# Selection Rules for Chemical Reactions Using the Orbital Phase Continuity Principle

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**Abstract:** Some recent *ab initio* calculations on simple molecular reactions are examined and found to indicate that in order for a reaction to have a low-activation energy certain *phase relationships* must occur between the orbitals of the reactants and the orbitals of the products. Herein this simple principle is developed and applied to several reactions of conjugated and nonconjugated molecules. For thermal reactions, the resulting selection rules are in general agreement with the generalized Woodward–Hoffmann rules [some exceptions occur for reactions involving open-shell molecules, *e.g.*, $O_2(^1\Delta_g)$ and $NH(^1\Delta)$] and with experiment. However, the *orbital phase continuity principle* (OPCP) does *not* depend upon molecular symmetry and hence can be applied easily to reactions involving *no* symmetry. The OPCP is based on the *generalized valence bond* (GVB) *self-consistent field* method, which leads to orbitals more akin to the valence bond description than to the Hartree–Fock or molecular orbital description. Thus, in a sense the use of OPCP for selection rules for chemical reactions might be considered the valence-bond analog of the Hoffmann–Woodward approach (for MO wave functions).

One of the ultimate goals of theoretical chemistry is to elucidate the mechanisms of chemical reactions. In order to do so, it is not enough to calculate that one reaction path would involve a large barrier and another path a small one, and thus that the latter path might be favored. Rather one wants to understand the states of molecules and complexes sufficiently well that one can *predict, without detailed calculations*, which path would be favored. Thus we require more than just energies and properties from theoretical wave functions of molecules; we want to extract from the wave function the key parts that determine the stability and structure of the molecule and that determine whether and how the molecule can react and bond with other molecules.

In the last few years there has been significant progress toward this end, especially by Hoffmann and Woodward,[2] who base their analysis on approximate forms of Hartree–Fock type wave functions, examining the higher occupied and lower unoccupied molecular orbitals.[3] By considering the ordering of these orbitals for the reactants and products and by examining the correlations of the orbitals between these limits, Hoffmann and Woodward[2] have formulated a set of rules that leads to reliable predictions for several important classes of reactions. As a result, their work has stimulated a vast amount of experimental work to test their predictions and theoretical work to extend it to other systems.

Most of these theoretical investigations have been based on the Hartree–Fock method (or approximations to it) and for good reason. The Hartree–Fock method allows an interpretation of the complicated many-electron wave function in terms of simple orbitals that change in rather simple ways when the molecule is ionized or is elevated to an excited state. In addition, it has been possible to carry out calculations using this method (or approximations to it) on molecules of reasonable size. However, the Hartree–Fock method has a well-known deficiency in not being able to describe properly the breaking or forming of a normal two-electron bond. For example, for $H_2$ at equilibrium the Hartree–Fock method leads to an energy 3.63 eV = 83.7 kcal/mol[4] below that of two separated H atoms, in reasonable agreement with the exact binding energy (including the zero-point energy) of 4.75 eV = 109.4 kcal/mol.[5] As the molecule is pulled apart, however, the Hartree–Fock wave function behaves incorrectly, and for $R = \infty$ the Hartree–Fock energy is 7.7 eV *above* that of two separated H atoms.[6] The problem here is that the Hartree–Fock method describes a bond in terms of one doubly occupied orbital, whereas for $R = \infty$, two singly occupied orbitals (one on each center) are required.

In order to avoid this problem we have employed another method,[7] referred to here as the *generalized valence bond* (GVB) method.[8] In this method every orbital is allowed to be different and singly occupied, no orthogonality conditions are placed on the orbitals, each orbital is solved for self-consistently in the field due to other orbitals, and the form of the wave function ensures that the total wave function possesses the proper spin symmetry (*e.g.*, singlet or triplet). The valence bond (VB) wave function is a special case of GVB in

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[1] Alfred P. Sloan Foundation Fellow. Partially supported by a grant (GP-15423) from the National Science Foundation.

[2] (a) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 87, 2046, 4388, 4389 (1965); (b) R. B. Woodward and R. Hoffmann, *ibid.*, 87, 395, 2511 (1965); (c) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

[3] Actually, such analyses consider only those molecular orbitals that can be described as a linear combination of valence atomic orbitals on each atom. Thus, for the $\pi$ states of a conjugated molecule, one would allow one $p_z$ orbital per C atom. This is adequate for describing qualitatively the occupied orbitals for the ground state but can be totally inadequate for even the first excited singlet state where the spatial character of the excited orbital might be quite different from that of a 2p orbital (see section III for further discussion).

[4] S. Fraga and B. J. Ransil, *J. Chem. Phys.*, 35, 1967 (1961).

[5] W. Kolos and L. Wolniewicz, *ibid.*, 41, 3663 (1964).

[6] W. A. Goddard III, *ibid.*, 48, 5337 (1968).

[7] W. A. Goddard III, *Phys. Rev.*, 157, 81 (1967); R. C. Ladner and W. A. Goddard III, *J. Chem. Phys.*, 51, 1073 (1969).

