Vibrational Modes, Orbital Symmetries, and Unimolecular Reaction Paths[1]

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Abstract: The conditions for favorable unimolecular reaction paths developed by Bader[2] and one of the authors[3] are used, together with a semilocalized molecular orbital model, to determine the allowed routes in the pyrolysis of cyclobutane and cyclohexene. It is found that the coplanar 2s + 2s decomposition of cyclobutane should proceed more favorably in two steps, with a predominant contribution from the E_u carbon–carbon stretching mode, than in the concerted B_{1g} mode. On the other hand, 2s + 2s concerted decomposition by puckering in the B_{1u} mode combined with (A_{1u} + E_g) twisting is favored. These conclusions are in agreement with the predictions of Woodward and Hoffmann.[4] The favored paths in cyclobutane are essentially determined by the harmonic terms in the potential energy surface and correspond to symmetry coordinates with low force constants. In the Diels–Alder retrogression of cyclohexene, however, the force constant for the allowed concerted motion is not much smaller than that for the forbidden process. The method should be useful for predicting the course of other unimolecular reactions.

Perturbation theory can be used to express the various differentials of the molecular electronic energy with respect to some nuclear coordinate Q, for instance, a vibrational symmetry coordinate. In the expressions which are obtained,[2,3] the energy differentials appear as sums of a classical term involving the electron density at equilibrium and of quantum-mechanical "relaxation" terms which express the rearrangement of the electron density as the nuclear distortion occurs. For instance, the force constant is the difference between a positive, "classical" force constant and a negative relaxability which includes matrix elements between the ground-state wave function and the wave functions for the various excited states of the molecule. Such an expression is particularly convenient when comparing the force constants of symmetry modes which involve *symmetry-equivalent internal valency* coordinates (bond lengths or bond angles), such as the carbon–carbon stretching modes in benzene or cyclobutane, the HCH bending modes in ethylene, etc. Indeed the classical energy expenditure for such modes is very nearly the same.[5] The relaxability can then discriminate between the force constants for the various modes. Large differences in these constants will reflect large interactions (and interaction constants) between the symmetry-equivalent internal valency coordinates.

Under these conditions, and under the reasonable assumption that low positive second- and large negative third-order energy differentials at equilibrium will ensure a low energy barrier along the corresponding coordinate, it is possible to write the conditions for a favorable reaction path along a given coordinate. The conditions are fourfold, as follows (for a totally symmetric ground state): (1) there is at least one excited state of same symmetry as the normal mode corresponding to the reaction coordinate;[2] (2) the excitation energy is as low as possible;[2] (3) the electronic transition density from the ground state to this excited state is localized in the region of nuclear motion;[3] (4) the corresponding excitation energy decreases as the reaction coordinate proceeds.[3] These conditions are valid only for comparison of motions where the classical energy expenditure is the same.

In large polyatomic molecules the conditions can be applied with the following procedure. One first seeks out one-electron excitations, whose transition densities *can exert important forces* ("transition forces") *in the direction of required nuclear motion* (condition 3). Then one verifies whether some of these excitations verify conditions 1 and 2. If one or several appropriate excitations can be found, the reaction is already favored by the harmonic terms in the potential energy. Condition 4, finally, must be verified to ensure that the path is not abruptly hindered as the molecule departs further from equilibrium. We shall now proceed to apply these conditions to the pyrolysis of cyclobutane and of cyclohexene. But first we describe a simple orbital model which is convenient for this type of problem.

A Semilocalized Molecular Orbital Model

The molecular reactants of interest here are the "saturated" products of cycloadditions or electrocyclic reactions in which π electrons are converted into σ elec-

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[2] R. F. W. Bader, *Mol. Phys.*, 3, 137 (1960); *Can. J. Chem.*, 40, 1164 (1962); see also R. G. Pearson, *J. Am. Chem. Soc.*, 91, 1252 (1969).

[3] L. Salem, *Chem. Phys. Letters*, 3, 99 (1969).

[4] (a) R. B. Woodward and R. Hoffmann, *Accounts Chem. Res.*, 1, 17 (1968); *Angew. Chem. Intern. Ed. Engl.*, in press. (b) In recent experiments, A. T. Cocks, and H. M. Frey, *J. Chem. Soc.*, *A*, 1671 (1969), find a much lower rate of pyrolysis for 1,1,3,3-tetramethylcyclobutane than for 1,1-dimethylcyclobutane. This would indicate a large 1,3 interaction in the transition state.

[5] The difference in the force constants of symmetry modes Q which involve symmetry-equivalent internal coordinates is measured by the interaction constants. These interaction constants determine the extent to which the force constants for the Q's depart from the value for the isolated internal valency coordinate. Now interaction constants, though determined essentially by relaxabilities, *do not have an entirely nonclassical origin.* The "classical" term[3] $(\partial^2 V/\partial Q^2)_{00}$ itself contains differentials of nonbonded nuclear repulsions (see eq 4 of Bader's first paper[2]) which contribute to the interaction constants. Hence the "classical" force constants for the different symmetry modes Q are not quite equal. The very small differences depend essentially on the effective nuclear charges for the nuclear motion (accompanied by orbital following), which should be nearly zero for the relative motion of nonbonded nuclei. Furthermore these differences should be insensitive to the electronic details of the bonds. For the B_{1g} and E_u modes studied here, the difference vanishes exactly.

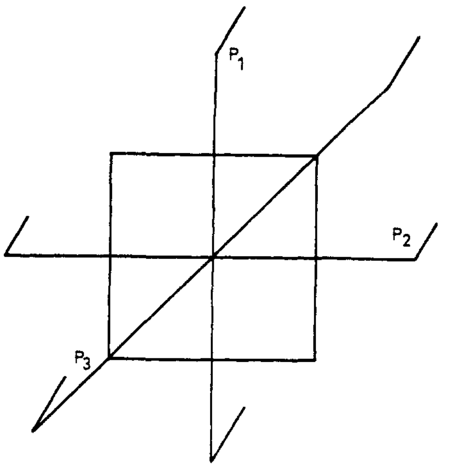

Figure 1. Planes of symmetry in planar cyclobutane.

