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Magnetic Field and Magnetic Isotope Effects in Organic Photochemical Reactions. A Novel Probe of Reaction Mechanisms and a Method for Enrichment of Magnetic Isotopes

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The possibility that the reactivity and efficiency of reactions involving radical pairs will depend on nuclear spin states (or laboratory magnetic fields) is a rather fascinating idea in view of the tiny interactions that exist between electron spins and nuclear spins (or electron spins and laboratory magnetic fields).

Many chemists are accustomed to thinking of nuclei as passive mass points, whose inertia only allows them to follow but not to influence electronic processes in a significant way.[1] However, besides mass, nuclei possess a second important property (or nonproperty): magnetism or magnetic spin (or diamagnetism or lack of magnetic spin). The latter property is not usually considered in a discussion of reaction mechanisms. Similarly, the possible influence of laboratory magnetic fields on chemical reactions represents an intriguing notion but most chemists would be hard pressed to cite any famous documented cases (or even any obscure, undocumented examples).[2]

A simple thermodynamic argument has been employed to summarily dismiss any serious possibility of significant magnetic field or magnetic isotope effects on the rates and/or efficiencies of chemical processes. The logic goes as follows: The strongest laboratory magnetic fields ($\sim$100 000 G) can induce at most energy changes of $\sim$0.03 kcal/mol even in paramagnetic molecules.[3] Such energy changes are negligible relative to the commonly encountered activation energies of chemical reactions ($\gtrsim$10 kcal/mol). The magnetic strengths and corresponding energy changes that can be induced by even the strongest nuclear magnets ($\lesssim$100 G) are, of course, even tinier ($\lesssim$0.00003 kcal/mol). Neither laboratory nor nuclear magnets can be expected to produce measurable effects on the energetics of chemical processes; therefore, there can be no serious possibility of magnetic field effects or magnetic isotope effects on chemical processes.

This is a pretty good argument, as far as it goes, and it would be difficult to refute if the rates and efficiencies of chemical reactions depended only on energetic considerations. However, reaction rates and efficiencies depend not only on energetic factors but also on entropic factors. In terms of the Arrhenius formulation of rates, a rate constant is given by $k = Ae^{-\Delta E/RT}$. *Substantial magnetic effects on the A factor are possible if states that possess different magnetic properties (i.e., triplet states and singlet states) are involved in a rate-determining step whose rate constant is given by k.*

Intersystem Crossing in Radical Pairs

The Wigner spin conservation rule states that during an elementary chemical step, electron and nuclear spins are conserved.[4] For most organic systems this rule forbids singlet to triplet or triplet to singlet intersystem crossing (S–T ISC or T–S ISC, respectively) in an elementary chemical reaction. The rule breaks down when an "elementary step" involves states whose lifetimes are long enough to allow the relatively slow ISC mechanisms (spin–orbit coupling and electron–nuclear hyperfine interactions) to operate. Reactions involving carbon radical pairs represent a large class for which the spin conservation rule fails, i.e., for which electron and nuclear spins are not conserved. The collapse of the spin conservation rule for organic radical pairs leads to several striking and unusual phenomena: (1) the observation (via NMR) of "non-Boltzmann" distributions of nuclear spins in the products of chemical reactions, i.e., *chemically induced nuclear polarization* (CIDNP);[5] (2) the observation of different reaction probabilities and efficiencies for radical pairs possessing nuclear spins relative to those possessing no nuclear spin, i.e., *a magnetic spin isotope effect on chemical reactions*;[4] (3) the observation of a dependence of the reaction probability and efficiency of a radical pair on the strength of a relatively weak (<1000 G) externally applied magnetic field, i.e., *magnetic field effects on chemical reactions*.[2]

In this Account we present a brief, qualitative description of the theory of ISC in radical pairs which, when considered in the framework of the molecular

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(1) G. E. Dunn, "Isotope Effects in Organic Chemistry", Vol. 3, E. Buncel and C. C. Lee, Eds., Elsevier, New York, 1977, p 1.

(2) Reviews of magnetic effects on chemical reactions: (a) P. W. Atkins and T. P. Lambert, *Annu. Rep. Chem. Soc. A*, 67 (1975); (b) R. Z. Sagdeev, K. M. Salikhov, and Y. M. Molin, *Russ. Chem. Rev.*, **46**, 297 (1977); (c) A. L. Buchachenko, *ibid.*, **45**, 375 (1976); R. G. Lawler and G. T. Evans, *Ind. Chim. Belg.*, **36**, 1087 (1971).

(3) P. Atkins, *Chem. Br.*, 214 (1976).

(4) A. L. Buchachenko, *Russ. J. Phys. Chem.*, **51**, 1445 (1977).

(5) Reviews of the theory of CIDNP: (a) R. Kaptein, *Adv. Free Radical Chem.*, **5**, 381 (1975); (b) G. Closs, *Proc. Int. Congr. Pure Appl. Chem., 23rd*, **4**, 19 (1971); (c) A. L. Buchachenko and F. M. Zhidomirov, *Russ. Chem. Rev.*, **40**, 801 (1971); (d) P. G. Frith and K. A. McLauchlan, *Annu. Rep. Chem. Soc. A.*, 378 (1975).

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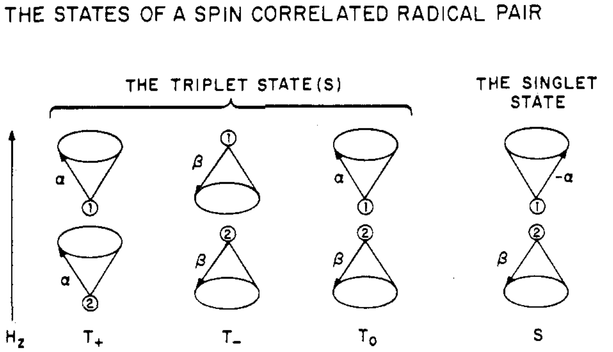

Figure 1. Schematic vector description of the three magnetic sublevels of a triplet radical pair and the singlet state of a radical pair.

mechanics of a radical pair and the concept of cage reactions, provides a simple unified theoretical basis for understanding CIDNP, the magnetic spin isotope effect, and magnetic field effects on chemical reactions. Examples will be given in which the magnetic spin isotope effect is employed (1) to separate ^{13}C (a magnetic isotope) from ^{12}C (a nonmagnetic isotope) with an efficiency that far surpasses that which is possible via any mechanism involving a conventional mass isotope effect and (2) to separate selectively ^{17}O (a magnetic isotope) from ^{16}O *and* ^{18}O (nonmagnetic isotopes), a selectivity that is impossible via a conventional mass isotope effect. Finally, examples will be provided for which the magnetic field effect is utilized to control the efficiency of cage reactions of radical pairs.

