Chemically Induced Dynamic Nuclear Polarization (CIDNP). II. The Radical-Pair Model

Ronald G. Lawler

Metcalf Research Laboratories, Brown University, Providence, Rhode Island 02912

Received March 12, 1971

The present Account is intended as an introduction to the quantitative features of the radical-pair model for CIDNP.[1-5] Special emphasis is placed on identifying the physical parameters needed to describe CIDNP phenomena observed under ordinary high-resolution nmr conditions and stating assumptions needed at present to make solution of the associated physical problems tractable. The subject matter thus covered lies at an intriguing intersection of the physics of magnetic resonance and the chemistry of organic free radicals. Although present and future developments in this field depend upon the use of concepts, methods, and experimental data from both disciplines, this presentation is aimed primarily at the group which has so far provided most of the experimental examples of CIDNP: organic chemists. Mathematical derivations, insofar as they presently exist, may be found elsewhere.[2-5]

We begin in section I by discussing briefly the factors which influence nmr line intensities and stating the basic assumptions underlying the radical-pair model. The problem is reduced largely to one of chemical kinetics. In section II we point out the critical steps in two schemes for generation and reaction of free-radical pairs and derive approximate expressions for the relative yields of products with different nuclear spin states. In section III we discuss the role of nuclear-spin-induced singlet–triplet mixing in determining reaction efficiencies of radical pairs and show how the initial electron spin multiplicity of a pair influences its reactivity. Section IV treats quantitatively one application of the model. Section V presents some general rules for predicting the effects of CIDNP on first-order nmr spectra. Finally, in section VI extension of the model to other types of phenomena is mentioned briefly.

I. Nmr Intensities and the Radical-Pair Model

In a slow-passage, high-resolution nmr experiment the intensity, $I_{nm}(H_0)$, of a transition between nuclear states n and m at magnetic field position H_0 is given by[6]

$$I_{nm}(H_0) = C|(n|I_x|m)|^2 g_{nm}(H_0)(N^n - N^m) \quad (1)$$

where C is an instrumental parameter assumed to be the same for all transitions, $|(n|I_x|m)|^2$ is a transition probability connecting n and m by means of the x component of the nuclear spin angular momentum, I, $g_{nm}(H_0)$ is a shape function which is often nearly the same for all lines, and N^n, N^m are the populations of the two states. If it is possible to take account of the first three factors, e.g., by assuming they are the same for all lines or by measurement or calculation, we see that an nmr spectrometer becomes simply a device for measuring the *relative concentrations* of two molecular species, n and m, which differ in the magnitude of their nuclear spin angular momenta.

It sometimes proves convenient to express the population differences in terms of the *polarization*,[7] P_{nm} (eq 2). For two levels which differ only in one unit of

$$P_{nm} = (N^n - N^m)/(N^n + N^m) \quad (2)$$

angular momentum in a sample of protons at 25° in a 60-MHz spectrometer the "thermal polarization" at equilibrium, $P_{nm}{}^0$, is 5×10^{-6}. This serves to define the *enhancement factor*, V_{nm}, for the transition.

$$V_{nm} = \frac{P_{nm}}{P_{nm}{}^0} - 1 \quad (3)$$

The original explanation[8,9] of CIDNP assumed that the "concentrations" of the nuclear spin species were driven away from equilibrium by selective exchange of energy with the surroundings via simultaneous relaxation of electron and nuclear spins. For a variety of

Ronald G. Lawler, a proud native of the state of Washington, received his higher education in California (B.Sc., California Institute of Technology; Ph.D., University of California, Berkeley), and then moved East for postdoctoral work (Columbia University, 1963–1965) and his present position at Brown University where he is Associate Professor of Chemistry. Shortly after the manuscript for this Account was completed, he continued his eastward drift by spending 7 months at the University of Leiden in the Netherlands. In addition to CIDNP, his research interests include electron spin resonance spectroscopy, isotope effects, and organic free radical, radical ion and dinegative ion chemistry and physics.

(1) H. R. Ward, *Accounts Chem. Res.*, **5**, 18 (1972).

(2) (a) G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); (b) G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2184 (1970).

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

(4) (a) H. Fischer, *Z. Naturforsch. A*, **25**, 1957 (1970); (b) H. Fischer, *Chem. Phys. Lett.*, **4**, 611 (1970).

(5) R. G. Lawler, to be published.

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapters 3, 6.

(7) The term "polarization" has traditionally been used by physicists to describe the fractional difference between the total number of "spin up" and "spin down" nuclei in a sample (C. D. Jeffries, "Dynamic Nuclear Orientation," Wiley-Interscience, New York, N. Y., 1963, Chapter 1). We restrict it here, however, to the relative populations of two levels. Some types of CIDNP, such as the "multiplet effect," do not represent "nuclear polarization" in the broader sense because the total number of spin up and spin down nuclei in the sample is the same as it would be in a sample at thermal equilibrium, even though the population differences between pairs of levels may exceed the equilibrium value by several orders of magnitude. In this sense the acronym CIDNP is a misnomer and has been retained only as a convenient, and by now widely accepted, label for the phenomenon.

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

(9) (a) J. Bargon and H. Fischer, *Z. Naturforsch. A*, **22**, 1556 (1967); (b) H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969).

reasons,[8],[9b] this cross-relaxation or Overhauser effect model has now been abandoned.

When one reflects that all examples of CIDNP to date have occurred in molecules which could be construed to be the *products* of chemical reactions, a conceptually very simple alternative explanation for the observed enhancements comes to mind: such effects will arise if the *yield* of product is greater for some spin states of the nuclei than for others; that is, *if the rate of formation of product depends on the nuclear spin states of the molecules undergoing reaction.*

The electrostatic interaction of electrons with nuclear charges and with each other is primarily responsible for determining reaction rate constants. Thus, a suitable mechanism for such nuclear spin selective reactions must be one in which, at a critical step in the reaction pathway, the nuclear magnetic moments can exert a force on the electrons which is comparable in magnitude to the electrostatic forces determining chemical reactivity. The starting point for the radical-pair model, first published by Closs[2] and Kaptein and Oosterhoff,[3] is the supposition that these conditions are satisfied during the very weak interaction of unpaired electrons during free-radical encounters at the distances characterizing radical-pair separation in a solvent cage. Control of chemical reactivity is then exercised through the ability of nuclear spins to induce the mixing of singlet and triplet electronic states of the radical pair.

II.   Kinetic Formulation

Delaying for the moment a more detailed discussion of how singlet–triplet mixing may arise and how it influences reactivity, we will first explore the consequences of hypothesizing a nuclear-spin-dependent reaction efficiency for radical pairs. In effect, what we will do is describe the life history of a molecular fragment, HR_1^n, containing one or more nuclei in combined state n, as it moves from a reactant molecule, R^n, through a radical pair, P^n, to give alternatively a cage combination product, C^n, or a free radical, F^n, which ultimately reacts with a scavenger to give a "cage escape" or scavenging product, S^n.

