

16. Reactions of the Radical Pairs. The I→P Step of the Paradigm

Let us consider the product forming step in the general photochemical paradigm, i.e., the I→P process shown in Figure 1. From the discussion of this chapter, we see that this step, for which the primary photochemical product is a geminate triplet dynamic radical pair, $^3\text{I}_{\text{GRP}}$, is not a simple elementary step involving passage of a representative point over a single energy barrier. Instead the I→P "step" is a complex set of steps involving molecular diffusion dynamics, spin dynamics and chemical dynamics and extensive motion of the representative point back and forth along the energy surface. It is convenient to classify the pathways from I to P as two types:

- (1) formation of products produced from reactions of geminate pairs, and
- (2) products produced from random pairs. Geminate pairs are born together and can be traced back to a primary photochemical event of the same parent molecule, whereas random pairs result from encounters or "free radical" partners that were generated in independent primary photochemical events. Geminate products produced by reactions of geminate radical pairs are often termed "cage" products or "recombination" products, but these terms are ambiguous, since random pairs also require encounters and formation of a caged pair to form products, and often the same products are produced by geminate or random pairs.

There are two methods, one chemical and one spectroscopic that can be employed to distinguish between the products of geminate and random radical pairs. The chemical method involves sorting the geminate and random pair reactions through **chemical scavenging** experiments which selectively scavenge the free radicals leading to random pairs leaving behind only products due to geminate pair reactions. The spectroscopic method involves the sorting of the geminate and random pair reactions through the NMR determination of the nuclear spin orientation in the products. The latter method, termed chemically induced dynamic nuclear polarization (CIDNP) provides a nice example of how the interplay of molecular, spin and chemical dynamics results in an unusual spectroscopic observation which provides detailed information on the structure and dynamics of the radical pair leading to isolated products, i.e., the I→P step of Figure 1.

We employ our case study pair, $\text{I} = \text{ACO} \cdot \cdot \text{B}$, to exemplify how chemical and spectroscopic methods can be employed to sort out the reactions of geminate and random pairs.

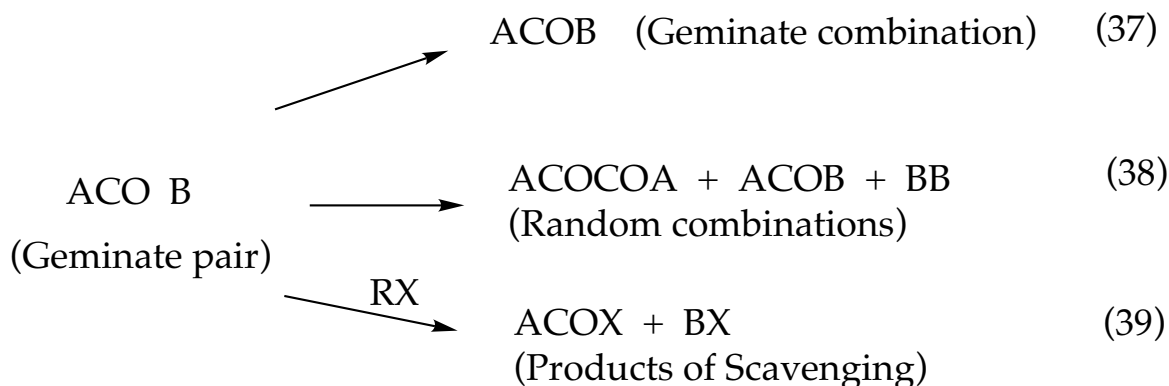
Chemical Sorting Geminate and Random Radical Pair Reactions. Scavenging of Free Radicals.

Singlet radical pairs, random or geminate, undergo two typical reactions when they are in the contact state (Region 1) in a solvent cage:

- (1) combination and (2) disproportionation. The former involves bond formation between the radicals to generate a molecule, and the latter involves hydrogen transfer between the radicals to form two molecules. We need only consider one of the two in our case study and we select the simpler process,

combination. However, we emphasize that the discussion is appropriate for either combination or disproportionation products of radical pairs.

Let us assume that the triplet, geminate pair, $\text{ACO} \cdot \cdot \text{B}$, produced by the primary process of α -cleavage of $^3\text{ACOB}$, may undergo two pathways to form radical pair combination products: (1) geminate pair recombination to form the combination product ACOB (Eq. 37.) and (2) random pair combination to form ACOCOA , ACOB and BB (Eq. 38).



