## Chapter 7

## Examples of Photochemical Reactions

In this chapter six photochemical reactions will be analyzed by the methods of Chapter 6.

### 7.1. Dimerization of Two Ethylenes

From the treatment of ground-state thermal reactions (Chapter 1-3) the fourcenter concerted dimerization of two $S_{0}$ ethylene molecules is forbidden by symmetry. Recall that in $C_{2 v}$ symmetry the orbital-correlation diagram for this reaction is that shown in Figure 7-1. If the ground state ( $\pi^{2} \pi^{2}, \sigma^{2} \sigma^{2}$ ) and singly excited ( $\pi^{2} \pi^{*} \pi, \sigma^{2} \sigma^{*} \sigma$ ) configurations of reactants and products and the configurations with which they correlate are included, the configuration-correlation diagram shown in Figure 7-2, in which the $C_{\mathbf{2 v}}$ symmetries of these configurations are also indicated, is obtained. Not all of the configuration correlations are shown because it is important to examine first in more detail the type of photochemical event we wish to simulate. Following this examination, certain of these configurations can be eliminated.

Photochemical dimerization of ethylene might be viewed as a collision between $\left(\pi \pi^{*}\right)^{1}$ excited ethylene molecule and a ground-state $\pi^{2}$ ethylene under $C_{2 v}$ symmetry. Analysis of the reaction requires expressing this localized (non-symmetry-adapted) excited species in terms of symmetry orbitals. Using the reverse of the transformation from a localized orbital to a symmetry-adapted orbital, the proposed experimentally prepared $\pi_{\mathrm{A}}^{2}\left(\pi \pi^{*}\right)_{\mathrm{B}}^{1}$ state (in which A and $B$ refer to the two isolated ethylene molecules) can be expressed as follows:

$$
\pi_{\mathrm{B}}=\pi_{a_{1}}+\pi_{b_{2}}, \quad \pi_{\mathrm{A}}=\pi_{a_{1}}-\pi_{b_{2}}
$$

and

$$
\pi_{\mathrm{B}}^{*}=\pi_{b_{1}}^{*}+\pi_{a_{2}}^{*}, \quad \pi_{\mathrm{A}}^{*}=\pi_{b_{1}}^{*}-\pi_{a_{2}}^{*}
$$

from which the localized (ethvlene + ethvlene*) configuration can he written


Figure 7-1
Orbital-correlation diagram for dimerization of ethylene.

$$
\pi_{A}^{2}\left(\pi \pi^{*}\right)_{B}^{1}=\left(\pi_{a_{1}}-\pi_{b_{2}}\right)\left(\pi_{a_{1}}-\pi_{b_{2}}\right)\left[\left(\pi_{a_{1}}+\pi_{b_{2}}\right)\left(\pi_{b_{1}}^{*}+\pi_{a_{2}}^{*}\right)\right]^{1}
$$

Keeping in mind that a singlet $\left(\pi \pi^{*}\right)^{1}$ state is represented by a combination of two Slater determinants, these orbital occupation patterns represent Slater determinant wavefunctions. This property of the wavefunctions, combined with the Pauli principle, allows one to eliminate the $\pi_{a_{1}} \pi_{a_{1}} \pi_{a_{1}}$ and $\pi_{b_{2}}^{3}$ pieces of this wavefunction; however, this local-orbital description still contains many symmetry pieces (e.g., $\pi_{a_{1}}^{2} \pi_{b_{2}} \pi_{b_{1}}^{*}$ has $\mathbf{A}_{2}$ symmetry). The analysis of the various symmetry pieces of this localized function is analogous to decomposing the six ${ }^{2} P$ states of $\mathrm{Na}^{*}$ into four ${ }^{2} \Pi$ and two ${ }^{2} \Sigma$ states when $\mathrm{Na}^{*}$ collides with $\mathrm{H}_{2}$ in $C_{2 v}$ symmetry.

The goal of this analysis is to determine whether there exists at least one photochemically accessible path for the reaction. An answer could be obtained by first analyzing the symmetry elements that are in the $\pi_{\mathrm{A}}^{2}\left(\pi \pi^{*}\right)_{\mathrm{B}}^{1}$ state, then constructing all configuration-correlation diagrams consistent with all of these symmetries, and looking for symmetry-imposed barriers arising on any of these surfaces. This procedure would be exceedingly tedious but can be simplified by the following method.

The orbital configuration diagram in Figure 7-1 shows that an excitation from the $b_{2} \pi$ orbital to the $b_{1} \pi^{*}$ orbital would have the best chance of producing an energetically downhill reaction surface because the $b_{2}$ and $b_{1}$ orbitals undergo a crossing (which incidentally causes the thermal reaction to be forbidden). Certainly this $b_{2} \rightarrow b_{1}$ excitation is a part of the local-orbital wavefunction described earlier (in that the $\pi_{\mathrm{A}}^{2}\left(\pi \pi^{*}\right)_{\mathrm{B}}^{1}$ function contains a $a_{1}^{2} b_{2} b_{1}$ component. This component is the one most likely to lead to stable products. Thus, a configuration-correlation diagram is constructed that contains only


Figure 7-2
Configuration-correlation diagram for dimerization of ethylene.
$b_{2} \times b_{1}=A_{2}$ symmetry that arise from the $b_{2} \rightarrow b_{1}$ excitation. Those configurations having $B_{1}$ and $B_{2}$ symmetry are eliminated from the configurationcorrelation diagram in Figure 7-2. These eliminated configurations include $b_{2} \rightarrow a_{2}$ and $a_{1} \rightarrow b_{1}$ excitations that do not promote an electron from an orbital whose energy is increasing into an orbital whose energy is decreasing. The resulting simplified configuration-correlation diagram, which is not meant to be quantitatively accurate, is shown in Figure 7-3. If experimental data for the $\pi \pi^{*}$ and $\sigma \sigma^{*}$ excitation energies of ethylene and cyclobutane and for the thermochemical $\Delta E$ for this reaction were available, the configuration-correlation diagram could be made more quantitative.

Because of the ( $b_{2}, b_{1}$ ) orbital crossing, the four configurations drawn in the configuration-correlation diagram would be degenerate at this crossing geometry at the level at which interelectron repulsion effects are ignored. However, the electron repulsions are not negligible and split the four configurations into four resulting states. At the crossing geometry, the triplet state is probably lowest in energy. The excited state, which is formed in the primary photochemical event, is-because of the forbidden nature of $S_{0}+h \nu \rightarrow T_{n}$


Figure 7-3
Simplified configuration-correlation diagram for dimerization of ethylene.
these requirements, though this state may only be the one most reactive component of the $\pi_{A}^{2}\left(\pi \pi^{*}\right)_{B}^{1}$ local-orbital excitation state.

After formation of the ${ }^{1} A_{2}$ state, internal conversion can occur near the point enclosed in the box in Figure 7-3. As the two ethylenes collide, via an $a_{2}$ accepting-mode distortion, internal conversion to the upper ${ }^{1} A_{1}$ state can be followed by "hopping" to the lower ${ }^{1} A_{1}$ surface at the funnel (labeled $F$ ), thereby giving either reactant or product molecules in their ${ }^{1} A_{1} \sigma^{4}$ ground state! The precise amount of ground-state reactant and ${ }^{1} A_{1}$ and ${ }^{1} A_{2}$ products depends upon the quantitative nature of the potential surfaces. Nowhere along the path from ${ }^{1} A_{2}$ to ${ }^{1} A_{1} *$ to ${ }^{1} A_{1}$ is a reaction barrier encountered. The $S_{1}$ surface may be thermodynamically uphill if the $\sigma^{2} \sigma \sigma^{* 1}$ state of cyclobutane lies above the $\pi^{2} \pi \pi^{* 1}$ state of the ethylene dimer. In such a case, an appreciable quantum yield of product would not be expected until the photon energy used to populate the $S_{1}$ state is sufficient to exceed the energy gap between the ( $\left.\pi \pi^{*}\right)^{1}$ absorption threshold and the point at which the $S_{1}$ state intersects the upper ${ }^{1} A_{1}$ curve. The crucial element in making this reaction photochemically allowed is the excitation of an electron from an orbital that moves uphill along $Q_{r}$ to a downhill moving orbital. Notice that the purpose in constructing the configuration-correlation diagram was to see whether the system can efficiently (through internal conversion or funnels) get from the ${ }^{1} A_{2}$ surface (at the Franck-Condon-populated reactant geometry) to the product ground-state

internal conversion will be sufficiently fast that the product molecules need not be formed on the ${ }^{1} A_{2}$ surface.