[8] In order to display the relationship of the wave function to the group operators, $G_i^{\gamma}$, used to effect the proper spin and Pauli symmetry, this method is often referred to as the GI method[7] or else as the spin-coupling optimized GI (or SOGI) method if the spin representation is optimized. Since it is the interpretation of the orbitals rather than the details of the construction of the wave function that is paramount here, we will simply refer to the wave function as the *generalized valence-bond* wave function (see also ref 9).

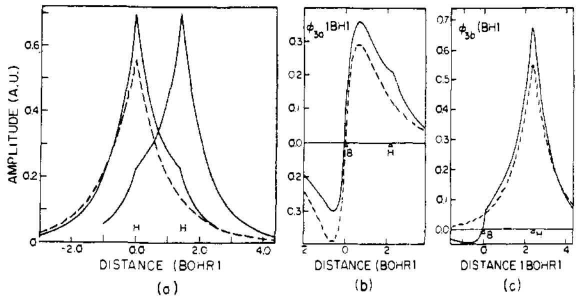

Figure 1. The GVB bonding orbitals for (a) the $H_2$ ($^1\Sigma_g$) molecule and (b, c) the BH ($^1\Sigma$) molecule. The dashed lines indicate the free atomic orbitals.

which (1) the orbitals are taken as (hybridized) atomic orbitals rather than allowed to delocalize onto the various atoms of the molecule, (2) orbitals not involved in bonds are often taken as doubly occupied, and (3) the orbitals are not solved for self-consistently. The Hartree–Fock (HF) method is also a special case of GVB in which the bonding orbitals are usually taken as double occupied but are solved for self-consistently.

In Figure 1a are the GVB orbitals for $H_2$ where we see that one orbital is localized more[7] on the left proton and the other is localized more on the right one. (In HF there would be one double occupied, symmetric orbital.) As the molecule is pulled apart, these orbitals gradually change into pure atomic functions on each center (indicated by the dashed line of Figure 1a). In Figures 1b and 1c are the bonding orbitals of BH; one of them is more localized on the B and the other is more on the H.[9] Again, as the molecule is pulled apart, these orbitals gradually become pure atomic orbitals (indicated by the dashed lines). For typical molecules the GVB orbitals are qualitatively similar to hybridized and somewhat delocalized valence-bond orbitals.[7,9]

For those unaccustomed to GVB type wave functions some features of the discussions below may be made clearer by expanding the GVB wave function in terms of valence bond configurations using localized orbitals. Such expansions will be made at several points below, where for convenience we will write VB configurations in terms of tableaux,[7] so that

$$\begin{array}{|c|c|}\hline a & b \\ \hline c & d \\ \hline e & f \\ \hline \end{array} \qquad (1)$$

for example, indicates a singlet many-electron wave function in which orbitals $\phi_a$ and $\phi_b$ are coupled into a singlet pair, $\phi_c$ and $\phi_d$ into a singlet pair, and $\phi_e$ and $\phi_f$ into a singlet pair. In VB theory the orbitals $\{\phi_a, \phi_b \ldots\}$ are usually taken as atomic orbitals, whereas in GVB the orbitals of eq 1 are solved for self-consistently. The resulting GVB orbitals are usually fairly localized for nonconjugated molecules but often become rather delocalized in the transition region for a reactive system. In addition to optimizing the orbitals of eq 1 the spin coupling of the GVB wave function is optimized (analogous to using the optimum combination of Rumer diagrams in the VB wave function); however, we shall not dwell on such details.

We have applied the GVB method to the study of a few simple reactions and have found some important characteristics that are expected to apply to a large number of chemical reactions.[10] The object of this paper will be to investigate the implications of these results for selection rules of chemical reactions.

## I. The Orbital Phase Continuity Principle

Before discussing the changes in orbitals during reactions, we should note a few relations between orbitals that are important for bond formation. Strong bonds as in $H_2$ or BH involve an orbital from each center *symmetrically coupled*[11] and oriented such that they have high overlap.[12a] Following the changes in the orbitals as the internuclear distance decreases from infinity, we find that in the self-consistent field calculation the orbitals readjust so as to increase the overlap. On the other hand, for a system such as He + H the two orbitals (say $\phi_a$ and $\phi_b$) of the He are already coupled symmetrically

$$\begin{array}{|cc|}\hline a & b \\ \hline \end{array}$$

consequently, because of Pauli's principle (and because electrons have spin one-half) the orbital of the H (say $\phi_c$) cannot be symmetrically coupled

$$\begin{array}{|ccc|}\hline a & b & c \\ \hline \end{array}$$

with the He pair of orbitals. In the allowed coupling

$$\begin{array}{|c|c|}\hline a & b \\ \hline c & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array}$$

the dominant terms in the intermolecular energy are repulsive and favor small overlap of the orbitals.[12b] Thus, the self-consistent readjustments of the orbitals tend to reduce the overlap between the H orbital and the He pair of orbitals.