The two products ACOCOA and BB (Eq. 38) cannot be geminate products based on simple atomic composition considerations, i.e., each requires the dissociation of two precursor ACOB molecules. However, the ACOB product could arise from either a geminate combination (Eq. 37) or a random combination (Eq. 38). These two possibilities can be distinguished through chemical scavenging of free radicals. Suppose a molecule RX (here X may be a halide such as Cl or Br) reacts very rapidly with each of the free radicals $\text{ACO} \cdot$ and $\text{B} \cdot$. If the rate of reaction of the free radicals with RX is fast enough, then at a high enough concentration of RX , all of the radicals that do not undergo geminate combination to form ACOB (Eq. 37) can be scavenged by RX to form the products shown in Eq. 39. **When this is the case, the ACOB formed through the combination of free radicals will be absent from the reaction mixture and the ACOB formed must result entirely from geminate combination.** We note that Eqs. 37 and 38 are spin dependent reactions because the product molecules are singlets, i.e., they are forbidden when the pair is in the triplet state. However, the scavenging reaction, Eq. 39 is spin independent since the reactants and products are doublets (although the orientation of the doublet spin in the reactants and products must be identical).

The efficiency of geminate combination reactions (Eq. 37) is termed the "cage effect" and may be defined in terms of the fraction of geminate pairs that are generated to those undergoing recombination. However, the fraction of geminate pairs formed is difficult to determine experimentally. Instead, the quantum yield for the cage effect is often determined. The quantum yield for the cage effect is defined as the number of geminate combinations relative to the number of photons absorbed. It is also possible to define the cage effect in terms of the probability of combination without determining the fraction of geminate pairs formed. This technique involves the use of an optically active ketone and

the measurement of racemization that occurs as a function of the extent of photolysis.

Spectroscopic Sorting Geminates and Random Radical Pair Reactions. Chemically Induced Dynamic Nuclear Polarization (CIDNP).

NMR spectra taken during a photochemical reaction sometimes result in unusual features: some signals possess a phase which is in emission rather than an absorption and some signals possess an enhanced absorption intensity which is much stronger than expected for the number of moles of material in the sample. Furthermore, when the source of photochemical excitation is removed, the emission and enhanced absorption signals disappear rapidly but can be regenerated when the exciting source is reestablished. Extensive investigations have shown that these unusual NMR features occur only for signals due to the products of reactions of free radicals and radical pairs, e.g., such as those of Eqs. 37-39. The "dynamic radical pair" theory we have employed in this chapter was, in fact, developed to explain the phenomena of NMR spectra showing emission and enhanced absorption, which is termed "*chemically induced dynamic nuclear polarization*" or more usually referred to as CIDNP.

We now briefly review the Wigner spin selection rules for elementary chemical steps that form a natural conceptual framework for understanding the fundamental principles of CIDNP.

Wigner Selection Rules for Reactions of Radical Pairs.

An elementary chemical step is conceptually defined as the passage of a representative point over a single bond making or bond breaking barrier on an energy surface. Wigner's Spin Selection Rule states that spin angular momentum must be conserved (unchanged) in any elementary chemical step. Thus, *electron and nuclear spin must be conserved during any elementary chemical step, such as the making or breaking of a chemical bond in a combination reaction such as Eq. 37.* The same principle holds for radiative or radiationless transitions since the conservation of angular momentum is as fundamental as the law of conservation of energy.

The application of Wigner's rule to the geminate reactions of dynamic radical pairs leads to the following principles of CIDNP:

- (1) Combination reactions depend on the **electronic spin** state of the dynamic radical pair, reaction from the singlet being allowed and reaction from the triplet being forbidden;
- (2) Combination reactions depend on the **nuclear spin** of the dynamic radical pair, the rate of intersystem crossing of a dynamic radical pair depending on the orientations of the nuclear spins that are hyperfine coupled to the electron spins in the radical pair.

Thus, although the electron spin controls bond formation and therefore combination reactions directly, the nuclear spin indirectly determines the rate of bond formation through hyperfine coupling which influences the rate of intersystem crossing. According to the principles stated above, a triplet radical pair (geminate or random) cannot undergo combination reactions (the product, Eq. 37, is a singlet!) and therefore **a triplet geminate radical pair is chemically inert**. In order to form a product the triplet geminate pair must undergo ISC to a singlet geminate radical pair. As we have seen in the previous section, different nuclear spin orientations cause electron spins to precess at different rates. We shall now see how the influence of nuclear spin orientation on electron spin precession in turn can cause intersystem crossing to occur faster for some nuclear orientations than for others, so that combination or "cage" reactions starting from a triplet pair will occur faster for the spin orientations that cross more rapidly to the singlet state. Thus, the two CIDNP principles lead to the conclusion that **the reactivity of a radical pair depends on the spin orientation of the nuclei present in the pair**. We now employ the vector model to understand the nuclear spin dependence of chemical reactivity.

Vector Model of CIDNP.

