

11. Magnetic Resonance and Spin Chemistry. A Paradigm and a Case History

At the beginning of the Chapter (Figure 1) a paradigm was proposed that a majority of investigated organic photochemical reactions involve photochemical primary processes initiated in the lowest triplet state, T_1 , to produce a geminate triplet radical pair (or triplet biradical) which then proceeds to products in secondary reactions. Since many photochemical reactions of organic molecules occur from the triplet electronically excited state and produce triplet geminate radical pairs (or biradicals) as the primary photochemical products, it is important to have a general paradigm to guide the mechanistic interpretation and experimental methods for understanding and investigating such reactions. Figure 26 reviews the key intermediates in such a paradigm. We are now interested in showing how the techniques and concepts of magnetic resonance (radiative transitions between magnetic energy levels) and spin chemistry (radiationless transitions between magnetic energy levels) can elucidate photochemical reaction mechanisms.

In Figure 26 we will consider the following stages of a case history photochemical process:

- (1) the intersystem crossing step, $S_1 \rightarrow T_1$;
- (2) the primary photochemical step, $T_1 \rightarrow {}^3\text{RP}$;
- (3) the intersystem crossing step, ${}^3\text{RP} \rightarrow {}^1\text{RP}$;
- (4) the product forming step, ${}^1\text{RP} \rightarrow \text{P}$.

The paradigm we shall develop will be analogous for weakly coupled radical pairs and weakly coupled flexible biradicals, so that for the sake of simplicity, the discussion will mainly refer only to radical pairs. One should keep in mind that in nearly all of the discussion the word "flexible biradical" can be substituted for "radical pair". It is also important to note at this point that if a photochemical reaction is investigated in a NMR spectrometer or in a ESR spectrometer the intermediates in Figure 26 are in a high magnetic field, so that the magnetic energy diagrams must consider the effect of the field on steps 1-4 below.

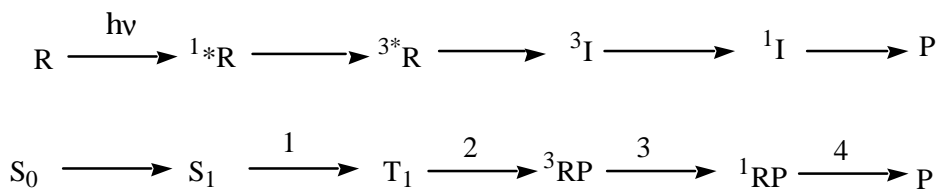


Figure 26. Simplified paradigm of a photochemical process proceeding through a triplet electronically excited state, T_1 .

Regions of Chemical Space and Spin Space Explored During a Photochemical Reaction.

We have seen in Chapter XX that electronic surface energy diagrams are extremely useful in visualizing the electronic features of photochemical reactions. We shall now combine the "chemical space" of electronic energy surfaces and "spin space" of the vector model to examine a case history of a photochemical reaction. It will be shown that the intersystem crossing step, $S_1 \rightarrow T_1$ occurs "vertically" in a region of the energy surface for which the exchange interaction is very large. Thus, this step can be treated in terms of a vertical jump (spectroscopic) of a representative point between energy surfaces described for radiative and radiationless transitions. The remaining steps, $T_1 \rightarrow {}^3RP \rightarrow {}^1RP \rightarrow P$, involve bond breaking, separation and reencounters of radical pairs and bond formation so that 3RP and 1RP constitute a **dynamic radical pair**. These processes involve both horizontal and vertical motion of the representative point on energy surfaces separated by various values of J . We shall see that the variation of J strongly influences the magnetic resonance spectroscopy and the spin chemistry of the dynamic radical pair.

Photochemical α -Cleavage of Ketones as a Case Study

We shall now use a "case study", the α -cleavage reaction of a ketone in its triplet state, to bring together the principles of the vector model to understand magnetic resonance spectroscopy and spin chemistry. Figure 27 shows the four steps 1-4 of the general paradigm of Figure 26 expressed in terms of a ketone, ACOB. We shall examine each of these steps to develop a working paradigm for photochemical reactions proceeding through triplet states of organic molecules.

We proceed with an analysis as follows: (1) For step 1, we shall examine the mechanism of the intersystem crossing step, $S_1 \rightarrow T_1$, in zero field and in high field. We shall ask how is angular momentum conserved in this step which involved an obvious change in spin, i.e., what mechanism of coupling is responsible for inducing the spin change? We shall also consider the magnetic resonance spectroscopy of the T_1 state that is formed and how this spectroscopy can provide both information on the mechanism of coupling that is responsible for the intersystem crossing and the electronic structure of the T_1 state. We shall see that the intersystem crossing step actually "locks" spin information into the triplet and that this spin information may be transferred to the radical pair produced in step 2; (2) For step 2, we shall examine the elementary step of bond breaking in zero field and in high field. We shall also see that step 2 and step 3 are intimately connected through the paradigm of a dynamic radical pair and

that the concept of the dynamic radical pair is required to understand the magnetic resonance and spin chemistry of the system; (3) For step 4, we shall show that the intersystem crossing step of the dynamic radical pair "locks" nuclear spin information into the products, P.

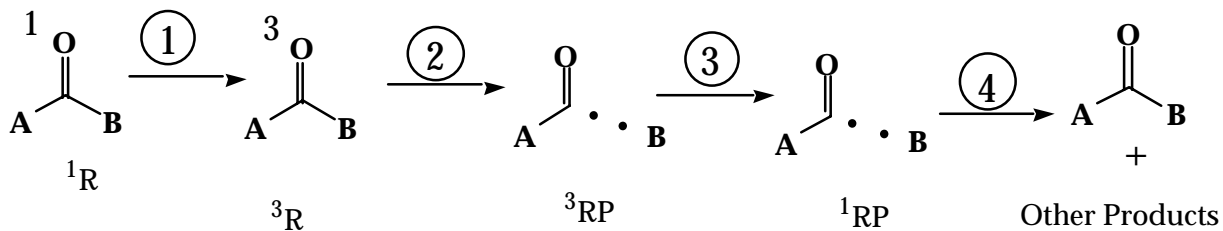


Figure 27. Paradigm for the α -cleavage reaction of ketones.