Two alternative pathways for reaction of HR_1^n *via* radical pairs are outlined in Figure 1, and a specific example of each is shown. In Scheme A HR_1^n resides initially in an initiator molecule which forms a *geminate* radical pair as the first step in the sequence. In Scheme B the reactant containing the fragment reacts initially in a chain transfer step with another radical (or possibly by diffusion away from a radical pair) and forms a radical pair only after a *diffusive* encounter with another radical. The rate constants responsible for the kinetic behavior of the systems are shown for each step. The products whose nmr spectra would actually be observed are shown in boxes. Thermal relaxation steps which try to restore normal populations in both the free radicals and in products are shown with wavy lines and proceed with rate constants $(T_1^n)^{-1}$.

Note that the only nuclear spin dependence is assumed to lie in the efficiencies, $\phi_C^{n,m}$ and $\phi_F^{n,m}$, of forming a cage combination product or free radical, respectively, from a radical pair. That is, the life history of a radical pair initially in the nuclear spin state n is described here in terms of the probabilities $\phi_C^{n,m}$ and $\phi_F^{n,m}$ that it will eventually form either a combination product or a free radical in spin state m. If the nuclear spin state does not change during an encounter, which is the case in high fields,[2-5] then n and m are the same and the molecules taking part in the reaction may be characterized by an unchanging label consisting of a set of nuclear spin quantum numbers.

As complicated as these schemes may appear at first glance, they show the *minimum* number of elementary steps which must be included to account for enhancement in both combination and scavenging products. Since free-radical reactions tend to be notoriously complex, almost any real system will have several of these schemes operating simultaneously. For example, in a reaction of an initiator carried out without the possibility of chain transfer (scavenging) steps, e.g., example A without I_2, the combination product, C, would be formed by Schemes A and B simultaneously. Likewise, if example A had employed an ethyl group rather than methyl, two combination products, the coupling product and ethylene, a disproportionation product, would be obtained. Example B also shows that in favorable cases (some of which have been observed,[10] in contrast to the, so far, hypothetical example shown here) a scavenging product may be the same as the reactant and give rise to enhancement in R! Real systems will also generally deviate from the idealized pseudo-first-order kinetics implied here. In fact, many of the reactions exhibiting CIDNP have been run under nonisothermal conditions, have complex orders in reactants, or are heterogeneous. Furthermore, in multiple spin systems the assumption of exponential thermal relaxation describable by a single T_1 is not even valid.[11] For these reasons quantitative descriptions of real reactions are likely to be much more difficult than the idealized treatment presented below would seem to indicate.

The kinetic equations for geminate and diffusive modes of radical-pair reaction have been solved[5] for nuclear-spin-state populations under steady-state conditions in the high-field limit where nuclear spins do not flip during a radical encounter (*i.e.*, $\phi^{n,m}$ is zero unless $n = m$). If we further assume that the populations, R, of levels in the reactant are the same (which ignores thermal polarization in the reactant), we obtain the following expressions for the population differences between two levels in combination and scavenging products.

(10) (a) H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Amer. Chem. Soc.*, **91**, 746 (1969); (b) H. R. Ward, R. G. Lawler, and R. A. Cooper, *Tetrahedron Lett.*, 527 (1969); (c) A. R. Lepley and R. L. Landau, *J. Amer. Chem. Soc.*, **91**, 748 (1969).

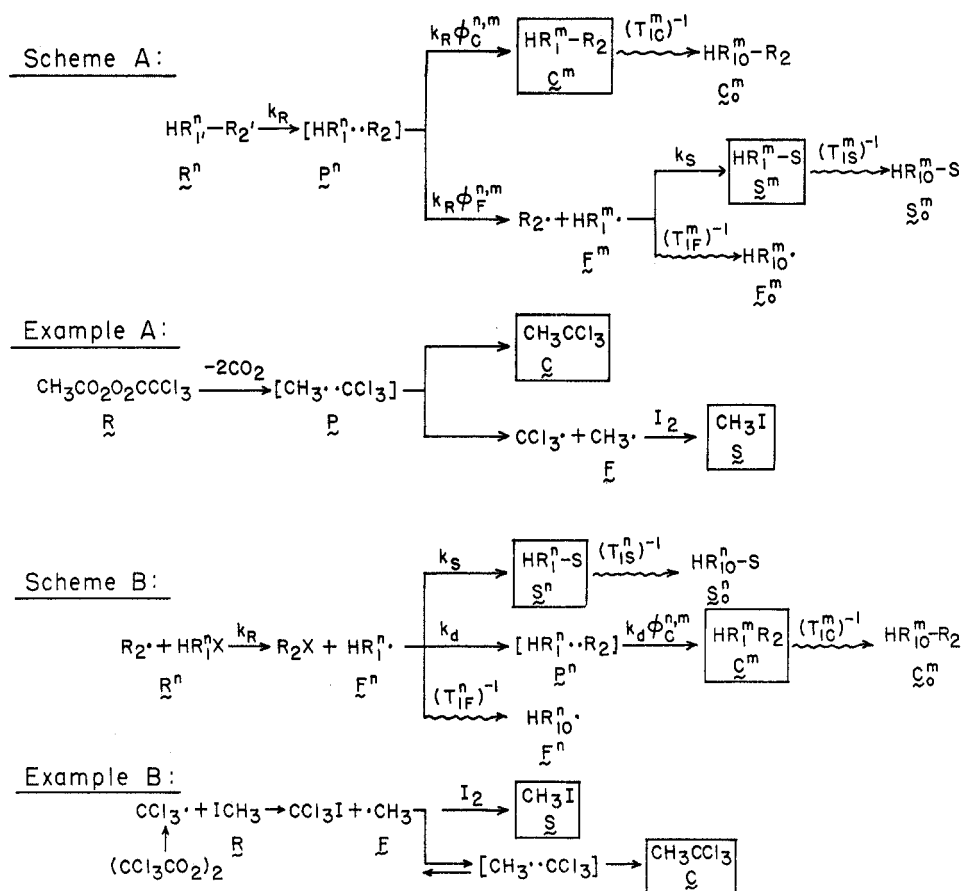(11) R. Freeman, S. Wittekoek, and R. R. Ernst, *J. Chem. Phys.*, **52**, 1529 (1970).