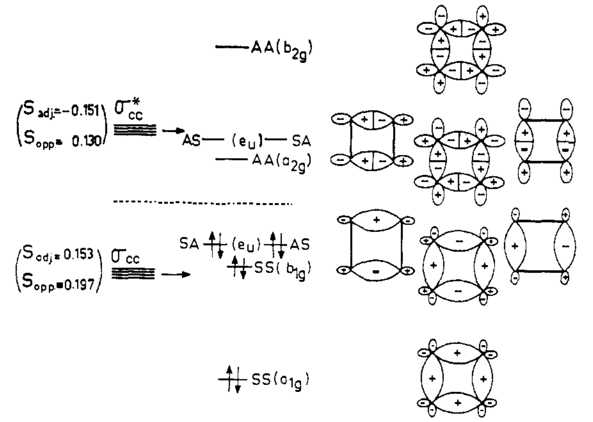

Figure 2. Semilocalized CC orbitals in cyclobutane.

trons: cyclobutane, cyclohexene, cyclobutene. A useful description starts with orbitals which are localized in the various bonds, CC or CH. Such a *bond-orbital* description has been used successfully in a recent analysis[6] of the rotational barrier in ethane. The bond orbitals of quasi-planar cyclobutane, for instance, are the bonding σ_{CC} and σ_{CH} and the antibonding σ^*_{CC} and σ^*_{CH} orbitals. The weak nonorthogonality of these orbitals makes them an appropriate basis for molecular combinations which are *semilocalized.* These semilocalized orbitals cover the entire nuclear framework but are restricted to a given set of bonds so that they still have a certain *local* character. Such orbitals seem to be a logical choice for the study of vibrational symmetry coordinates which are expressed likewise as linear combinations of *local* valency coordinates. In particular it is relatively easy to select the proper pairs of semilocalized orbitals for which the transition density lies precisely in a given region of internal valency motion.

The semilocalized orbitals can often be determined by symmetry arguments alone, and their relative energy is estimated by consideration of the overlap between the various component bond orbitals. In cyclobutane the four σ_{CC} orbitals are combined to give four semilocalized combinations, and similarly for the σ^*_{CC} orbitals. The σ_{CH} orbitals are first combined by pairs on each carbon atom to give a σ_{CH_2} and a π_{CH_2} orbital. The latter are then mixed to give semilocalized σ_{CH_2} and π_{CH} molecular orbitals; similarly semilocalized $\sigma^*_{CH_2}$ and $\pi^*_{CH_2}$ orbitals are obtained. Of course in a complete molecular orbital calculation the σ_{CC} and σ_{CH_2} semilocalized orbitals will mix. The description of the σ-bonding orbitals as localized *either* in the CC bonds *or* in the CH bonds, whereas the correct molecular orbitals will be localized on *both* sets of bonds, but with a larger amplitude on one of the two sets, shows precisely the limits of the theory. We now consider the procedure in more detail in the case of cyclobutane with the carbon skeleton assumed in a near-equilibrium planar configuration.

Figure 1 shows the important planes of symmetry P_1 and P_2 which serve to classify the semilocalized orbitals for quasi-planar cyclobutane. These symmetry planes are identical with those used by Hoffmann and Woodward in their symmetry classification of the orbitals in the *cis–cis* dimerization of ethylene.[7] Plane P_2 cuts through the bonds which will eventually break. Also shown is plane P_3, passing through opposite carbon atoms, and which will be used as an additional element for symmetry classification. We first consider the σ^*_{CC} and σ_{CC} bond orbitals. Initially, before the interaction between electrons and nuclei in different bonds is accounted for, these orbitals fall into two degenerate groups of four orbitals, as shown on the left-hand side of Figure 2. The bond–bond interaction lifts the degeneracy, and proper semilocalized orbitals can be constructed which cover the entire carbon–carbon skeleton. The proper combinations of bond orbitals are entirely determined by symmetry; they are drawn schematically on the right-hand side of the figure,[8] and their symmetry denomination (S, symmetric, or A, antisymmetric, relative first to P_1 and secondly to P_2) together with their D_{4h} group-theoretical denomination, is given on the orbital energy pattern. The latter is obtained approximately by assuming that the matrix element of the Hamiltonian between two bond orbitals is proportional to their overlap.[9] For the bonding σ_{CC} orbitals, the overlap between opposite bond orbitals is larger than that between orbitals on adjacent bonds, so that the degenerate pair of semilocalized orbitals ($\sigma_{C_1C_2}$–$\sigma_{C_3C_4}$) and ($\sigma_{C_2C_3}$–$\sigma_{C_4C_1}$) probably lies highest in energy. The antibonding σ^*_{CC} orbitals are essentially characterized by a *negative* overlap between adjacent bond orbitals, so that the semilocalized combination with alternating signs ($\sigma^*_{C_1C_2} - \sigma^*_{C_2C_3} + \sigma^*_{C_3C_4} - \sigma^*_{C_4C_1}$) lies lowest in energy.

In order to obtain the semilocalized CH orbitals, one must first combine CH orbitals on the same carbon atom, as shown in Figure 3. Thus σ_{CH}, which lies above the plane, and $\sigma'_{CH'}$, which lies below the plane, can form a positive symmetric σ_{CH_2} combination and a negative antisymmetric π_{CH_2} combination. The antibonding σ^* orbitals can be combined in a similar fashion to give $\sigma^*_{CH_2}$ and $\pi^*_{CH_2}$ combinations. The σ_{CH_2} and $\sigma^*_{CH_2}$ "group" orbitals are then combined to form semilocal-

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[6] (a) O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *J. Chem. Phys.*, **49**, 2592 (1968); (b) J. R. Hoyland, *J. Am. Chem. Soc.*, **90**, 2227 (1968); *J. Chem. Phys.*, **50**, 473 (1969).

[7] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

[8] In this figure the CC bond orbitals have been drawn along the bond axes. In actual fact the orbitals are slightly bent relative to the bond direction, as shown in Figures 8 and 10. Similarly the σ_{CH_2} and π_{CH_2} orbital axes are not quite perpendicular to the molecular plane, as Figures 4 and 5 would suggest.

[9] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

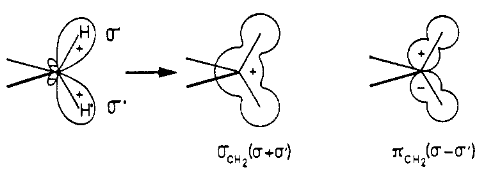

Figure 3. Formation of localized σ_{CH_2} and π_{CH_2} orbitals (σ^* and σ'^* can be combined similarly to form σ^* and $\pi^*_{CH_2}$ orbitals).

ized molecular orbitals. The proper combinations are again determined by symmetry and are shown in Figure 4. Here the overlap between adjacent group orbitals is the determining factor, and the orbital energy pattern, both bonding and antibonding, resembles the Hückel π-orbital energy pattern for cylcobutadiene. The same holds for the energy pattern of the semilocalized π_{CH_2} and $\pi^*_{CH_2}$ orbitals, which is shown in Figure 5. Note that in both cases (σ_{CH_2} and π_{CH_2}) the symmetry denomination of the antibonding orbitals repeats that of the bonding orbitals—contrary to the σ_{CC} case.

Coplanar Decomposition of Cyclobutane

The pyrolysis of cyclobutane to yield two ethylene molecules (Figure 6) can conceivably occur in two distinct manners[4] (we mention later a third possibility). If opposite carbon bonds are stretched while the carbon skeleton stays roughly coplanar, the two product ethylene molecules separate *cis* relative to each other (2s + 2s retro-addition). If, however, the molecule decomposes by puckering combined with CH_2 twisting, the reaction is a 2s + 2a retro-addition, *cis* with respect to one ethylene but *trans* with respect to the other. We consider in turn these two modes of decomposition, and first the coplanar scission.

