Part 3

Theory and Applications Pertaining to Photochemical Processes

Chapters 1-4 treated thermal reactions. In Chapters 5 and 6 the theoretical concepts needed to understand photochemical reactions are explained. Chapter 5 begins by reviewing the gualitative experimental features that characterize most photochemical processes. The purpose of this review is to focus attention on those aspects of particular excited-state potential energy surfaces that play crucial roles in rate-determining processes because the slow rate-determining steps determine the outcome of photochemical reactions. An important principle is the Kasha rule (Kasha. 1950) that radiationless transitions among excited singlet states usually occur very quickly compared either to fluorescence or to a chemical reaction. Thus, it is only necessary to consider the lowest-excited-singletstate potential energy surface, since it is on this surface that the system may eventually undergo chemical reaction. Chapter 5 also shows that the strategy for using symmetry concepts to probe photochemical problems is very much the same as for thermal reactions. It is still necessary to seek symmetry-imposed activation barriers in the appropriate (excited) potential energy surface. In addition, avoided (or real) crossings of the excited- and ground-state surfaces must be sought, since the system yields the commonly observed ground-state products through these funnels.

Chapter 6 presents a quantitative analysis of the rates of internal conversion and intersystem crossing. This treatment will provide understanding of how such rates depend upon the shapes and energy spacings of the potential energy surfaces between which the radiationless process takes place, though the treatment does not provide the mechanics to compute the rates from first principles. This analysis will show that radiationless rates will be rapid when the surfaces approach one another closely with similar slopes and when there are high frequency vibrational modes available for digesting the excess electronic energy. In the case of intersystem crossing, considerations of orbital angular momentum favor certain transitions [e.g., $(n\pi^*) \rightarrow (n\pi^*)$] over others $[^1(n\pi^*) \rightarrow (n\pi^*)]$. Knowing how these radiationless rates depend upon physical characteristics

of the ground and excited states of the molecule enables one to design molecules with particular photochemical behavior and to interpret experimental data from many photoreactions.

In Chapter 7 the principles introduced in the Chapters 5 and 6 will be applied in a qualitative manner to several photoreactions.

Readers not entirely familiar with the Franck-Condon principle and other concepts relating to photon-absorption processes should read Appendix B before beginning Chapters 5–7.

Chapter 5

Introductory Remarks about Photochemical Reactions

5.1. Nature of Low-Energy Excited States

Electronic excitation arising from the absorption of one or more photons usually gives rise to an excited state having the same *spin symmetry* as the absorbing (ground) state. Transitions that do not conserve spin are more likely when the absorbing molecule contains one or more heavy atoms that allow the various spin states to be mixed via spin-orbit coupling (Turro, 1978). Excited states of different spin symmetry can also be populated via collisional energy transfer from an excited sensitizer molecule or atom (e.g., benzophenone or mercury).

The vast majority of stable compounds that can easily be used as reactionstarting materials have closed-shell singlet ground states (S_0) . Therefore, for most of the material in this chapter we assume that the ground state is a singlet. However, most of the conclusions are valid also for molecules having other types of ground states.

One-electron excitations arising from one-photon transitions can give rise to either singlet $(S_1, S_2, ...)$ or triplet $(T_1, T_2, ...)$ excited states. By convention these states are ordered on an electronic energy basis when assigning the labels S_1 , T_1 , and so on. Usually the triplet state arising from a given orbital transition (e.g., $n\pi^*$ or $\pi\pi^*$) lies below its corresponding singlet state. The most common explanation for this arrangement is that the triplet state contains two electrons of the same m_s value and this lowers the energy by exchange interaction relative to the singlet—that is, the two electrons of the triplet state are kept apart by the Pauli exclusion principle. However, this explanation is not complete. For excited states in which a bonding-to-antibonding orbital transition occurs, the charge distribution character of the singlet and triplet states can differ significantly, and this difference in electron distribution must also be considered.