What would happen if the ${ }^{3} A_{2}\left(\pi \pi^{*}\right)$ state were populated in the primary excitation event by triplet sensitization? If the configuration-correlation diagram in Figure 7-3 is quantitatively accurate, the $T_{1}$ surface moves downhill from reactants to products, and some phosphorescence from the ${ }^{3} A_{2}\left(\sigma \sigma^{*}\right)^{3}$ state of cyclobutane is expected (assuming that the species does not first decompose to yield another product). In regions of $Q_{r}$ space in which the ${ }^{3} A_{2}$ surface intersects the lower ${ }^{1} A_{1}$ surface (Figure 7-3), it is also possible that intersystem crossing could lead to the formation of ground-state reactants, because the lower ${ }^{1} A_{1}$ surface is intersected on its reactant side. Recall that this intersystem crossing will be efficient only if one of the rotations $R_{x}, R_{y}$, and $R_{z}$ has the same symmetry as the direct product $A_{2} \times A_{1}=a_{2}$. Because the $C_{2 v}$ point group does have a rotation with $a_{2}$ symmetry, intersystem crossing should be efficient. In summary, from the intersection of $T_{1}$ with $S_{0}$ on the left side, intersystem crossing should give ground-state reactant molecules. From the right-hand intersection of $T_{1}$ and $S_{0}$, products will form. Phosphorescence of products will also occur. The quantum yields for each of these three processes will depend upon the exact values of the radiative and intersystem crossing rate constants-such quantitative evaluations cannot be made from symmetry-based arguments.

### 7.2. Closure of $\mathbf{1 , 3}$-Butadiene to Cyclobutene

The orbital-correlation diagrams for the disrotatory (DIS) and conrotatory (CON) paths for closure of 1,3-butadiene are shown in Figure 7-4, in which $e$ and $o$ indicate even and odd symmetry under $\sigma_{v}$ or $C_{2}$. In Chapter 4 the CON pathway for the thermal reactions was shown to be allowed and the DIS path to be forbidden. It will be seen in this section that the allowed pathway for the photochemical reaction differs. We begin by constructing a configurationcorrelation diagram that includes only the most important configurationsnamely, the ground state and the state most likely to lead to photoreaction. The fact that the energetically favorable $\pi \rightarrow \pi^{*}$ excitation has $o \rightarrow e$ symmetry for the DIS path is used next. For this reaction coordinate, the configurationcorrelation diagram, which is not necessarily quantitatively accurate, is shown in Figure 7-5. If the relative-energy scale were correct in this figure-which depends on the strengths of the $\sigma$ and $\pi$ bonds and the strain energy of the cyclobutene-excitation of butadiene to the singlet $\pi^{2}\left(\pi \pi^{*}\right)^{1}$ state would not yield cyclobutene at excitation energies near the $\pi \pi^{* 1}$ threshold. Absorption of photons of higher energy might cause a reaction if the excess internal energy were maintained in the reaction coordinates. The reaction is not cummetrv-


Figure 7-4
Orbital-correlation diagrams for CON and DIS closure of 1,3-butadiene.


DIS

Figure 7.5
Configuration-correlation diagram for DIS closure.
amount to intersect with the upper totally symmetric surface. In contrast, the reverse $S_{1}$ photoreaction should occur readily because the $\pi^{2}\left(\pi \pi^{*}\right)^{1}$ state can cross to the upper totally symmetric ( $\sigma^{2} \pi^{* 2}$ ) surface and thereby permit funneling to the ground-state surface. The funneling can then produce either reactants


Figure 7-6
Configuration-correlation diagram for CON closure.

The CON reaction path, which is thermally allowed, is photochemically forbidden when the excitation includes promotion of an electron from the second orbital of the butadiene to the lowest $\pi^{*}$ orbital. The relevant configurationcorrelation diagram for the CON path is shown in Figure 7-6. It shows that in addition to the fact that reaction along the $S_{1}$ state of the butadiene to produce cyclobutene is endothermic-as was the case for the DIS process-an additional symmetry-imposed barrier to reaction on this $S_{1}$ surface is also present. Because no funnel route connecting $S_{1}$ to $S_{0}$ is present, it is unlikely that the system will return to $S_{0}$ at a geometry that characterizes cyclobutene; it is much more likely that the molecule will either fluoresce or return to $S_{0}$ via internal conversion near the reactant geometry, because it cannot move away from this geometry when it is on $S_{1}$. The thermal reaction is allowed in the CON case, as shown by the $S_{0}$ surface not moving uphill along $Q_{r}$. The same behavior of $S_{0}$ also makes the excited-state reaction to yield $S_{0}$ products forbidden. For the same reasons, excitation of the triplet $\pi^{2}\left(\pi \pi^{*}\right)^{3}$ butadiene should also fail to form cyclobutene.

The Dewar-Zimmerman rules can also be applied to certain photochemical reactions if the resonance stahility rules are simplv reversed (Pearson. 1976).

so this reaction is thermally forbidden and photochemically allowed. Analogously, the suprafacial $[1,3]$ sigmatropic migration of a hydrogen atom is a 4-electron Hückel system

and would also occur photochemically. These simple rules cannot be universally valid because they do not contain references about the orbital into which the electron is excited. The range of applicability of the Dewar-Zimmerman prediction is limited to situations in which the occupied and virtual orbitals participating in the excitation are energy ordered, either as


### 7.3. HOMO-LUMO (SOMO) Overlap

## for the Diels-Alder Reaction

In using the criterion of HOMO-LUMO overlap to study thermal reactions, the HOMO and LUMO orbitals for each of the two reactant species are examined. For a Diels-Alder reaction, the orbitals are the diene $\pi_{2}$ and $\pi_{3}^{*}$ orbitals (Figure 7-7a) and the ene $\pi$ and $\pi^{*}$ orbitals (Figure 7-7b). The energy of the ordering of these orbitals and the ground-state reactant orbital occupations are depicted in Figure 7-7c. These diagrams show that $\pi_{2} \rightarrow \pi^{*}$ and $\pi \rightarrow \pi_{3}$ excitations include favorable HOMO-LUMO interactions in that the low-energy excitations produce a charge flow that allows the old bonds to break as the new bonds form. Hence, the thermal Diels-Alder reaction is allowed.

To use the HOMO-LUMO overlap tool for the photochemical reaction, the orbitals are first occupied in a manner appropriate to the excited state. For


Figure 7-7
(a) Diene $\pi_{2}$ and $\pi_{3}$ orbitals. (b) Ene $\pi$ and $\pi^{*}$ orbitals. (c) Energy ordering of the orbitals in (a) and (b).
singlet configuration $\pi^{2}\left(\pi_{2} \pi_{3}\right)^{1}$ is considered. The orbitals $\pi_{2}$ and $\pi_{3}$ are now singly occupied molecular orbitals (SOMO) that can act either as electron donors or acceptors in the HOMO $\rightarrow$ LUMO excitation sense. Although all possible single excitations should be considered when determining how electron density can flow between two reactants to break old bonds and make new bonds, orbital energy differences (according to perturbation theory) influence the contributions to the overall electron density flow, and thus indicate that the $\pi \rightarrow \pi_{2}$ and $\pi_{3} \rightarrow \pi^{*}$ excitations are probably more important. A $\pi_{2} \rightarrow \pi$ excitation would nut three elertrons in the $\pi$ orhital fwhirh is not allowed hy
higher energy. The $\pi_{2} \rightarrow \pi_{3}, \pi_{3} \rightarrow \pi_{2}$, and $\pi \rightarrow \pi^{*}$ orbital promotions do not cause charge to flow between reactants, but they are entirely intrafragment excitations. Notice that, analogous to the perturbation treatment of charge flow in the ground state, here these orbital promotions are analyzed with respect to their producing useful electron flow starting from an excited state. Examination of the energetically favored $\pi^{2} \rightarrow \pi_{2}$ and $\pi_{3} \rightarrow \pi^{*}$ orbital excitations shows that these orbital-promotion pairs do not produce a favorable overlap that allows new product bonds to form. Hence, the photochemical reaction should be forbidden. Certainly all of the orbital excitations have some influence on the charge flow that accompanies this reaction, but the most significant factor is whether there are low-energy single excitations that form new bonds as old bonds break.