Figure 7 shows the three C–C stretching symmetry coordinates for planar cyclobutane (D_{4h} point group). These modes are

$$Q^{A_{1g}} = \frac{1}{2}(C_1C_2 + C_2C_3 + C_3C_4 + C_4C_1)$$

$$Q^{B_{1g}} = \frac{1}{2}(C_1C_2 - C_2C_3 + C_3C_4 - C_4C_1)$$

$$Q^{E_u{}^a} = \frac{1}{\sqrt{2}}(C_1C_2 - C_3C_4)$$

$$Q^{E_u{}^b} = \frac{1}{\sqrt{2}}(C_2C_3 - C_4C_1)$$

where C_1C_2 is the bond length between carbon atoms 1 and 2. Now the motions to which the organic chemist is accustomed are expressed directly in terms of the bond-length changes. For instance, a distinction can be made between the *concerted* opening of opposite bonds

$$\frac{1}{\sqrt{2}}(C_1C_2 + C_3C_4) = \frac{1}{\sqrt{2}}(Q^{A_{1g}} + Q^{B_{1g}})$$

and the *two-step* motion in which one bond alone opens in the first step.

$$C_1C_2 = \frac{1}{2}(Q^{A_{1g}} + Q^{B_{1g}} + \sqrt{2}Q^{E_u{}^a})$$

This two-step motion leads to a biradical intermediate.

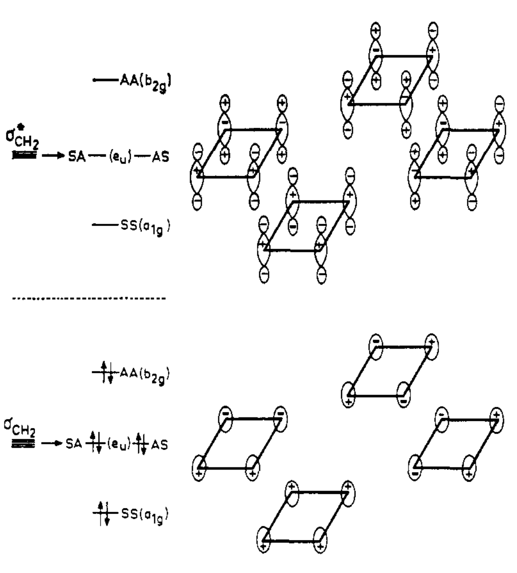

Figure 4. Semilocalized σ_{CH_2} orbitals.

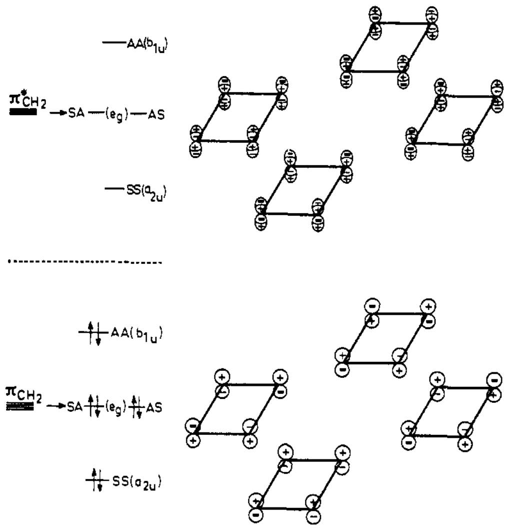

Figure 5. Semilocalized π_{CH_2} orbitals.

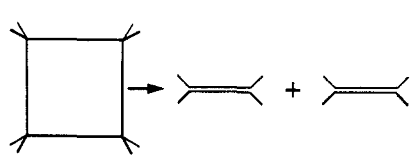

Figure 6. Pyrolysis of cyclobutane.

Although both the concerted and two-step motions involve a mixture of symmetry coordinates, it is clear that a unique symmetry mode characterizes each one: the B_{1g} mode the concerted motion, the E_u mode the two-step motion. In the familiar Woodward–Hoffmann symmetry notation, the B_{1g} (concerted) mode is SS, while the $E_u{}^a$ (two-step) is AS. However, the totally symmetric A_{1g} mode is also SS and to distinguish the B_{1g} mode from the A_{1g} mode it is necessary to introduce the symmetry (S or A) relative to the plane P_3 (Figure 1). The B_{1g} mode is SS (A) whereas the A_{1g} mode is SS (S).

We now investigate whether the conditions[2,3] given in the introduction predict a favorable reaction path of SS (A) symmetry or AS symmetry. Since the motion

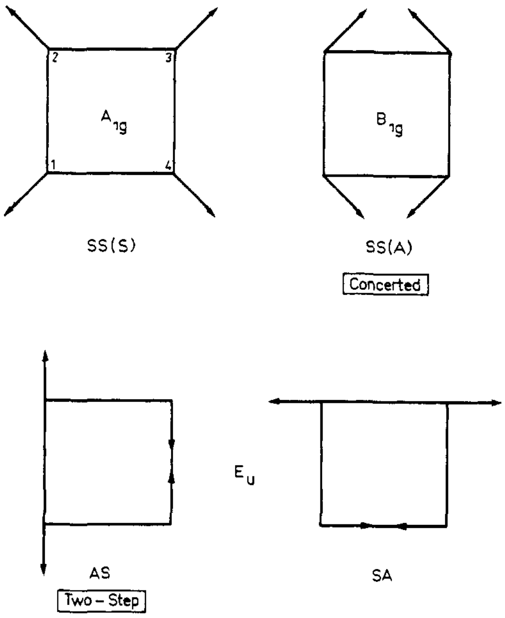

Figure 7. CC stretching symmetry coordinates for planar cyclobutane.

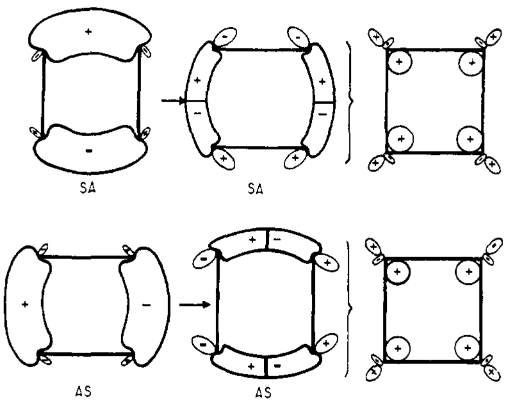

Figure 8. $\sigma_{CC} \rightarrow \sigma^*_{CC}$ transitions giving rise to SS transition densities.

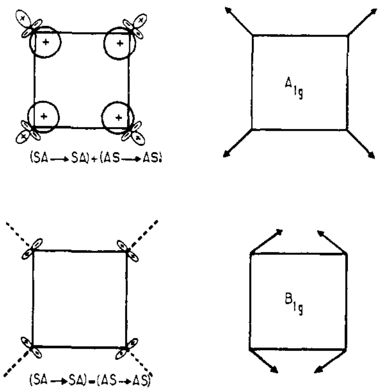

Figure 9. Components of $e_u \rightarrow e_u$ transition leading to A_{1g} and B_{1g} motion.

