduce these by integrating over the electron spin coordinates, which are of no interest for a specified product.[17] We thereby obtain density matrix blocks $\rho_{i',i}$ which describe the nuclear spin characters of portions of the radical pair ensemble with selected electronic spin character at the moments of radical pair destruction.

$$\rho_{i',i} = \sum_X\sum_{X'}P_{X'i',Xi}\delta_{XX'} \qquad (13)$$

The Kronecker δ expresses the mutual orthogonality of the electronic spin functions.

For our purposes, the following reduced density matrix blocks are important.

$$\rho^S_{i',i} = P_{Si',Si}$$
$$\qquad (13a)$$

$$\rho^T_{i',i} = P_{T_+i',T_+i} + P_{T_0i',T_0i} + P_{T_-i',T_-i}$$

The trace of $\rho^S_{i',i}$ is the probability that a randomly chosen radical pair of the original ensemble will be describable as an electronic singlet at the moment of its destruction, and the trace of $\rho^T_{i',i}$ has a similar meaning with respect to triplet character. It is in connection with these reduced density matrix blocks that the CKO hypothesis, that the probability of col-

(16) Since we are following the fate of the entire ensemble to its complete destruction, and since the ensemble members are noninteracting, we need not assume that all radical pairs are created simultaneously in real time. The computed probabilities will be independent of whether they are simultaneously created or not. We are not treating the kinetics of radical pair formation nor relaxation occurring in radicals or products at any stage. In principle, these processes could have been included in a formulation of the type we describe, but we set them aside for independent consideration.

(17) For electronic singlet products with high negative values of J, the nuclear and electronic eigenfunctions are separable to a high degree of approximation, the electronic portion having no bearing on the product nmr spectrum. Because we are treating neither relaxation nor electron spin polarization, we need not be concerned with the electronic functions associated with radicals which permanently separate from associated radical pairs.

lapse of a radical pair to singlet product is proportional to its singlet character at the time of its destruction, is introduced.

If the probability that a pure singlet radical pair will collapse to product is $k\tau$, then

$$\gamma_{i',i} = k\tau\rho^S_{i',i} \tag{14}$$

where $\gamma_{i',i}$ is a product density matrix in the nuclear basis $\{\phi_i\}$.

To populate the product nuclear spin eigenstates, a transform of $\gamma_{i',i}$ to the basis $\{\phi_k\}$ is required. If

$$\phi_k = \sum_i v_{i,k}\phi_i \tag{15}$$

then

$$\gamma_{k',k} = \sum_i \sum_{i'} \gamma_{i',i} v_{i,k} v_{i',k'} \tag{16}$$

and for the singlet collapse product

$$n_k = N\gamma_{k,k} \tag{17}$$

from which the nmr signal enhancement can be computed (eq 2).

For the radical pairs which suffer permanent diffusive separation, a parallel treatment is given.

$$\theta_{i',i} = \rho^T_{i',i} + (1 - k\tau)\rho^S_{i',i} \tag{18}$$

Here $\theta_{i',i}$ is a density matrix, analogous with $\gamma_{i',i}$, which describes the nuclear spin character of permanently separated radical pairs (neglecting the possibility of relaxation). Equation 18 reflects the facts that some of the radical pairs which are describable as singlets at the moments of their destructions *can* separate and that all radical pairs describable as electronic triplets at those times *must* separate. A transform to a new basis is again required.

$$\theta_{k',k} = \sum_i \sum_{i'} \theta_{i',i} v_{i,k} v_{i',k'} \tag{19}$$

In analogy with eq 17

$$n_k = N\theta_{k,k} \tag{20}$$

The $\{\phi_k\}$ employed here are not, of course, the same as for a product of radical pair collapse.

Construction of the Initial Radical Pair Density Matrix. First, consider the case of radical pair precursors which have well-defined electronic states. These will, in general, be singlet or triplet molecules which react or decompose to give the radical pairs. Since an ensemble of such precursors consists of molecules in well-defined eigenstates $\{\phi_{Xj} = \phi_X\phi_j\}$, a density matrix describing the precursor ensemble will be diagonal in the basis $\{\phi_{Xj}\}$, the diagonal elements being the population fractions in the various eigenstates. The choice of population fractions for the diagonal elements, and not numbers proportional to them, ensures a normalization such that the interpretations of the meanings of the various denisty matrices discussed in previous sections are correct.