Some Fundamental Postulates about Cage Reactions Involving Radical Pairs

Several postulates help to set a foundation for a basic understanding of the fundamental mechanism of magnetic effects on the chemistry of radical pairs. We shall only consider organic molecules containing hydrogen and second-row elements. **Postulate** 1: When the bond connecting two groups (R_1–R_2) undergoes homolytic cleavage, the primary radical pair $\dot{R}_1\ \dot{R}_2$ is produced with complete conservation of spin. **Postulate** 2: Singlet radical pairs can undergo "cage" reactions such as recombinations and disproportionations, but triplet radical pairs cannot undergo cage reactions directly, i.e., they must first intersystem cross to singlet radical pairs. **Postulate** 3: The chemical reactivity of a radical pair depends on the hyperfine interactions of the orbitally uncoupled electrons of the radical pair with nuclear spins (magnetic isotope effects) or laboratory magnets (magnetic field effects).

The Vector Model of Spin Mechanics

For concreteness we shall consider a triplet radical pair $^3(\dot{R}_1\ \dot{R}_2)$ that is produced (postulate 1) via homolytic cleavage of a triplet molecule $^3(R_1–R_2)$. The intersystem crossing $^3(\dot{R}_1\ \dot{R}_2) \rightarrow {}^1(\dot{R}_1\ \dot{R}_2)$ may be influenced by magnetic isotope and/or magnetic field effects (postulate 3). If this is the case, then the cage reactions of the radical pair will be influenced by magnetic effects since only $^1(\dot{R}_1\ \dot{R}_2)$ radical pairs but not $^3(\dot{R}_1\ \dot{R}_2)$ can form cage products (postulate 2).

The triplet radical pair consists of three distinct states that may be classified in terms of magnetic[6] sublevels. The latter may be visualized by considering the vector model of electron spin (Figure 1). Let α denote an electron spin that is pointing in the direction of an arbitrary magnetic field, H_z, and let β denote an electron spin that is pointing in a direction opposed to H_z. The three triplet levels of a radical pair are labeled T_+, T_-, and T_0 and have spin configurations $\alpha\alpha$, $\beta\beta$, and $\alpha\beta$. The singlet state has a spin configuration $-\alpha\beta$. (These functions are, of course, abbreviated symbols of the correct spin functions.)[4] The T_0 state has net spin-angular momentum but the projection of this momentum along H_z is zero (the magnetic quantum number $M_S = 0$). The singlet state S of the radical pair is similar to the T_0 triplet sublevel in that it possesses an α spin and a β spin. The only vectorial difference between T_0 and S is due to the "phasing" of the spins; in T_0 the vectors are 0° out of phase, whereas in S the vectors are 180° out of phase. The conversion of T_0 to S requires the "rewinding" of one spin vector relative to the other by 180°. In the absence of an external magnetic field, the spin vectors of a triplet pair ($\dot{R}_1$ and $\dot{R}_2$) are at some indefinite overall orientation but at a well-defined (triplet) relative orientation or phase. This means that although the three magnetic sublevels T_+, T_-, and T_0 are "strongly mixed" (rapidly interconverting), the net spin of the triplet is always equal to 1.

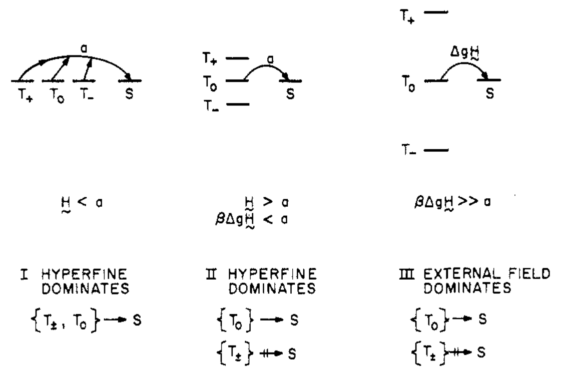

Figure 2. At zero magnetic field, all three triplet levels may undergo electron–nuclear hyperfine-induced intersystem crossing to S. When the magnetic field strength is much larger than the magnitude of the hyperfine interaction, T_+ and T_- are "split" away from S and are incapable of undergoing hyperfine-induced crossing to S. T_0, however, remains degenerate with S and hyperfine-induced $T_0 \rightarrow S$ crossing is still possible. When the external field interaction is much larger than the hyperfine interaction, ISC is determined by the external magnetic field strength.

An interesting consequence of the application of a strong magnetic field to a radical pair is the "splitting" of T_+ and T_- from T_0 (Figure 2). However, T_0 and S remain degenerate. This means that $T_+ \rightleftarrows S$ and $T_- \rightleftarrows S$ transitions in the radical pair may be "quenched" by the application of a strong magnetic field because interconversions of $T_\pm \rightleftarrows S$ are slowed down and only $T_0 \rightleftarrows S$ transitions remain probable.

A General Qualitative Theory of CIDNP, Magnetic Isotope Effects, and Magnetic Field Effects for Reactions Involving Radical Pairs

The modern theory of CIDNP provides all of the essential concepts required for an understanding of magnetic isotope and magnetic field effects on reactions involving radical pairs.[5] Two important aspects of the theory involve a "sorting" principle and a "correlation" principle. These principles state that for a radical pair nuclear spin states ($+^1/_2$ or $-^1/_2$ spins), electronic spin states (singlet or triplet), and triplet sublevels (T_+, T_-,

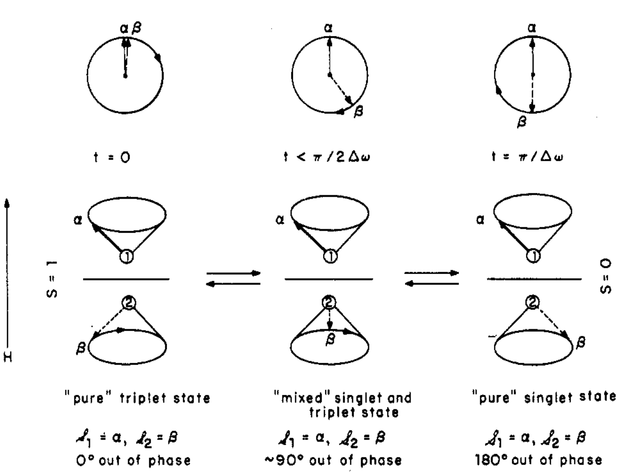

Figure 3. Schematic vector description of the rephasing mechanism for $T_0 \rightleftarrows S$ intersystem crossing in a radical pair. Bottom: At $t = 0$ the system is a "pure" triplet, at a later time ($t < \pi/2\Delta\omega$) the system is a "mixed" state and at $t = \pi/\Delta\omega$ the system is a "pure" singlet state. Top: A view of the spin vectors in terms of a spin clock.

and T_0) may be "sorted" from one another if the pair can undergo geminate *cage* reactions of a "correlated" radical pair in competition with an *escape* process that either destroys the correlation or involves a reaction of the radical pair.