Singlet $(\pi\pi^*)^1$ excited states can be represented approximately by Slater determinant wavefunctions of the form

$$\frac{1}{\sqrt{2}}\left[|\ldots \pi \alpha \pi^* \beta| - |\ldots \pi \beta \pi^* \alpha|\right]$$
(5.1)

(Cook, 1978; Pilar, 1968; Turro, 1978). Using the following (approximate) representations of the π and π^* orbitals in terms of the individual atomic orbitals (P_A and P_B) and the amplitudes (x and y) on each atom,

$$\pi \cong x P_{\rm A} + y P_{\rm B} \tag{5.2}$$

$$\pi^* \cong y P_{\rm A} - x P_{\rm B},\tag{5.3}$$

to express the active electron parts of the Slater determinants in terms of their atomic components, we find

$$(\pi\pi^*)^1 \cong \{2xy[P_A P_A - P_B P_B] + (y^2 - x^2)[P_B P_A - P_A P_B]\} \frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} .$$
(5.4)

The same analysis of the triplet state determinant gives

$$(\pi\pi^*)^3 = |\dots \pi\alpha\pi^*\alpha| = [(x^2 + y^2)(P_{\rm B}P_{\rm A} - P_{\rm A}P_{\rm B})] \frac{\alpha\alpha}{\sqrt{2}}.$$
 (5.5)

In writing equations 5.4 and 5.5, the last two columns of appropriate Slater determinants are simply expanded; the other columns contain the *passive* orbitals, which need not be explicitly addressed here. For π bonds that are not extremely polar $x \cong y$, in which case the $(\pi\pi^*)^1$ state is dominated by the *ionic* terms $(P_A P_A - P_B P_B)$, whereas the $(\pi\pi^*)^3$ state contains only radical or *covalent* terms $(P_B P_A - P_A P_B)$. This strong difference in the two charge densities plays an important role in making the $\pi\pi^*$ triplet state lower in energy than the singlet (which has both electrons in the same region of space).

The description of the relative energetics of the singlet and triplet states just given has been simplified by assuming that the π and π^* orbitals can be expressed in terms of the same atomic orbitals. More sophisticated *ab initio* calculations on singlet $\pi\pi^*$ states indicate that it is more correct to think of the π and π^* orbitals as having different radial extent or size (McMurchie and Davidson, 1977). However, detailed investigations of this problem indicate that the formulation in terms of the ionic and covalent charge-density picture is qualitatively correct. It is important to keep in mind that, as a result of the large difference in electron distribution, these excited states may have physical and chemical properties that are very different from those of the ground state and that depend upon spin multiplicity (Pearson, 1976; Turro, 1978).

5.2. Energy Redistribution in the Singlet Manifold

We now consider what happens to the energy that has been stored in the electronic framework of the system after an excited state is formed. In an isolatedmolecule gas-phase system (Rice, 1971) the total energy must be conserved within the degrees of freedom of the electronic-and-nuclear motion (vibration, rotation, translation) of the molecule. In condensed media, it is possible eventually (on time scales appropriate to vibrational relaxation, $\sim 10^{-12} - 10^{-10}$ sec) for energy to be dissipated to the surrounding medium.

Two experimental observations indicate the processes that occur with the highest rate (those fast enough to lead to observed phenomena). First, it is observed that fluorescence $(S_n \rightarrow S_0 + h\nu)$ almost never occurs from higher singlet states $(S_n, n > 1)$ (however, see Beer and Longuet-Higgins, 1955). Even when S_2, S_3, \ldots are excited from S_0 , the fluorescence usually comes from S_1 , a fact known as Kasha's rule (1950). This rule states that when S_2 , S_3 ... are excited, some of this *electronic* energy must be digested (on a time scale that is fast with respect to fluorescence, namely, $< 10^{-6} - 10^{-10}$ sec) by the degrees of freedom associated with nuclear motion, since in this isolated molecule the total energy must remain constant. This process of digesting electronic energy $(S_{n+1} \rightarrow S_n)$ is called *internal conversion*; its physical origin will be explored in more detail in the following chapter.