These precursors decompose suddenly, in the CKO model, to give the radical pairs. Like a wave function, the density matrix cannot change discontinuously in time, so the initial density matrix for the radical pair ensemble is identical with the density matrix describing the precursor molecules at their moments of reaction or decomposition to give the radical pairs. Thus, the

matrix of elements $P_{X'j',Xj}(0)$ is diagonal in the basis $\{\phi_{Xj}\}$. To obtain the matrix $P_{X'i',Xi}(0)$ merely requires the appropriate similarity transformation. If

$$\phi_{Xj} = \sum_i u_{i,j}\phi_{Xi} \tag{21}$$

then

$$P_{X'i',Xi}(0) = \sum_j \sum_{j'} P_{X'j',Xj}(0) u_{j,i} u_{j',i'} \tag{22}$$

In the simplest and most common cases of interest, the precursor nuclear eigenstates are populated according to Boltzmann distributions. Because the population differences are very small, only small errors are introduced if the nuclear eigenstates are assigned equal fractional populations 2^{-p}, where p is the number of protons. Then

$$P_{X'j',Xj}(0) = 2^{-p}w_X\delta_{X'j',Xj} \tag{23}$$

where w_X is the fractional population of ϕ_X. For electronic singlet precursors, $w_S = 1$, $w_{T_+} = 0$, $w_{T_0} = 0$, and $w_{T_-} = 0$. For electronic triplet precursors, $w_S = 0$, $w_{T_+} = 1/3$, $w_{T_0} = 1/3$, and $w_{T_-} = 1/3$.

$\mathbf{P}(0)$ is diagonal, of course, in the basis of precursor eigenstates. Each block of $P_{X'j',Xj}(0)$, associated with a particular ϕ_X, is proportional to a unit matrix. For example

$$P_{Sj',Sj}(0) = 2^{-p}w_S\delta_{j',j} \tag{24}$$

where the Kronecker δ is interpreted as representing the elements of a unit matrix. Since similarity transforms leave unit matrices invariant

$$P_{X'i',Xi}(0) = 2^{-p}w_X\delta_{X'i',Xi} \tag{25}$$

Comparison with eq 23 reveals that the change in nuclear basis leaves the initial radical pair density matrix unchanged. Thus, for this case one need not be concerned with the nuclear eigenfunctions of the precursor. One merely assigns equal populations $2^{-p}w_X$ to all members of any convenient basis $\{\phi_{Xi}\}$, the initial radical pair density matrix being diagonal in any such basis.

Now we consider radical pairs formed from randomly diffusing radicals. Neglecting again population differences imposed by Boltzmann distributions, the initial radical pair density matrix would be proportional to a unit matrix in any complete basis.

$$P_{X'i',Xi}(0) = (1/4)2^{-p}\delta_{X'i',Xi} \tag{26}$$

However, a calculation based on such an initial condition does not give reasonable results.[18] Instead, it must be assumed that not all the initially singlet radical pairs survive their initial collisions or encounters. The fraction f of the singlets which react immediately in this way leads directly to unpolarized product. The singlet population of the remaining radical pairs, which undergo the usual time developments, is depleted. For the time developing radical pairs

$$P_{X'i',Xi}(0) = (1 - \delta_{SX}f)2^{-(p+2)}\delta_{X'i',Xi} \tag{27}$$

The electronic blocks of this matrix are also proportional to unit matrices. Therefore, we find again that $P_{X'i',Xi}(0)$ is invariant to any transformation of the nuclear portion of the basis.

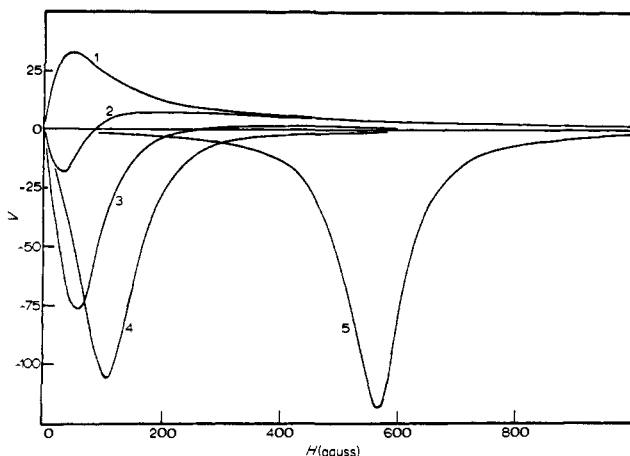(18) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2186 (1970).

Figure 1. Calculated signal enhancements V for a product of collapse of one-proton radical pairs formed from freely diffusing radicals $vs.$ the magnetic field of the chemical reaction, H. Parameters used: $A = +27$ G; $f = 0.02$; $\tau = 10^{-9}$ sec; $J = 0$ (curve 1), -2×10^8 rad/sec (curve 2), -5×10^8 rad/sec (curve 3), -10×10^8 rad/sec (curve 4), and -50×10^8 rad/sec (curve 5).

It should be noted that the trace of the matrix (eq 27) is not unity; it is $1 - (f/4)$. This reflects the fact that radical pairs have already vanished at $t = 0$, and it preserves the proper normalization. However, when one calculates the product density matrix $\gamma_{i',i}$, he must take care to note that it contains a term in addition to that indicated in eq 14, the new term representing product formed from the immediately collapsing radical pairs.

$$\gamma_{i',i} = 2^{-(p+2)} f \delta_{i',i} + k\tau\rho^S{}_{i',i} \qquad (28)$$

There is no new contribution to the matrix $\theta_{i',i}$, for which eq 18 remains correct.

