

### 13. Primary Photochemical Reactions. Spinomers

Step 2 in the paradigm of the case history of our ketone photochemistry (Figure 27) is the formation of a geminate radical pair by  $\alpha$ -cleavage. In order to understand the subsequent spin chemistry and magnetic resonance spectroscopy associated with this geminate radical pair and the other reactive intermediates, as well as the final product, we must examine in some detail the spin structure and dynamics of the radical pair  $\text{ACO}\cdot\cdot\text{B}$ . For the spin structure we introduce the concept of **electronic and nuclear spinomers**, species which have **identical chemical structures** but differ in some measurable aspect of their spin structure. We shall see that the chemical structure of a radical pair  $\text{ACO}\cdot\cdot\text{B}$  has a complex spin structure when we consider nuclear spin, electron spin, and the influence of applied magnetic fields. Thus, what looks like a simple structure  $\text{ACO}\cdot\cdot\text{B}$  can actually be viewed as corresponding to a large number of distinct spinomers. We shall also see that the molecular dynamics (relative diffusional and rotational motions) of  $\text{ACO}\cdot\cdot\text{B}$  will play an important role in the spin chemistry and magnetic resonance spectroscopy of the system. The distance dependence of the exchange interaction,  $J$  (which causes the S and T states to separated in energy) and the influence of  $J$  on intersystem crossing and mixing of magnetic energy levels are dominant factors in determining the spin chemistry and magnetic resonance spectroscopy of various spinomers of a dynamic radical pair.

After a consideration and description of the spinomers for some simple examples of the  $\text{ACO}\cdot\cdot\text{B}$  system, we shall return to an analysis of steps 2, 3 and 4 (Figure 27) of the case history system.

#### **Electronic and Nuclear Spinomers.**

The geminate radical pair,  $\text{ACO}\cdot\cdot\text{B}$  is often described in textbooks with a dot presenting an odd electron on each radical. This model is lacking in any spin characteristics. Thus, at the spinless level, it is expected that a collision between two radicals will lead to the rapid and efficient radical-radical reactions such as formation of a bond to form  $\text{ACO-B}$ . In this simple model there is no basis for lack of reactivity between two radicals. Taken to its logical conclusion, when radicals are produced in pairs by the cleavage of a bond, they would be expected to react efficiently by bond reformation, since there is no apparent barrier to recombination reactions. This conclusion is contrary to the results of many photoreactions for which triplet radical pairs are produced, but have very inefficient geminate reactivity and form free radicals efficiently. Let us now see what happens to the structure of a primitive, spinless model of the geminate radical pair  $\text{ACO}\cdot\cdot\text{B}$  when we (1) couple a single nuclear spin ( $^{13}\text{C}$  on the carbonyl carbon) to one of the odd electrons; (2) introduce correlated electronic

spins to represent the 2 odd electrons; and (3) introduce a strong applied magnetic field.

### **Enumeration of Spinomers of the $\text{ACO} \cdot \cdot \text{B}$ Geminate Radical Pair.**

It will be assumed that the  $\text{ACO} \cdot \cdot \text{B}$  radical pair possesses a well defined chemical structure in terms of bond connectivities. Keeping these connectivities fixed, we seek to enumerate the number of distinct spin structures that are possible when we consider: (1) an isotopomeric  $\text{ACO} \cdot \cdot \text{B}$  pair with a carbonyl carbon atom that is either  $^{12}\text{C}$  or  $^{13}\text{C}$ ; (2) the correlation of the unpaired electrons; and (3) the application of a magnetic applied field.

We start with a "spinless" radical pair,  $\text{ACO} \cdot \cdot \text{B}$ . The effect of considering isotopes at the carbonyl carbon is to generate two isotopomeric pairs:  $\text{A}^{12}\text{CO} \cdot \cdot \text{B}$  and  $\text{A}^{13}\text{CO} \cdot \cdot \text{B}$  (Figure 30). These pairs are conventionally termed **isotopomers** (chemical structures possessing the same elemental composition, but different isotopic composition). Without consideration of spin, at the level of the "dot" representation of odd electrons, these two isotopomeric pairs are expected to be comparably reactive except for a weak mass isotope effect.