Scheme A:

$$HR_{I'}^{n}-R_{2'} \xrightarrow{k_R} [HR_I^{n}\cdots R_2] \begin{cases} \xrightarrow{k_R\phi_C^{n,m}} \boxed{\begin{array}{c} HR_I^{m}-R_2 \\ \underline{C}^m \end{array}} \xrightarrow{(T_{IC}^{m})^{-1}} \begin{array}{c} HR_{I0}^{m}-R_2 \\ \underline{C}_0^m \end{array} \\ \xrightarrow{k_R\phi_F^{n,m}} \begin{array}{c} R_2\cdot + HR_I^{m}\cdot \\ \underline{F}^m \end{array} \begin{cases} \xrightarrow{k_S} \boxed{\begin{array}{c} HR_I^{m}-S \\ \underline{S}^m \end{array}} \xrightarrow{(T_{IS}^{m})^{-1}} \begin{array}{c} HR_{I0}^{m}-S \\ \underline{S}_0^m \end{array} \\ \xrightarrow{(T_{IF}^{m})^{-1}} \begin{array}{c} HR_{I0}^{m}\cdot \\ \underline{F}_0^m \end{array} \end{cases} \end{cases}$$

Example A:

$$CH_3CO_2O_2CCCl_3 \xrightarrow{-2CO_2} [CH_3\cdot \cdot CCl_3] \begin{cases} \boxed{\begin{array}{c} CH_3CCl_3 \\ \underline{C} \end{array}} \\ \rightarrow CCl_3\cdot + CH_3\cdot \xrightarrow{I_2} \boxed{\begin{array}{c} CH_3I \\ \underline{S} \end{array}} \end{cases}$$

$\underline{R}$ $\underline{P}$ $\underline{F}$

Scheme B:

$$R_2\cdot + HR_I^{n}X \xrightarrow{k_R} R_2X + HR_I^{n}\cdot \begin{cases} \xrightarrow{k_S} \boxed{\begin{array}{c} HR_I^{n}-S \\ \underline{S}^n \end{array}} \xrightarrow{(T_{IS}^{n})^{-1}} \begin{array}{c} HR_{I0}^{n}-S \\ \underline{S}_0^n \end{array} \\ \xrightarrow{k_d} [HR_I^{n}\cdots R_2] \xrightarrow{k_d\phi_C^{n,m}} \boxed{\begin{array}{c} HR_I^{m}R_2 \\ \underline{C}^m \end{array}} \xrightarrow{(T_{IC}^{m})^{-1}} \begin{array}{c} HR_{I0}^{m}-R_2 \\ \underline{C}_0^m \end{array} \\ \xrightarrow{(T_{IF}^{n})^{-1}} \begin{array}{c} HR_{I0}^{n}\cdot \\ \underline{F}^n \end{array} \end{cases}$$

$\underline{R}^n$ $\underline{F}^n$ $\underline{P}^n$

Example B:

$$CCl_3\cdot + ICH_3 \rightarrow CCl_3I + \cdot CH_3 \begin{cases} \xrightarrow{I_2} \boxed{\begin{array}{c} CH_3I \\ \underline{S} \end{array}} \\ \rightleftharpoons [CH_3\cdot\cdot CCl_3] \rightarrow \boxed{\begin{array}{c} CH_3CCl_3 \\ \underline{C} \end{array}} \end{cases}$$

$(CCl_3CO_2)_2$ $\underline{R}$ $\underline{E}$

Figure 1. Pathways by which a proton-containing fragment, HR_I, may undergo geminate (Scheme A) or diffusive (Scheme B) encounters with another radical and give rise to selective formation of coupling (HR_I–R_2) and scavenging (HR_I–S) products according to the nuclear spin state of the fragment. Symbols are explained in the text (section II).

Geminate encounter (Scheme A)

$$(C^n - C^m) = (C_0^n - C_0^m) +$$
$$(k_R/T_{1C}^{-1})(\phi_C^{n,m} - \phi_C^{m,m})R \quad (4a)$$

$$(S^n - S^m) = (S_0^n - S_0^m) -$$
$$(k_R/T_{1S}^{-1})[k_S/(k_S + T_{1F}^{-1})](\phi_C^{n,n} - \phi_C^{m,m})R \quad (4b)$$

Diffusive encounter (Scheme B)

$$(C^n - C^m) = (C_0^n - C_0^m) +$$
$$(k_R/T_{1C}^{-1})[k_d/(k_S + k_d\langle\phi_C\rangle)](\phi_C^{n,n} - \phi_C^{m,m})R \quad (5a)$$

$$(S^n - S^m) = (S_0^n - S_0^m) -$$
$$(k_R/T_{1S}^{-1})[k_d/(k_S + k_d\langle\phi_C\rangle)][k_S/(k_S +$$
$$k_d\langle\phi_C\rangle + T_{1F}^{-1})](\phi_C^{n,n} - \phi_C^{m,m})R \quad (5b)$$

Here we have introduced $\langle\phi_C\rangle$ as the observable cage effect for a terminal combination step and have also assumed that the effects of nuclear spins on ϕ_C are small.

Within the framework of this purely kinetic model and the hypothesis of nuclear spin dependent rate constants we may make the following observations.

(1) The relative enhancements of nmr transitions within a single product are determined only by the combination efficiencies, $\phi_C^{n,n}$, and spin–lattice relaxation times.

(2) Fragments in combination and scavenging products give spectra with oppositely signed enhancement factors. That is, if a given transition is emission in a combination product, it will be enhanced absorption in the same fragment in a scavenging product, and vice versa.

(3) The relative magnitudes of enhancement in scavenging and combination products should depend on scavenger concentration because the competition between T_{1F}^{-1} and k_S affects S but not C. This has, in fact, recently been employed as a means of determining ratios of scavenging and nuclear spin relaxation rate constants in free radicals.[12] Enhancement generated in diffusive encounters, however, will be affected in both combination and scavenging products by scavenging processes.

(4) If enhancements are large enough that thermal polarization makes a negligible contribution to the spectrum, the relative intensities of lines from S and C products are independent of the yields of the two kinds of product. This is demonstrated dramatically in Figure 1 of the accompanying Account[1] where equal and opposite intensities of lines from CH_3I and CH_3CCl_3 in example A are observed during the reaction in spite of the fact that approximately six times as much of the former product is actually formed (i.e., $\langle\phi_C\rangle = 0.15$).[13]

(12) G. L. Closs and A. D. Trifunac, J. Amer. Chem. Soc., 92, 7229 (1970).

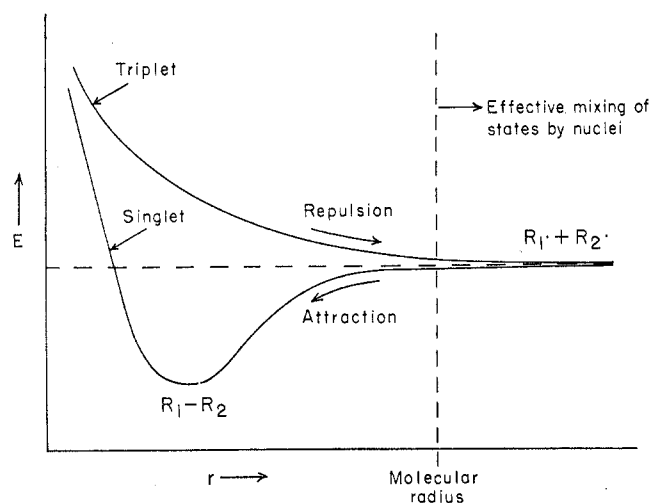(13) P. Livant, unpublished results.

Figure 2. Schematic representation of potential energy curves for the lowest singlet and triplet electronic states of a two-electron bond which dissociates to form two free radicals.