Description of Computer Calculations. The method presented here has been embodied in a series of Fortran programs for the CDC 6400 digital computer.

GCKO calculates the radical pair ensemble behavior, using symmetry and magnetic factoring of the secular determinants. The parameters of the Hamiltonian, the number and total spins of the nuclear composite particles, and the radical pair effective lifetime τ are input on punched cards. The density matrix is calculated, a partial reduction performed, and the result stored on magnetic tape.

NIMCO completes the calculation of product nmr spectra. The product nuclear spin Hamiltonian parameters and precursor information are input on punched cards. The program also used the tape produced by GCKO. The nuclear eigenfunctions are obtained for the field of the reaction and their populations are calculated. These populations are transferred adiabatically to the spectrometer field[19] and the enhancement factors are calculated. By using the full symmetry available it is possible to perform the adiabatic transfer by simply assuming a noncrossing rule within each block of the secular determinant, assigning the populations to the energy levels in order of increasing energy in all fields.

(19) Glarum pointed out that the transfer of samples from low magnetic fields into high spectrometer fields should be adiabatic for pertinent nmr coupling constants of the usual, appreciable sizes: S. H. Glarum, presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, paper ORGN 40; private communication from S. H. Glarum, 1970.
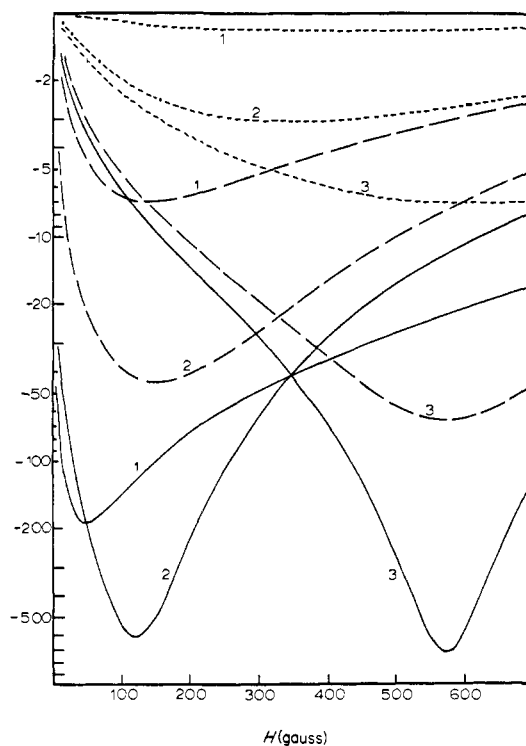

Figure 2. Similar to Figure 1 except for log scale for V and parameters. Parameters: $A = -22$ G; $f = 0.19$; $\tau = 10^{-9}$ sec (solid curves), 3×10^{-10} sec (curves of long dashes), and 10^{-10} sec (short dashes); $J = 0$ (curves 1), -10×10^8 rad/sec (curves 2), and -50×10^8 rad/sec (curves 3).

Finally, the polarized nmr spectra are calculated and displayed by printer graphics.

The calculational sections of both programs involve matrix diagonalization by the Jacobi technique. Spectral intensities are calculated by a section adapted from LAOCOON.

The upper limit of the programs' capacities is presently four composite nuclear particles of spin $^1/_2$ or two spins $^1/_2$ and $^7/_2$. As an example of the computer time required, the fits illustrated in Figure 5 required 26 sec for 11 field values. The Jacobi diagonalization is the rate-limiting computational step; it is currently being replaced by a faster Givens technique subroutine.

One-Proton Radical Pairs. General Aspects. Because they are the simplest systems of interest and because they serve as models for more complex systems, we consider the calculated behavior of one-proton radical pairs. Two cases are presented, $A = -22$ G and $A = +27$ G, representing 1 and 2 protons, respectively, of alkyl radicals.

For zero reaction fields, the calculated polarizations are zero, and they tend to zero for high reaction fields, as expected. In fact, the calculations for a wide variety of radical pairs conform, for high reaction fields, to the approximate T_0–S CKO model.

In Figures 1 and 2 are shown the results of calculations of the polarizations of a product of collapse of one-proton radical pairs formed from freely diffusing radicals in low magnetic fields. The polarizations resemble those calculated for radical pairs with triplet precursors, as expected,[18] with lower absolute magnitudes. The parameters f and $k\tau$ both act as factors

which scale the absolute intensity of the calculated polarizations without affecting the shapes of the curves plotted. We have arbitrarily set $k\tau = 1$, throwing all the scaling into the parameter f. Other parameters are given with the figures.

Although effective values of $-J$ as large as 50×10^8 rad/sec seem unlikely, we have included calculations based on this value as well as smaller ones to illustrate the effects of J variation. It is seen that the calculated curves show considerable dependence on J, A, τ, and H. These facts are of potential use in determining the "best" values of parameters of the CKO model (or of other radical pair models.) Studies of low-field polarization provide data which supplement the high-field studies and which might serve to give definition to parameters to which the high-field results are relatively insensitive. Also, the data from low-field studies are, in principle, valuable for the discrimination that it might provide among radical pair models.