Next, let us introduce the effect of electronic spin correlation (resulting from electron exchange, J) without respect to the separation of the spins in space (this is important and we shall deal with it when we consider the **dynamic** radical pair below). By introducing electron spin and electron spin correlation, each isotopomer must now be considered as one of two **electronic spinomers**: a triplet, T, or a singlet, S. In the absence of an applied magnetic field, the initial "spinless" structure for a radical pair becomes **four** different electron correlated spinomers, two triplet and two singlet spinomeric structures:  $^{12}\text{S}$ ,  $^{13}\text{S}$ ,  $^{12}\text{T}$  and  $^{13}\text{T}$  (Figure 30). These structures are expected to have different reactivity toward bond forming reactions.

Now let us introduce the effect of a strong magnetic field,  $\mathbf{H}_0$ , which will cause a Zeeman coupling of the field to the electron and nuclear spins. The Zeeman effect orients the magnetic moments of all the electronic and nuclear spins of the pairs along the field direction. For the  $\text{A}^{12}\text{CO} \cdot \cdot \text{B}$  pair, the two electronic spinomers,  $^{12}\text{T}$  and  $^{12}\text{S}$ , will split into the **four Zeeman electronic spinomers** (Figure 30):  $^{12}\text{S}$ ,  $^{12}\text{T}_-$ ,  $^{12}\text{T}_0$ , and  $^{12}\text{T}_+$ . For the  $\text{A}^{13}\text{CO} \cdot \cdot \text{B}$  pair, the two structures  $^{13}\text{S}$  and  $^{13}\text{T}$  will break up into **eight nuclear-electronic Zeeman spinomers** (Figure 30):  $^{13}\text{S}^{\alpha,\beta}$ ,  $^{13}\text{T}_-^{\alpha,\beta}$ ,  $^{13}\text{T}_0^{\alpha,\beta}$ , and  $^{13}\text{T}_+^{\alpha,\beta}$ , where the superscript indicates the nuclear spin orientation in the field. Thus, our analysis of the hypothetical radical pair leads to the conclusion that the simple idea of a radical pair,  $\text{ACO} \cdot \cdot \text{B}$ , involving simply two orbitally unpaired electrons becomes quite

interesting and complex when electron correlation, a magnetic field, and even one nuclear spin is introduced. This hypothetical pair, a three spin system, contains most of the important features of spin systems.