The same conclusion would be reached if the ene had been excited rather than the diene. The orbital occupancy would then be given by $\pi_{2}^{2}\left(\pi \pi^{*}\right)^{1}$, and the relevant energetically favored excitations would be $\pi^{*} \rightarrow \pi_{3}^{*}$ and $\pi_{2} \rightarrow \pi$, both of which lead to unfavorable overlap and, hence, a forbidden reactionthat is, no formation of new bonds.

### 7.4. Excited Reactants Can Correlate Directly with Ground-State Products

By promoting an electron from a doubly occupied orbital whose energy is increasing along the reaction coordinate to one whose energy decreases, an $S_{1}$ surface might be obtained that has no symmetry-imposed barriers. In such a case, the system moves from the $S_{1}$ surface to the $S_{0}$ surface of products by intersystem crossing at the point where the $S_{1}$ surface intersects $S_{0}$ (or the upper cone of $S_{0}$ ) in a manner favoring product formation.

However, cases are known in which internal conversion is not needed. Consider, for example, the photochemical abstraction of a hydrogen atom from an alkane by an excited carbonyl group


Treating the active orbitals as the $\mathrm{CO} \pi$ and $\pi^{*}$, the $\mathrm{O} p$-like lone pair ( $n_{o}$ ), and the $\mathrm{H}-\mathrm{C} \sigma$ and $\sigma^{*}$ orbitals, the orbital-correlation diagram shown in Figure $7-8$ can be made, in which only the approximate symmetry plane of the $\mathrm{H}_{2} \mathrm{CO}$ moiety is used to label the orbitals. The orbitals on the C and O of the product that lie perpendicular to the COH plane are labeled $\pi_{\mathrm{C}}$ and $\pi_{\mathrm{o}}$. This symmetry label is only correct while the earhnnvi aroun remaine nianar

$\mathrm{H}_{2} \mathrm{CO}+\mathrm{HCR}_{3}$
$\mathrm{H}_{2} \mathrm{COH}+\mathrm{CR}_{3}$
Figure 7-8
Orbital-correlation diagram for H -atom abstraction by carbonyl.

because when this radical becomes nonplanar, the orbitals no longer have pure $\pi$ symmetry, $\pi_{\mathrm{O}}$ becomes a lone pair on oxygen, and $\pi_{\mathrm{C}}$ becomes a radical orbital on carbon having a mixed $p$ and $s$ character.

The orbital-correlation diagram in Figure 7-8 seems to indicate that the thermal reaction is allowed. However, notice that the $\sigma_{\mathrm{CH}}^{2} \pi_{\mathrm{Co}}^{2} n_{\mathrm{O}}^{2}$ configuration correlates with the $\sigma_{\mathrm{OH}}^{2} \pi_{\mathrm{O}}^{2} \sigma_{\mathrm{CR}_{3}}^{2}$ configuration of the products and that the product configuration also corresponds to the ionic products $\mathrm{H}_{2} \mathrm{COH}^{+}$and $\mathrm{C}^{-} \boldsymbol{R}_{3}$. Clearly, these ionic species could not be the ground state of the products unless extreme solvation effects were present. (We shall not consider how solvation can affect the $S_{n}$ and $T_{n}$ surfaces; this is a separate, but very important, topic that is beyond the scope of the present work.) Hence, the orbital-correlation diagram does not predict that ground-state reactants can smoothly give rise to ground-state (radical) products.

The various low-energy configurations that can arise by occupying the reactant and product molecular orbitals in various ways are shown in the singlet configuration-correlation diagram shown in Figure 7-9. Notice that this diagram is different from those that have been encountered in that the singlet


Figure 7-9
Configuration-correlation diagram for H -atom abstraction by carbonyl.
$\left(n \pi^{*}\right)^{1}$ excited configurations of the reactants directly correlate with the ground-state configuration of the product. This means that an efficient direct mechanism is available for bringing about the reaction

$$
S_{0}+h \nu \rightarrow S_{1} \text { (reactants) } \rightarrow S_{0} \text { (products). }
$$

No internal conversion or funneling is needed, and photochemical excitation of a $\left(n \pi^{*}\right)^{11} A_{2}$ reactant can lead directly to ground-state radical products.

Had we included the triplet $\left(n \pi^{*}\right)^{3}$ configuration of the reactants on this configuration-correlation diagram, it would have correlated directly with the triplet $\sigma^{2} \pi^{2} \sigma \pi$ state of the product. Thus, triplet sensitized carbonyls should also abstract hydrogen atoms from alkanes as long as the triplet $\left(n \pi^{*}\right)^{3}$ state of the reactants is above the ground (singlet or triplet radical) state of the products (Turro, 1978).

### 7.5. Benzene Photochemistry

In this example, three rearrangements of benzene shown in Figure 7-10 are considered. The dewarbenzene and prismane are drawn both in their proper three-dimensional structures and symbolically as valence isomers of planar benzene to emphasize the bonding relationships among these species. We begin the analysis by proposing reaction coordinates for each of the above reactions that preserve $C_{2 v}$ symmetry and by labeling and ordering the active orbitals of the three species.

In order of increasing energy from left to right, for benzene (see Cotton, 1963), the $\pi$ molecular orbitals are


Figure 7-10 Valence isomers of benzene.

in which the + and - signs label the relative signs of the $\left(p_{\pi}\right)$ atomic orbitals. The $\sigma$ and $\pi$ orbitals of dewarbenzene are

and the three $\sigma$ orbitals of prismane are


These sets of orbitals lead to the orbital-correlation diagram shown in Figure 7-11. The diagram is not drawn to be quantitatively accurate but indicates that $\sigma$ bonds are stronger than $\pi$ bonds; furthermore, the orbital-correlation diagram contains no information about the strain energy of 1,4-dewarbenzene or prismane. Construction of a configuration-correlation diagram appropriate for the ground and low-lying singlet excited states of these three valence isomers is begun by listing the configurations expected to be most important, indicating the essential configurations for each of the three species and the cor-


## TABLE 7-1

Correlation of Essential Configurations for Benzene Valence Isomers

| Configuration | Dominant species | Correlates with |
| :--- | :--- | :--- |
| $a_{1}^{2} b_{2}^{2} a_{1}^{2}$ | Prismane | $\pi^{4} \pi^{* 2}$ benzene and $\sigma^{2} \pi^{2} \pi^{* 2}$ dewarbenzene |
| $a_{1}^{2} b_{2}^{2} a_{1} b_{1}$ | Prismane | $\pi^{5} \pi^{*}$ benzene and $\sigma^{2} \pi^{2} \pi^{* 2}$ dewarbenzene |
| $a_{1}^{2} b_{2}^{2} b_{1}^{2}$ | Benzene | $\sigma^{4} \sigma^{* 2}$ prismane and $\sigma^{2} \pi^{2} \pi^{* 2}$ dewarbenzene |
| $a_{1}^{2} b_{2}^{2} b_{1} a_{1}$ | Benzene | $\sigma^{5} \sigma^{*}$ prismane and $\sigma^{2} \pi^{2} \pi^{* 2}$ dewarbenzene |
| $a_{1}^{2} a_{1}^{2} b_{1}^{2}$ | Dewarbenzene | $\sigma^{4} \sigma^{* 2}$ prismane and $\pi^{4} \pi^{* 2}$ benzene |
| $a_{1}^{2} a_{1}^{2} b_{1} b_{2}$ | Dewarbenzene | $\sigma^{5} \sigma^{*}$ prismane and $\pi^{4} \pi^{* 2}$ benzene |
| $a_{1}^{2} a_{1} b_{1}^{2} b_{2}$ | Dewarbenzene | $\sigma^{4} \sigma^{* 2}$ prismane and $\pi^{5} \pi^{*}$ benzene |

Note: The * indicates an electronically excited molecule or orbital.