III. Nuclear-Spin-Dependent Radical-Pair Reaction Efficiencies, ϕ_C

Reactivities of Singlet and Triplet States. A basic assumption underlying the concept of nuclear-spin-selective reactions is simply: *radical pairs in singlet electronic states react to form combination products more rapidly than pairs in triplet states.* The rationale for this hypothesis is illustrated in Figure 2 which shows schematically potential energy curves for the lowest singlet and triplet states of a two-electron chemical bond, *e.g.*, H_2, C–C bond in ethane, etc. It is seen that two fragments in a singlet state which are brought together attract each other to form a bond. A pair in a triplet state will, however, repel each other. This anticipated difference in reactivity between singlet and triplet radical pairs has been the subject of several investigations.[14] One of the most successful was that of Fox and Hammond who noted a substantial lowering of the cage effect for recombination of cyanocyclohexyl radicals when they were generated by triplet photosensitized decomposition of a suitable precursor.[15]

Nuclear-Spin-Induced Singlet–Triplet Mixing. A second assumption of the radical-pair model is that nuclear hyperfine fields may cause a radical which initially was in a pure singlet state to develop triplet character, and *vice versa.* A qualitative explanation of how this can come about is given in the accompanying Account.[1] We present here a more quantitative treatment of this type of "intersystem crossing."[16]

The basic question which needs to be answered is the following: If we know the wave function for a radical pair at $t = 0$ when it was formed either by bond breaking or by a diffusive encounter, what is the wave function at some later time, t? In particular, if we initially knew the *probabilities* of finding the pair in the singlet and triplet states with nuclear-spin-state n, what are the probabilities of finding the system in these (or other) states at a later time? This is the central problem in time-dependent quantum mechanics and requires solution of the time-dependent Schrödinger equation

$$i \frac{\partial \psi(S,t)}{\partial t} = \mathcal{K}(S,t)\psi(S,t) \qquad (6)$$

where $\psi(S,t)$ is the wave function for the electron and nuclear spin coordinates, S, and $\mathcal{K}(S,t)$ is the time-dependent spin Hamiltonian (in radians/second) of the system.

It is customary to write $\mathcal{K}(S,t)$ as a sum of phenomenological terms representing the coupling of electron and nuclear magnetic moments to each other and to external fields.[17] We thus may write the following spin Hamiltonian[2b,3] for a radical pair with two unpaired electrons, 1 and 2, and magnetic nuclei with spins I_N, in a magnetic field, H_0

$$\mathcal{K}(S,t) = \mathcal{K}_{EZ} + \mathcal{K}_{NZ} + \mathcal{K}_{EN} + \mathcal{K}_{EE}(t) \qquad (7)$$

where

$\mathcal{K}_{EZ}$ = electron Zeeman interaction =

$$\hbar^{-1}\beta H_0(g_1 S_1{}^z + g_2 S_2{}^z) \quad (8a)$$

$\mathcal{K}_{NZ}$ = nuclear Zeeman interaction =

$$\hbar^{-1}H_0 \Sigma \beta_N g_N I_N{}^z \quad (8b)$$

$\mathcal{K}_{EN}$ = electron–nuclear hyperfine coupling =

$$\Sigma(A_{1N}\mathbf{S}_1 \cdot \mathbf{I}_N + A_{2N}\mathbf{S}_2 \cdot \mathbf{I}_N) \quad (8c)$$

$\mathcal{K}_{EE}(t)$ = electron–electron exchange coupling =

$$-J(t)[{}^1/_2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2] \quad (8d)$$

We have ignored nuclear–nuclear couplings, which would be small, have assumed all interactions to be isotropic, an unjustified but simplifying assumption,[4] and have placed all of the time dependence in the electron exchange coupling.[18] It is the latter interaction which is responsible for the difference in energy between singlet and triplet electronic states, the separation being $2J$; J is the "exchange integral," which is assumed to have a negative value.

The magnitudes of the time-independent g factors and hyperfine splittings for isolated radicals are well known from conventional magnetic resonance measurements.[19] The value of J as a function of interelectron

(14) P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 5883 (1970).

(15) J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964).

(16) The physical concepts underlying the idea of nuclear spin selection *via* intersystem crossing seem to have been anticipated in a discussion of the formation of excited states during recombination of radiolysis intermediates [B. Brocklehurst, *Nature (London)*, **221**, 921 (1969)]. The possibility of observing effects of a magnetic field on the rate of electron exchange (H. Shimizu, *J. Chem. Phys.*, **42**, 3599 (1965); C. S. Johnson, Jr., *Mol. Phys.*, **12**, 25 (1967)) and triplet–triplet annihilation (R. E. Merrifield, *J. Chem. Phys.*, **48**, 4318 (1968)) processes has also been discussed.

(17) R. McWeeny, "Spins in Chemistry," Academic Press, New York, N. Y., 1970.

(18) J. H. VanVleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford Press, London, 1932, p 318. Note that this interaction appears as a scalar product of the type often encountered in angular momentum problems and interpreted as a magnetic interaction. It is really of electrostatic origin, however, and results from the combined effects of electron repulsion and the Pauli exclusion principle.

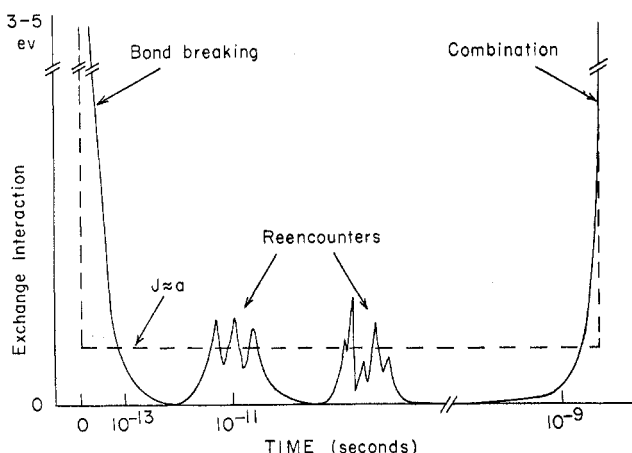(19) For a comprehensive listing of these parameters covering the

Figure 3. Schematic time dependence of the exchange interaction, J, for a caged radical pair in solution. The dotted line represents the approximation of sudden bond making and breaking and constant J employed in the quantitative treatment of the radical-pair model.

distance, i.e., a quantitatively correct Figure 2, is, however, known only for very simple molecules such as H_2.[20,21] Furthermore, its time variation depends on the details of motions of molecules in liquids which are poorly understood at present. However, a reasonable estimate of the time dependence of J is sketched in Figure 3 for a radical pair formed initially by rapid cleavage of one or more chemical bonds (geminate pair). After an initial rapid (10^{-13} sec) decrease in J as the fragments separate to a molecular diameter or more where J may be comparable to or smaller than the hyperfine couplings, the fragments are driven by Brownian motion back and forth with a time between diffusive displacements of ca. 10^{-11}–10^{-12} sec.[22] J will vary randomly about some average value at about this frequency[23] until eventually the pair either reacts, i.e., J becomes extremely large again, or diffusively separates to a distance where one or both partners are

scavenged or pair up with radicals from other encounters. Given the radical concentrations and scavenging rates in typical systems the original pair can be considered to exist for 100–1000 diffusive steps, i.e., for 10^{-9}–10^{-10} sec.[24]