Figure 38 presents a schematic vector model that will assist in understanding how the orientation of nuclear spin could influence the rate of intersystem crossing of a geminate triplet pair and how the different rates of ISC for different nuclear orientations lead to the ^{13}C CIDNP spectrum observed when A^{13}COB is photolyzed in an NMR spectrometer. We must point out that we are observing ^{13}C NMR, which results from the spinomeric pair $\text{A}^{13}\text{C}_\alpha\text{O B}$ and $\text{A}^{13}\text{C}_\beta\text{O B}$ and that the spinomeric pair $\text{A}^{12}\text{CO B}$ does not enter into the analysis (because ^{12}C does not have a nuclear spin and therefore does not have an NMR!). Next we point out that the experiment is being performed in the high field of an NMR spectrometer so that the energy surface of Figure 33 applies in our analysis of CIDNP. Finally we note that the same ideas will apply to ^1H or other magnetic nuclei occurring in organic molecules (^{31}P , ^{19}F , etc.).

Let us now follow the vector description of the two unpaired electron spins from the molecular triplet state through the formation of products from geminate pairs and free radicals. In the triplet state, $^3\text{ACOB}$, the two electron spins are tightly coupled by the exchange interaction (Region 1 of Figure 33). The triplet geminate radical pair produced by α -cleavage is originally born as a primary contact pair (Region 2 of Figure 33), and must become a solvent separated pair (Region 3 of Figure 33) in order to undergo $\text{T}_0 \rightarrow \text{S}$ intersystem crossing. In Figure 38 we show these situations in terms of tightly coupled electronic spins in the molecular triplet and in the contact pair and loosely coupled spins in the solvent separated state. The trajectories from the contact state to the solvent separated state and the subsequent reencounter is termed a **random walk diffusion of a dynamic radical pair**. If during these random walks a triplet geminate pair undergoes ISC to form a singlet geminate pair, upon reencounter (return to Region 2) in the contact state a recombination reaction can occur, i.e., the originally cleaved bond can reform. In Figure 38 we visualize

this process as it would occur in a strong magnetic field, i.e., one for which only the T_0 and S states of the pair are capable of undergoing ISC, because only these two states are capable of becoming degenerate in a strong magnetic field.

In Figure 38 the spinomer, $A^{13}C_{\beta}O$ B is shown undergoing a faster $T_0 \rightarrow S$ ISC than the $A^{13}C_{\alpha}O$ B pair. If this is correct, the geminate product of combination (ACOB) will be enriched in β nuclear spins and the scavenging product (ACOX) will be enriched in α spins! We now need to justify the hypothesis that the β orientation of ^{13}C nucleus lead to a faster ISC than the α orientation of ^{13}C nuclei. Let us now see how inspection elementary quantum mechanical relations and the ESR spectra of Figure 37 leads to the conclusion that the $A^{13}C_{\beta}O$ B pair undergoes ISC faster than the $A^{13}C_{\alpha}O$ B pair.