Figure 7-11
Orbital-correlation diagram for rearrangements of benzene.


## Figure 7-12

Configuration-correlation diagram for benzene and prismane.

This information is then used to construct configuration-correlation diagrams for the three reactions (Figures 7-12, 7-13, and 7-14). Since the lowest energy orbitals of all three systems have $a_{1}$ symmetry and are doubly occupied, the two electrons in these orbitals are neglected in constructing the configuration-correlation diagrams. In each diagram the configurations that


## Dewarbenzene

Figure 7-13
Configuration-correlation diagram for dewarbenzene and prismane.
contribute to $S_{0}$ of reactants or products and those that give rise to low-lying singly excited states are displayed. Arrows directed steeply upwards indicate that the particular configuration correlates with a doubly or more highly excited configuration on the other side of the diagram.

These configuration-correlation diagrams indicate that the ${ }^{1} B_{1}$ excited state of benzene would not lead to dewarbenzene for photon energies near the ${ }^{1} B_{1}$ absorption threshold; although the process is not symmetry-forbidden, it is a very uphill process that leads to the doubly excited $b_{2}^{2} a_{1} b_{1}$ state of dewarhenzene. Alane the unhill movement the ${ }^{1} R$. curfane arnssec the ${ }^{1} R$.


Figure 7-14
Configuration-correlation diagram for benzene and dewarbenzene.
surface. If the photon energy were sufficient to place the system high enough on the ${ }^{1} B_{1}$ surface, the system could hop-by a vibration of $b_{1} \times b_{2}=a_{2}$ symmetry-to the ${ }^{1} B_{2}$ surface. The system might then move on this ${ }^{1} \sim_{2}$ surface, eventually crossing again to the ${ }^{1} A_{1}$ ground-state surface. Since the ${ }^{1} B_{2}$-to- ${ }^{1} A_{1}$ surface crossing occurs on the reactant side of the ${ }^{1} A_{1}$ surface, ground-state benzene should be the main product.

Alternatively, this same benzene-excitation process could yield either ground-state benzene or prismane because the ${ }^{1} B_{1}$ surface crosses the ${ }^{1} A_{1}$ surface along the reaction coordinate connecting benzene and prismane. On the other hand, one of the benzene ${ }^{1} B_{2}$ configurations correlates directly with a low-lying ${ }^{1} B_{2}$ configuration of dewarbenzene and should thus give an allowed reaction that might yield some $S_{0}$ dewarbenzene (but no prismane), the relative amounts depending on the exact values of quantum yields. If the ${ }^{1} A_{1} S_{0}$ surface is intersected by the ${ }^{1} B_{2}$ surface on the benzene side, then intersystem aroccine will monet likelv land ton areund-state hensene $n$ n the other hand if
the top of the $S_{0}$ surface lies below the ${ }^{1} B_{2}$ surface, formation of ground-state dewarbenzene is equally likely.

Excitation to the lowest ${ }^{1} A_{2}$ state of dewarbenzene should yield an appreciable amount of ground-state prismane, since the lowest ${ }^{1} A_{2}$ configuration of each species correlates directly and crosses the funnel region of the ${ }^{1} A_{1}$ ground state. At higher photon energies, excitation of a ${ }^{1} B_{2}$ state of dewarbenzene can give rise to formation of ground-state benzene; this is the reverse of the reaction just discussed.

The number of events that might occur when a photon is absorbed is quite large even for a system having few low-energy excited states. A small number of occupied orbitals out of which an electron can be excited and a small number of low-energy virtual orbitals can give rise to a large number of singly excited states. Moreover, a number of geometrical distortions (that is, proposed reaction coordinates) may have to be considered in following reactant states through to various product states (as in the case just discussed). The crossings of the excited potential-energy curves having low energy among one another and with the ground state $\left(S_{0}\right)$ surface along the possible reaction coordinates determine the quantum yields of the numerous available reactive, radiative, and radiationless pathways. Although the symmetry and nodal-pattern tools do not allow a quantitative prediction of the yields of the competing events, they allow one to guess the events that are likely and those that are not likely because of symmetry-imposed barriers.

## 7.6. $\mathrm{C}+\mathrm{H}_{2} \rightarrow \mathrm{CH}_{2}$

In this example, the reactions ${ }^{1} A_{1} \mathrm{CH}_{2} \rightarrow \mathrm{H}_{2}+\mathrm{C}$ and ${ }^{3} B_{1} \mathrm{CH}_{2} \rightarrow \mathrm{H}_{2}+\mathrm{C}$ are investigated in an assumed $C_{2 v}$ reaction pathway. To form the appropriate correlation diagrams the following information is needed (all energies are in $\mathrm{kcal} /$ mole):

$$
\begin{array}{ll}
\mathrm{C}\left({ }^{3} P\right) \rightarrow \mathrm{C}\left({ }^{1} D\right), & \Delta E=29.2 \\
\mathrm{C}\left({ }^{1} D\right) \rightarrow\left({ }^{1} S\right), & \Delta E=32.7 \\
\mathrm{C}\left({ }^{3} P\right)+\mathrm{H}_{2} \rightarrow \mathrm{CH}_{2}\left({ }^{3} B_{1}\right), & \Delta E=-78.8 \\
\mathrm{C}\left({ }^{1} D\right)+\mathrm{H}_{2} \rightarrow \mathrm{CH}_{2}\left({ }^{1} A_{1}\right), & \Delta E=-97.0 .
\end{array}
$$

Using the coordinate system shown in Figure 7-15, the hydrogen $\sigma_{g}$ and $\sigma_{u}$ orbitals and the carbon $2 s, 2 p_{x}, 2 p_{y}$, and $2 p_{z}$ orbitals are labeled as either $a_{1}$, $b_{1}$ or $b_{2}$, as are the $\sigma, \sigma, \sigma^{*}, \sigma^{*}, n$, and $p_{\pi}$ orbitals of $\mathrm{CH}_{2}$. For the reactants,


Figure 7-15
Coordinate system for discussion the reaction $\mathrm{C}+\mathrm{H}_{2} \rightarrow \mathrm{CH}_{2}$.
the $\sigma_{g}$ and $\sigma_{u}$ orbitals have $a_{1}$ and $b_{2}$ symmetry, respectively. The nitrogen orbitals and their symmetries are $2 s\left(a_{1}\right), 2 p_{z}\left(a_{1}\right), 2 p_{y}\left(b_{2}\right)$, and $2 p_{x}\left(b_{1}\right)$. For $\mathrm{CH}_{2}$ the symmetric combinations of the two $\mathrm{CH} \sigma$ and $\sigma^{*}$ bonds have $a_{1}$ symmetry, the antisymmetric $\sigma$ and $\sigma^{*}$ combinations have $b_{2}$ symmetry, the nonbonding ( $n$ ) orbital has $a_{1}$ symmetry, and the $p_{\pi}(x)$ orbital has $b_{1}$ symmetry.

An orbital-correlation diagram for the $\mathrm{CH}_{2} \rightarrow \mathrm{C}+\mathrm{H}_{2}$ reactions can be drawn in which the orbitals are ordered by their relative energies. The same orbital-correlation diagram applies to both reactions; only in the configurationand state-correlation diagrams does one distinguish between the triplet and singlet species. The orbital-correlation diagram is constructed by connecting orbitals having the same symmetry, as shown in Figure 7-16. To proceed, ${ }^{3} P$, ${ }^{1} D$, and ${ }^{1} S$ wavefunctions of the carbon atoms must be symmetry-analyzed. We write these wavefunctions-first in terms of $2 p_{m}$ where $m=1,0,-1$ orbitals and then in terms of $2 p_{x y, z}$ orbitals. These wavefunctions are the following:

1. Three Slater-determinant wavefunctions belonging to the ${ }^{3} P$ state, each of which has an $M_{s}$ value of 1 . (Any value of $M_{s}-1,0$, or -1could be chosen because the reaction of ${ }^{3} P \mathrm{C}$ to produce ${ }^{3} B_{1} \mathrm{CH}_{2}$ is independent of $M_{s}$.)
2. Five ${ }^{1} D$ Slater-determinant wavefunctions
3. One ${ }^{1} S$ Slater-determinant wavefunction

Then, the configuration-correlation diagrams for the above singlet and triplet reactions can be constructed.

