## Answers

## Problems Relating to Thermal Processes (Chapter 4)

1. The relevant HOMO and LUMO of the ten-membered ring are the antisymmetric $\sigma_{A}$ bonding and symmetric antibonding $\sigma_{S}^{*}$ orbitals involving the CH bonds. The HOMO and LUMO of the smaller ring are the $\pi_{s}$ and $\pi_{A}^{*}$ orbitals, which are symmetric and antisymmetric, respectively, under reflection through the plane of symmetry that is preserved throughout the reaction. Suprafacial attack would result in favorable HOMO-LUMO interactions ( $\sigma_{A} \leftrightarrow \pi_{A}^{*}$ and $\sigma_{S}^{*} \leftrightarrow \pi_{S}$ ), whereas antarafacial attack would not.

The bond-symmetry rule also indicates that suprafacial attack is allowed because the occupied orbitals of the reactants ( $\sigma_{S}, \sigma_{A}$, and $\pi_{S}$ ) match in symmetry those of the products ( $\pi_{S}, \sigma_{S}$, and $\sigma_{A}$ ), where the $\pi$ bond is now in the ten-membered ring, and $\sigma_{S}$ and $\sigma_{A}$ now refer to CH bonds in the smaller ring.

In applying the Dewar-Zimmerman method, one finds for suprafacial attack, a Hückel transition state having six electrons (two CH bonds and one $\pi$ bond). Again, the suprafacial attack is predicted to be allowed.
2. Using the bond-symmetry rule, one sees that the occupied active orbitals of the cyclopenteneone are the symmetric $\sigma_{s}$ and antisymmetric $\sigma_{A} \mathrm{CC}$ bonding orbitals and the symmetric $p_{s}$ orbital. The plane of symmetry used to make these labels is the only one that persists throughout the reaction path. In the products the active orbitals are the CO lone pair on carbon, which is symmetric $\sigma(\mathrm{CO})_{s}$, and the two occupied $\pi$ orbitals of 1,3-butadiene, which are symmetric $\pi_{s}$ and antisymmetric $\pi_{A}$, respectively. The reactant and product orbitals match in symmetry; hence, the decomposition reaction should be thermally allowed.

In the other case, the relevant occupied orbitals of the cyclohexadieneone are the two CC bonds $\sigma_{S}$ and $\sigma_{A}$ and the two $\pi$ bonds $\pi_{s}$ and $\pi_{s}^{\prime}$ (both of which are symmetric). In the products, the orbitals are $\sigma_{s}(\mathrm{CO})$ and the three occupied orbitals of benzene, which are $\pi_{S}, \pi_{s}^{\prime}$, and $\pi_{A}$ (see section 7.6). Again, the bondsymmetry rule indicates that the thermal decomposition reaction is allowed.
3. This reaction is symmetry-forbidden-it is nothing but two independent [ $2_{s}+2_{s}$ ] cycloaddition reactions. Such reactions were shown to be forbidden in sections 4.4 and 4.8. The reason this problem might lead to confusion is that when using the orbital- and configuration-correlation diagram method, one is tempted to connect the $\pi_{12}-\pi_{56}$ symmetry-adapted orbital, which is antisymmetric under the plane $M 1$, with the $\sigma_{38}-\sigma_{47}$ orbital, which is also odd under $M 1$. However, as becomes clear when one utilizes the orbital-following device, $\pi_{12}-\pi_{56}$ and $\sigma_{38}-\sigma_{47}$ cannot be so connected-they belong to totally distinct portions on this molecule.

By placing two forbidden $\left[2_{s}+2_{s}\right]$ reactions in close spatial proximity, one might incorrectly correlate the reactant and product orbitals. It is not proper to correlate orbitals that are localized on one part of the reactant molecule with those that belong to a different part of the product molecule.
4. If $n$ is odd, the $H$ atom can undergo a suprafacial shift to give HDFC $=\mathrm{C}(-\mathrm{C}=\mathrm{C})_{n}-\mathrm{CR}_{1} \mathrm{R}_{2}$; when $n$ is even, the antarafacial hydrogen shift to the terminal carbon is allowed. In either case, one obtains two isomers that differ geometrically at the $-\mathrm{CR}_{1} \mathbf{R}_{2}$ end and that are enantiomers at the HDFC - end. The two isomers arise in each case because of the free rotation about the $\mathrm{C}-\mathrm{CHR}_{1} \mathrm{R}_{\mathbf{2}}$ bond in the reactant molecule.
5. Methyl-group migration is allowed because the orbital of the $\mathrm{CH}_{3}$ group, which plays a role analogous to that of the $1 s$ orbital of the hydrogen atom, has $s p^{3}$ character. This orbital has both a positive and a negative lobe. By connecting its positive lobe to the orbital of the neighboring carbon atom and its negative lobe to the $p_{\pi}$ orbital of the terminal carbon atom, one achieves a Möbius transition state having four electrons. Thus, the suprafacial methylgroup shift is allowed. Of course, the configuration of the substituents around the methyl group is inverted once the transfer to the 3-carbon takes place.
6. Denoting the three orbitals of the hydrogen atoms by $1 s_{\mathrm{HA}}, 1 s_{\mathrm{HB}}$, and $1 s_{\mathrm{HC}}$ and applying the $a_{1}$ and $e$ symmetry projectors (see Appendix C), one obtains the following (unnormalized) symmetry-adapted orbitals:

