Problems Relating to Thermal Processes (Chapter 4)

1. The relevant HOMO and LUMO of the ten-membered ring are the antisymmetric σ_A bonding and symmetric antibonding σ_s^* orbitals involving the CH bonds. The HOMO and LUMO of the smaller ring are the π_s and π_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 (σ_s , σ_A , and π_s) match in symmetry those of the products (π_s , σ_s , and σ_A), where the π bond is now in the ten-membered ring, and σ_s and σ_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 π 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 σ_s and antisymmetric σ_A 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 $\sigma(CO)_s$, and the two occupied π orbitals of 1,3-butadiene, which are symmetric π_s and antisymmetric π_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 σ_s and σ_A and the two π bonds π_s and π'_s (both of which are symmetric). In the products, the orbitals are σ_s (CO) and the three occupied orbitals of benzene, which are π_s , π'_s , and π_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 M1, with the $\sigma_{38} - \sigma_{47}$ orbital, which is also odd under M1. 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 $[2_s + 2_s]$ 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 $HDFC=C(-C=C)_n-CR_1R_2$; 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 $-CR_1R_2$ end and that are enantiomers at the HDFC— end. The two isomers arise in each case because of the free rotation about the C-CHR₁R₂ bond in the reactant molecule.

5. Methyl-group migration is allowed because the orbital of the CH_3 group, which plays a role analogous to that of the 1s orbital of the hydrogen atom, has sp^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_{π} 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 $1s_{HA}$, $1s_{HB}$, and $1s_{HC}$ and applying the a_1 and e symmetry projectors (see Appendix C), one obtains the following (unnormalized) symmetry-adapted orbitals:

$$X_{a_1} = (1s_{HA} + 1s_{HB} + 1s_{HC})$$
$$X_e = \begin{cases} 2 \cdot 1s_{HA} - 1s_{HB} - 1s_{HC} \\ 2 \cdot 1s_{HB} - 1s_{HA} - 1s_{HC} \end{cases}$$

The four nitrogen orbitals can also be symmetry-projected:

$$X'_{a_1} = 2s_N$$
$$X''_{a_1} = 2p_{zN}$$
$$X'_{e} = \begin{cases} 2p_{xN} \\ 2p_{yN} \end{cases}$$

(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 (ϕ_1) , nonbonding (ϕ_4) and antibonding (ϕ_7) molecular orbitals having a_1 symmetry. Likewise, the two pairs of *e* orbitals combine to give pairs of bonding (ϕ_2, ϕ_3) and antibonding (ϕ_5, ϕ_6) molecular orbitals having *e* symmetry.

The ground state of NH₃ has an electronic wavefunction that is dominated by the configuration $\phi_1^2 \phi_2^2 \phi_3^2 \phi_4^2$ (the $1s_N^2$ electrons are neglected). This configuration has 1A_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-) Jahn-Teller 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 NH₃ 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

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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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Appendix A

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