The most interesting aspect of the low-field calculations is the predicted turnover of the direction of polarization with magnetic field variation, described earlier.[8] The turnover is predicted only for positive values of A, and it is not predicted by the approximate CKO model which considers only $T_\pm$–S mixing. We defer further discussion of the details of one-proton polarization pathways to a later section, but we note at this point that we have observed, in reactions of alkyl iodides with sodium mirrors in DME, polarization turnovers which may reflect this prediction, though the reactions are presently incompletely understood.[20]

Adrian's Diffusion Model. Though we do not attempt here to discriminate among radical pair models, some of the calculations and experimental results we will consider do have a bearing on the diffusion model for radical pairs proposed by Adrian.[15] He supposes that the time development of the spin characters of radical pairs occurs during a period of moderate separation following an initial encounter or geminate pair production event. There is a significant probability that such radicals will reencounter before finally separating, and the probability of reaction during the second encounter is taken to be proportional to the electronic singlet character at the time of the second encounter. This will have developed differently for different associated nuclear spin functions, leading to product polarization.

Adrian prefers to assign J the value zero during the period in which time development occurs. The time development itself is treated exactly as in the CKO model, so the qualitative predictions of the two models, which differ only in the methosd of averaging, should be the same.

We will show below that $J = 0$ will not accommodate some of our experimental results. We have previously reached this conclusion on a basis which does not now appear to be firm.[8] The new basis for rejecting $J = 0$ depends on further considerations of the mechanism of the reaction, together with a detailed analysis of the origin of the polarization. We will examine the calculations for a model one-proton radical pair in more detail; then we will consider the predicted polarization in the light of recent evidence relating to the

effect of the kinetics of the chemical reaction on the observed polarization.[21a]

Polarization Pathways. For the common cases of interest, the initial radical pair density matrix is diagonal in any basis $\{\phi_{Xi}\}$ ($X = T_+$, T_0, T_-, or S) and for any magnetic field, low or high. This does not mean that any such basis consists of precursor eigenfuntions. Rather, it is a consequence of the assumption of equal populations of the pertinent precursor eigenstates, as discussed earlier. The initial radical pair density matrix can be *imagined* to represent populations of eigenstates $\{\phi_{Xi}\}$. One can then consider the contributions to polarization of "intersystem crossings" like $T_0\alpha \rightarrow S\alpha$ and $T_-\alpha \rightarrow S\beta$, or their reverse "processes." The total polarization is correctly given by a properly weighted sum of polarizations attributable to precursor molecules arbitrarily assigned to each basis function.

While this is an artificial dissection, it can be convenient. The "selection rules" for T_0–S crossings are different from those for $T_\pm$–S crossings, and there are observable consequences of this fact.[9]

Polarization Pathways for One-Proton Radical Pairs. For a one-proton radical pair, there are four intersystem crossings which provide pathways for polarization of the product of radical pair collapse.

$$T_0\alpha \longrightarrow S\alpha$$
$$T_0\beta \longrightarrow S\beta$$
$$T_+\beta \longrightarrow S\alpha$$
$$T_-\alpha \longrightarrow S\beta$$
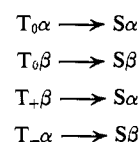
Intersystem crossings involving $T_+\alpha$ and $T_-\beta$ are forbidden, and crossings $T_+\beta \rightarrow T_0\alpha$ and $T_-\alpha \rightarrow T_0\beta$ are not relevant to formation of the product of radical pair collapse, which occurs from singlet radical pairs only. The intersystem crossings occur in both directions, but the net amounts, for cases of diffusion-formed radical pairs, are in the directions shown above.

Figures 3 and 4 give the relative amounts of product formed through the several kinds of intersystem crossings. The vertical arrows are vectors representing the directions and relative magnitudes of the contributions of the $T_0 \rightarrow S$ and $T_\pm \rightarrow S$ crossings to the product nmr signal, nmr emission being represented by an arrow pointing down, absorption by an arrow pointing up.

When $J = 0$, the two $T_\pm \rightarrow S$ crossings occur equally in all fields, leading to no contribution to the product nmr signal. The sole contribution in this case is due to the inequivalent $T_0 \rightarrow S$ crossings! This is surprising because calculations based on the approximate T_0–S CKO model (neglecting $T_\pm$ functions altogether) predict equal amounts of the two $T_0 \rightarrow S$ crossings (for $\Delta g = 0$), while similar calculations based on an

(20) A particular case is the reaction of isopropyl iodide with a sodium mirror, giving polarized biisopropyl.[1]