The Mechanism of Intersystem Crossing in Radical Pairs

In the presence of magnetic fields, the correlated electronic spins of a triplet pair $\dot{R}_1$ $\dot{R}_2$ will tend to precess about the direction of the strongest field to which they can couple. If these fields are exactly the same for $\dot{R}_1$ and $\dot{R}_2$, then the precession rates ω_1 and ω_2 of the two spins are identical, the difference in precessional rates $\Delta\omega$ is zero, and the relative triplet phase is preserved forever. If, on the other hand, the magnetic fields experienced by the spins of $\dot{R}_1$ and $\dot{R}_2$ are different, then $\Delta\omega \neq 0$, and the initial triplet phasing transforms into a "mixed" triplet–singlet phasing and eventually becomes a singlet phasing, i.e., a triplet–singlet intersystem crossing (ISC) occurs.

The qualitative dependence of the rate of $T_0 \rightarrow S$ conversions can be illustrated in terms of the vector model of magnetic moments obtained from classical physics.[6] Let the z axis correspond to a direction defining the orientation of the spin vectors. The projections of the electron spins in the xy plane produce a vector description of the time evolution of T_0 and S that resembles a "spin clock" (Figure 3).[7] For a "pure" T_0 state the spin clock only reads 12 o'clock, and for a "pure" S state the spin clock only reads 6 o'clock. When the electron exchange energy (J) of the two unpaired electrons is large relative to the electron–nuclear hyperfine constant a, the radical centers are in close proximity (solvent cage), and the clock can read only 12 or 6, i.e., T_0 and S do not mix. When $J < a$, i.e., when the radical centers are far apart (solvent separated), T_0 and S are degenerate and may mix. In such a situation the spin clock may read any time.

Suppose we start ($t = 0$) with the spin clock reading 12 (e.g., a triplet radical pair in a solvent cage) and then, as a result of diffusive separation of the radical pair, we allow J to decrease to a value smaller than a (e.g., the primary geminate pair $\dot{R}_1$ and $\dot{R}_2$ diffuse out of the cage but remain spin correlated). All that is now needed in order to convert T_0 into S (or S into T_0) is a rotation about the direction of H_z of one of the spin vectors *relative* to the other. This will occur when the net magnetic field torques on the spin vectors are different. In addition to applied external fields, the spin vectors experience magnetic fields arising from nearby nuclear spins and from electron orbital motion. Although the electron spins on $\dot{R}_1$ and $\dot{R}_2$ behave independently, their common origin provides a "spin correlation" or phase relationship between the spin vectors as they start to precess. The nearby nuclear spins make magnetic "communication" with the electron spins via electron–nuclear hyperfine coupling, whose magnitude is given by a, the hyperfine constant. The orbital motion of the electron makes magnetic communication with the electron spins via spin–orbit coupling, whose magnitude is reflected by the g factor of the individual radicals.

Time Scales for Intersystem Crossing in Radical Pairs

Let us now consider the time scale for triplet–singlet rephasing in radical pairs. For concreteness consider first the conversion of T_0 to S. The time τ_{TS} it takes T_0 to convert to S equals the time required to rephase the two spin vectors by π radians. If $\Delta\omega$ equals the differential rate of precessions in radians/second, then $\tau_{TS} = \pi/\Delta\omega$. We can also define a probability per unit time (analogous to a rate constant) for $T_0 \rightarrow S$ interconversion as τ_{TS}^{-1}.

$$\begin{aligned} \tau_{TS} &= \pi/\Delta\omega \text{ (time for } T_0 \rightarrow S \text{ rephasing)} \\ k_{TS} &= \Delta\omega/\pi \text{ (rate for } T_0 \rightarrow S \text{ rephasing)} \end{aligned} \tag{1}$$

Suppose that the primary geminate radical pair $\dot{R}_1$ and $\dot{R}_2$ does not possess magnetic nuclei, but does possess different g factors (g_1 for $\dot{R}_2$ and g_2 for $\dot{R}_2$). In this case, $\Delta\omega$ and k_{ST} are related to the laboratory magnetic field by the relationship[3]

$$\Delta\omega \cong (g_1 - g_2)\beta H = \Delta g\beta H \tag{2}$$

$$k_{TS} \sim (3 \times 10^6)\Delta g H \tag{3}$$

where H is in gauss and k_{TS} is in radians per second.

For typical organic radicals $\Delta g \sim 0.000$–0.001. In the earth's magnetic field ($H \sim 1$ G), $k_{TS} \sim 3 \times 10^3$ s^{-1}, a very small rate compared to the rates of other processes available to radical pairs. However, in very strong laboratory fields ($H \sim 100\,000$ G), $k_{TS} \sim 3 \times 10^8$ s^{-1}. In this case, external field induced intersystem crossing may become competitive with other processes available to the triplet radical pair.

If $\dot{R}_1$ or $\dot{R}_2$ contains a magnetic nucleus whose hyperfine coupling constant is a, then k_{TS} will be proportional to some power of a even at zero external field. For an order of magnitude estimation[8]

$$k_{TS} \sim (3 \times 10^6)a \tag{4}$$

where a is in gauss and k_{TS} is in radians/second. Typical values of a for organic radicals fall in the range 10–100 G, so that $k_{TS} \sim (3 \times 10^7)$–$(3 \times 10^8)$ rad/s for