The $M_{5}=1$ functions all have two unpaired $\alpha$ electrons. If the $1 s^{2}$ and $2 s^{2}$ spin orbitals, which are common to the first four columns of each Slater determinant are ignored, for ${ }^{3} P\left(M_{1}, M_{\mathrm{s}}\right)$


Figure 7-16
Orbital-correlation diagram for the reaction $\mathrm{C}+\mathrm{H}_{\mathbf{2}} \rightarrow \mathrm{CH}_{\mathbf{2}}$.

$$
{ }^{3} P(1,1)=\left|2 p \alpha_{+1} 2 p_{0} \alpha\right|
$$

and

$$
\begin{aligned}
& { }^{3} P(0,1)=\left|2 p_{+1} \alpha 2 p_{-1} \alpha\right| \\
& { }^{3} P(-1,1)=\left|2 p_{0} \alpha 2 p_{-1} \alpha\right|
\end{aligned}
$$

The five ${ }^{1} D$ determinantal functions are obtained as follows. The ${ }^{1} D(2,0)$ and ${ }^{1} D(-2,0)$ functions are the only determinants arising from $p^{2}$ that have $M_{\mathrm{L}}= \pm 2$ and are

$$
{ }^{1} D(2,0)=\left|2 p_{+1} \alpha 2 p_{+1} \beta\right| \text { and }{ }^{1} D(2,0)=\left|2 p_{-1} \alpha 2 p_{-1} \beta\right| .
$$

The other ${ }^{1} D\left(M_{\mathrm{L}}, 0\right) M_{\mathrm{L}}=1,0,-1$ functions are obtained by applying the $L$ lowering operator to ${ }^{1} D(2,0)$ or the $L_{+}$raising operator to ${ }^{1} D(-2,0)$. In so doing, we use the fact that $L_{+}$acting on an eigenfunction of $L^{2}$ and $L_{z}$ yields a multiple of the eigenfunction having one higher or lower $L_{x}$ eigenvalue. Thus, $L_{-}^{1} D(2,0) \sim{ }^{1} D(1,0)$, and $L_{+}^{1} D(-2,0) \sim^{1} D(-1,0)$.

The operators $L_{ \pm}$are most conveniently expressed as sums of orbital-level

$2 p^{2}$ aspects are treated. Since $l_{ \pm}$operating as an orbital having $(l, m)$ eigenvalues gives $\hbar \sqrt{l(l+1)-m(m \pm 1)}$ times the orbital with eigenvalues $(l, m \pm 1)$,

$$
\begin{aligned}
L_{-}^{1} D(2,0) & =\left[l_{-}(5)+l_{-}(6)\right]\left|2 p_{+1} \alpha 2 p_{+1} \beta\right| \\
& =\hbar \sqrt{2}\left[\left|2 p_{0} \alpha 2 p_{+1} \beta\right|+\left|2 p_{+1} \alpha 2 p_{0} \beta\right|\right] \sim^{1} D(1,0)
\end{aligned}
$$

and

$$
\begin{aligned}
L_{+}{ }^{1} D(-2,0) & =\left[l_{+}(5)+l_{+}(6)\right]\left|2 p_{-1} \alpha 2 p_{-1} \beta\right| \\
& =\hbar \sqrt{2}\left[\left|2 p_{0} \alpha 2 p_{-1} \beta\right|+\left|2 p_{-1} \alpha 2 p_{0} \beta\right|\right] \sim^{1} D(-1,0)
\end{aligned}
$$

To obtain ${ }^{1} D(0,0)$ we can apply $L_{-}$to ${ }^{1} D(1,0)$ or $L_{+}$to ${ }^{1} D(-1,0)$. For example,

$$
\begin{aligned}
L_{-}^{1} D(1,0)= & \hbar \sqrt{2}\left[\left|2 p_{-1} \alpha 2 p_{+1} \beta\right|+2\left|2 p_{0} \alpha 2 p_{0} \beta\right|\right. \\
& \left.+\left|2 p_{+1} \alpha 2 p_{-1} \beta\right|\right] \hbar \sqrt{2} \sim^{1} D(0,0) .
\end{aligned}
$$

These combinations of Slater determinants are not normalized; to normalize them is straightforward, for example,

$$
{ }^{1} D(0,0)=\frac{1}{\sqrt{6}}\left[\left|2 p_{+1} \alpha 2 p_{-1} \beta\right|+\left|2 p_{-1} \alpha 2 p_{+1} \beta\right|+2\left|2 p_{0} \alpha 2 p_{0} \beta\right|\right] .
$$

The one ${ }^{1} S(0,0)$ Slater-determinant function can be obtained as the remaining combination of the determinants having $M_{L}=0, M_{\mathrm{s}}=0$ that is orthogonal to ${ }^{1} D(0,0)$ and ${ }^{3} P(0,0)$. Recall that ${ }^{1} D(0,0)$ is given above. ${ }^{3} P(0,0)$ can be obtained from ${ }^{3} P(0,1)$ by applying $S_{\text {- }}$ :

$$
\begin{aligned}
{ }^{3} P(0,0) \sim S_{-}{ }^{3} P(0,1) & =\left(S_{-}(5)+S_{-}(6)\right)\left|2 p_{+1} \alpha 2 p_{-1} \alpha\right| \\
& =\hbar \sqrt{1}\left[\left|2 p_{+1} \beta 2 p_{-1} \alpha\right|+\left|2 p_{+1} \alpha 2 p_{-1} \beta\right|\right] .
\end{aligned}
$$

Clearly ${ }^{1} D(0,0)$ has the form $2 z+x+y$, whereas ${ }^{3} P(0,0)$ contains $x-y$; hence, ${ }^{1} S(0,0)$ must have the form $z-x-y$, or

$$
{ }^{1} S(0,0)=\frac{1}{\sqrt{3}}\left[\left|2 p_{0} \alpha 2 p_{0} \beta\right|-\left|2 p_{+1} \alpha 2 p_{-1} \beta\right|-\left|2 p_{-1} \alpha 2 p_{+1} \beta\right|\right]
$$

To exnrese the ${ }^{1} D{ }^{3} P\left(M\right.$. 1) and ${ }^{1} S$ wavefunctionc in terme of $2 n \ldots$ or-
and $\left(2 p_{x} \pm i 2 p_{y}\right) 2^{-1 / 2}$ for $2 p_{ \pm 1}$; this will generate Slater determinants including $2 p_{x y, z}$ orbitals. It is important to understand the reason for bringing about this transformation from $m_{l}=1,0,-1$ to $x, y, z$ space. The $2 p_{m}$ orbitals and their determinental wavefunctions are appropriate for the spherically symmetrical carbon atom in which $L_{z}=\Sigma_{i} l_{z}(i)$ commutes with the electronic Hamiltonian. However, in the presence of the $\mathrm{H}_{2}$ molecule in $C_{2 v}$ symmetry, $L_{z}$ no longer commutes with the electronic Hamiltonian, though the operations of the $C_{2 v}$ point group ( $E, \sigma_{v}, \sigma_{\nu^{\prime}}, C_{2}$ ) do. Because the $2 p_{x y, z}$ orbitals are symmetryadapted with respect to $C_{2 v}$ symmetry, these orbitals must be used in the wavefunctions.