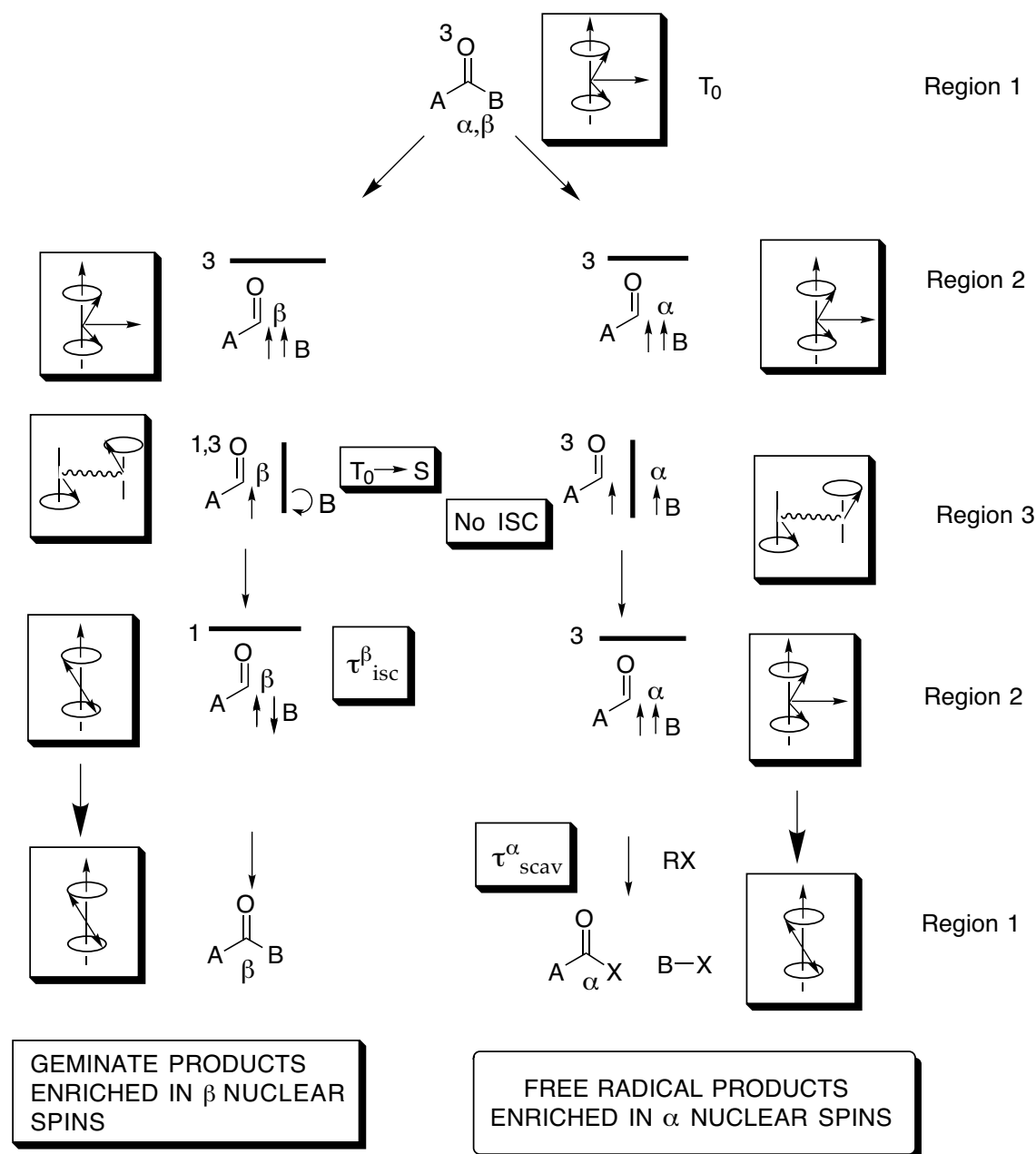


Figure 38. Vector model of the nuclear spin sorting that occurs in the dynamic radical pair. See text for discussion.

The connection between ESR spectroscopy and CIDNP

As discussed above, since both ESR spectra and NMR spectra are experimentally observed at high fields, the pertinent energy diagram for the dynamic radical pair under condition of magnetic resonance observation is given by Figure 33. At high field we are dealing only with T₀-S ISC (since T₊ and T₋ are split off resonances from S) and strong coupling of the electron and nuclear spins to the z-axis. Thus, at high field, the issue of ISC is which spinomeric radical pair,

$A^{13}C_{\alpha}O\cdot$ B or $A^{13}C_{\beta}O\cdot$ B, undergoes more rapid **spin rephasing** about the z-axis? In other words, which spinomeric pair has the greatest difference in precessional frequencies, $\Delta\omega$? For example, if $\Delta\omega = 0$, then both partners of the pair will possess identical precessional rates, and the electron spins would never get out of phase and ISC would not occur! **It is the difference in magnetic fields due to g factors and hyperfine coupling that cause the spins to precess at different rates so that $\Delta\omega$ is not equal to 0.** Recalling that the precessional rates of an electron spin depends on the orientation of the nuclear spin (Figure 37), we can now determine which spinomeric pair is rephased more rapidly by simply considering the frequencies at which the lines occur in the ESR spectra of the spinomeric pairs. We will then consider the more generalized form of the rephasing process.

In Figure 39 the ESR spectrum of the $A^{13}C_{\alpha,\beta}O\cdot$ radical is shown as two lines occurring at frequencies ω_1^{α} and ω_1^{β} . The line at ω_1^{α} corresponds to the "pure" electron spin transition $D_{-}^{\alpha} \rightarrow D_{+}^{\alpha}$ and the line at ω_1^{β} corresponds to the "pure" electron spin transition $D_{-}^{\beta} \rightarrow D_{+}^{\beta}$. For each of these transitions the nuclear orientation is unchanged. The ESR spectrum of the B \cdot radical is shown as a single line at ω_2 .