Since a time-dependent term in $\mathcal{3C}$ of the above type is very difficult to handle, the assumption has been made[3] that $J(t)$ is a step function, dropping instantly from a value for a typical bond (3–5 eV) to a time-independent value comparable to or smaller than the hyperfine interaction. This approximation is shown by the dotted line in Figure 3. The solution of eq 6 with time-independent $\mathcal{3C}$ then becomes a straightforward problem.[2-5,25] It is thus found[5] that in the limit where H_0 is much larger than J and the hyperfine splittings (i.e., greater than several hundred gauss), the probability, $\rho_{sn}(t)$, of finding the pair in the singlet electronic state and nuclear spin state n is given by

$$\rho_{sn}(t) = \rho_{sn}(0) - (\delta_n{}^2/\omega_n{}^2)[\rho_{sn}(0) - \rho_{tn}(0)]\sin^2\omega_n t \quad (9)$$

where $\rho_{sn}(0)$ and $\rho_{tn}(0)$ are the probabilities that the pair in nuclear state n was in the singlet or triplet T_0 state, respectively, at $t = 0$, $\delta_n = (1/2)[\omega_e(g_1 - g_2)/2 + \Sigma(A_{1N} - A_{2N})m_N]$, $\omega_e = 2\beta\hbar^{-1}H_0$, $\omega_n = (J^2 + \delta_n{}^2)^{1/2}$, and m_N is the magnetic quantum number for the Nth nucleus.

Equation 9 says that the singlet probability of a radical pair oscillates in time (as in the classical model[1]) with a frequency which depends on both the exchange interaction and the nuclear-spin-dependent mixing coefficient, δ_n. The amplitude of oscillation also depends on these quantities but, in addition, is proportional to the difference in initial populations of the singlet and triplet states. In fact, no S_0–T_0 mixing will occur in a pair born with equal probabilities of occupation of these states. The maximum amplitude of mixing will occur when J is zero and when the pair is initially in either the pure S_0 or T_0 states. We will assume the former condition to hold for illustrative purposes inasmuch as it gives an upper limit to the rate of the S_0–T_0 mixing. The initial probabilities will depend on the circumstances of pair formation.

Three sets of initial probabilities would be expected to be important.

Singlet born pairs

$$\rho_{sn}(0) = 1$$
$$\rho_{tn}(0) = 0 \quad (10a)$$

Triplet born pairs

$$\rho_{sn}(0) = 0$$
$$0 \leqslant \rho_{tn}(0) \leqslant 1 \quad (10b)$$
$$\langle\rho_{tn}(0)\rangle = 1/3$$

Random encounter pairs

$$0 \leqslant \rho_{sn}(0) \leqslant 1$$

literature through March 1964 see H. Fischer, "Magnetic Properties of Free Radicals," Landolt-Bornstein, New Series, Vol. 1, Springer-Verlag, New York, 1965.

(20) J. E. Harriman, M. Twerdochlib, M. B. Milleur, and J. O. Hirschfelder, Proc. Nat. Acad. Sci. U. S., 57, 1558 (1967); W. Kolos and L. Wolniewicz, J. Chem. Phys., 43, 2429 (1965); J. N. Murrell and J. J. C. Teixeira-Dias, Mol. Phys., 19, 521 (1970).

(21) Esr measurements on stable biradicals [S. H. Glarum and J. H. Marshall, J. Chem. Phys., 47, 1374 (1967); G. R. Luckhurst, Mol. Phys., 10, 543 (1966)] and on radical pairs trapped in crystalline solids [K. Itoh, H. Hayashi, and S. Nagakura, ibid., 17, 561 (1969)] and glasses [S. I. Weissman and N. Hirota, J. Amer. Chem. Soc., 86, 2538 (1964)] and measurements of spin exchange rates between radicals in solution [W. Plachy and D. Kivelson, J. Chem. Phys., 47, 3312 (1967)] indicate that the exchange interaction may be comparable to the hyperfine interaction at distances of the order of a molecular diameter.

(22) A. M. North, "Collision Theory of Chemical Reactions in Liquids," Methuen, London, 1964.

(23) The time dependence of J plays an explicit and central role in the modification of the radical pair model put forward by H. Fischer[4] and S. Glarum [Symposium on CIDNP, Houston, Tex., Feb 24–25, 1970]. They assume large changes in J during the lifetime of an encounter pair while the theory discussed here assumes that after an initial large change these changes are small and distributed about a time-independent mean value. Since J, and especially its time dependence, are so poorly understood at present, it is perhaps not surprising that they can be manipulated to make either model predict enhancements of the correct order of magnitude. F. J. Adrian [J. Chem. Phys., 53, 3374 (1970)] has recently questioned the physical basis of the Fischer–Glarum modification of the radical-pair model.

(24) R. M. Noyes, J. Amer. Chem. Soc., 77, 2042 (1955).

(25) D. Bohm, "Quantum Theory," Prentice-Hall, Englewood Cliffs, N. J., 1951, p 507.

$$0 \leqslant p_{tn}(0) \leqslant 1 \qquad (10c)$$

$$\langle \rho_{sn}(0) \rangle = \langle \rho_{tn}(0) \rangle = {}^1/_4$$

Radical-Pair Reaction Efficiencies. A radical pair, P, formed at $t = 0$ either from a reactant or by a diffusive encounter of free radicals, will eventually disappear by a combination of diffusive separation and chemical reaction. The following expressions for the efficiency of combination, $\phi_C{}^{nn}$, are derived[5] assuming (a) the high-field limit, (b) negligible exchange interaction, (c) predominant destruction of radical pairs by diffusion rather than reaction, and (d) a frequency of S_0–T_0 mixing, δ_n, which is less than the rate constant, τ^{-1}, for diffusive separation. a_S is the cage effect for a pair which remains in a pure singlet state indefinitely.

Singlet born pairs

$$\phi_C{}^{n,n} \cong a_S[1 - 2\delta_n{}^2\tau^2] \qquad (11a)$$

Triplet born pairs

$$\phi_C{}^{n,n} \cong + ({}^2/_3)a_S\delta_n{}^2\tau^2 \qquad (11b)$$

Random encounter pairs

$$\phi_C{}^{n,n} \cong (a_S/4)[1 + 2a_S\delta_n{}^2\tau^2] \qquad (11c)$$

Inspection of eq 11 gives rise to the following qualitative observations regarding the relative magnitudes of the nuclear-spin-dependent parts of $\phi_C{}^{n,n}$ for the three types of initially formed pairs.

(1) The nuclear-spin-dependent parts of $\phi_C{}^{n,n}$ for singlet and triplet or random born pairs are always of *opposite sign*. Thus, products from singlet born pairs will have signs of enhancement opposite to those from triplet or random born pairs.

(2) The nuclear spin dependence in all three cases, and therefore the nmr enhancement, decreases with decreasing cage effect. Although eq 11 do not show it, the nuclear spin dependence also vanishes for singlet born pairs as a_S approaches unity. In contrast, as long as $\delta_n \ll \tau^{-1}$, the nuclear spin dependence for triplet or random pairs increases continuously with increasing a_S. In the presence of strong singlet–triplet mixing, however, the nuclear spin dependence vanishes for all three cases as a_S tends to 1. In this case every radical pair reacts, regardless of its nuclear spin state.