The transformations of the three ${ }^{3} P\left(M_{L}, 1\right)$, five ${ }^{1} D\left(M_{L}, 0\right)$, and one ${ }^{1} S(0,0)$ wavefunctions to $x, y, z$-space are the following. The transformations of the $P$ wavefunctions are

$$
\begin{aligned}
{ }^{3} P(1,1) & =\left|2 p_{+1} \alpha 2 p_{0} \alpha\right|=2^{-1 / 2}\left[\left|2 p_{x} \alpha 2 p_{z} \alpha\right|+i\left|2 p_{y} \alpha 2 p_{x} \alpha\right|\right] \\
{ }^{3} P(-1,1) & =2^{-1 / 2}\left[\left|2 p_{x} \alpha 2 p_{z} \alpha\right|-i\left|2 p_{y} \alpha 2 p_{z} \alpha\right|\right] \\
{ }^{3} P(0,1) & =2^{-1}\left[\left|2 p_{x} \alpha 2 p_{x} \alpha\right|+\left|2 p_{y} \alpha 2 p_{y} \alpha\right|+i\left|2 p_{y} \alpha 2 p_{x} \alpha\right|-i\left|2 p_{x} \alpha 2 p_{y} \alpha\right|\right] \\
& =i\left|2 p_{y} \alpha 2 p_{x} \alpha\right|
\end{aligned}
$$

For ${ }^{3} P(0,1)$ we used the facts that Slater determinants are antisymmetric

$$
\left|2 p_{x} \alpha 2 p_{y} \alpha\right|=-\left|2 p_{y} \alpha 2 p_{x} \alpha\right|
$$

and that they obey the Pauli principle

$$
\left|2 p_{x} \alpha 2 p_{x} \alpha\right|=0
$$

The three ${ }^{3} P\left(M_{L}, 1\right)$ functions are degenerate when the $\mathbf{H}_{2}$ molecule is not present, so any combinations of these three functions would also be degenerate. In particular,

$$
\begin{aligned}
& {\left[{ }^{3} P(1,1)+{ }^{3} P(-1,1)\right] 2^{-1 / 2}=\left|2 p_{x} \alpha 2 p_{z} \alpha\right| \equiv{ }^{3} P(x z, 1)} \\
& \frac{1}{i}\left[{ }^{3} P(1,1)-{ }^{3} P(-1,1)\right] 2^{-1 / 2}=\left|2 p_{y} \alpha 2 p_{z} \alpha\right| \equiv{ }^{3} P(y z, 1)
\end{aligned}
$$

and

$$
\frac{1}{x} P(0,1)=\left|2 p_{y} \alpha 2 p_{x} \alpha\right| \equiv{ }^{3} P(y x, 1)
$$

are all degenerate. However, the three new functions $(y z, x z$, and $y x)$ are more useful because they are symmetry-adapted for $C_{2 v}$ symmetry: ${ }^{3} P(x z, 1)$ ${ }^{3} P(y z, 1)$ and ${ }^{3} P(y x, 1)$ have $B_{1}, B_{2}$ and $A_{2}$ symmetry, respectively. These symmetries are obtained as the direct products of the symmetries of the orbitals. For example, ${ }^{3} P(y x, 1)$ has $A_{2}$ symmetry because the direct product of $b_{2}(y)$ and $b_{1}(x)$ has $A_{2}$ symmetry. Notice that it is not correct to conclude that the ${ }^{3} \mathrm{P}$ state functions would span the same symmetry space as three $2 p$ orbitals do ( $p_{x}$ has $b_{1}, p_{y}$ has $b_{2}$ and $p_{z}$ has $a_{1}$ symmetry). A second reason that the $x z, y z$, and $y x$ determinants are more useful for the $C_{2 v}$ case is that they correspond to a single orbital occupancy from which configuration-correlation diagrams are easily generated.

Let us now consider the five degenerate ${ }^{1} D\left(M_{L}, 0\right)$ wavefunctions.

$$
\begin{aligned}
{ }^{1} D(2,0)= & \left|2 p_{+1} \alpha 2 p_{+1} \beta\right|=\frac{i}{2}\left[\left|2 p_{x} \alpha 2 p_{y} \beta\right|+\left|2 p_{y} \alpha 2 p_{x} \beta\right|\right] \\
& +\frac{1}{2}\left[\left|2 p_{x} \alpha 2 p_{x} \beta\right|-\left|2 p_{y} \alpha 2 p_{y} \beta\right|\right] \\
{ }^{1} D(-2,0)= & \left|2 p_{-1} \alpha 2 p_{-1} \beta\right|=\frac{1}{2}\left[\left|2 p_{x} \alpha 2 p_{x} \beta\right|-\left|2 p_{y} \alpha 2 p_{y} \beta\right|\right] \\
& -\frac{i}{2}\left[\left|2 p_{x} \alpha 2 p_{y} \beta\right|+\left|2 p_{y} \alpha 2 p_{x} \beta\right|\right] . \\
{ }^{1} D(1,0)= & 2^{-1 / 2}\left[\left|2 p_{0} \alpha 2 p_{+1} \beta\right|+\left|2 p_{+1} \alpha 2 p_{0} \beta\right|\right] \\
= & \frac{1}{2}\left[\left|2 p_{z} \alpha 2 p_{x} \beta\right|+\left|2 p_{x} \alpha 2 p_{z} \beta\right|+i\left|2 p_{z} \alpha 2 p_{y} \beta\right|+i\left|2 p_{y} \alpha 2 p_{z} \beta\right|\right] \\
{ }^{1} D(-1,0)= & \frac{1}{2}\left[\left|2 p_{z} \alpha 2 p_{x} \beta\right|+\left|2 p_{x} \alpha 2 p_{z} \beta\right|-i\left|2 p_{z} \alpha 2 p_{y} \beta\right|-i\left|2 p_{y} \alpha 2 p_{z} \beta\right|\right] \\
{ }^{1} D(0,0)= & 6^{-1 / 2}\left[2\left|2 p_{0} \alpha 2 p_{0} \beta\right|+\left|2 p_{+1} \alpha 2 p_{-1} \beta\right|+\left|2 p_{-1} \alpha 2 p_{+1} \beta\right|\right] \\
= & 6^{-1 / 2}\left[2\left|2 p_{z} \alpha 2 p_{z} \beta\right|+\left|2 p_{x} \alpha 2 p_{x} \beta\right|+\left|2 p_{y} \alpha 2 p_{y} \beta\right|\right] .
\end{aligned}
$$

Since degenerate functions can be combined without affecting their degeneracy, ${ }^{1} D( \pm 2,0)$ can be combined to yield functions having symmetries ${ }^{1} D(x x, 0)-$ ${ }^{1} D(y y, 0)$ and ${ }^{1} D(x y, 0)$. Likewise, ${ }^{1} D( \pm 1,0)$ can be combined to yield ${ }^{1} D(x z, 0)$ and $D(y z, 0)$ symmetry functions. These new combinations are useful because they are symmetry-adapted: For example, the symmetries of ${ }^{1} D(x x, 0)-$ ${ }^{1} D(y y, 0),{ }^{1} D(x y, 0),{ }^{1} D(x z, 0)$, and ${ }^{1} D(y z, 0)$ are $A_{1}, A_{2}, B_{1}$ and $B_{2}$, respectively;


Figure 7-17
Configuration-correlation diagram for singlet and triplet.

The ${ }^{1} S(0,0)$ wavefunction has the property that

$$
\begin{aligned}
{ }^{1} S(0,0) & =3^{-1 / 2}\left[\left|2 p_{0} \alpha 2 p_{0} \beta\right|-\left|2 p_{+1} \alpha 2 p_{-1} \beta\right|-\left|2 p_{-1} \alpha 2 p_{+1} \beta\right|\right] \\
& =3^{-1 / 2}\left[\left|2 p_{x} \alpha 2 p_{z} \beta\right|-\left|2 p_{x} \alpha 2 p_{x} \beta\right|-\left|2 p_{y} \alpha 2 p_{y} \beta\right|\right],
\end{aligned}
$$

which has $A_{1}$ symmetry in $C_{2 v}$ since each of its components has $A_{1}$ symmetrythat is, $a_{1} \times a_{1}=A_{1}, b_{1} \times b_{1}=A_{1}, b_{2} \times b_{2}=A_{1}$.

The configuration-correlation diagram, together with the relevant avoided crossings, is shown in Figure 7-17. In constructing this diagram, the relative energy orderings of various configurations must be kept in mind. For example, the $\sigma^{2} n^{2} p_{x} \sigma$ configuration is placed lower then the $\sigma^{2} n^{2} \sigma \sigma^{*}$ one, which, in turn, is lower than $\sigma^{2} n^{2} p_{x} \sigma^{*}$.