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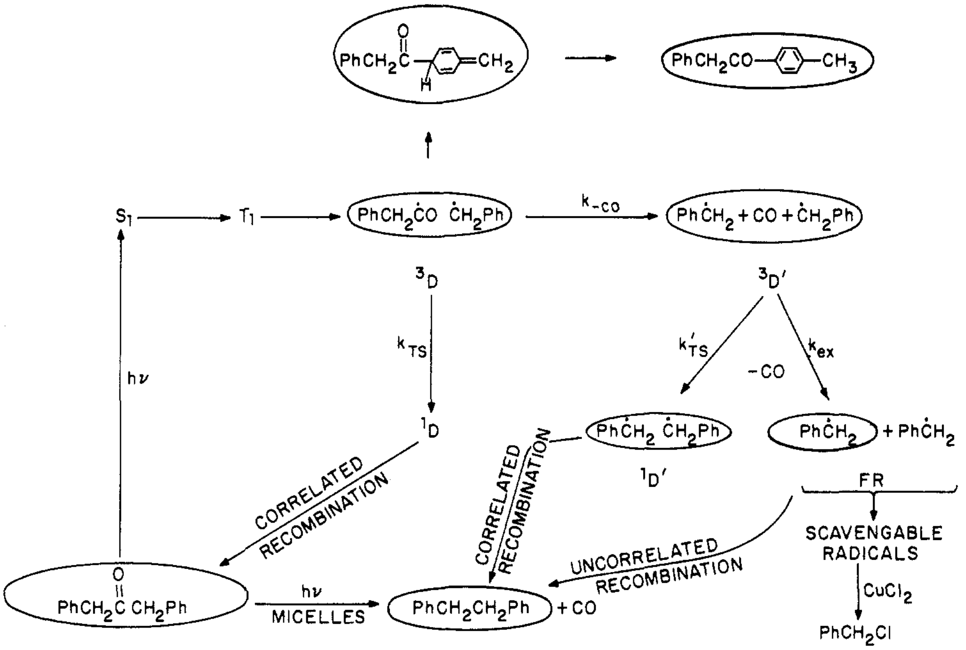
(6) The vector model of electron spin as applied to intersystem crossing in radical pairs is reviewed by H. R. Ward, *Acc. Chem. Res.*, **5**, 18 (1972), and by Atkins.[3]

(7) For a clear discussion of the "spin clock" idea see R. Kaptein, "Chemically Induced Magnetic Polarization", L. T. Muus, Ed., D. Reidel, Dordrecht, Netherlands, 1977, p 1.

(8) A. L. Buchachenko, *Russ. Chem. Rev.*, **45**, 761 (1976).

Scheme I. Mechanism for the Photolysis of DBK in Micellar Solution



a single nucleus–electron hyperfine interaction.

Two Mechanisms for Intersystem Crossing in a Radical Pair: Spin Flipping and Spin Rephasing

From eq 3 and 4 we learn that there are at least two mechanisms for ISC in a radical pair. The first (eq 3) involves only a rephasing of the electron spin vectors and is brought about by an imbalance in the inherent precession rates of the vectors (Δg), and causes k_{ST} to increase as H increases. *No nuclear spin flip is involved in this mechanism.* Suppose, however, that $\dot{R}_1$ contains a magnetic nucleus of spin = $\pm^1/_2$ and a hyperfine coupling constant of a_1. Equation 3 then becomes

$$k_{ST} \sim (3 \times 10^6)(\Delta g H \pm \tfrac{1}{2}a_1) \qquad (5)$$

Clearly, if a_1 is positive, then $k_{ST}^{+1/2} > k_{ST}^{-1/2}$ where the k's refer to radical pairs possessing spins $+^1/_2$ and $-^1/_2$, respectively. Since radical pairs possessing nuclear spins of $+^1/_2$ undergo *faster* ISC than radical pairs possessing nuclear spins of $-^1/_2$, the former undergo cage reaction more efficiently than the latter and *a mechanism for "sorting" nuclear spin states is available*! As a result, the cage products are "enriched" in $+^1/_2$ nuclear spins and the escape products are enriched in $-^1/_2$ nuclear spins. We say that the nuclei of the cage and escape products are "polarized" (i.e., do not possess a Boltzmann distribution), and we have a rudimentary understanding of the theory of CIDNP.

The second mechanism for ISC in a radical pair (eq 4) requires a simultaneous flip of a nuclear spin and an electron spin. Clearly, this mechanism is unavailable to a nucleus which does not possess spin. We perceive that in the absence of a magnetic field ($H = 0$), radical pairs possessing magnetic nuclei can undergo ISC faster than those which possess nonmagnetic nuclei. *A mechanism is thus available for sorting magnetic nuclei from nonmagnetic nuclei.*

Application of an external magnetic field, in addition to increasing ISC via the Δg mechanism, energetically splits T_+ and T_- from T_0 and S via Zeeman splitting of the triplet sublevels. T_0 and S states remain degenerate even when a strong laboratory field is applied (Figure 2). It is expected that when $H > a$, ISC from T_+ and T_- to S will become inefficient. As a result, cage reaction will occur predominantly from T_0. However, T_+ and T_- will still be able to undergo an escape process. In effect, *application of a magnetic field provides a mechanism for "sorting" the chemistry of T_+ and T_- from that of T_0!*

An Example: Magnetic Isotope Effects in the Photolysis of Dibenzyl Ketone

Photolysis of $PhCH_2COCH_2Ph$ (DBK) in benzene solution ($\lambda_{ex} > 300$ nm, room temperature) results in a quantitative yield of CO and 1,2-diphenylethane.[9] The reaction pathway (Scheme I) has been demonstrated to involve homolytic α cleavage of T_1 of DBK to produce a triplet radical pair ($PhCH_2\dot{C}O$ and $Ph\dot{C}H_2$) as primary products. The quantum yield is high ($\Phi \sim 0.8$). The small reaction inefficiency may be explained by assuming that a certain fraction of cage recombination to regenerate DBK is occurring. Indeed, CIDNP studies (^1H and ^{13}C) are consistent with a finite amount of cage recombination of $PhCH_2\dot{C}O$ and $Ph\dot{C}H_2$ radicals.[5a,9b]

The pertinent ESR parameters[10] for the radical pair $PhCH_2\dot{C}O\ \dot{C}H_2Ph$, produced from the photolysis of dibenzyl ketone, are listed in Figure 4. From the data $\Delta g = 0.0018$ and the largest single value of a is 125 G for the $R\dot{C}{=}O$ carbon atom. If a dibenzyl ketone molecule contained ^{13}C at this carbon, we would expect k_{TS} of the triplet radical pair to be determined (at "low H") by the hyperfine interaction of ^{13}C (of $R\dot{C}O$) and the odd electron of the $PhCH_2\dot{C}O$. For a triplet radical pair containing ^{13}C corresponding to a natural abun-

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[9] (a) P. S. Engel, *J. Am. Chem. Soc.*, 92, 6074 (1970); W. K. Robins and R. H. Eastman, *ibid.*, 92, 6076 (1970); (b) H. Langhals and H. Fischer, *Chem. Ber.*, 111, 543 (1978); B. Blank, P. G. Mennitt, and H. Fischer, *Pure Appl. Chem.*, 4, 1 (1971).

[10] A. Berndt, H. Fischer, and H. Paul, "Magnetic Properties of Free Radicals", Landolt-Börnstein, Vol. 9, Part b, Springer-Verlag, Berlin, 1977: $Ph\dot{C}H_2$, p 543; $PhCH_2\dot{C}O$, p 321.