(21) (a) In a private communication, F. J. Adrian showed analytically that $T_\pm \rightarrow S$ intersystem crossings in radical pairs do not lead to predicted product polarization if $J = 0$. The fact that our generalized calculations do lead to predictions of polarization, even for $J = 0$, led us to examine the details of the polarization pathways. (b) A description of the approximate calculations and the resulting predictions is given in ref 8. The results of such calculations are strongly basis dependent. It is possible to choose the basis functions appropriately to obtain meaningful predictions for reactions carried out in high fields or in zero field, but it is not clear that this is possible for an arbitrarily chosen low field. The failure of the approximate calculations involving mixing of basis functions in pairs can be attributed to an improper choice of basis. More likely, even the best basis choice would be inadequate; mixing in pairs necessarily implies neglect of some off-diagonal elements of the Hamiltonian matrix.
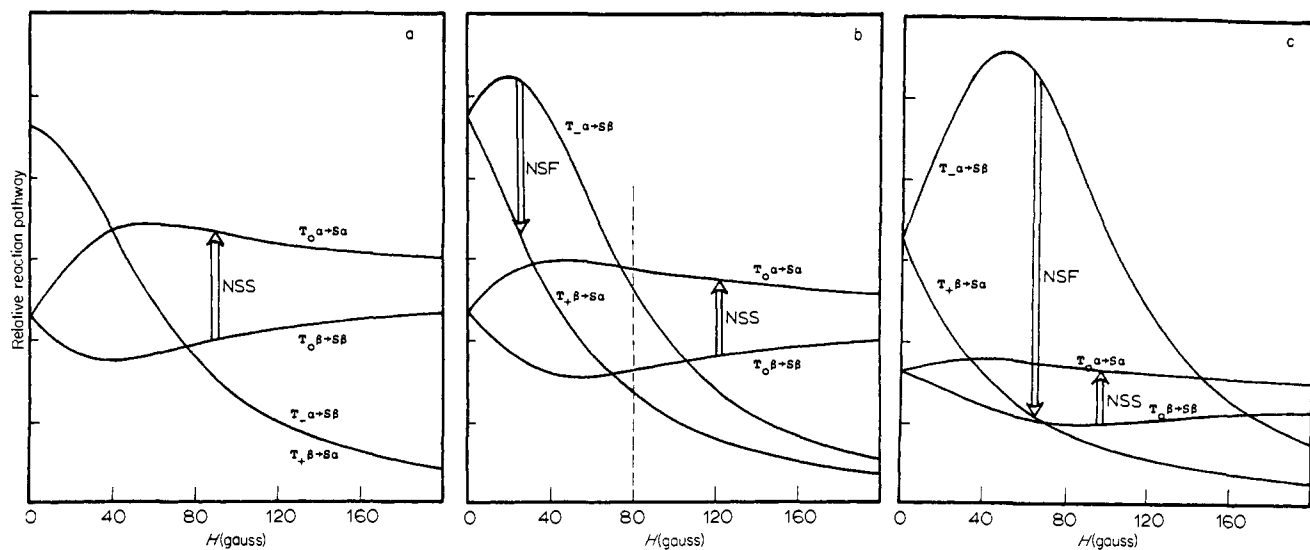
Figure 3. Relative contributions of intersystem crossings to formation of one-proton radical pair collapse product vs. reaction magnetic field H. Parameters: same as for Figure 1, with Figure 3a corresponding to curve 1, Figure 1; Figure 3b, curve 2; Figure 3c, curve 3. The vertical broken line indicates the turnover point in Figure 1. The vertical arrows represent the relative nmr signal enhancements, both magnitude and direction, resulting from the two different kinds of intersystem crossings.
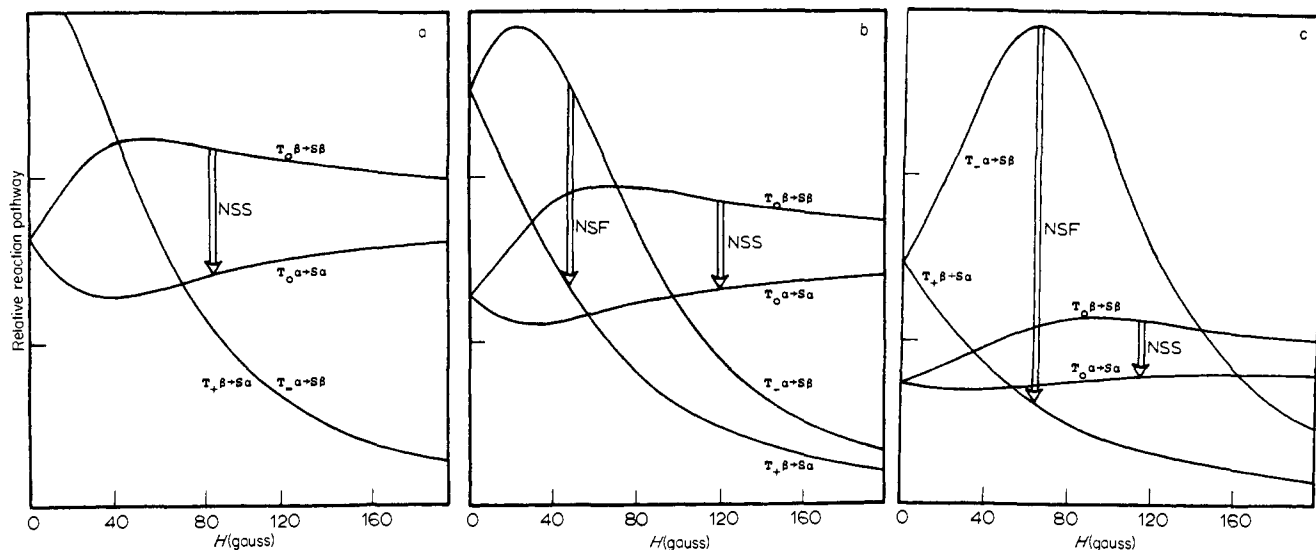