To determine which spinomeric geminate pair undergoes more rapid ISC we need to compute which possesses the larger value of $\Delta\omega$, where $\Delta\omega$ is the difference in the precessional rates of each spinomer. $\Delta\omega$ is simply the absolute difference in the precessional rate (ω_1^{α} and ω_1^{β}) for each spinomeric $A^{13}CO$ radical and the precessional rate of the B radical (ω_2). From Eqs. 35 and 36, we may compute the **difference in precessional rates for the spinomeric pairs** from Eq. 40 and 41.

$$\Delta\omega_{\alpha} = \omega_1^{\alpha} - \omega_2 = (g_1\mu_e H_Z + a/2)/\hbar - (g_2\mu_e H_Z)/\hbar =$$

$$\Delta\omega_{\alpha} = [(g_1 - g_2)\mu_e H_Z + a/2]/\hbar = [\Delta g\mu_e H_Z + a/2]/\hbar \quad (40)$$

$$\Delta\omega_{\beta} = \omega_1^{\beta} - \omega_2 = (g_1\mu_e H_Z - a/2)/\hbar - (g_2\mu_e H_Z)/\hbar$$

$$\Delta\omega_{\beta} = [(g_1 - g_2)\mu_e H_Z - a/2]/\hbar = [\Delta g\mu_e H_Z - a/2]/\hbar \quad (41)$$

From Eqs. 40 and 41 we see that the absolute magnitudes of $\Delta\omega_{\alpha}$ and $\Delta\omega_{\beta}$, which determine the differences in ISC rates at high field, depend on the following factors: (1) the magnitude of the difference in g factors of the radicals forming the pair; (2) the sign of the difference in g factors; (3) the magnitude of the hyperfine coupling constant, a; and (4) the sign of a. Thus, whether $\Delta\omega_{\alpha}$ is larger or smaller than $\Delta\omega_{\beta}$ depends on both magnitudes and signs, so that the ISC rates of the spinomeric pairs will depend on the same factors. Let's see how this all works out for our case study pair.

The sign of a for the $A^{13}CO$ radical is positive. Since the g factor for the $A^{13}CO$ radical ($g = 2.001$) is smaller than the g factor for the B radical ($g = 2.003$), $\Delta g (= g_1 - g_2)$ is negative. Inspection of Eqs. 40 and 41 show that from the ESR parameters of the spinomeric $A^{13}CO$ B radical pairs, the absolute value of $\Delta\omega_\beta$ is **larger** than the absolute value of $\Delta\omega_\alpha$, because in Eq. 41 two quantities are being added together and both are **negative**, whereas in Eq. 40 the same quantities are being added but one is **negative** and the second is **positive**. The same conclusion is reached graphically from inspection of the ESR spectra shown in Figure 39. The magnitudes of $\Delta\omega_\alpha$ may be read from the ESR spectra directly as the difference between the lines ω_1^α and ω_2 and $\Delta\omega_\beta$ may be read from the ESR spectra directly as the difference between the lines ω_1^β and ω_2 . It can be seen by inspection of Figure 39 that the difference between ω_1^β and ω_2 is **greater** than the difference between ω_1^α and ω_2 . This is, of course, what is expected since Eqs. 40 and 41 simply are mathematical representations of the ESR spectrum of the spinomer pairs.

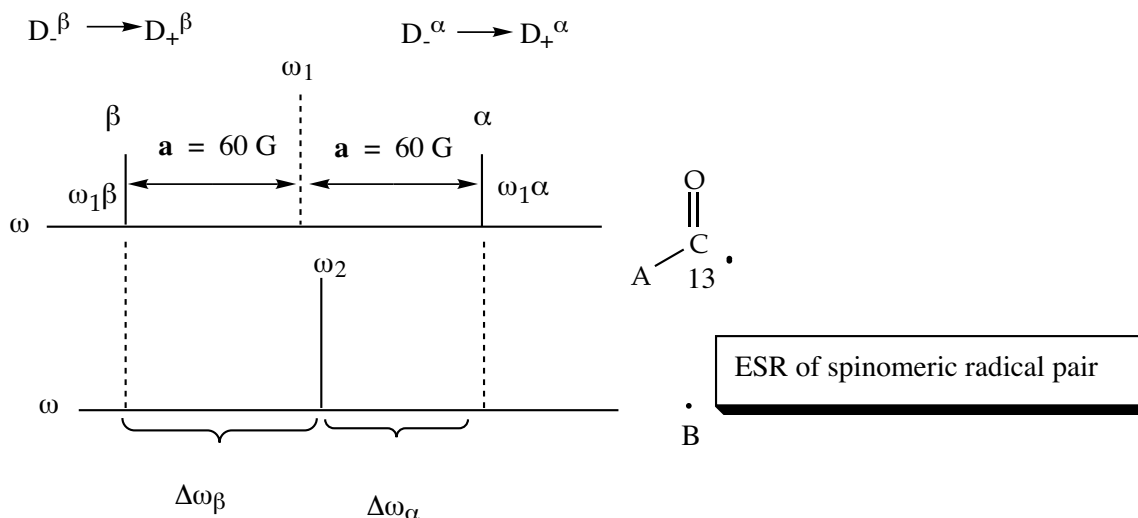


Figure 39. Comparison of the ESR spectrum of the radical pair and the NMR spectrum of the ACO radical.