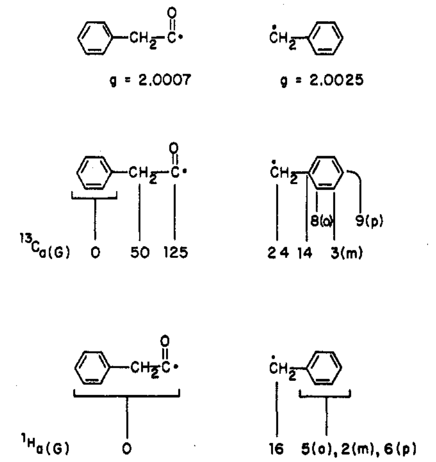

Figure 4. Important ESR parameters for the $PhCH_2\dot{C}O$ and $Ph\dot{C}H_2$ radicals.

dance (~1.1%), k_{TS} will be determined mainly by the ^1H hyperfine interactions of the $Ph\dot{C}H_2$ radical (note that the ^1H hyperfine interactions on the $PhCH_2\dot{C}O$ radical are ~0 G). To the extent that radical pairs containing ^{13}C at the $R\dot{C}O$ carbon undergo more rapid $T_0 \rightarrow S$ intersystem crossing than those pairs possessing ^{12}C at the $R\dot{C}O$ carbon, *the DBK regenerated by cage reaction should be enriched in* ^{13}C. The enrichment should be selective at the $R\dot{C}O$ carbon atom, since $a(^{13}C)$ for $PhCH_2{}^{13}CO$ is the largest for any ^{13}C atom of either radical in the pair (more precisely, a significant enrichment of the CH_2 carbon of DBK should also occur, since the $a(^{13}C)$ in $Ph^{13}CH_2\dot{C}O$ is ~50 G).

Experimentally, photolysis of DBK in benzene to very high conversions (~99%) followed by mass spectral analysis of the remaining DBK revealed that a small enrichment in ^{13}C had occurred.[11] When DBK containing a natural abundance of ^{13}C is employed, the effect is barely outside of the experimental error. However, if synthetically enriched DBK is employed, the measured enrichment is well outside of experimental error. The percent enrichment is found to depend on the extent of conversion. For example, when the sample initially contains 25.38% ^{13}C (total), at 45% conversion the percent ^{13}C is 25.60% and at 89% conversion it is 26.88%. This corresponds to a 5.6% net enrichment.[11b] The magnetic isotope effect on chemical reactivity may be compared to the mass isotope effect on chemical reactivity by employing a single stage separation factor α, a quantity which is independent of the extent of conversion. For our purposes, α is a measure of the relative rate constants of the isotopic species for an irreversible rate-determining step.

$$\alpha = \frac{\text{rate of disappearance of } ^{12}\text{C compound}}{\text{rate of disappearance of } ^{13}\text{C compound}} \quad (6)$$

Bernstein[12] has derived a formula for determining α (for first-order thermal reactions involving isotopes) from an appropriate plot of percent enrichment as a function of percent conversion. Applying his formula to the photolysis of DBK in benzene, we obtain a value of $\alpha = 1.05 \pm 0.02$. The largest $^{12}C/^{13}C$ mass isotope effects reported are of this magnitude.[1] Thus, although the enrichment in ^{13}C is real (on the basis of the above observations alone) it cannot be unambiguously associated with a magnetic isotope effect.

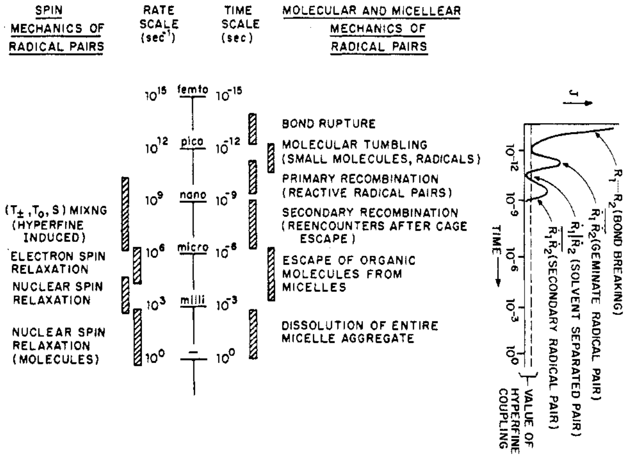

Figure 5. Rate and time scales for important processes involving spin dynamics and molecular and micellar mechanics.

Why Is the α Value for ^{13}C Enrichment So Small and What Can Be Done about It?

In analogy to the basis of CIDNP, the magnetic isotope effect originates in a reaction of radical pairs when for a key partitioning step an "escape" process competes with hyperfine-induced intersystem crossing and eventual cage reactions. If escape is too fast and irreversible, the number of molecules undergoing cage reaction is very small. In the case of DBK photolysis, the two most likely candidates for escape are diffusive separation and decarbonylation. $PhCH_2\dot{C}O$ radicals can be trapped, and the lifetimes of these radicals have been estimated to be ~10^{-7}–10^{-8} s at room temperature.[13] On the other hand, escape of radical pairs from a solvent cage in benzene should take ~10^{-10} s. Thus, in nonviscous homogeneous solution, diffusive separation from the initial solvent cage, a process that is required in order for hyperfine interactions to become effective, is followed by irreversible escape and formation of free radicals. If one can produce an environment for the triplet radical pair that (a) allows for diffusive separation to distances that allow J to "vanish" and for the hyperfine interaction to become effective but (b) prevents or inhibits irreversible diffusive escape, then the competition between hyperfine-induced intersystem crossing and escape will be modified and α should be increased.

Influence of Viscosity and Micellization on ^{13}C Isotopic Enrichment

It can thus be surmised that the observation of significant magnetic field effects on the reactions of radical pairs will require a proper detailed balance of time scales and the manipulation of various parameters such as diffusion coefficients of the radical pair, hyperfine interactions, ΔgH interactions, and electron-exchange interactions. Typical time scales and rates for these processes are summarized in Figure 5.

As the solvent viscosity is increased, the probability of recombination after a short diffusive escape should

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(11) (a) A. L. Buchachenko, *Russ. J. Phys. Chem.*, **51**, 1445 (1977); (b) N. J. Turro and B. Kraeutler, *J. Am. Chem. Soc.*, **100**, 7432 (1978); (c) A. Pines and L. Sterna, Lawrence Berkeley Laboratory, Annual Report, 1977.

(12) R. B. Bernstein, *J. Phys. Chem.*, **56**, 893 (1952); *Science*, **126**, 119 (1957).

(13) G. Brunton, A. C. McBay, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 4447 (1977), and ref 9.