(3) The nuclear spin dependence for random encounter pairs decreases as the square of a_S, in contrast to a first-power dependence on a_S for singlet or triplet born pairs. Qualitatively,[1] this is a consequence of the necessity that reaction occur in order to destroy some singlet pairs and allow S_0–T_0 mixing to occur. Note, however, from eq 5a, that in the case where radicals are lost predominantly by recombination this may be compensated by the increased concentration of free radicals available for random encounters. In fact, in the case where independently generated radicals disappear only by diffusive encounters, the enhancement in a combination product should be *equal* and *opposite* to that produced in an equivalent singlet born geminate pair. This leads to the interesting prediction (from
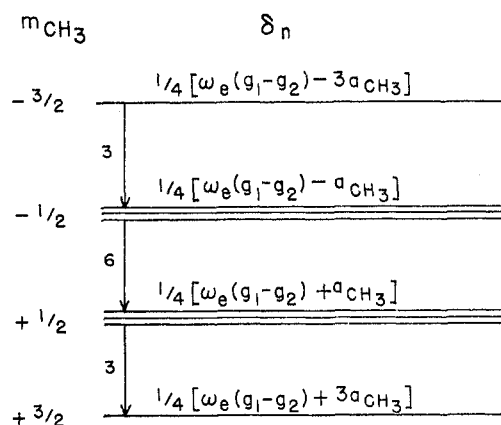

Figure 4. Energy levels, transitions, and mixing coefficients, δ_n, for a methyl group which resided in a radical intermediate with g-factor g_1, hyperfine splitting A_{CH_3}, paired up with a structureless radical with g-factor g_2. The total nuclear magnetic quantum number for the three protons is indicated for each level on the left. Numbers to the left of the downward arrows are the degeneracies of each transition.

eq 11a, 11c, 4a, and 5a) that no enhancement should be observed from reactions involving identical radical fragments when no scavenging processes are available. This is in accord with the failure to observe CIDNP from reaction 12[26] unless a scavenger, such as an olefin

$$n\text{-}C_4H_9Br + n\text{-}C_4H_9Li \longrightarrow$$
$$\text{1-butene} + n\text{-butane} + n\text{-octane} \qquad (12)$$
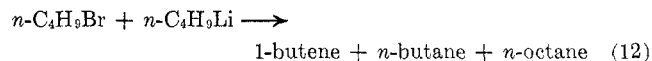
or alkyne, is present.

IV. Calculation of Nmr Intensities

In this section we attempt to bring together the ideas and formulas presented in the previous sections by applying the radical-pair model to a specific example. We consider the enhancement expected from 1,1,1-trichloroethane produced in example A of Figure 1 (eq 13). Since this is a combination product arising from

$$CH_3CO_2CO_2CCl_3 \longrightarrow [CH_3\cdot\cdot CCl_3] \longrightarrow CH_3CCl_3 \qquad (13)$$
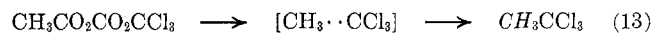
a geminate pair, we expect the kinetic behavior described by eq 4a for each nmr transition. The eight nuclear spin states for the three equivalent protons in the methyl group are shown in Figure 4. In calculating the reaction efficiencies, $\phi_C{}^{n,n}$, for each level from eq 11a we adopt a convention that the methyl group contains electron 1. The quantity $\delta_n{}^2$ is then computed for each state. Note that the $m_{CH_3} = \pm{}^1/_2$ levels are triply degenerate because of the magnetic equivalence of the protons in this example. Also indicated in Figure 4 are the number of single spin-flip transitions between each set of levels. In this example all 12 transitions occur at the same field position. In this representation each transition probability, $|(n|I_x|m)|^2$, has the value[6] $^1/_4$. Ignoring the contribution to the spectrum from the unpolarized product, we then have, from eq 1, for the observed intensity, $I_{CH_3}(H_0)$, of the nmr line

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

$$I_{CH_3}(H_0) = 3I_{3/2 \to 1/2} + 6I_{1/2 \to -1/2} + 3I_{-1/2 \to -3/2} =$$

$$-(3/2)Cg(H_0)(k_R/T_{1CH_3}{}^{-1})a_S A_{CH_3}\omega_e(g_1 - g_2)\tau^2 R \quad (14)$$

The instrumental constant, C, the shape function, $g(H_0)$, and the concentration, R, of one spin state in the acyl peroxide reactant may be approximately determined in this example because the intensity, $I_R(H_0')$, of the reactant line is simultaneously observed during the reaction (Figure 1 of ref 1). That is,

$$I_R(H_0') = 3Cg(H_0')(2p^0 R) \quad (15)$$

where $p^0 = 5 \times 10^{-6}$ is the thermal polarization.

One can now either substitute a value for each quantity on the right-hand side of eq 14 and calculate the intensity or use the observed intensity to determine one of these quantities. Since we know the relative intensities of product and reactant spectra in this example, we will use them to calculate a value of τ, the least well-known quantity in eq 14. From the spectrum we know that $(I_{CH_3}/I_R) = -0.6$, and it has been independently determined[13] that $(k_R/T_{1CH_3}{}^{-1}) \cong 10^{-3}$ and $a_S \cong \langle \phi_C \rangle$ $= 0.15$. Furthermore, from esr experiments it is known that $A_{CH_3} = -4.0 \times 10^8$ radians/sec[27] and that[27,28] $g_{CH_3} - g_{CCl_3} = -0.0065$. In the field of a 60-MHz nmr spectrometer $\omega_e = 2.5 \times 10^{11}$ radians/sec. We thus obtain a value for the "cage lifetime," τ, of 3×10^{-10} sec, which is quite reasonable.[22] It should be recalled, however, that this estimate is based on the possibly unrealistic assumption that the exchange interaction is zero during most of the cage lifetime and that pairs react only by spin-dependent pathways. This value of τ is therefore a lower limit since exchange coupling or alternative pathways for reaction would require that the pair remain together for a longer time to produce the observed enhancement.

An alternative way of expressing the experimental results is in terms of the enhancement factor, V_{CH_3} (eq 16). This is an ambiguous measure of enhancement,

$$V_{CH_3} = (I_{CH_3}/I_{CH_3}{}^0) - 1 \quad (16)$$

however, because it is time dependent. For a slow reaction ($k_R \ll T_{1CH_3}{}^{-1}$), I_{CH_3} varies only slowly with time while $I_{CH_3}{}^0$, the intensity of product with thermal polarization, increases linearly with time during the early stages of the reaction. Consequently V_{CH_3} decreases steadily as time goes on. V_{CH_3} may, however, be estimated by calculating what it would be after a time T_{1CH_3}. In the present example an amount of CH_3-CCl_3 corresponding to $\langle \phi_C \rangle k_R T_{CH_3} = 0.015\%$ of the starting material would have been formed in this length of time. Since $(I_{CH_3}/I_R) = -0.6$, this corresponds to a minimum enhancement factor of approximately -4000. Clearly, however, a reliable value of V depends strongly on good quantitative understanding of the kinetics of the reactions and relaxation times.