A second important observation is that the products of most photochemical reactions of molecules that contain more than a few (\sim 5) atoms need not be electronically excited. Thermal and photochemically induced chemiluminescent reactions do occur, but they are exceptions. Most photochemical reactions yield directly (without much fluorescence) a high fraction of the products in their ground (S_0) state. This experimental fact indicates that photoreactions do not occur entirely on an excited-state potential energy surface (most likely, S₁) followed by radiative decay (fluorescence) of the products; rather, the excited-state reactants often end up on the ground-state potential energy surface of the product molecule(s). How then can an excitedstate reaction ever be symmetry-forbidden if the ground-state energy of the products lies below the energy of the photochemically prepared state? To answer this question it is necessary to understand how internal conversion occurs. A more detailed analysis of internal conversion will show that, if the S_0 and S₁ potential energy surfaces vary with some reaction coordinate (geometrical distortion) as in Figure 5-1, then the initially excited S_1 molecules will have a good chance to react and to yield ground-state (S_0) products by hopping from the S_1 surface to S_0 near the close approach of S_0 and S_1 . In Chapter 6 it will be shown that the rate of hopping depends on the number of internal degrees of freedom that the molecule can use to digest the electronic energy. Near the

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avoided crossing, there is little electronic energy to be digested, so internal conversion is facilitated at these geometries. For small molecules with low densities of internal states (vibration, rotation, translation) the rate of hopping is slower and the system is more likely to remain on S_1 . Remember that, in gasphase radiationless transitions, total energy must be conserved. Therefore, the system gains internal energy even though the diagram in Figure 5-1 shows the system hopping from S_1 to S_0 , thereby losing electronic energy. This internal energy can be vibrational motion along Q_r , or it can be vibration or rotation along degrees of freedom orthogonal to Q_r (not shown in the figure). The larger the number of vibrational modes, the less likely it is for the energy to remain for a substantial length of time in the Q_r degrees of freedom. In condensed media, the excess vibrational-rotational energy can also be dissipated to surroundings in $10^{-10}-10^{-12}$ sec.

On the other hand, if the S_0 and S_1 surfaces have the properties shown in Figure 5-2, the initially prepared S_1 molecules will have to overcome an *additional* activation barrier for reaction to occur. Such S_1 surfaces would then lead to photochemically forbidden reactions: the excited molecule will be trapped on the reactant side of the barrier. If the photon energy placed the system high enough on the S_1 surface to overcome the barrier, the S_1 molecule may undergo internal conversion to S_0 near an avoided crossing or actual intersection of S_0 and S_1 . As will be seen later, the excited S_1 molecules can most efficiently hop (undergo internal conversion) to S_0 at such near crossings of S_0 and S_1 (Michl, 1972, 1974, 1975). After reaching the S_0 surface, the system can either yield products or the reactants can be restored. The quantum yields for these two processes will depend upon both the precise shape of the S_1 and S_0 surfaces and the photon energy. The nature of the distortion coordinates that





coordinate is obtained, it is necessary to seek symmetry-imposed reaction barriers that arise on the S_1 surface between the reactant geometry (as determined by the Franck-Condon principle; see Herzberg, 1966, and Appendix B) and the funnel geometry through which the reaction proceeds. As in Chapter 1-3, this again means finding where the potential surface (S_1) passes through extrema (barriers and minima) as a result of avoided crossings.

Appendix B outlines the theory of an electronic transition in which a ground-state (S_0) molecule absorbs a photon and moves to an excited surface S_n $(n \ge 1)$. Both the common Franck-Condon approach and a partly classical picture are presented; these tools allow one to guess the geometry at which a molecule will enter an excited-state (S_n) potential energy surface. These entry geometries must be known before walking along the S_1 surface as outlined above can be undertaken.

5.3. Processes Involving Triplet States

Thus far, our attention has been restricted to processes that take place on the singlet-state manifold. If spin-orbit effects were entirely negligible, the triplet states would not become populated after the primary photochemical event, and these spin-forbidden states could be ignored. However, triplet excited states are important because even a small amount of spin-orbit coupling can cause intersystem crossings $(S_n \rightarrow T_m)$, especially when the S_n and T_m surfaces approach or intersect. Moreover, the excited triplet states can also be directly populated in the primary event either by using electron impact on the neutral S_0 or by forming the doublet anion of S_0 (S_0) and subsequently detaching an electron from the doublet anion of S_0 (S_0) and subsequently detaching an