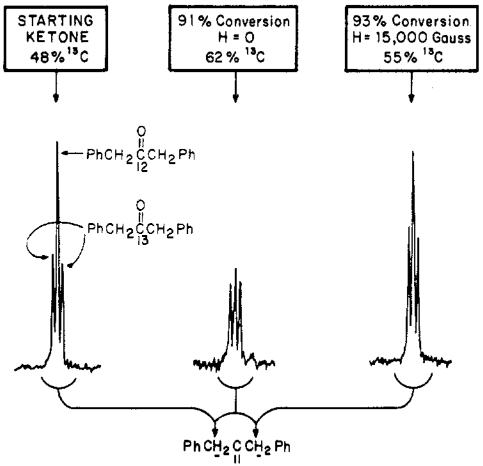

Figure 6. ^{1}H NMR spectra of ^{13}C-labeled dibenzyl ketone. (Left) Starting ketone; (middle) ketone recovered after 91% photolysis in micellar solution in the earth's magnetic field; (right) ketone recovered after 93% photolysis in micellar solution in a strong magnetic field. A similar result is observed with magnetic fields of several hundred gauss.

increase. A microenvironment which is relatively nonviscous but which possesses a boundary that "reflects" the diffusing particles back toward a cage encounter would also enhance the probability of reencounter of the correlated radical pair. A specific example of such a microenvironment is that provided by micellar aggregates.[14]

Photolysis of DBK at room temperature in solvents of increasing viscosity results in corresponding increases in the value of α. For example, when the solvent is changed from benzene (η = 0.6 cP) to dodecane (η = 1.35 cP) to cyclohexanol (η = 30 cP), α increases from 1.04 to 1.05 to 1.07, respectively.[11c] Thus, although α increases as a function of viscosity, the magnitude of the effect is not very large.

In contrast, photolysis of DBK in aqueous detergent solutions containing micelles results in a dramatic increase in α. For example, in detergent solution of hexadecyltrimethylammonium chloride (HDTCl) or sodium dodecyl sulfate, α values of $\sim$1.4 are observed. Since mass isotope effects involving ^{12}C and ^{13}C rarely show $\alpha > 1.03$, values of α of the order of 1.4 are enormous. Furthermore, the value of α approaches 1.0 (i.e., the magnetic isotope effect vanishes) at very strong fields, presumably because the Δg mechanism (eq 3) completely determines the rate of intersystem crossing (Figure 2, case III).

Experimental support for the isotopic enrichment is summarized convincingly and completely in Figure 6. The "triplet" appearance of the CH_2 group of DBK arises from the occurrence of a central singlet (due to $CH_2{}^{12}CO$) and of two satellites (due to $CH_2{}^{13}CO$). The satellites are caused by H–C–^{13}C spin–spin coupling. At the left of Figure 6 the signal is shown for the methylene group of DBK containing 48% ^{13}C in the carbonyl carbon. The ratio of the area of the center peak to the sum of the areas of the satellite peaks represents the $^{12}C/^{13}C$ ratio of the carbonyl carbon atom. Photolysis of DBK in micellar solution to 91% disappearance followed by recovery and ^{1}H NMR analysis of the remaining DBK leads to the spectrum shown in the middle of Figure 6. *Note that the $^{12}C/^{13}C$ ratio has drastically decreased.*

Evidently, reaction in the micelle increases the extent of cage recombination and thereby increases the effectiveness of ^{13}C-induced intersystem crossing in radical pairs. If this is true, then (1) the quantum yield of disappearance of DBK should be much smaller in micelle solutions relative to homogeneous solution and (2) the quantum yield of disappearance of $PhCH_2{}^{12}COCH_2Ph$ (^{12}DBK) should be significantly larger than that for $PhCH_2{}^{13}COCH_2Ph$ (^{13}DBK). Experimentally, these conclusions are completely confirmed.[15]

Magnetic Field Effects on the Photolysis of Dibenzyl Ketone

The rate of decarbonylation of $PhCH_2\dot{C}O$ radicals at room temperature is estimated[13] to be $\sim 10^8\ s^{-1}$. Since the exit rate of small organic molecules from HDTCl micelles[16] should be $< 10^5\ s^{-1}$, decarbonylation of the $PhCH_2\dot{C}O\ \dot{C}H_2Ph$ triplet radical pair (^{3}D in Scheme I) will occur much faster than escape of the radical pair from the micelle. In effect, loss of CO produces a new *correlated* triplet pair, i.e., $Ph\dot{C}H_2\ \dot{C}H_2Ph$ (^{3}D′ in Scheme I). Application of an external field will decrease the rate of ISC of both ^{3}D and ^{3}D′ because T_+ and T_- will be split away from S and will not be able to undergo efficient ISC (Figure 2, case II). Thus, when an external field is applied, escape of radicals from the micelle will compete more efficiently with cage recombination reactions. Therefore, in the presence of a positively charged water-soluble scavenger, radicals that escape the micelle will be efficiently trapped and will be prevented from forming diphenylethane (DPE) or reforming dibenzyl ketone (DBK).

Experimentally, the quantum yield of disappearance of DBK is the same in the presence and absence of Cu^{2+} (an efficient trap of $Ph\dot{C}H_2$ radicals) so that the primary radical pair $PhCH\dot{C}O\ \dot{C}H_2Ph$ *does not* undergo significant escape. However, the quantum yield for formation of DPE drops drastically as Cu^{2+} is added. A cage effect of 25% can be calculated from these results. A plot of the quantum yield of DPE in the presence of an applied field shows that the cage effect[17] drops from 25% at 0 G to about 14% at fields greater than 1000 G. A magnetic field dependence of the quantum yield for formation of a minor product, an isomer of DBK (see Scheme I for its mechanism of formation), is also observed.[17]

Correlation of Quantum Yields with Isotopic Enrichment

A quantitative relationship has been established between the value of α obtained from ^{13}C isotopic enrichment experiments and that from quantum yield data for photolysis of DBK.[17b] It is thus possible to

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[14] J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, 1975.

[15] N. J. Turro, B. Kraeutler, and D. R. Anderson, *J. Am. Chem. Soc.*, 101, 7435 (1979).

[16] M. Almgren, F. Grieser, and J. K. Thomas, *J. Am. Chem. Soc.*, 101, 279 (1979).

[17] (a) M. F. Chow, C. Chung, and G. Weed, *J. Am. Chem. Soc.*, in press. The observation of extrema at <1000 G in product profiles vs. *H* fulfills one of the criteria suggested for unambiguously establishing the operation of magnetic field effects on chemical reactions: R. Lawler, *J. Am. Chem. Soc.*, **102**, 430 (1980). (b) B. Kraeutler and N. J. Turro, *Chem. Phys. Lett.*, **70**, 266 (1980).