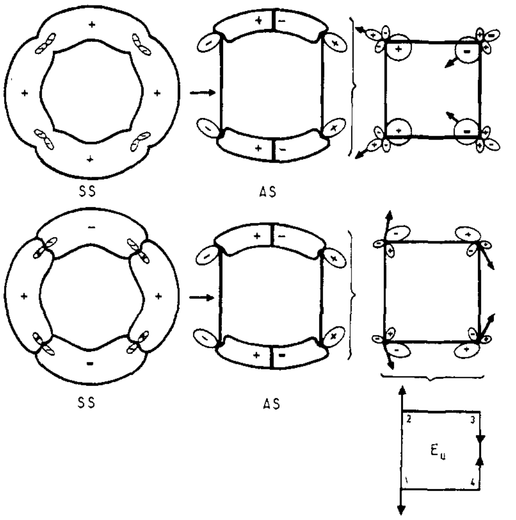

Figure 10. $\sigma_{CC} \rightarrow \sigma^*_{CC}$ transitions giving rise to AS transition densities (the translational components are ultimately cancelled out[10]).

involves C–C bond breaking with displacements of the carbon atoms *in* the molecular plane, the appropriate excited states must involve one-electron transitions between σ_{CC} and σ^*_{CC} semilocalized orbitals. This ensures that the transition density will be localized in the CC bond regions, which are precisely the regions of nuclear motion. Consideration of Figure 2 shows that there are two transitions of SS symmetry and four transitions of AS symmetry.

$$\sigma_{CC}(SA) \longrightarrow \sigma^*_{CC}(SA),\ \sigma_{CC}(AS) \longrightarrow \sigma^*_{CC}(AS) \quad (SS)$$

$$2\sigma_{CC}(SS) \longrightarrow \sigma^*_{CC}(AS),\ \sigma_{CC}(SA) \longrightarrow 2\sigma^*_{CC}(AA) \quad (AS)$$

Let us first consider the two transitions of SS symmetry. The transition density is proportional to the product of the two orbitals involved in the transition. Now the $\sigma_{CC}(SA)$ and $\sigma^*_{CC}(SA)$ molecular orbitals are localized on different pairs of bonds so that the transition density vanishes everywhere except near the corners of the square formed by the four carbon atoms, where adjacent σ_{CC} and σ^*_{CC} bond orbitals have appreciable overlap. Figure 8 shows the approximate transition density for both transitions of SS symmetry. It is clear that neither transition density alone leads to nuclear motion in the A_{1g} or B_{1g} modes. However, the positive combination of the two excitations has a transition density which leads to SS(S) or A_{1g} motion, as shown in Figure 9. Similarly the negative combination leads to SS(A) or B_{1g} motion. These results follow directly from group theory, which requires the over-all $e_u \rightarrow e_u$ excitation to include an A_{1g} and a B_{1g} state. Therefore both the B_{1g} motion we were seeking and the A_{1g} motion are favored, according to the first and third conditions of the introduction.

Let us now consider the four excitations which give rise to AS transition densities. Figure 10 shows the transition densities from the two bonding SS semilocalized orbitals to the AS antibonding orbital. These transition densities now favor unambiguously an E_u^a motion in which one bond alone breaks.[10] The first and third conditions for a favorable reaction path are therefore again satisfied. It is interesting to discuss here the fourth condition, which represents the require-

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(10) The additional translational components which arise from such transition densities (A with respect to a symmetry plane and u with respect to the center of inversion) are similar to the translational forces which arise in homonuclear diatomics from $\sigma_g \rightarrow \sigma_u^*$ transitions which are also A and u. The apparent energy gain for this translational motion is cancelled out by the energy loss contributed by the "classical" force constant term.

ment for large anharmonicity.[3] In a first approximation only the 12 and 34 bond orbitals are affected by the E_u motion. One bond orbital (12) is raised while the other (34) is lowered. Hence there is approximately no energy change in either of the two SS semilocalized orbitals. Since the σ^*(AS) orbital is also unaffected, the excitation energies remain constant, so there should be no significant anharmonicity factor. (However, as the system approaches the diradical stage, the potential energy must flatten out, because the correct two-step motion, which has an admixture of A_{1g} and B_{1g} modes, involves only the lengthening of bond 12.)

In summary both the "concerted" B_{1g} motion and the E_u motion which lead to a diradical intermediate can be relaxed by $\sigma_{CC} \rightarrow \sigma^*_{CC}$ transitions. However, the extent to which the favorable relaxation occurs differs vastly for the two modes. To begin with there are four excitations which favor E_u and only *one* which favors B_{1g}. Furthermore the transition forces leading to B_{1g} motion should be *small*, the B_{1g} transition density having the distinctive feature that the contribution near a given carbon atom comes only from the overlap of orbitals centered on adjacent atoms (if t_1 and t_1' are the tetrahedral hybrids pointing from atom 1 respectively toward its adjacent carbons 2 and 4, and t_2 and t_4 the hybrids pointing toward atom 1, the A_{1g} transition density involves $t_1t_1' - t_2t_4$, the B_{1g} density $-t_1t_4 + t_1't_2$, and a typical E_u density $-t_1^2 + t_1t_1' + t_1t_4 - t_1't_2$; overlap densities of type t_1t_4 or $t_1't_2$ are relatively small).[10a] Finally the lowest $\sigma_{CC} \rightarrow \sigma^*_{CC}$ excited state is precisely the σ_{CC} (e_u) $\rightarrow \sigma^*_{CC}$ (a_{2g}) excited state which is useful in the E_u relaxation. It is most likely, therefore, that the two-step motion will be preferred to the concerted one. The essential factor, as expressed by the first three conditions for favorable reactions paths, is the *harmonicity* of the potential energy: the force constant must be much larger for a concerted decomposition than for a two-step decomposition. These results agree with the normal coordinate analysis of Lord and Nakagawa,[11] which gives force constants of 3.659×10^5 and $[1.391 \times 10^5]$ dynes/cm for the B_{1g} and E_u modes, respectively. They also indicate that there is a large positive interaction constant[5] between the stretching of opposite CC bonds in cyclobutane.

It is remarkable that Woodward and Hoffmann's result[7] for the cycloaddition of two ethylene molecules can be obtained by sole consideration of the saturated adduct. The present method even demonstrates the feasibility of the two-step motion, whereas the Woodward–Hoffmann diagram demonstrates only the forbiddenness of the concerted motion. A curious feature of this method is that it involves orbitals which are not present in the Woodward–Hoffmann correlation diagram. Figure 11 shows the *full* correlation diagram for the 2s + 2s dimerization[4] of ethylene, in which the σ_{CC} orbitals of the ethylenic bonds have been included. In cyclobutane the correct higher σ(SS) bonding and lower σ^*(AA) antibonding orbitals are those given in Figure 2. They would have to be combined each with its partner of identical symmetry to obtain the "Woodward–Hoffmann" orbitals localized in bonds 12 and 34 alone, together with two other orbitals localized in the ethylenic bonds (14 and 23).