Figure 4. Similar to Figure 3, but for $A = -22$ G rather than $+27$ G.

approximate CKO model which neglect T_0 functions altogether predict unequal amounts of the two $T_\pm \rightarrow$ S crossings.[21b] The latter calculations do predict qualitatively the same kinds of polarizations for products of radical pair collapse as do calculations with the general model if $J = 0$. For triplet or diffusion-formed radical pairs with $J = 0$, the prediction of each model is nmr emission if $A < 0$ and nmr absorption if $A > 0$.

One might imagine, then, that the discrepancy between the polarization pathways implied by the two models would be inconsequential; what matter that an internal dissection of the total effect gives surprising results if the total effect itself is reasonably calculated? The fact is, however, that for $J = 0$ the total effects are calculated quite differently in the approximate and general models when one considers the radicals which suffer permanent diffusive separation.

The $T_\pm \rightarrow$ S intersystem crossings involve nuclear spin flips, but the $T_0 \rightarrow$ S crossings do not. Through
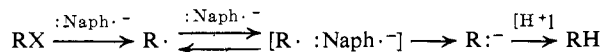
$T_0 \rightarrow$ S crossings, the polarization results from "nuclear spin selection" (NSS),[22a] and the radical pairs suffering permanent diffusive separation are polarized oppositely from those suffering collapse to product.[10,11] Polarization through $T_\pm \rightarrow$ S crossings, on the other hand, involve nuclear spin "flips" (NSF), and through this kind of pathway the radical pairs suffering permanent diffusive separation are polarized in the same direction as those collapsing to product.[8] Therefore, if polarizations of collapse products are similar for the two kinds of pathways, the polarizations of the separating

(22) (a) H. R. Ward, R. G. Lawler, and R. A. Cooper, presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, paper ORGN 69. (b) A case of polarization resulting from $T_\pm$-S crossings even in a high magnetic field has been discussed in connection with a reaction leading to dimers of trimethylenemethane derivatives. See J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, J. Amer. Chem. Soc., 93, 1544 (1971); and G. L. Closs, ibid., 93, 1546 (1971). It is not clear whether the polarization results from the action of pairs of triplet trimethylenemethanes or from initially triplet diradical trimethylenemethane dimers.[8]

radicals will be opposed for the two pathways. Further, as will be seen below, certain reaction mechanisms may lead to the suppression of NSS ($T_0 \rightarrow$ S) polarization but not NSF ($T_\pm \rightarrow$ S) polarization.[22b]

It is interesting to note from Figures 3 and 4 that $T_0 \rightarrow$ S contributions to the polarization diminish as larger negative values of J are assumed. This accords, perhaps, with our earlier observation that as $-J$ increases, the agreement between the general and approximate $T_\pm$-S calculations improves.

Influence of the Mechanism and Kinetics of Reactions of Alkyl Halides with Sodium Naphthalene on the Observed Polarization of a Reduction Product. For present purposes, the important part of the mechanism of reactions of alkyl halides with sodium naphthalene in DMA is the following.

$$RX \xrightarrow{:Naph\cdot^-} R\cdot \underset{\xleftarrow{\hspace{1cm}}}{\overset{:Naph\cdot^-}{\xrightarrow{\hspace{1cm}}}} [R\cdot \ :Naph\cdot^-] \longrightarrow R:^- \xrightarrow{[H^+]} RH$$

This mechanism completely suppresses NSS ($T_0 \rightarrow$ S) polarization by ensuring the eventual conversion of all initially formed alkyl radicals to product with their original nuclear spin states.[9] However, it does not suppress NSF ($T_\pm \rightarrow$ S) polarization. Therefore, if there were not contributions to polarization from $T_\pm \rightarrow$ S pathways, no polarization would be observable in the reduction product RH.

The experimental evidence supporting these assertions is reported elsewhere.[9] In brief, the reaction of isopropyl chloride with sodium naphthalene in 5000 G gives propane which is not polarized. Multiplet effects arising through NSS ($T_0 \rightarrow$ S) pathways would have been expected had there not been effectively complete retrapping of escaped radicals before nuclear spin relaxation had occurred. When the reaction is carried out in a 60-G field, pure emission nmr spectra are observed for the propane formed. Basically, the lack of suppression of NSF ($T_\pm \rightarrow$ S) polarization is due to the fact that escaped radicals are partly channeled to product in the first encounters with new sodium naphthalene moieties. If this occurs before relaxation, the product polarization is reinforced, not cancelled.