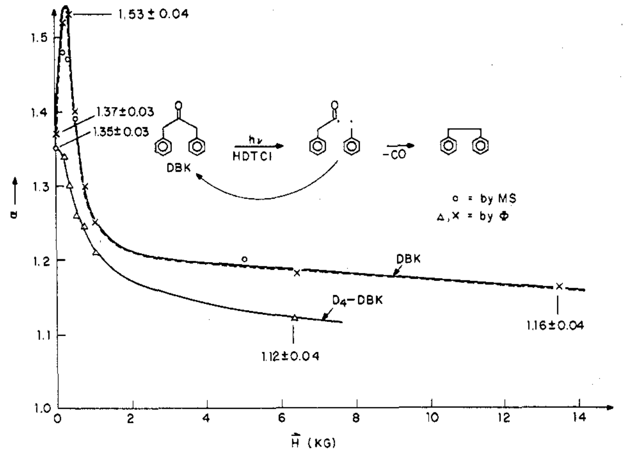


Figure 7. Magnetic field effects on the values of α as a function of magnetic field strength. The same curve is found for α values determined by mass spectral analysis (circles) or by quantum yield measurements (X). The lower curve is for photolysis of $C_6H_5CD_2COCD_2C_6H_5$. Notice that the behavior of α for this compound is quantitatively different than it is for DBK.

measure α by two completely independent analytical methods: mass spectrometric analyses of recovered DBK and conventional quantum yield determinations. The former do not involve knowledge of the light intensity, whereas the latter require quantitative knowledge of the *absolute* light intensity. In Figure 7, the measured value of α as determined by these two methods is shown as a function of magnetic field strength. The agreement between the two methods is excellent and serves as convincing support for the mechanism given in Scheme I and for the absence of artifacts related to optical properties of the system. Furthermore, the occurrence of a maximum in the α vs. H profile at ~150 G clearly identifies the origin of α as a magnetic isotope effect.[17a]

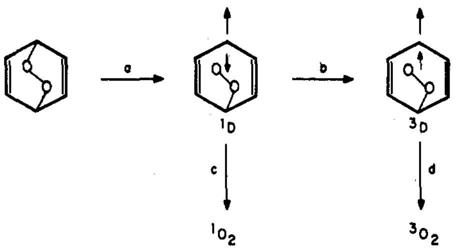
Enrichment in Other "Restricted Spaces"

Are micelles unique as vehicles for unusually large enrichments? We think not, since we have recently observed large values of α (1.2–1.3) when the photolysis of DBK is conducted in polymer films (i.e., poly(methyl methacrylate)) or in porous glass. Furthermore, the value of α drops significantly (~1.1) when the polymer or porous glass photolyses are conducted in a strong magnetic field. It thus appears that the radical pair is constrained to a certain "restricted space" such as that provided by micelles, the fluid portions of polymer films or the cavities of porous glass.

Magnetic Isotope and Magnetic Field Effects on the Formation of Singlet Oxygen from Thermolysis of Endoperoxides

The thermolysis of certain endoperoxides of aromatic compounds produces molecular oxygen quantitatively. From a study of activation parameters it has been found that these reactions proceed via two pathways:[18] (1) a concerted mechanism in which $^1O_2$ is produced quantitatively and (2) a diradical mechanism in which both $^3O_2$ and $^1O_2$ are produced. Magnetic field and magnetic isotope effects potentially provide a novel and convincing tool for distinguishing concerted and diradical mechanisms. *Only the diradical pathways are influenced by magnetic effects.* For example, consider the simplified diradical mechanism for endoperoxide thermolysis shown in Scheme II. If thermolysis leads initially to a singlet diradical ^1D, this species may undergo either ISC to ^3D (path b) or fragmentation of $^1O_2$ (path c). As in the case of radical pairs, magnetic fields may influence reactions of diradicals via a Δg effect or via a hyperfine effect. The Δg effect will increase the rate of step b relative to step c, thereby producing ^3D with greater efficiency. Hence, *a higher yield of $^3O_2$ and a lower yield of $^1O_2$ is expected* when endoperoxides (which decompose via diradicals) are thermolyzed in a magnetic field. Furthermore, no effect of external magnetic field is expected if a concerted decomposition occurs. Figure 8 shows a plot of the $^1O_2$ yield vs. H for a 1,4-endoperoxide (1) that undergoes concerted thermolysis and a 9,10-endoperoxide (2) that undergoes thermolysis via a diradical.[19] It is gratifying to find that there is no magnetic field effect on the $^1O_2$ yield for thermolysis of 1 but that a striking *decrease* in the yield of $^1O_2$ is observed for 2 as for variation of field strength in the range 9000–15000 G.

Scheme II. Simplified Diradical Mechanism for the Thermolysis of Endoperoxides



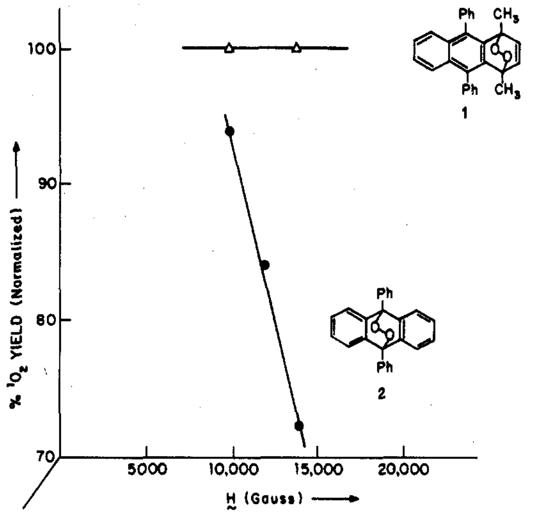


Figure 8. Magnetic effects on the $^1O_2$ yield from thermolysis of some endoperoxides.

A spectacular prediction can be made concerning magnetic isotope effects on the thermolysis of endoperoxides: If a diradical pathway (Scheme II) is followed, diradicals possessing ^{17}O atoms will have a higher probability of following path b than diradicals possessing only ^{16}O or ^{18}O atoms, because ^{17}O is a magnetic isotope but ^{16}O and ^{18}O are nonmagnetic isotopes. Experimentally this means that endoperoxide molecules which contain ^{17}O will produce $^1O_2$ *less* efficiently and $^3O_2$ more efficiently. Thus, if a selective and efficient

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(18) N. J. Turro, M. F. Chow, and J. Rigaudy, *J. Am. Chem. Soc.*, **101**, 1300 (1979).

(19) N. J. Turro and M. F. Chow, *J. Am. Chem. Soc.*, **101**, 3701 (1979).