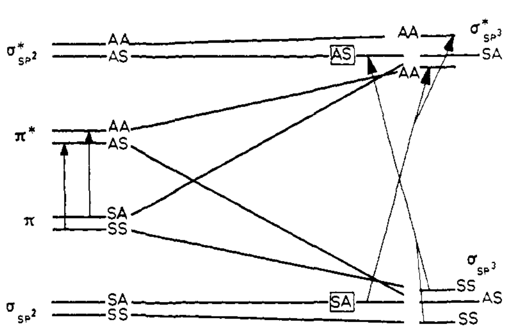

Figure 11. Full correlation diagram for 2s + 2s dimerization of ethylene. Arrows indicate transitions allowing for AS relaxability.

The relevant excitations which allow AS motion are shown by arrows in Figure 11. For the weakly interacting ethylene molecules, excitations between π and π^* orbitals suffice to obtain AS motion. However, each excitation in cyclobutane involves at least one orbital (enscribed in a square) which does not correlate with the initial, purely π, Woodward–Hoffmann orbitals: an AS antibonding orbital for one pair of excitations, an SA bonding for the other pair. A tentative explanation for the apparent discrepancy between the inclusion of these orbitals here and their neglect in the usual correlation diagram is the following. The occurrence in the molecular relaxability of a transition density to a given excited orbital implies that the corresponding excited-state wave function mixes with the ground-state function as the reaction proceeds. Here the mixing-in of antibonding AS character in the ground-state wave function of cyclobutane is equivalent to an increase in energy of an AS bonding orbital—and this is precisely the behavior of the Woodward–Hoffmann σ(AS) orbital in cyclobutane, which correlates with a π^* antibonding orbital. Similarly excitation from an SA orbital implies that the ground state loses bonding SA character, which must be acquired in counterpart by some SA excited orbital. Again this is exactly what happens in the Woodward–Hoffmann correlation diagram: the σ^*(SA) orbital in cyclobutane correlates with a bonding π(SA) orbital. The behavior of the cyclobutane relaxability is therefore coherent with the orbital behavior in the Woodward–Hoffmann correlation diagram.

Decomposition of Cyclobutane by Puckering Combined with CH_2 Twisting

We now consider the alternative, $\sigma^2s + \sigma^2a$, mode for decomposition of cyclobutane (Figure 12). According to Woodward and Hoffmann[4] the pyrolysis of cyclobutane along this reaction coordinate can occur in a concerted manner. We therefore proceed to investigate whether the conditions given in the introductory section are satisfied. The motion, in which only one axis of symmetry is conserved, is a complicated mixture in which quite a few normal modes intervene. Particularly important are the puckering motion of the ring and the twisting motion of the methylene groups attached to

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(10a) Note Added in Proof. This argument does not account for the lower force constant of the B_{1g} mode relative to the A_{1g} mode (4.238×10^5 dynes/cm). The lower energy of the (SA $\rightarrow$ SA)-(AS $\rightarrow$ AS) configuration, when electron repulsion is included, may be responsible here.

(11) R. C. Lord and I. Nakagawa, *J. Chem. Phys.*, 39, 2951 (1963). The E_u "ring deformation" mode actually includes hydrogen motion. To proceed from the force constant for this motion to one for the pure bond-stretching mode, some additional assumption would have to be made: R. C. Lord, private communication, 1969.

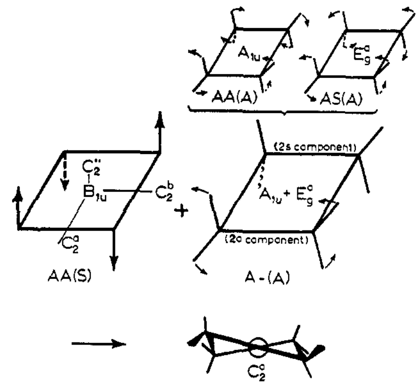

Figure 12. 2s + 2a motion in cyclobutane.

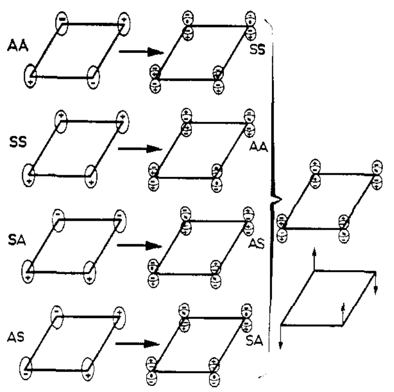

Figure 13. $\sigma_{CH_2} \rightarrow \pi^*_{CH_2}$ transitions leading to AA transition densities of π symmetry (a similar result holds for $\pi_{CH_2} \rightarrow \sigma^*_{CH_2}$ transitions).

the CC bond which breaks up in antarafacial manner. The other two CH_2 groups also twist, but to a lesser extent since the stereochemistry at the suprafacial component is conserved.

The puckering coordinate has B_{1u} symmetry and can be written[11]

$$Q^{B_{1u}} = \frac{1}{2}(Z_1 - Z_2 + Z_3 - Z_4)$$

where Z_1 is the coordinate, along an axis perpendicular to the molecular plane, of carbon atom 1, etc. With respect to P_1 and P_2 it has AA symmetry. However, several symmetry elements are still conserved: P_3, and three twofold axes $C_2{}^a$, $C_2{}^b$, and C_2''. Further with respect to the *molecular* plane the motion has π symmetry. Appropriate excitations must therefore also have π symmetry, with the corresponding transition densities localized as much as possible just above and below the carbon atoms, *i.e.*, along the Z axes. Clearly the best orbitals for such a purpose are the σ_{CH_2} and π_{CH_2} group orbitals, and appropriate transitions are those from σ_{CH_2} to $\pi^*_{CH_2}$, or π_{CH_2} to $\sigma^*_{CH_2}$, semilocalized orbitals. Figure 13 shows that there are four one-electron excitations of the former type which have the appropriate AA symmetry. The common, over-all transition density for these excitations is shown on the right-hand side of the figure, together with the favored nuclear motion. The puckering is effectively favored. The same results hold for the $\pi_{CH_2} \rightarrow \sigma^*_{CH_2}$ excitations.