Agreement between the General Calculations and the Observed Polarizations in Reactions of Alkyl Halides with Sodium Naphthalene. Basis for Rejecting $J = 0$. Figures 3 and 4 illustrate how the general calculation, coupled with the considerations outlined in the preceding section, account for the observed kinds of polarizations from alkyl halide–sodium naphthalene reactions. Since polarization *is* observed, J cannot be zero; no contribution of the $T_\pm \rightarrow$ S pathway is predicted for that case.[23]

In general calculations, the $T_\pm \rightarrow$ S polarization component is always negative, giving nmr emission, regardless of the sign of A, the magnitude of the reaction field H, or the magnitude of a negative J. This is in complete agreement with the experimental observations.[8,9] It is particularly noteworthy that the experimentally observed polarizations exhibit no turnovers as the magnetic field is varied. Such turnovers might have been expected (see Figure 3) for protons with

(23) Adrian has recently shown that his method can predict $T_\pm \rightarrow$ S polarization if provision is made for some time development *during* encounters (when $J \neq 0$) as well as between encounters (when J is taken to be zero): private communication from F. J. Adrian, 1971.
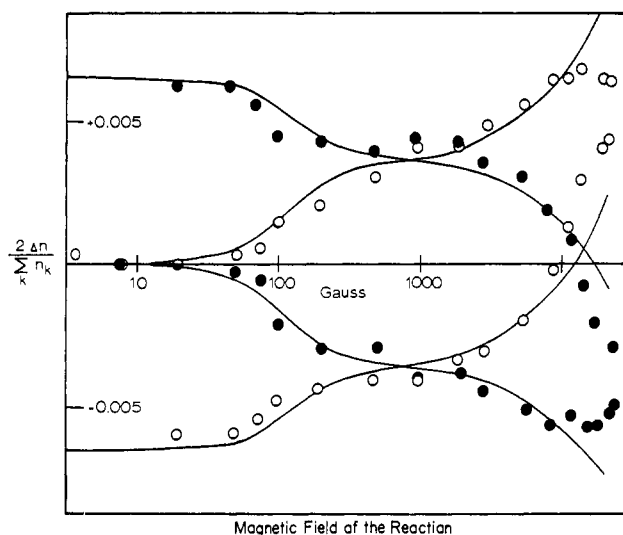

Magnetic Field of the Reaction

Figure 5. Calculated fit to experimental data (circles) of Fischer and Lehnig.[14a] The product is 2,3,3-trichloropropanoic acid formed from nongeminate $Cl_2CH\cdot$ and $\cdot CHClCOOH$ radicals. Open circles represent nmr transitions due primarily to H-2, while filled circles represent those due primarily to H-3. Nmr spectra were obtained on a 100-Mc instrument. For the significance of the units of the ordinate, see eq 2; the data were supplied to us in this form.[14a] Parameters: g ($Cl_2CH\cdot$) = 2.008; g ($\cdot CHClCOOH$) = 2.00677; A ($Cl_2CH\cdot$) = -15 G; A ($\cdot CHClCOOH$) = -20.2 G; $\tau = 5 \times 10^{-10}$ sec; $f = 0.36$; $k\tau = 1$; $J = 0$. These are far from unique parameters. As mentioned in the text, $k\tau$ and f serve only to scale the calculations, and τ serves mostly this function, although it does affect the shape of the curves also. The parameters describing $\cdot CHClCOOH$ were taken to be fixed by esr data.[14a] The parameters describing $Cl_2CH\cdot$ were adjusted. It seems possible to obtain approximately the same quality of fit with A ($Cl_2CH\cdot$) = -13 G as with -15 G; -17 G (used by Fischer and Lehnig) leads to a slightly poorer fit. Within a range of about 0.001, g ($Cl_2CH\cdot$) = 2.008 seems optimal; it is the value used by Fischer and Lehnig. $J = 0$ gives a better fit than $J = -2 \times 10^8$ rad/sec, but the differences are probably within experimental error. $J = -5 \times 10^8$ rad/sec gives rise to significant deviations from the experimental data.

positive hyperfine coupling constants if the NSS component of polarization had not been suppressed.