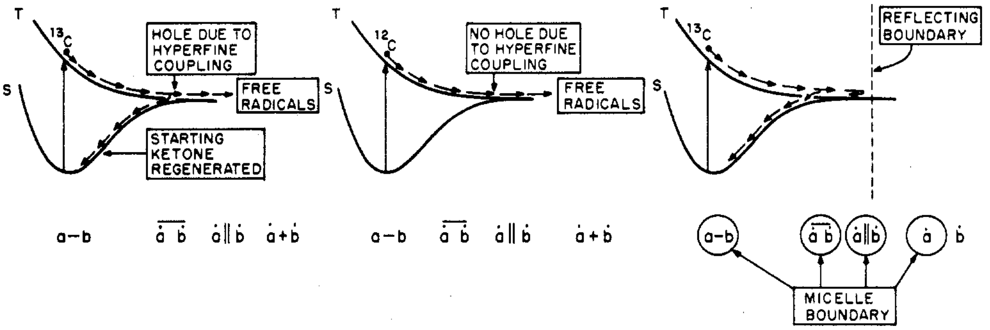

Figure 9. Schematic surface representation of the hyperfine mechanism for ^{13}C enrichment of DBK in micelles. In the figure a represents the $PhCH_2CO$ group and b refers to the $PhCH_2$ group.

trap of $^1O_2$ is present during reaction, the "untrappable" molecular oxygen will be enriched in ^{17}O!

Two types of measurements were made[20] to test the validity of these ideas: (a) the ^{17}O and (^{16}O + ^{18}O) content of untrappable molecular oxygen was analyzed by mass spectrometry and (b) the yield of trapped $^1O_2$ was evaluated by quantitative determination of the amount of reacted acceptor when DPA–$^{16}O_2$, DPA–$^{18}O_2$, or DPA–$^{17}O_2$ were employed. It was found that the yield of $^1O_2$ formation is smaller for ^{17}O than for ^{16}O or ^{18}O containing DPA–O_2. Furthermore, it was found that both DPA–^{16}O and DPA–^{18}O produce the *same* yield of $^1O_2$, while DPA–^{17}O produces less $^1O_2$. This result rules out a significant mass isotope effect as the basis for different quantum yields.[17]

Since the amount of reacted trap is monitored in the yield measurements, they only provide an *indirect* test of the isotopic enrichment. A *direct* measurement involves determination of the isotopic composition of the untrappable molecular oxygen produced in the thermolysis of DPA–O_2. The results demonstrate that the untrappable molecular oxygen is indeed enriched in ^{17}O relative to the control sample.[20]

Finally, endoperoxides which undergo concerted thermolysis were found not to produce ^{17}O molecular oxygen in equivalent experiments.

Concluding Remarks

The observation of magnetic isotope and magnetic field effects on the photolysis of DBK in micellar solution is not an isolated finding. Numerous other ketones (phenyl adamantyl ketone, phenyl benzyl ketone, etc.) have been found to exhibit analogous behavior.[21,22] The ideas employed in the DBK system are summarized schematically in Figure 9 in terms of potential-energy surfaces.[23] The reaction coordinate represents breaking of the OC–CH_2 bond. As the OC–CH_2 bond breaks, the representative point "slides" down the electronically repulsive triplet surface. When the bond is broken the triplet surface becomes essentially degenerate with the ground-state singlet surface. A magnetic interaction is required before the representative point can make a "jump" from the T surface to the S surface. Such a jump can be induced by hyperfine interaction only when the point is far to the right, i.e., when the triplet and singlet are nearly degenerate and $J < a$. The "jump" from T to S requires a "hole" in the T surface, through which the point may fall.

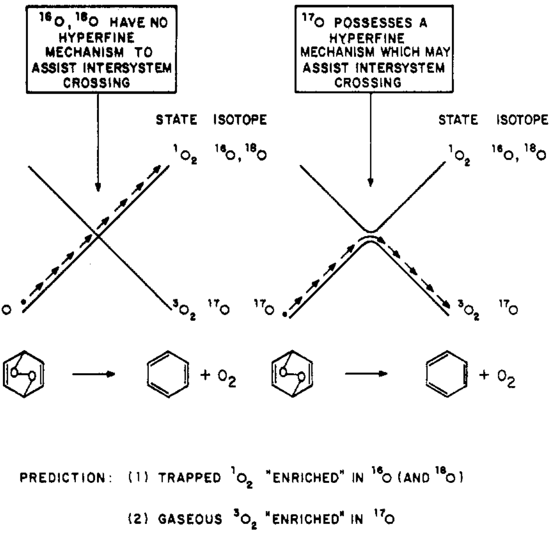

Figure 10. Schematic surface representation of the hyperfine mechanism for ^{17}O enrichment of O_2 via thermolysis of endoperoxides.

The role of the micelle may be viewed as providing a boundary which "reflects" the representative point back toward the hyperfine induced hole after an "overshoot" has occurred. Thus, diffusive escape is temporarily thwarted and a ^{13}C-containing molecule receives extra chances to find a hole which allows return to ground-state DBK. Eventually, of course, escape by decarbonylation will take place if neither diffusive escape nor bond formation occur.

In the case of ^{17}O enrichment, the hyperfine interaction provides a surface avoiding (Figure 10, right) for ^{17}O-containing diradicals where a surface crossing exists (Figure 10, left) for ^{16}O- or ^{18}O-containing diradicals.[24]

The ideas discussed above may be employed, in principle, to design chemical reactions that will separate magnetic isotopes from their nonmagnetic colleagues. The key features are the requirement of a singlet–triplet crossing (or touching) along the reaction coordinate, the availability of a hyperfine hole at the molecular geometry corresponding to the hole, and sufficient time for the representative point to find the hole when it arrives in the region of "phase space" corresponding to the hole. Magnetic field and magnetic isotope effects provide a complement to CIDNP for probing mechanisms of

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[20] N. J. Turro and M. F. Chow, *J. Am. Chem. Soc.*, **102**, 1190 (1980).

[21] N. J. Turro, B. Kraeutler, and D. R. Anderson, *Tetrahedron Lett.*, **21**, 3 (1980).

[22] N. J. Turro and J. Mattay, *Tetrahedron Lett.*, **21**, 1799 (1980).

[23] For a discussion of the representative point concept, see N. J. Turro, "Modern Molecular Photochemistry", Benjamin-Cummings, Menlo Park, CA, 1978, p 52.

[24] During the refereeing of this paper a report appeared describing ^{17}O enrichment via a clever application of the radical pair coupling and decomposition of peroxy radicals: V. A. Belyakov, V. I. Mal'tsev, E. M. Galimov, and A. L. Buchachenko, *Dokl. Akad. SSSR*, **243**, 924 (1978).

radical reactions. In contrast to CIDNP which requires NMR measurement during reaction, magnetic field and magnetic isotope effects reveal themselves in terms of chemical products which may be analyzed at the chemist's convenience by conventional methods. Moreover, it should be noted that unusual isotope effects that have been interpreted in terms of conventional mass effects should be reconsidered as possible magnetic isotope effects and subjected to the magnetic field criterion.

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