There remains to consider how the orbital energies are affected by the nuclear motion. As the puckering sets in, the overlap between adjacent CH_2 groups will decrease. The energy of the degenerate (SA, AS) pairs of semilocalized σ_{CH_2} or $\pi^*_{CH_2}$ orbitals, which are over-all "nonbonding," will not change in first approximation. The σ_{CH_2}(SS) orbital is raised, while the $\pi^*_{CH_2}$(AA) orbital is lowered, and the corresponding excitation energy decreases; however, this is compensated by the energy increase in the $\sigma_{CH_2}(AA) \rightarrow \pi^*_{CH_2}(SS)$ transition. Altogether, then, anharmonicity does not seem to play a major role. Again the motion is favored by a low force constant (0.610×10^5 dynes/cm).[11]

The twisting modes of the CH_2 groups which combine to give the appropriate motion of the two groups attached to the antarafacial C_1C_4 σ component have respectively A_{1u} (AAA) and E_g (ASA) symmetry.

$$A_{1u} = \frac{1}{2}(\text{twist}_1 + \text{twist}_1 + \text{twist}_3 + \text{twist}_4)$$

(fully conrotatory)

$$E_g{}^a = \frac{1}{2}(\text{twist}_1 - \text{twist}_2 - \text{twist}_3 + \text{twist}_4)$$

$$\frac{1}{\sqrt{2}}(A_{1u} + E_g{}^a) = \frac{1}{\sqrt{2}}(\text{twist}_1 + \text{twist}_4)$$

This motion destroys the plane P_3 as element of symmetry as well as C_2'' and the twofold axis $C_2{}^b$ crossing through the midpoints of the bonds which break. Figure 12 shows that the only remaining symmetry element is the twofold axis C_{2a} passing through the bonds which become ethylenic.[4]

We now apply the procedure outlined in the introductory section to the two hydrogens attached to a same carbon atom which move in opposite directions. The relevant transitions must therefore be $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$. Furthermore the $\sigma(\pi)$ and $\pi(\sigma)$ orbitals must be semilocalized respectively on the CH_2 groups and on the CC bonds, with transition densities in the region of the CCH angles and which tend to pull the hydrogens into the carbon plane. The appropriate transitions are therefore $\pi_{CH_2} \rightarrow \sigma^*_{CC}$ and $\sigma_{CC} \rightarrow \pi^*_{CH_2}$. Consideration of Figures 2 and 5 shows that, in the $\pi_{CH_2} \rightarrow \sigma^*_{CC}$ manifold, for example, the lowest bonding π_{CH_2}(SS) to lowest antibonding σ^*_{CC}(AA) transition has the appropriate AAA symmetry, as does the negative combination of SA → AS and AS → SA transitions. Similarly the bonding π_{CH_2}(SA) to lowest antibonding σ^*_{CC}(AA) transition and a combination of the AA → SA and SS → AS transitions have the appropriate ASA symmetry. Transitions to the top antibonding AA orbital are not effective because they have S symmetry relative to P_3. Again the electron density can relax relatively easily and the twisting motion is allowed.

Hence the 2s + 2a retrogression appears to be a favorable reaction path for pyrolysis. At this stage, however, it is important to seek out in what manner this path differs from that for the forbidden 2a + 2a retrogression.[4] Careful consideration shows that the 2a + 2a motion involves the *same* puckering mode, but that the CH_2 twisting motion is the pure conrotatory A_{1u} mode. In this manner the twofold symmetry axes $C_2{}^b$ and C_2'' are also conserved. Do our calculations fail to draw

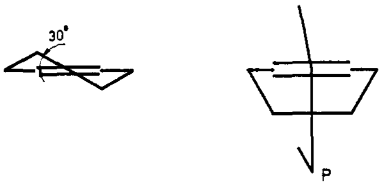

Figure 14. Stable cyclohexene[13] and cyclohexene "prepared" for scission to butadiene + ethylene.

any distinction between the two retrogressions? There is apparently one significant difference. The excitation energy for the $\pi_{CH_2}(SA) \rightarrow \sigma^*_{CC}(AA)$ transition which contributes to E_g twisting is smaller than for the $\pi_{CH_2}(SS) \rightarrow \sigma^*_{CC}(AA)$ transition which contributes to A_{1u} twisting (the other two transitions have similar average excitation energies). This is in agreement with the difference in the observed force constants: 0.710×10^5 dynes/cm for the E_g mode and an estimated value of 0.914×10^5 dynes/cm for the A_{1u} mode.[11] Such a difference is quite significant for twisting motions of symmetry-equivalent groups, and the over-all motion should involve a large E_g component.

Diels–Alder Retrogression of Cyclohexene[12]

We now turn to a 4 + 2 adduct, cyclohexene, for which the unimolecular decomposition is expected to occur in a concerted fashion.[7] Stable cyclohexene has the half-chair conformation shown on the left-hand side of Figure 14. The angle of deviation from planarity is 30°.[13] In the Diels–Alder retrogression which ultimately yields ethylene and butadiene, the molecule is probably "prepared" in the boat conformation shown on the right-hand side of the figure. Also shown is the plane of symmetry P which exists in this equilibrium conformation.

The relevant motions of the carbon skeleton are given in Figure 15. In the concerted, S motion all the bonds tend to lengthen or to shorten according to their destiny in the products. The double bond lengthens and the adjacent single bonds shorten, in accordance with the situation in butadiene. Bonds 34 and 56 ultimately break. The two-step motion, in which only one bond breaks in the first stage, is a mixture of vibrational coordinates in which the A motions I and II (Figure 15) play a critical role.

$$\mathrm{I} = \frac{1}{2}(-C_2C_3 + C_3C_4 - C_5C_6 + C_6C_1)$$

$$\mathrm{II} = \frac{1}{2}(C_2C_3 + C_3C_4 - C_5C_6 - C_6C_1)$$

(The second coordinate actually includes changes in the CCC bond angles because it is impossible to lengthen two adjacent bonds and shorten two opposite ones while keeping all angles at 120°.) The positive combination of I and II leads to the A motion $(1/\sqrt{2})(C_3C_4 - C_5C_6)$ which resembles the E_u stretching mode of cyclobutane.

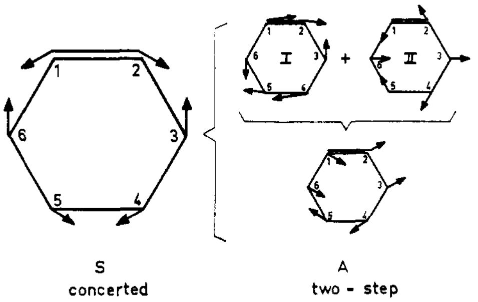

Figure 15. Concerted and two-step motion of the carbon skeleton.

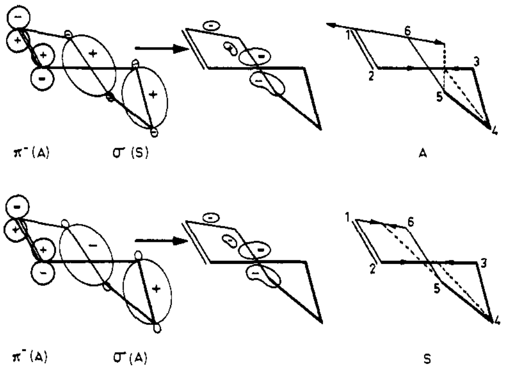

Figure 16. "$\sigma \rightarrow \pi^*$" transition densities[14] in cyclohexene.