Finally, let us consider how the vector model leads to the same qualitative conclusion concerning the faster ISC of the pair possessing the β spin. The magnetic field "felt" by the electron spin of B is independent of nuclear spin and depends only on the magnitude of the applied field and the value of g_1 .

However, the magnetic field "felt" by the electron spin of the $A^{13}CO$ radical depends not only on the magnitudes of the applied field and the value of g_1 but also on the value of the orientation of the nuclear spin. When the nuclear spin is in the α orientation, the magnetic moment due to the nuclear spin is along the z -axis, the electron of $A^{13}C_\alpha O$ feels a **stronger** field than the applied field (see vector diagram of figure 37). When the nuclear spin is in the β orientation, the electron of $A^{13}C_\beta O$ feels a **weaker** field than the applied field (see vector diagram

of figure 37). Because the ACO radical has a smaller g factor than the B radical, the ACO radical inherently precesses more slowly than the B radical. If a magnetic field is added to the ACO radical it will precess more rapidly and at a rate that is more similar to the B radical. Therefore the **difference** in precessional rates will become smaller and ISC will become **slower**. On the other hand, if a magnetic field is subtracted from the ACO radical it will precess more slowly and at a rate that is less. Therefore, the **difference** in precessional rates will become larger and ISC will become **faster** than the B radical. These ideas are captured by the vector model in Figure 37 where the projection of the nuclear spin on the z-axis is shown for the α and β orientations. For the α orientation the electron spin on $A^{13}C_{\alpha}O$ feels a field 60 Gauss stronger than H_Z , and for the β orientation the $A^{13}C_{\beta}O$ radical feels a field 60 Gauss weaker than H_Z .

In Figure 36, the transitions between E^- levels (or transitions between E^+ levels) correspond to NMR transitions (e.g., $\beta_e\alpha_N \rightarrow \beta_e\beta_N$) because for these transitions, **the nuclear spins, not the electron spins undergo reorientation**. Although the NMR spectra of radicals are technically difficult to observe because of line broadening resulting from the electron spin coupling to the nuclear spin, the radical $A^{13}CO$ does in principle possess an NMR spectrum, which is shown schematically in Figure 39. The separation of the levels in Figure 36 do not take the nuclear Zeeman coupling into account. When this is done, the energy gaps for nuclear transitions become different in energy and the difference in transition frequencies is equal to the hyperfine coupling constant. Just as the ESR spectrum of the electron spin of the $A^{13}CO$ radical is split into two lines separated by the coupling constant of 60 gauss, **the NMR spectrum of the nuclear spin of the $A^{13}CO$ radical is also split by the same amount**. The NMR spectrum of the $A^{13}CO$ radical may be considered in the same way that any AX NMR spectrum is considered, except that the nucleus is coupled to an electron possessing an enormous "chemical shift" many orders of magnitude larger than any nuclear chemical shift. For example, the "center" of the NMR spectrum of the $A^{13}CO$ radical in a magnetic field of 10,000 gauss is at a frequency of ca. $10 \times 10^6 \text{ s}^{-1}$ (Megahertz), whereas the "center" of the ESR spectrum of the $A^{13}CO$ radical in a magnetic field of 10,000 gauss is ca. $28,000 \times 10^6 \text{ s}^{-1}$ (Megahertz). The typical variation of chemical shifts for ^{13}C NMR spectra is ca. 100×10^{-6} (10,000 gauss) = 1 gauss. The hyperfine splitting of 120 gauss of the radical is thus two orders of magnitude greater than the entire normal range of NMR chemical shifts for molecules.

CIDNP Resulting from Nuclear Spin Orientation Dependent ISC

We have now justified the more rapid ISC for the triplet $A^{13}C_{\beta}O \cdot \cdot B$ geminate dynamic radical pair relative to the $A^{13}C_{\alpha}O \cdot \cdot B$ geminate radical pair. For an extreme case, if the rate of triplet to singlet ISC for the β spin containing pairs were fast enough, we could imagine that after a time (τ_{ISC}^{β}) all of these pairs might undergo combination reactions upon reencounters after ISC. If the rate of ISC of the pairs containing the α spins is slow relative to the time τ_{ISC}^{β} ,

the partners in the pair will separate to form free radicals that can be completely scavenged within a time $\tau^{\alpha}_{\text{SCAV}}$. In this extreme scenario, the $A^{13}\text{C}_{\beta}\text{O} \cdot \cdot \text{B}$ pairs undergo exclusive recombination to form $A^{13}\text{C}_{\beta}\text{OB}$ after a time of ca. $\tau^{\beta}_{\text{ISC}}$ and the free radicals $A^{13}\text{C}_{\alpha}\text{O}$ would be scavenged to form $A^{13}\text{C}_{\alpha}\text{O}$ after a time of ca. $\tau^{\alpha}_{\text{SCAV}}$. This extreme case is shown schematically at the top of Figure 40.