We could go through a similar analysis for the scavenging product, CH_3I, in this example, but eq 4a,b show that there is a simple reciprocal relationship between the combination and scavenging enhancements when nuclear relaxation in the free radical is negligible and the spin–lattice relaxation times in the two products are the same, as they appear to be in the present case.

V. Some General Considerations Regarding Absolute and Relative Nmr Enhancements

The first thing to note is that the steady-state relative populations in eq 4a through 5b are all of form 17,

$$(N^n - N^m) - (N_0{}^n - N_0{}^m) =$$
$$K(\phi_C{}^{n,n} - \phi_C{}^{m,m})R \quad (17)$$

where K is a function of several kinetic constants and R is the population of a single nuclear spin level in the reactant. If there are l such levels

$$R = [\text{reactant}]/l \quad (18)$$

The population difference for a transition, corrected for contributions, N_0, from thermal polarization, is then simply proportional to the difference in cage reaction efficiencies for the two levels. In the high-field, low J, and small a_S limits these are given by eq 11a–c. Therefore, the intensity of a transition between two levels labeled with the same nuclear spin quantum numbers in the pair and product will be

$$I_{nm} = \Lambda_{nm}(\delta_n{}^2 - \delta_m{}^2)\tau^2 + I_{nm}{}^0 \quad (19)$$

where Λ_{nm} is a product of quantities from eq 1, 4, 5, and 11. For the example in the previous section

$$\Lambda_{nm} = -C|\langle n|I_x|m \rangle|^2 g_{nm}(H_0)(k_R/T_{1C}{}^{-1})(2a_S)R \quad (20)$$

First-Order Intensities. In multiple spin systems where all nuclei in a product are not equivalent one frequently observes enhancement in which lines on opposite sides of the center of a spin–spin multiplet have oppositely signed enhancement. To explain this so-called "multiplet effect"[1] we consider the case where a set of equivalent nuclei, A, reside on the fragment containing electron 1 and become coupled in the product to another set of equivalent nuclei, B, which may be on either fragment 1 or 2 in the radical pair. A first-order transition of A which would normally absorb radiation is one in which m_A changes to $m_A - 1$ and m_B is unaffected. Substituting for δ_n for these two levels we obtain eq 21,

$$I_{m_A \to m_A-1} = (1/2)\Lambda_{m_A \to m_A-1}A_A[\omega_e(g_1 - g_2)/2 \pm$$
$$A_B m_B + A_A(m_A - (1/2))] \quad (21)$$

where the plus and minus signs before the second term inside the brackets refer to B on fragments 1 or 2, respectively. If B were absent, eq 21 would give the intensity of one of the 12 transitions for the example in eq 14. The third term vanishes when one sums over all of the A transitions.

The first term in eq 21 gives rise to net polarization, as in example A, with a sign which depends on the signs of both A_A and $g_1 - g_2$. The multiplet effect originates in the second term, since each line of an A

(27) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

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

Table I[a]
Contributions to the Sign of the Enhancement of a Line Arising from a Set of Equivalent Nuclei, A, on Fragment 1, Which May Be Coupled to Another Set of Equivalent Nuclei, B

Type of precursor	Type of product	Sign of A_A
Singlet (−)	Combination (+)	$A_A > 0$ (+)
Triplet or random (+)	Scavenged (−)	$A_A < 0$ (−)

Net polarization			Multiplet effect		
Sign of g	Location of B	Sign of A_B	Sign of J_N	Position of line	
$g_1 > g_2$ (+)	On 1 (+)	$A_B > 0$ (+)	$J_N > 0$ (+)	High field (+)	
$g_1 < g_2$ (−)	On 2 (−)	$A_B < 0$ (−)	$J_N < 0$ (−)	Low field (−)	

Examples (positions of signs correspond to table entries)

$CH_3CO_2CO_2CCl_3 \longrightarrow [CH_3 \cdot \cdot CCl_3] \longrightarrow CH_3CCl_3$
(−)   (−)   (+)   (−)

Predict *emission*

$CH_3CH_2I + CH_3CH_2Li \longrightarrow [2CH_3CH_2 \cdot] \longrightarrow$

$CH_3CH_2 \cdot \xrightarrow{RI} CH_3CH_2I$ (low field side
(−)   (−) of multiplet)
(+)   (−)   (+)   (+)
                               (−)

Predict *absorption*

[a] The sign of the enhancement is found by algebraically multiplying the signs of each contribution.

multiplet corresponds to a different value of m_B. Equation 21 thus shows that the enhancement of a multiplet line is proportional to m_B and has a sign which depends both on the relative signs of A_A and A_B and on the sign of m_B itself. Proper assignment of m_B to lines in a multiplet requires, in turn, that the sign of J_N, the nuclear spin–spin coupling, be known. For this purpose it is convenient to remember that if J_N is *positive* the *low-field lines* in a multiplet have *negative m* values.

From the above we see that there are several factors (eight in all) which determine whether a given line in a spectrum is positively or negatively enhanced. These factors and the contributions they make to the sign of the enhancement are tabulated in Table I. A somewhat more explicit table of this type and additional examples of its use are given in the accompanying Account.[1]

Relative Intensities in the Multiplet Effect. In the limit where $g_1 = g_2$, for example, in reaction 22,[1] eq 21

$CH_3CH_2Li + CH_3CH_2I \longrightarrow [2CH_3CH_2 \cdot] \longrightarrow$

$CH_3CH_2 \cdot \xrightarrow{RI} CH_3CH_2I$ (22)
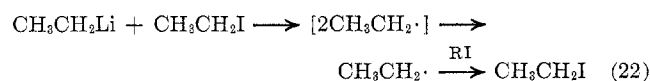
makes possible a simple rule for calculating the first-order *relative* intensities of lines arising from two coupled sets of protons:

$$I_{A,rel} = I^0_{A,rel} m_B$$
$$I_{B,rel} = I^0_{B,rel} m_A \qquad (23)$$

where $I^0_{A,rel}$ and $I^0_{B,rel}$ are the relative intensities of the lines in the unenhanced spectrum, which will normally be multiples of the binomial coefficients. For

example, in the first-order spectrum of ethyl iodide the quantum numbers for the seven multiplet lines listed from low field to high are $m_{CH_3} = -^3/_2, -^1/_2, +^1/_2, +^3/_2; m_{CH_2} = -1, 0, +1$, and the normal relative intensities of these lines are 2, 6, 6, 2; 6, 12, 6. Equation 23 then predicts enhanced relative intensities of $-3, -3, +3, +3; -6, 0, +6$. The relative intensities within a single multiplet are the same as those derived empirically by Lepley.[29] The absolute signs are, of course, arbitrary and the actual enhancement will depend on the factors in Table I. Comparison with Figure 2 of ref 1 shows that the experimentally observed intensity ratios are only in qualitative agreement with the predicted ratios. Factors which can account for these discrepancies, which we have already warned about in the previous sections, include variation of reaction rate in different parts of the spectrum during this fast reaction, unequal rates of spin–lattice relaxation for different lines, overlap with unpolarized product (reactant in this case), and contributions from non-first-order transitions. The linearity in δ_n^2 of eq 11a–c is also an oversimplification[2-5,23] which breaks down in some cases.[30,31]

VI. Other Implications of the Radical-Pair Model

There are several effects, as yet little explored, which are related to the model presented here. Investigations have only just begun into the effects expected[31b] and observed[31] when reactions are run in low fields and spectra are recorded in high fields. Likewise, the phenomenon of chemically induced *electron* polarization is almost certainly related to radical-pair interactions, but relatively few experimental data[27,32] are presently available and the theoretical problems[3,4b,32f,33] associated with the effects have not yet been satisfactorily solved. Similarly, the potential consequences of the magnetic interactions in radical pairs described here for chemical reactions run under normal conditions have as yet received little attention.[34] These areas constitute a rich source of second-generation experiments which are sure to shed much additional light on the phenomenon of CIDNP as well as on the whole area of free-radical physics and chemistry.