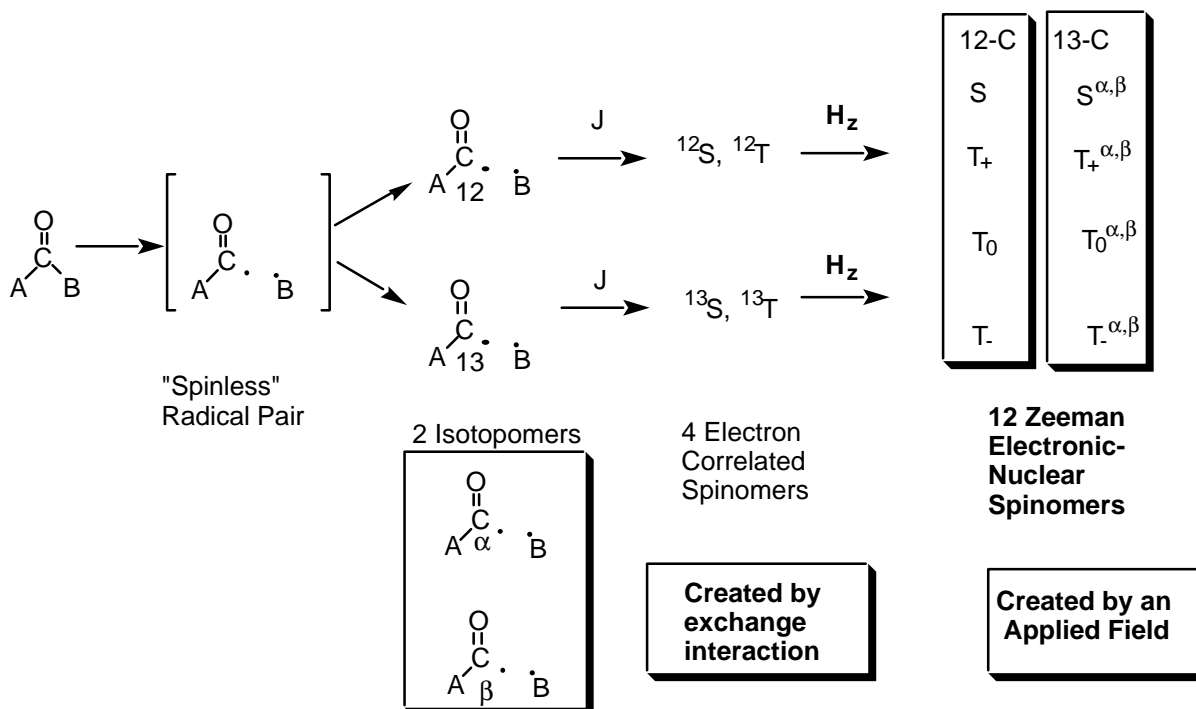


Figure 30. Evolution of spinomers as the result of introducing electron exchange, a magnetic isotope and an applied field.

It is important to recognize that **each of the 12 spin states shown in Figure 30 correspond to completely independent and distinct spin species.** A radical pair can be in one of these states or the other, but cannot be simultaneously in more than one of these states at any instant. For example, each state potentially possesses a distinct rate of intersystem crossing, a distinct ESR spectrum and distinct chemical reactivity. There will be a certain rate of interconversion of spinomers for each of the two isotopomers. For example, the four electronic Zeeman spinomers of the  $A^{12}CO \cdot B$  pair will possess a certain rate of interconversion, but only the S state will be capable of undergoing radical pair combination reactions. All of the 8 nuclear-electronic Zeeman spinomers of the  $A^{13}CO \cdot B$  are capable of interconversion, but only the  $S^{\alpha,\beta}$  pair is reactive toward radical pair combination reactions. The S states will not display any ESR signal (they do not possess net electron spin to couple with an applied field!). The  $^{13}C$  containing radicals will show ESR spectra with hyperfine splitting and the  $^{12}C$  containing radicals will not show hyperfine splitting. We shall see that even in solution the selection rules for interconversion of spinomers are strict and that angular momentum and magnetic energy must always be conserved.

As a further example of the differences between isotopomers and spinomers, a radical pair containing  $^{14}\text{C}$  at the carbon is an isotopomer of the  $\text{A}^{12}\text{CO} \cdot \text{B}$  radical pair, but not a spinomer because both  $^{12}\text{C}$  and  $^{14}\text{C}$  have a nuclear spin of 0. Thus, magnetically,  $^{12}\text{C}$  and  $^{14}\text{C}$  behave qualitatively the same, so that in terms of spin the  $\text{A}^{14}\text{CO} \cdot \cdot \text{B}$  pair is identical to the  $\text{A}^{12}\text{CO} \cdot \cdot \text{B}$  pair, but qualitatively different from the  $\text{A}^{13}\text{CO} \cdot \cdot \text{B}$  pair!

We now consider an extension of the radical pair model to a more realistic dynamic radical pair by introducing the critical feature of molecular dynamics which recognizes the feature that, in solution, the two partners of a pair undergoing random diffusional motion influences the electron correlation due to electron exchange and the magnetic interactions which are distance dependent.