If the ^{13}C NMR spectrum of the system were observed after time $\tau^{\alpha}_{\text{SCAV}}$, there would be no radicals left and the "P \rightarrow I" process would be complete. Figure 40 shows schematically the population of the nuclear spin levels at this point. From Figure 40 we note that the β level of the combination product, ACOB would be overpopulated. Because of the overpopulation of the β level, stimulated downward transitions would be more favored than stimulated upward transitions and the spectrum of the geminate coupling product would appear as an emissive line (Figure 40) rather than the usual, much weaker absorption spectrum of a solution containing an equivalent molar amount of ACOB (Boltzmann spectrum shown bottom left of Figure 40). The **position** of the line is the same for both Boltzmann and polarized spectra because it is the energy level **populations**, not the energy gaps between levels (which determine line position) that are influenced by the processes producing CINDP.

If the ^{13}C NMR spectrum is taken after scavenging occurs, the spectrum would result from stimulation of nuclear spin levels that are tremendously overpopulated in the α level (Figure 40). Thus, stimulated upward transitions would occur but the intensity of the transitions and the observed signal would be far greater than is observed under normal (Boltzmann) conditions. Thus, the ^{13}C NMR spectrum of the scavenged products would appear in enhanced absorption. If there were no nuclear spin relaxation which occurred in the radicals before geminate reaction and scavenging reaction, the enhancement intensities of emission and absorption would be roughly equal because they would be much stronger than the signal