Calculation of Experimental Data for a Reaction of Two-Proton Radical Pairs. Finally, we illustrate an application of the method and programs described herein. We calculate the field dependence of the nmr spectrum of $Cl_2CHCHClCOOH$ formed in reactions of nongeminate $Cl_2CH\cdot$ and $\cdot CHClCOOH$ radicals, attempting a fit to the experimental data of Fischer and Lehnig[14a] (see Figure 5). This provides a test of our entire package of computer programs, as well as the method, in that the program package performs the calculations in one nuclear basis, populates the product nuclear spin states in the reaction field by means of an appropriate density matrix transformation, correlates low-field and high-field product nuclear spin states, effects the adiabatic transfer of low-field populations to high field, and computes the predicted second-order nmr spectrum. Further, we cover the entire range of magnetic fields with one kind of calculation.[24,25]

(24) While this manuscript was in its final stage of preparation, we received the doctoral thesis of R. Kaptein, University of Leiden, The Netherlands, 1971. In Chapter X, by R. Kaptein and J. A. den Hollander, an approach similar to the one described here is outlined, using a diffusion model to supply the method of averaging, and various results are discussed. It is noteworthy that these authors have found a simple example of the polarization turnover with variation in reaction magnetic field ($CHCl_3$ formed in the photolysis of diisopropyl

ketone in CCl₄), and that they have been able to obtain a good fit for the observed variation by means of their calculations. We are grateful to Dr. Kaptein for providing us with a copy of his thesis, which represents a magnificent body of work.

(25) NOTE ADDED IN PROOF. Fischer and Lehnig[14a] have determined the esr parameters of $Cl_2CH\cdot$ as $g = 2.00829 \pm 0.00010$ and $A = 16.79 \pm 0.05$ G. See H. Fischer and M. Lehnig, *J. Phys. Chem.*, **75**, 3410 1971); this paper reports the work cited in our ref 14a.

Fluorescence of Aromatic Benzoxazole Derivatives

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Contribution from the Research Laboratory, Kodak Limited, Wealdstone, Harrow, Middlesex, England. Received May 21, 1971

Abstract: Absorption spectra, emission spectra, and fluorescence yields were measured for a group of benzoxazolyl-substituted aromatic hydrocarbons. From the data, radiative and nonradiative lifetimes of the first-excited singlet state are calculated and compared to those of the unsubstituted molecules. It is found that benzoxazolyl groups enhance fluorescence by increasing the rate of the radiative process without too much affecting the probability of the nonradiative transitions. Stilbene and tolan are exceptions in this respect; the introduction of benzoxazolyl groups in these molecules considerably decreases the rate of nonradiative deactivation. This behavior is connected with the configurational changes which occur in stilbene and in tolan on optical excitation. From flash spectrometric experiments on fluorescent benzoxazole derivatives in polystyrene matrices it can be inferred that the nonradiative deactivation of the excited singlet state of these molecules proceeds mainly by intersystem crossing to the triplet; internal conversion to the ground state is of minor importance. Direct spin–orbit coupling between the excited ππ* singlet state and a nπ* triplet state leads to fast intersystem crossing in benzoxazole and to a short nonradiative lifetime (0.8 nsec). In the composite heteroaromatic fluorescers direct spin–orbit coupling is eliminated by a change in the relative positions of the ππ* and the nπ* levels. Intersystem crossing proceeds here by spin–vibronic coupling, an effect similar to "intensity borrowing" in radiative transitions.

With the advent of fluorescent whitening agents, wavelength converters, and scintillators, the synthesis of highly fluorescent compounds has gained new impetus. Currently a whole subsection of *Chemical Abstracts* is devoted to the subject.[1] The great majority of the new fluorescers are composite aromatic systems containing one or several heteroaromatic components. Some heterocycles such as furan, oxazole, oxadiazole, and thiazole recur particularly often in industrial fluorescers. They do not fluoresce themselves but have a powerful fluorescence enhancing effect when coupled to aromatic hydrocarbons or other conjugated systems.

Although this effect is responsible for the fluorescence capability of a whole class of substances, it has not attracted attention because of a lack of experimental data. The syntheses of large numbers of industrial fluorescers have been described, but their spectra are rarely given and quantum yields of fluorescence are reported for only a few.[2] It seemed therefore of interest to investigate a representative group of composite heteroaromatics in some detail. We have chosen a series of aromatic derivatives of benzoxazole. The compounds listed in Table I were prepared as described

in the Experimental Section, their absorption and emission spectra were measured, and their fluorescence efficiencies determined. The rate (k_R) of the radiative depopulation of the first-excited singlet state of the molecules was calculated from the integrated absorption spectra by the method of Förster.[3] The sum of the rates of the nonradiative processes (k_N) was obtained from the radiative rate and the fluorescence yield (φ_f) by the relation

$$\varphi_f = k_R/(k_R + k_N) \qquad (1)$$

We have compared the rates of the radiative and the nonradiative transitions in the composite fluorescers with the corresponding rates in the parent hydrocarbons and in benzoxazole, and we have attempted a qualitative interpretation of the effect of structure on these rates. The results are reported in the present communication.

Results and Discussion

Experimental results relating to the singlet state of the fluorescent benzoxazole derivatives are collected in Table I. Apart from a reference number and the structural formula, Table I indicates the wavelength of the 0,0 band and the wavelength of maximum

(1) See section 40 of *Chemical Abstracts*, "Fluorescent Whitening Agents."

(2) I. D. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.

(3) Th. Förster, "Fluoreszenz Organischer Verbindungen," Göttingen, 1951.