We now enquire into the relevant excitations which obey the conditions for favorable reaction paths. Contrary to the case of cyclobutane, and because of the significant nonplanarity of the carbon skeleton (see Figure 16), transitions between carbon–carbon σ orbitals[14] need not guarantee a satisfactory motion of the carbon nuclei. The π and π* orbitals[14] in the double bond almost certainly play a determining role. The contrary would make it difficult to understand the expected alternation of behavior[7] when the conjugated system is extended. Also a study of the transition densities for σ_{CC} to σ^*_{CC} excitations in a quasi-planar model does not lead to any distinction between S and A motions. Finally the second of the four conditions, that of low-lying excited states, points toward the intervention of $\pi \rightarrow \pi^*$ or $\sigma \rightarrow \pi^*$ transitions. Since the former is localized only in the region of bond 12, we are brought to conclude that the important transitions occur between the σ orbitals of bonds 34 and 56 and the π orbitals of bond 12. These orbitals are precisely those of the Woodward–Hoffmann correlation diagram.[7] The relevant $\sigma_{CC} \rightarrow \pi^*_{C=C}$ excitations, for instance, occur between the symmetric $\sigma_{CC}(S)$ combination and $\pi^*(A)$ orbital (favoring an A motion) and between the antisymmetric $\sigma_{CC}(A)$ combination and $\pi^*(A)$ orbital, which favors an S motion. The transition densities are shown in Figure 16, together with the enhanced nuclear displacements. Although the transition densities are localized essentially in the region of bonds 23 and 61, these nuclear displacements reproduce fairly well the general features (bond lengthenings and shortenings) of respectively the concerted and the two-step motion (mainly I) of Figure 15.

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(12) (a) N. D. Zelinskii, B. M. Mikhailov, and Y. A. Arbuzov, *J. Gen. Chem. USSR*, **4**, 856 (1934); (b) F. O. Rice, P. M. Ruoff, and E. L. Rodowskas, *J. Am. Chem. Soc.*, **60**, 955 (1938); (c) L. Kuchler, *Nachr. Akad. Wiss. Goettingen, Math.-Physik. Kl. III*, 213 (1939); *Trans. Faraday Soc.*, **35**, 874 (1939); (d) M. Kraus, M. Vavruska, and V. Bazant, *Collection Czech. Chem. Commun.*, **22**, 484 (1957); (e) S. R. Smith and A. S. Gordon, *J. Phys. Chem.*, **65**, 1124 (1961); (f) M. Uchiyama, T. Tomioka, and A. Amano, *ibid.*, **68**, 1878 (1964).

(13) L. H. Scharpen, J. E. Wollrab, and D. P. Ames, *J. Chem. Phys.*, **49**, 2368 (1968). See also J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, **91**, 1898 (1969).

(14) The terminology σ and π is used here as a local symmetry denomination, since the planarity of the carbon skeleton has been lost.

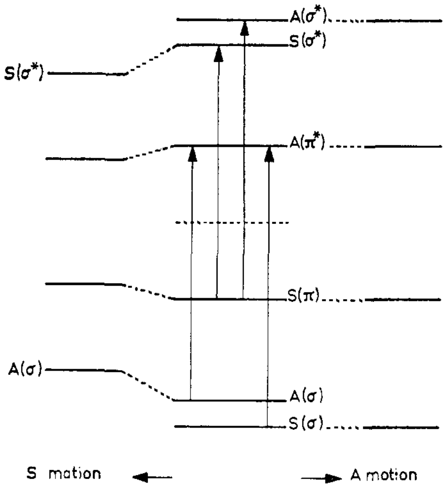

Figure 17. "Woodward–Hoffmann" orbitals in cyclohexene (effect of anharmonicity).

Now each motion is favored by one transition. However, the $\sigma(A) \rightarrow \pi^*(A)$ excitation energy is smaller than the $\sigma(S) \rightarrow \pi^*(A)$ energy. Similarly the $\pi(S) \rightarrow \sigma^*(S)$ state lies under the $\pi(S) \rightarrow \sigma^*(A)$ state. The difference between these excitation energies is difficult to assess, but should be of the order of 1 or 2 eV. Hence the force constant of the S motion is only slightly lower than that of the A motion.

The anharmonicity of the energy, as expressed by the fourth condition, does, however, seem to be different in the two types of motion. The energy pattern of the "Woodward–Hoffmann" orbitals in cyclohexene is given in Figure 17, together with the important $\sigma \rightarrow \pi^*_{C=C}$ and $\pi_{C=C} \rightarrow \sigma^*$ transitions. In the A motion the energy of the S(σ) orbital is unchanged as bond 56 is shortened and bond 34 lengthened. The A(π^*) orbital also has a constant energy as the double bond keeps a constant length. Hence there is no significant anharmonicity in the A motion—though again in the actual two-step process, as in the two-step pyrolysis of cyclobutane, there is a large anharmonicity as the localized orbital σ_{34} is raised while orbital π^* goes down, correlating with a nonbonding orbital in the intermediate diradical. In the S motion, however, the A(σ) orbital is raised because both bonds 56 and 34 are lengthened while bond 45 is shortened. At the same time the π^* orbital is lowered by the lengthening of the double bond. Similarly the S(σ^*) orbital is lowered while the π orbital is raised. Hence a significant decrease in excitation energy occurs as the reaction proceeds, and the S mode becomes more and more favorable as the molecule is distorted further from its initial configuration. Thus, even though in the equilibrium configuration the force constant for S motion is only slightly smaller than for the A motion, this difference *increases* as the molecule departs from equilibrium because of the significant anharmonicity in the S mode. Important anharmonicities should be typical of allowed thermal routes in which a bonding σ orbital correlates with a higher π orbital.

We conclude that the tendency for the Diels–Alder retrogression to proceed in a concerted rather than two-step fashion is rather weak during the initial stage of the reaction. The low selectivity which is imposed on the pathway of the Diels–Alder retrogression—in contrast to the highly concerted pathway imposed on the forward reaction[4,7]—may account in part for its very small (probably positive) entropy of activation.[12f,15] The Diels–Alder addition is highly "directed" and has a precise path with important motional restriction and a large negative entropy of activation. On the other hand, the retrogression proceeds in a somewhat "disorderly" fashion, by a variety of isoenergetic paths, until the transition state is reached or nearly so. Thus the retro reaction can hardly bring much restriction in degrees of freedom.