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When a triplet state becomes populated, it can undergo several processes. Higher triplet states $(T_n, n > 1)$ usually decay in a radiationless manner to T_1 on a time scale that is very fast relative either to backward intersystem crossing $-T_1 \rightarrow S_1$ or S_0 —or to radiative decay (phosphorescence)— $T_n \rightarrow S_m + h\nu$ both of which are slow spin-forbidden events. After undergoing internal conversion $(T_n \rightarrow T_1)$, the T₁-state molecules usually live for 10^{-3} -10 sec. During this time, which is much longer than the radiative lifetime of the S_1 state $(10^{-10}-10^{-6}$ sec), the triplet molecules can undergo chemical reaction or decay radiatively or by intersystem crossing to S_0 . Since T_1 usually lies below S_1 , it can no longer return to the excited singlet manifold. We will make this point clearer in the next chapter. The longer lifetime of the T_1 state plays an important role in its chemical reactivity-namely, time is available for reagents to arrange themselves in a geometrically favorable manner for initiation of reaction. The lifetime gives rise to one of the distinguishing features of triplet molecules-namely, the tendency to undergo two-step radical reactions rather than the concerted one-step reactions characteristic of singlets. For a reagent in the triplet state to react with a closed-shell (singlet) molecule and yield a closed-shell product-for example,

$$O-O$$

$$| |$$

$$O_2(^3\Sigma) + H_2CCH_2 \rightarrow H_2C-CH_2)$$

requires intersystem crossing. Such reactions are usually described by two steps. First, a triplet reagent bonds to the singlet molecule to form an intermediate triplet radical, for example,



which slowly undergoes intersystem crossing to become a singlet radical that finally allows the two radical fragments to close and form a bond.

When an excited molecule in a singlet or triplet state reaches the lowest T_1 state, the factors that determine whether it will react to form products and the products that will be formed are the same as those used in analyzing the fate of the S_1 -state molecules. The two preceding figures can be employed to explain the allowed and forbidden triplet reactions to yield singlet products by simply replacing S_1 by T_1 and making two modifications. First, the possibility for the T_1 and S_0 surfaces to intersect in a (3N-7)-dimensional space (for nonlinear molecules) must be considered; S_1 and S_0 can intersect in, at most, a (3N-8)-dimensional space. Second, when examining the rate of hopping from T_1 to S_0 , spin-orbit coupling effects must be included. The rates of $S_1 \rightarrow S_0$ internal

conversion and $T_1 \rightarrow S_0$ intersystem crossing are much different because the physical factors that govern these rates are different.

To predict whether a triplet-state reaction is allowed, one proceeds in the following way. First, the Franck-Condon principle is used to select those regions of nuclear configuration space that, upon the primary $(S_0 + h\nu \rightarrow S_n)$ event, are likely to be populated. The internal conversion $(S_n \rightarrow S_1)$ then occurs rapidly to give S_1 . Then, likely molecular deformation coordinates are sought, along which S_1 and T_1 approach closely or intersect and along which no high symmetry-imposed barriers on the S_1 surface occur. The intersystem crossing $(S_1 \rightarrow T_1)$ funnels will determine the molecular geometries at which T_1 is formed. Finally, starting at this point on the potential energy hypersurface at which T_1 is formed, additional deformations are sought, such that T_1 and S_0 intersect or approach closely and along which no high barriers exist on the T_1 surface. These $T_1 \rightarrow S_0$ funnels can yield either ground-state reactants or ground-state products, depending on the detailed nature of the $T_1 \rightarrow S_0$ funnel

Note that the approach in studying photochemical processes is similar to that for thermal reactions. Minima in S_1 and T_1 are sought because these minima often indicate where the excited surfaces (S_1 and T_1) come closest to S_0 . Although it is indeed possible for S_1 and T_1 to *intersect* S_0 , emphasis should not be placed on these crossing geometries; they contribute a subspace of smaller dimension than the dimension of S_0 , T_1 , or S_1 . The regions of space in which S_1 or T_1 comes close (within striking distance for the non-Born-Oppenheimer terms in the total Hamiltonian) are of higher dimension and thus more important. In addition to finding minima in S_1 or T_1 , the points at which S_1 and T_1 can cross or come close must be determined, and possible barriers in S_1 and T_1 must be sought.

Before proceeding to examples of photochemical reactions, it is necessary to explore further the physical mechanisms by which radiationless processes such as internal conversion and intersystem crossing occur. This knowledge is important because it will permit us both to predict when these events will be likely (occur at competitive rates) and to understand how isotopic substitution, heavy atoms, and vibrational state densities can be used to alter the rates at which they occur. This is the subject of Chapter 6.