Let us examine how the configurations have been correlated. The ${ }^{3} B_{1}$ $\sigma^{2} \sigma^{2} n p_{x}$ configuration of $\mathrm{CH}_{2}$ correlates with the $\sigma_{g}^{2} p_{y}^{2} 2 s p_{x}$ configuration of $\mathrm{C}+\mathrm{H}$, (see the orhital-configuration diagram in Figure 7-16) The latter mon
$\mathrm{H}_{2}+\mathrm{C}\left(1 s^{2} 2 s 2 p^{3}\right)$ and, as such, lies considerably above the ${ }^{1} S$ state of $\mathrm{C}\left(1 s^{2} 2 s^{2} 2 p^{2}\right)$.

The ${ }^{1} A_{1} \sigma^{2} \sigma^{2} n^{2}$ configuration of $\mathrm{CH}_{2}$ correlates with $\sigma_{g}^{2} 2 s^{2} 2 p_{y}^{2}$ (see Figure 7-16). This latter configuration is not purely ${ }^{1} D$ or ${ }^{1} S$. It is a combination of ${ }^{1} D$ and ${ }^{1} S$ functions-in particular

$$
\left|\sigma_{g}^{2} 2 s^{2} 2 p_{y}^{2}\right|=6^{-1}\left[6^{1 / 2}{ }^{1} D(0,0)-3^{1 / 2} 2^{1} S(0,0)\right]-2^{-1}\left[{ }^{1} D(2,0)+{ }^{1} D(-2,0)\right]
$$

which is $2 / 3{ }^{1} D$ and $1 / 3{ }^{1} S$ in character. Hence, the configuration-correlation diagram must be drawn with a barrier near the ${ }^{1} D$ asymptote to represent the fact that ${ }^{1} A_{1} \mathrm{CH}_{2}$ correlates with a (2/3:1/3) mixture of ${ }^{1} D$ and ${ }^{1} S \mathrm{C}$ (plus $\mathrm{H}_{2}$ ), which will eventually mix (with $2 p_{x}^{2}$ and $2 p_{x}^{2}$ ) to yield the ${ }^{1} D$ and ${ }^{1} S$ states.

The ${ }^{3} A_{2} \sigma^{2} n^{2} \sigma p_{x}$ and ${ }^{3} B_{2} \sigma^{2} n^{2} \sigma \sigma^{*}$ configurations of $\mathrm{CH}_{2}$ correlate with $\sigma_{g}^{2} 2 s^{2} p_{x} p_{y}$ and $\sigma_{g}^{2} 2 s^{2} p_{y} p_{z}$ configurations of $\mathrm{C}+\mathrm{H}_{2}$. The latter two triplet configurations are members of the three degenerate ${ }^{3} P(x y, 1),{ }^{3} P(y z, 1)$ and ${ }^{3} P(x z, 1)$ functions. The third member of this family-the ${ }^{3} P(x z, 1)$ configuration $\sigma_{g}^{2} 2 s^{2} p_{x} p_{z}$-which has ${ }^{3} B_{1}$ symmetry-correlates with the $\sigma^{2} n^{2} p_{x} \sigma^{*}$ configuration of $\mathrm{CH}_{2}$.

In like fashion, all five of the ${ }^{1} D$ and the ${ }^{1} S$ states of $\mathrm{C}+\mathrm{H}_{2}$ can be correlated with those of $\mathrm{CH}_{2}$. However, since we are considering only the lowest triplet and singlet states, this correlation is unnecessary. All that needs to be done is to seek low-energy configurations that have ${ }^{1} A_{1}$ or ${ }^{3} B_{1}$ symmetry in the $C_{2 v}$ point group.

We now examine whether the reactions $\mathrm{C}\left({ }^{3} P\right)+\mathrm{H}_{2} \rightarrow \mathrm{CH}_{2}$ and $\mathrm{C}\left({ }^{1} D\right)+$ $\mathbf{H}_{\mathbf{2}} \rightarrow \mathrm{CH}_{\mathbf{2}}$ have large activation barriers and determine the states of $\mathrm{CH}_{\mathbf{2}}$ that are produced in these reaction.

The configuration-correlation diagram in Figure 7-17 clearly illustrates that the ${ }^{3} B_{1}$ reaction- $\mathrm{C}+\mathrm{H}_{2} \rightarrow \mathrm{CH}_{2}$-should have a symmetry-imposed barrier. The transition state along this reaction path should lie closer to the $\mathrm{C}+\mathrm{H}_{2}$ reactants than to the $\mathrm{CH}_{2}$ products because the forward reaction is exothermic.

The ${ }^{1} A_{1}$ reaction $\mathrm{C}\left({ }^{1} D\right)+\mathrm{H}_{2} \rightarrow \mathrm{CH}_{2}$ also has a symmetry barrier in the configuration-correlation diagram, but this barrier is artifical. Recall that the ${ }^{1} A_{1} \sigma^{2} \sigma^{2} n^{2} \quad \mathrm{CH}_{2}$ configuration correlates with a $2 / 3: 1 / 3$ mixture of ${ }^{1} D$ and ${ }^{1} S$ configurations. Hence, as $\mathrm{CH}_{2}\left({ }^{1} A_{1}\right)$ is pulled apart along the assumed $C_{2 v}$ reaction path, the electronic wavefunction must mix the ${ }^{1} D(0,0),{ }^{1} D(+2,0)+$ ${ }^{1} D(-2,0)$, and the ${ }^{1} S(0,0)$ configurations. However, as the distance between the C and $\mathrm{H}_{2}$ species becomes so large that they no longer interact, the wavefunction smoothly evolves to have only ( $\left.{ }^{1} D\right) \mathrm{C}+\mathrm{H}_{2}$ symmetry.

Another aspect of the configuration correlation diagram shown in Figure $7-17$ is of interest. The lowest ${ }^{3} B_{1}$ surface, which has a substantial barrier, is crossed hv the ${ }^{3} A$, and ${ }^{3} R$, surfaces. so we may ask whether pseudo-Jahn-
vibrational distortion to give rise to mixing. The $\mathbf{C H}_{\mathbf{2}}$ molecule has no vibration with this symmetry. In constrast, the ${ }^{3} B_{1}{ }^{3} A_{2}$ crossing could give rise to a pseudo-Jahn-Teller effect through a distortion having $A_{2} \times B_{1}=B_{2}$ symmetry. The asymmetric stretch vibration of $\mathrm{CH}_{\mathbf{2}}$ has $b_{\mathbf{2}}$ symmetry; this means that as the $\mathrm{CH}_{2}$ is pulled apart, any asymmetric stretch motion could cause a transition from the ${ }^{3} B_{1}$ surface to the ${ }^{3} A_{2}$ surface, after which further dissociation could occur on ${ }^{3} A_{2}$ to give rise to $\mathrm{C}\left({ }^{3} P\right)+\mathrm{H}_{2}$. The result of such a surface transition would be a lowering of the activation energy of the dissociation reaction. The ${ }^{3} B_{1} \rightarrow{ }^{3} A_{2}$ transition need not take place in every collision. Those collisions in which the molecule ends up on the ${ }^{3} \boldsymbol{A}_{2}$ surface will experience a lower barrier.

Such pseudo-Jahn-Teller effects can also affect the reaction $\mathbf{C}\left({ }^{3} P\right)+\mathrm{H}_{2}$ $\rightarrow \mathrm{CH}_{2}$. Those C atoms whose orbital occupancy is $p_{x} p_{y}\left({ }^{3} A_{2}\right)$ can follow the ${ }^{3} A_{2}$ surface, which has no barrier, until the ${ }^{3} A_{2}{ }^{3} B_{1}$ crossing. At the crossing the asymmetric distortion can permit the system to move to the ${ }^{3} B_{1}$ surface and thereby form ground-state $\mathrm{CH}_{2}$ products. Those $\mathrm{C}\left({ }^{3} P\right)$ atoms whose orbital occupancies are $p_{x} p_{z}\left({ }^{3} B_{1}\right)$ or $p_{y} p_{z}\left({ }^{3} B_{2}\right)$ will encounter barriers as the $\mathrm{H}_{2}$ approaches. The ${ }^{3} B_{2}$ surface appears to have the smallest barrier (activation energy) but, as mentioned above, the ${ }^{3} B_{2}{ }^{3} B_{1}$ crossing cannot give rise to a surface transition because $\mathrm{CH}_{2}$ has no $B_{2} \times B_{1}=A_{2}$ vibration, and thus, ${ }^{3} B_{2}$ collisions are ineffective. ${ }^{3} B_{1}$ collisions can proceed directly (that is, with no pseudo-Jahn-Teller effects required) through the barrier on this surface to give ground-state $\mathrm{CH}_{2}$ products.