(29) A. R. Lepley, *J. Amer. Chem. Soc.*, **91**, 749 (1969).

(30) M. Lehnig and H. Fischer, *Z. Naturforsch. A*, **25**, 1963 (1970).

(31) (a) H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *J. Amer. Chem. Soc.*, **91**, 4928 (1969); (b) J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *ibid.*, **92**, 5761 (1970).

(32) (a) B. Smaller, J. R. Remko, and E. C. Avery, *J. Chem. Phys.*, **48**, 5174 (1968); (b) S. H. Glarum and J. H. Marshall, *ibid.*, **52**, 5555 (1970); (c) H. Paul and H. Fischer, *Z. Naturforsch. A*, **25**, 443 (1970); (d) P. W. Atkins, I. C. Buchanan, R. C. Gurd, K. A. McLauchlan, and A. F. Simpson, *Chem. Commun.*, 513 (1970); (e) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **53**, 1406 (1970); (f) P. W. Atkins, R. C. Gurd, K. A. McLauchlan, and A. F. Simpson, *Chem. Phys. Lett.*, **8**, 55 (1971).

(33) F. J. Adrian, paper presented at Second Symposium on Electron Spin Resonance in Chemistry, Athens, Ga., Dec 6–9, 1970.

(34) R. G. Lawler, paper presented at International Colloquium on CIDNP and Its Impact on the Study of Reaction Mechanisms, Brussels, Belgium, March 18–19, 1971.

Cyclobutane Ring Contractions Not Involving Carbonium Ions
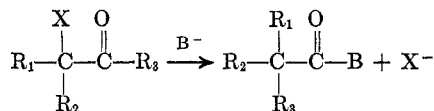
JEAN M. CONIA* AND JACQUES R. SALAUN

Laboratoire des Carbocycles, Universite de Paris-Sud, 91 Orsay, France

Received February 4, 1971

The facile interconversions which occur among related cyclobutane, cyclopropane, and open-chain structures *via* carbonium ion intermediates have been extensively studied. Analogous rearrangements of small-ring compounds *via* carbenes or free radicals are well known, but not so widely explored.[1-3] A type of cyclobutane ring contraction which does not involve a carbonium ion is the base-induced skeletal rearrangement of α-halogenated cyclobutanones into cyclopropanecarboxylic acid derivatives. Such ring contractions and related rearrangements are the subject of this Account.

α-Halo- and α-Tosyloxycyclobutanones and Nucleophilic Reagents

In the presence of nucleophilic reagents such as hydroxides, alkoxides, or amines, α-halogenated ketones undergo skeletal rearrangement into carboxylic acid salts, esters, or amides, respectively. This reaction was

$$R_1\text{---}\underset{R_2}{\underset{|}{\overset{X}{\overset{|}{C}}}}\text{---}\overset{O}{\overset{||}{C}}\text{---}R_3 \xrightarrow{B^-} R_2\text{---}\underset{R_3}{\underset{|}{\overset{R_1}{\overset{|}{C}}}}\text{---}\overset{O}{\overset{||}{C}}\text{---}B + X^-$$

discovered by Favorskii in 1894[4] and showed itself rapidly to be general for α-halocycloalkanones in rings of from six to ten carbon atoms.[5] The fact that α-halocyclopentanone fails to undergo the reaction is perhaps responsible for the long reluctance to attempt such a reaction with smaller rings: *i.e.*, α-halocyclobutanones. However, α-bromocyclobutanone (**1a**) was recently reported to rearrange with high yield and stereospecificity.[6]

Mono-, di- and trihalo ketones generally undergo this rearrangement. The reaction has proven to be a reliable and important route to derivatives of highly branched acyclic carboxylic acids, to various 1-substi-

1a, X = Br
b, X = Cl
c, X = OTs
2
3
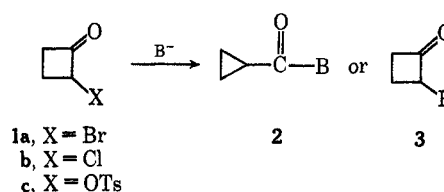
tuted cycloalkanecarboxylic acids, and for the contraction of specific rings in mono- or polycyclic and steroid systems.[5]

A survey of the literature reveals that the choice of base and solvent can profoundly affect the yield of rearranged products. Correlations have been established between the nature of the base and the products of the reaction.[7,8] Thus, the reaction of a nucleophilic reagent with an α-halo ketone can lead to substitution product, α-ethylenic ketone, epoxide, hydroxy ketal, saturated ketone, and/or rearranged acid derivatives. The product of the reaction can be often predicted as a function of the type of nucleophile.

From 2-bromocyclobutanone (**1a**), rather specific reactions lead either to ring contraction product **2** or to substitution product **3** (see Table I[6,9]). Reaction conditions which usually lead to an elimination product (dehydrohalogenation) did not give the expected cyclobutenone.[6]

The facility and specificity of this rearrangement, particularly with water itself, open a way to the synthesis of three-membered rings from four-membered systems (*vide infra*) which is just as useful as the interconversion of related cyclobutyl, cyclopropylcarbinyl, and homoallyl derivatives *via* carbonium ion reactions.[10]

(1) R. Breslow, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 233.

(2) J. Jaz, *Ind. Chim. Belge*, [2] **33**, 130 (1968).

(3) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(4) A. Favorskii, *J. Russ. Chem. Soc.*, **26**, 559 (1894); *Bull. Soc. Chim. Fr.*, **14**, 1188 (1895); *J. Prakt. Chem.*, **51**, 553 (1895).

(5) A. S. Kende, *Org. React.*, **11**, 261 (1961).

(6) J. M. Conia and J. L. Ripoll, *C. R. Acad. Sci.*, **251**, 1071 (1960); **252**, 423 (1961); *Bull. Soc. Chim. Fr.*, **755** (1963).

(7) B. Tchoubar, *ibid.*, 1363 (1955).

(8) G. Stork and I. J. Borowitz, *J. Amer. Chem. Soc.*, **82**, 4307 (1960).

(9) (a) J. Salaun and J. M. Conia, *Chem. Commun.*, **20**, 1358 (1970); (b) J. Salaun and J. M. Conia, submitted for publication.

(10) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951); R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).