Discussion of the Semilocalized Orbital Model

It is interesting to compare the simple results of the semilocalized molecular orbital approach with those of more accurate calculations. We have performed extended Hückel[9] and SCF molecular orbital calculations[16] on cyclobutane with a planar carbon skeleton. The orbitals fall into three groups: eight π orbitals localized on the CH_2 groups, eight σ orbitals localized mainly on the C–C bond regions, and eight σ orbitals largely localized in the CH_2 regions. Actually, symmetry alone *requires* the $\sigma(b_{1g})$ and $\sigma(a_{2g})$ orbitals to be pure C–C. The ordering of the levels within each group of eight orbitals is that predicted in the simple picture. An additional, interesting feature is that the band of CC orbitals is well separated from the band of CH_2 orbitals (more tightly bound, or more antibonding), while the π orbitals are interspersed throughout. The detailed calculations will be published elsewhere.

The more accurate calculations do give some quantitative insight that the present approach is unable to provide. For instance, the difference between the one-electron orbital energies of $\pi_{CH_2}(SA)$ and $\pi_{CH_2}(SS)$ in cyclobutane, which was assumed to account for the favored E_g twisting, is 1.4 eV in the extended Hückel calculation and 3.1 eV in the SCF calculation. Similarly the difference between the energies of $\sigma(A)$ and $\sigma(S)$ in cyclohexene can be estimated as 1.6 eV, by comparison with the $\sigma_{CC}(b_{1g}) - \sigma_{CC}(a_{1g})$ cyclobutane energy difference. The latter has approximately the same value (roughly 2β, where β is the matrix element between bonds 12 and 34 in cyclohexene) in extended Hückel theory if all the bond–bond matrix elements in the cyclobutane ring are assumed equal to β.

Discussion of Other Applications

The method for obtaining reaction paths by consideration of the excited states of the reactant can be used in other applications, for instance, electrocyclic reactions[17] which again involve the twisting of CH_2 groups. In cyclobutene, for instance, the σ_{CC} orbital pattern is similar to that of cyclobutane (Figure 2). However, since the symmetry element P_2 has been destroyed, the four bonding semilocalized σ_{CC} orbitals are respectively S, S, and (A,S). The $\pi^*_{CH_2}$ orbitals are only two in number since only two CH_2 groups subsist. There is an S combination and an A combination with roughly equal energies. However, the presence of the low-lying $\pi^*_{C=C}(A)$ orbital perturbs this situation: the orbitals

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[15] (a) A. Wasserman, "Diels-Alder Reactions," Elsevier Publishing Co., New York, N. Y., 1965, p 62; (b) W. C. Herndon and L. H. Hall, *Tetrahedron Letters*, 3095 (1967).

[16] The SCF calculations were performed with a program kindly provided by Dr. Richard Stevens of Harvard University.

[17] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

$\pi^*_{C=C}(A)$ and $\pi^*_{CH_2}(A)$ mix, yielding a particularly low-lying A combination which has some CH_2 character.

The important $\sigma \rightarrow \pi^*$ excitations occur between the four σ_{CC} orbitals and this $\pi^*(A)$ combination. The effects of the degenerate pair $\sigma_{CC}(A,S)$ cancel while the excitation from the lowest $\sigma_{CC}(S)$ orbital gives a transition density of correct symmetry but with no net force acting on the hydrogen atoms. Finally, therefore, we are left with the excitation from the second lowest $\sigma_{CC}(S)$ orbital to the antibonding $\pi^*(A)$ orbital. The favored motion has A symmetry and corresponds to a conrotatory ring opening.[17] The motion is further favored by the scission of the carbon–carbon bond, which raises the energy of the relevant σ_{CC} orbital.

It is interesting to summarize, for planar hydrocarbons, the important excitations between semilocalized orbitals and the motions which they enhance. For the sake of completeness, we include the wagging motion of CH_2 groups for which CC–CH_2 excitations are involved like in the twisting motion.

$$\sigma_{CC} \longrightarrow \sigma^*_{CC} \quad \text{CC bond stretching}$$

$$(\pi_{CH_2} \longrightarrow \pi^*_{CH_2}, \sigma_{CH_2} \longrightarrow \sigma^*_{CH_2}) \quad \text{(weakly, CC bond stretching)}$$

$$\sigma_{CH_2} \longrightarrow \pi^*_{CH_2}, \pi_{CH_2} \longrightarrow \sigma^*_{CH_2} \quad \text{ring puckering}$$

$$\sigma_{CC} \longrightarrow \pi^*_{CH_2}, \pi_{CH_2} \longrightarrow \sigma^*_{CC} \quad \text{CH}_2 \text{ twisting}$$

$$\sigma_{CC} \longrightarrow \sigma^*_{CH_2}, \sigma_{CH_2} \longrightarrow \sigma^*_{CC} \quad \text{CH}_2 \text{ wagging}$$

Transitions of $\pi_{CH_2} \rightarrow \pi^*_{CH_2}$ and $\sigma_{CH_2} \rightarrow \sigma^*_{CH_2}$ types should only have secondary importance in the determination of the carbon–carbon stretching motions; they contribute to the electronic relaxation only through the H–H overlap regions. However, in a conjugated molecule such as benzene the $\pi_{CC} \rightarrow \pi^*_{CC}$ transitions become a crucial factor: the B_{2u} carbon–carbon stretching mode has the lowest force constant,[18] in agreement with the nature of the lowest excited singlet state.

Can the method be applied to photochemical reactions? In principle a motion which is allowed in the molecular ground state should be forbidden precisely in that excited electronic state which allows for the electronic relaxation during the motion. Indeed the corresponding term in the molecular relaxability[3] will change sign because the energy difference in the denominator is reversed. It is therefore relatively easy to predict the photochemical forbiddenness of various thermally allowed reactions, in agreement with the reversal of behavior proved by Woodward and Hoffmann.[4] However, it should be more difficult to predict the most favorable path for a molecule in a given excited state because of the large number of neighboring excited states, with only a small energy difference (condition 2) from the state under consideration.

Similar difficulties should be encountered in eventual applications to the products of mass spectrometric reactions, although perturbation theory, which determines the basic conditions of our method, does seem useful for these reactions.[19]

For these reactions, photochemical or mass spectrometric, which involve initial states which generally are not totally symmetric, condition 1 must be modified appropriately. In particular the states which now allow for electronic relaxation have a symmetry whose "symmetric direct product"[20] with the symmetry of the state under consideration yields the symmetry of the required mode.

It should be kept in mind that a limitation of this method is that it considers only vibrational motions and electronic states of the reactant molecule in its starting equilibrium configuration. Because the perturbation treatment assumes small vibrations, we are limited to a prediction of the most favored *incipient* paths along the potential surface for the reaction. In reactions which involve extensive structural changes, as for instance cyclopropane → propylene, the approach would not be expected to be useful. In all cases the method should be used with care.[21]

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(18) D. H. Whiffen, *Phil. Trans. Roy. Soc.* (London), **A248**, 131 (1955).

(19) R. C. Dougherty, *J. Am. Chem. Soc.*, **90**, 5780, 5788 (1968).

(20) R. M. Hochstrasser, "Molecular Aspects of Symmetry," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 172–173.

(21) For further discussion see L. Salem, *Chem. Britain*, in press