## Problems

1. You are studying the photochemical reaction in which 1,4 -dewarnaphthalene rearranges in a disrotatory ring opening to yield naphthalene. The relevant energy change is $\Delta E=-48 \mathrm{kcal} / \mathrm{mol}$.


$$
\Delta E=-48 \mathrm{kcal} / \mathrm{mole}
$$

a. Using the one symmetry plane that is conserved in the reaction, draw and label as even ( $a^{\prime}$ ) or odd ( $a^{\prime \prime}$ ) all of the active orbitals of the benzene moiety and of the

moiety. For example,

is $a^{\prime}$.
b. The energy ordering of the orbitals in the dewar structure is $a^{\prime}, a^{\prime}, a^{\prime}, a^{\prime \prime}, a^{\prime}, a^{\prime \prime}$, $a^{\prime}, a^{\prime \prime}, a^{\prime \prime}, a^{\prime \prime}$. Describe the physical characteristics (e.g., $\sigma$ or $\pi$, bonding or antibonding) of each of these orbitals in terms of the benzene and

moiety orbitals.
c. The energy ordering of the $\pi$ orbitals in naphthalene is $a^{\prime}, a^{\prime}, a^{\prime \prime}, a^{\prime}, a^{\prime \prime}, a^{\prime}, a^{\prime \prime}$, $a^{\prime}, a^{\prime \prime}, a^{\prime \prime}$. Draw an orbital-correlation diagram for the reaction, labeling each orbital as $a^{\prime}$ or $a^{\prime \prime}$ and state the nature ( $\sigma, \pi, \sigma^{*}$, or $\pi^{*}$ ) of each orbital.
d. The low-energy excited states of 1,4-dewarnaphthalene lie at $125 \mathrm{kcal} / \mathrm{mol}, 150$ $\mathrm{kcal} / \mathrm{mol}$, and $180 \mathrm{kcal} / \mathrm{mol}$ and are triplet, singlet, and singlet, respectively. Their spatial symmetries are $A^{\prime \prime}, A^{\prime}$, and $A^{\prime \prime}$, respectively. Assign configurations to each of these three excited states and state the configurations of naphthalene with which they correlate. In all cases use the ground state of naphthalene as the reference point of energy.
e. The low-energy excited states of naphthalene lie $60 \mathrm{kcal} / \mathrm{mol}, 90 \mathrm{kcal} / \mathrm{mol}$, and $100 \mathrm{kcal} / \mathrm{mol}$ above the ground state and have ${ }^{3} A^{\prime \prime},{ }^{1} A^{\prime}$, and ${ }^{1} A^{\prime \prime}$ symmetries, respectively. Assign configurations to each of these three states and state the configurations of 1,4 -dewarnaphthalene with which they correlate.
f. Draw a quantitatively correct configuration-correlation diagram using all of the above data. Give spin and space ( $A^{\prime}$ or $A^{\prime \prime}$ ) labels to all configurations. Show how the configurations will mix to give rise to states. You may assume the doubly excited configurations lie $180 \mathrm{kcal} / \mathrm{mol}$ or more above their ground state configurations.

Now, based upon your state-correlation diagram, answer the following:
g. When light of $2850 \AA$ is used to excite the dewarnaphthalene, why does one obtain primary fluorescence of the dewarnaphthalene?
h. What other fluorescence would you expect to see if the wavelength of the exciting light decreases to $2550 \AA$ ? Why? What does the observation of fluorescence at $3195 \AA$ tell you about how the internal energy has been distributed within the excited dewarnaphthalene molecule?
i. At a much longer time after creating the initial excited state of the dewarnaphthalene, why does one see phosphorescence only from naphthalene?
2. The photochemistry of formaldehyde has received much attention recently. It is a "testing molecule" for models of energy-sharing, photodissociation, and internal
conversion. Let us try to understand some of the interesting features of this small molecule.
a. Draw an orbital-correlation diagram for the $C_{2 v}$ decomposition $\mathrm{H}_{2} \mathrm{CO} \rightarrow \mathrm{H}_{2}+\mathrm{CO}$, labeling the orbitals according to their symmetry under the two reflection planes. Repeat this process for the $\mathrm{H}_{2} \mathrm{CO} \rightarrow \mathrm{H}+\mathrm{HCO}$ reaction, assuming the reaction to take place in a manner that preserves one symmetry plane. Include only the active orbitals in these diagrams.

The following facts are available: (1) The lowest $n \pi^{*}$ triplet and singlet excited states of $\mathrm{H}_{2} \mathrm{CO}$ lie $25,200 \mathrm{~cm}^{-1}$ and $28,200 \mathrm{~cm}^{-1}$ above the ground state. (2) The CH bond energy in $\mathrm{H}_{2} \mathrm{CO}$ is $88 \mathrm{kcal} / \mathrm{mol}$. (3) $\mathrm{H}_{2} \mathrm{CO} \rightarrow \mathrm{H}_{2}+\mathrm{CO}$ is exothermic by $11 \mathrm{kcal} / \mathrm{mol}$. (4) $\left.\mathrm{H}_{2} \mathrm{CO}\left({ }^{1} A\right) \rightarrow \mathrm{H}^{2} S\right)+\mathrm{HCO}$ (linear ${ }^{2} \pi$ ) is endothermic by $114 \mathrm{kcal} / \mathrm{mol}$. (5) The lowest $n \pi^{*}$ singlet excited state of CO lies $65,500 \mathrm{~cm}^{-1}$ above its ground state.
b. Draw configuration-correlation diagrams for the $C_{2 v} \mathrm{H}_{2} \mathrm{CO} \rightarrow \mathrm{H}_{\mathbf{2}}+\mathrm{CO}$ reaction and the $C_{s} \mathrm{H}_{\mathbf{2}} \mathrm{CO} \rightarrow \mathrm{H}+\mathrm{HCO}$ (bent) reaction. Label the configurations according to symmetry and indicate how the configurations combine to give rise to states.
c. It is known that excitation of the singlet $n \pi^{*}$ state of $\mathrm{H}_{\mathbf{2}} \mathrm{CO}$ with light between 28,200 and $30,600 \mathrm{~cm}^{-1}$ leads to internal conversion, fluorescence, and formation of ground state $\mathrm{H}_{2}+\mathrm{CO}$. By examining the $C_{2 v}$ correlation diagram, explain how $\mathrm{H}_{\mathbf{2}}+\mathrm{CO}$ could be formed. In particular, what kind of molecular deformation could be involved to allow (in a symmetry sense) the formation of ground-state $\mathrm{H}_{\mathbf{2}}+\mathrm{CO}$ ? Near $28,200 \mathrm{~cm}^{-1}, \mathrm{H}_{2} \mathrm{CO}^{*}$ undergoes fluorescence and internal conversion to ground-state $\mathrm{H}_{2} \mathrm{CO}$ in a ratio fo 1:20. In contrast, $\mathrm{D}_{\mathbf{2}} \mathrm{CO}(\mathrm{D}=$ deuterium) undergoes mostly fluorescence and very little internal conversion. Explain this difference between $\mathrm{H}_{2} \mathrm{CO}$ and $\mathrm{D}_{2} \mathrm{CO}$. (An isotope effect is not a sufficient explanation).
d. As the energy of the exciting light reaches $30,600 \mathrm{~cm}^{-1}$, formation of $\mathbf{H}+\mathrm{HCO}$ becomes possible. On symmetry grounds, what kind of molecular deformation could give rise to these radical products? Be sure to explain the fact that the resulting HCO is bent.
e. Describe the mechanism by which triplet $n \pi^{*} \mathrm{H}_{2} \mathrm{CO}$ (formed by triplet sensitization) quickly gives rise to ground-state singlet $\mathrm{H}_{\mathbf{2}} \mathrm{CO}$.