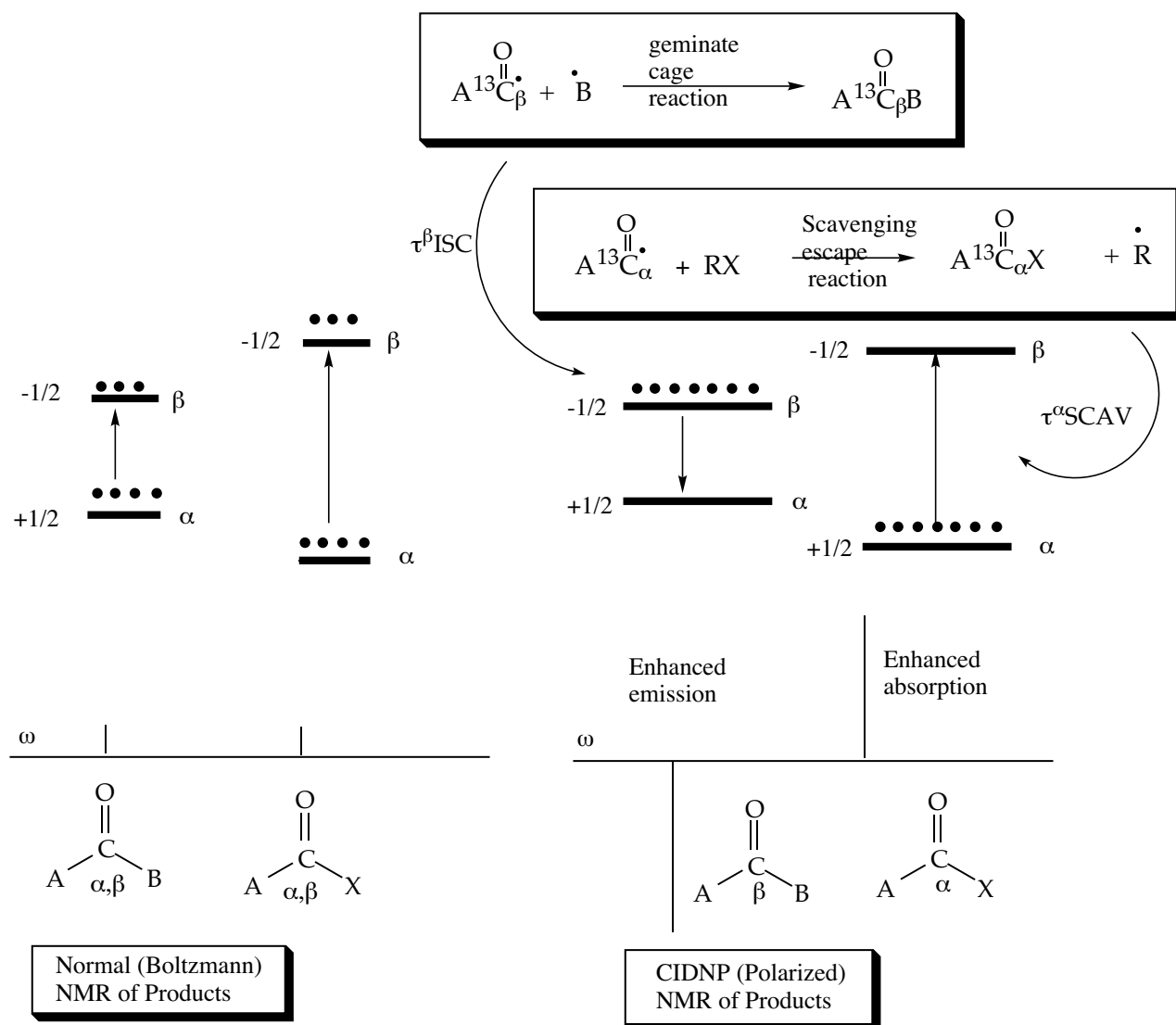


Figure 40. Conventional (left) and CIDNP spectra of the combination and scavenged products from the photolysis of ACOB in an NMR spectrometer. See text for discussion.

due to the Boltzmann intensity. Typical ^{13}C nuclear spin relaxation times are of the order of seconds, which sets an upper limit to the effective time after a photolysis that a CIDNP spectrum can be observed.

In summary, if hyperfine coupling determines the ISC of the $A^{13}CO^{\bullet} \cdot B$ radical pair and the formation of the geminate coupling product, $A^{13}COB$, the resulting NMR spectra possess some remarkable features: (1) the signal for the recombination product $A^{13}COB$ would be an "emissive" signal rather than the normal absorptive signal, and the scavenged $A^{13}COX$ product would be an absorptive signal that is much stronger in intensity than expected from the number of moles of product produced; (2) if the exciting light is extinguished, the

entire NMR spectrum would disappear in a matter of seconds or less as the ^{13}C nuclei undergo relaxation; (3) upon reirradiation, the NMR spectrum of an emission for the A^{13}COB product and a strong absorption for the A^{13}COX product would reappear; (4) these processes might be repeated over and over again with little loss of signal if the amount of ketone required to produce the signal is quite small relative to the ketone employed.

Kaptein's Rules. Applications of CIDNP to Photochemical Reactions

Eqs. 40 and 41 and the vector model form the basis of **Kaptein's rules** which allow a prediction of the origin of a product showing a certain CIDNP polarization, i.e., either geminate cage or escape, **if the primary geminate pair is a triplet (the most common case)**. The rules may also be applied to the less common situation for which a singlet radical pair is the primary product. In this case the rules for the sign of the CIDNP are reversed because the formation of a geminate cage product becomes disfavored by more rapid ISC of the geminate pair.

The vector model of Figure 22 shows schematically the $\text{T}_0 \rightarrow \text{S}$ ISC. The vector description shows that ISC requires a rotation of one electron spin vector relative to the other about the z-axis. ISC occurs when the electron spin vectors of the triplet, originally 0° out of phase, twist to become 180° or π radians out of phase. Let τ_α be the time it takes to make this twisting motion for the $\text{A}^{13}\text{C}_\alpha\text{O}$ radical and let τ_β be the time it takes to make this twisting motion for the $\text{A}^{13}\text{C}_\beta\text{O}$ radical. The two times τ_α and τ_β are equal to the inverse of the difference in precessional rates $\Delta\omega_\alpha$ and $\Delta\omega_\beta$ given by Eqs. 40 and 41, respectively.

In principle, Kaptein's rules (an abbreviated form given in Table 2) can be applied to determine any one of the three parameters for reaction starting from a geminate triplet radical pair, if the other two parameters are known: (1) the magnitude and sign of the difference in g factors; (2) the magnitude and sign of the hyperfine coupling constant; and (3) the geminate (cage combination) or free radical (cage escape) nature of products. Since spectroscopic parameters 1 and 2 are generally available from ESR spectra, the third, chemical, parameter is commonly determined by CIDNP experiments.

In some cases, parameters 1, 2 and 3 are known. In such situations, the multiplicity of the exciting state may be deduced from CIDNP data, since triplet precursors of radical pairs will lead to one set of predictions for the observed CIDNP spectrum and singlet precursors of radical pairs will lead to a different set of predictions, for the same set of known parameters.

Table 2. Abbreviated table of Kaptein's rules for polarization of geminate cage products.*

Spin State of Radical Pair	$\Delta g > 0$	$\Delta g > 0$	$\Delta g < 0$	$\Delta g < 0$
	$a > 0$	$a < 0$	$a > 0$	$a < 0$

Singlet	Emission	Enhanced Absorption	Enhanced Absorption	Emission
Triplet	Enhanced Absorption	Emission	Emission	Enhanced Absorption

*The opposite polarization is expected for scavenged escape products of the radical pair. Free radicals which encounter to produce combination products behave qualitatively the same as triplet geminate pair with respect to the prediction.