$$
\begin{aligned}
& X_{a_{1}}=\left(1 s_{\mathrm{HA}}+1 s_{\mathrm{HB}}+1 s_{\mathrm{HC}}\right) \\
& X_{e}=\left\{\begin{array}{l}
2 \cdot 1 s_{\mathrm{HA}}-1 s_{\mathrm{HB}}-1 s_{\mathrm{HC}} \\
2 \cdot 1 s_{\mathrm{HB}}-1 s_{\mathrm{HA}}-1 s_{\mathrm{HC}}
\end{array}\right.
\end{aligned}
$$

The four nitrogen orbitals can also be symmetry-projected:

$$
\begin{aligned}
& X_{a_{1}}^{\prime}=2 s_{\mathrm{N}} \\
& X_{a_{1}}^{\prime \prime}=2 p_{z \mathrm{~N}} \\
& X_{e}^{\prime}=\left\{\begin{array}{l}
2 p_{x \mathrm{~N}} \\
2 p_{y \mathrm{~N}}
\end{array}\right.
\end{aligned}
$$

(The $z$ axis is chosen to be the 3 -fold symmetry axis of the molecule.)
The three $a_{1}$ atomic orbitals combine to yield bonding ( $\phi_{1}$ ), nonbonding ( $\phi_{4}$ ) and antibonding ( $\phi_{7}$ ) molecular orbitals having $a_{1}$ symmetry. Likewise, the two pairs of $e$ orbitals combine to give pairs of bonding ( $\phi_{2}, \phi_{3}$ ) and antibonding ( $\phi_{5}, \phi_{6}$ ) molecular orbitals having $e$ symmetry.

The ground state of $\mathrm{NH}_{3}$ has an electronic wavefunction that is dominated by the configuration $\phi_{1}^{2} \phi_{2}^{2} \phi_{3}^{2} \phi_{4}^{2}$ (the $1 s_{\mathrm{N}}^{2}$ electrons are neglected). This configuration has ${ }^{1} A_{1}$ symmetry. The singly excited configuration $\phi_{1}^{2} \phi_{2}^{2} \phi_{3} \phi_{4}^{2} \phi_{5}$ gives rise to singlet and triplet states corresponding to all symmetries contained in the direct product $e \times e=e+a_{1}+a_{2}$ (see Appendix C). Of these, the $E$ state would be first-order Jahn-Teller unstable, whereas the other two ( $A_{1}$ and $A_{2}$ ) are not. The $A_{1}$ and $A_{2}$ states could be second-order (actually pseudo-) JahnTeller unstable through coupling, via a distortion of $e$ symmetry, with the $E$ state. The other singly excited configuration $\phi_{1}^{2} \phi_{2}^{2} \phi_{3} \phi_{4}^{2} \phi_{7}$ has $e \times a_{1}=e$ symmetry. This $E$ state should be first-order Jahn-Teller unstable with respect to distortions of $E \times E=E+A_{1}+A_{2}$ symmetry. Of these, the only vibrations of $\mathrm{NH}_{3}$ have $A_{1}$ and $E$ symmetry. The $A_{1}$ vibrations would not remove the degeneracy because they preserve the symmetry of the molecule; hence, only the distortion of $E$ symmetry will be effective.

## Problems on Photochemistry (Chapters 5-7)

The answers to problem 1 are given in the excellent book Problems in Quantum Chemistry by P. Jørgensen and J. Oddershede (Addison-Wesley, Reading, Mass., 1983). On page 238 of this book a discussion of the problem is given, as well as references to the experimental literature relating to this very interesting case.

Complete answers to the questions posed in problem 2 are probably not attainable at this time. Much debate remains about what is really happening in
the photochemistry of formaldehyde. For this reason, it is best to attempt to relate your answers to this problem to some of the best treatments of formaldehyde photochemistry, which are contained in the following references: J. C. Weisshaar and C. B. Moore, (1980), J. Chem. Phys., 72, 5415; H. L. Selzle and E. W. Schlag, (1979), Chem. Phys., 43, 111; D. F. Heller, M. L. Elert, and W. M. Gelbart, (1978), J. Chem. Phys., 69, 4061; J. D. Goddard and H. F. Schaefer III, (1979), J. Chem. Phys., 70, 5117; and many other references contained in these papers.

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