Consider the changes in the orbitals for the simple reaction

$$H_2 + D \rightleftharpoons H + HD \qquad (2)$$

The orbitals for several points along the reaction path are shown in Figure 2. At each point there are three electrons and therefore three orbitals. In both the reactant (Figure 2a) and product (Figure 2e) limits, two orbitals are $H_2$ bonding orbitals (as in Figure 1a) and the other is a free hydrogen orbital. The salient points to note here are the following. (1) The strongly bonding pair of orbitals of the reactants (Figure 2a) is bonding at each point along the reaction path, but the orbitals gradually shift from the left two nuclei, becoming delocalized over the three nuclei in the transition region[13] (Figure 2c), and eventually relocalizing

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(9) W. E. Palke and W. A. Goddard III, *J. Chem. Phys.*, **50**, 4524 (1969); R. J. Blint, W. A. Goddard III, R. C. Ladner, and W. E. Palke, *Chem. Phys. Lett.*, **5**, 302 (1970); R. J. Blint and W. A. Goddard III, *J. Chem. Phys.*, in press.

(10) (a) W. A. Goddard III and R. C. Ladner, *J. Amer. Chem. Soc.*, **93**, 6750 (1971); (b) W. A. Goddard III and R. C. Ladner, *Int. J. Quant. Chem.*, **3S**, 63 (1969).

(11) We say that a pair of orbitals $\phi_a$ and $\phi_b$ is symmetrically coupled if the many-electron wave function uses these orbitals in the form $[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)]$. The many-electron wave function also involves spin functions and orbitals for other electrons, but $\phi_a$ and $\phi_b$ are said to be symmetrically coupled if the total wave function is invariant under interchange of the orbitals.

(12) (a) The factors responsible for bond formation involve much more than just the overlap of the orbitals; however, the additional factors are generally favorable when orbitals on different centers have high overlap. [For further details, see C. W. Wilson, Jr., and W. A. Goddard III, *Chem. Phys. Lett.*, **5**, 45 (1970)]. (b) C. W. Wilson, Jr., and W. A. Goddard III, *Theor. Chim. Acta*, to be published.

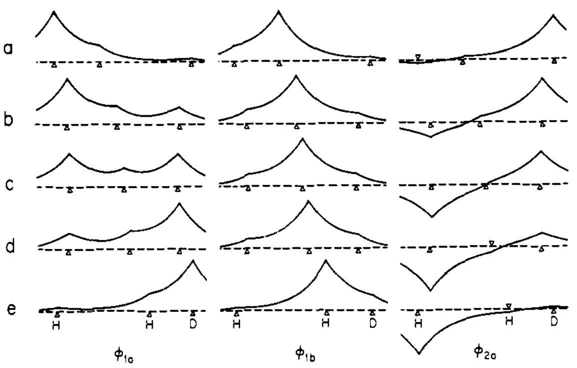

Figure 2. The GVB orbitals for the $H_2 + D \rightarrow H + HD$ exchange reaction. Each column corresponds to a different orbital, each row to a different nuclear configuration. Row c is at the saddle point.

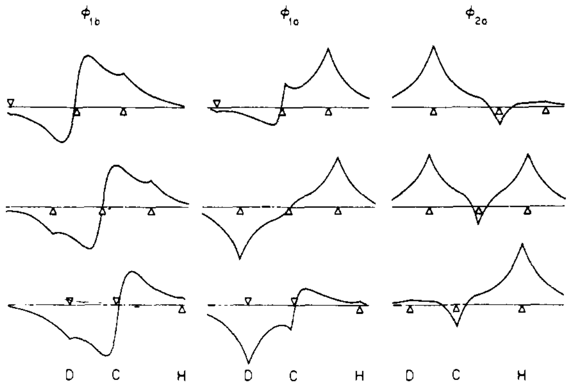

Figure 3. Sketch of the $\sigma$ orbitals for the $D + CH_4 \rightarrow CDH_3 + H$ exchange reaction.

onto the right two nuclei for the products (Figure 2e). In this case the phase relations between the bonding orbitals change continuously during the reaction in such a way as to keep a large overlap between the bonding orbitals. We can visualize these changes in terms of the bonding pair of orbitals shifting across the center nucleus. (2) Concomitant with the changes in eq 2, the nonbonding[14] orbital shifts from the right nucleus (Figure 2a), delocalizing over the left and right nuclei in the transition region (Figure 2c), and eventually relocalizing onto the left nucleus in the products (Figure 2e). (3) The shifting of the bonding pair of orbitals in item 1 primarily involves the left orbital moving from left to right in such a way as to keep a large overlap (~0.8) with its bonding partner centered on the central atom. Thus these orbitals are *gerade* (unchanged upon inversion) in the transition region[13] and have the same phase in the reactant and product states. It is essential that this bonding pair of orbitals remain highly overlapping and strongly bonding at all points along the reaction path in order for the activation energy to remain significantly lower than the $H_2$ bond energy. (4) The nonbonding orbital changes in such a way as to keep a small net overlap (0.0–0.3) with each of the orbitals of the bonding pair. Because the energy terms involving exchange of orbital $\phi_{2a}$ with $\phi_{1a}$ and $\phi_{1b}$ are repulsive, it is essential that this nonbonding orbital not have a large overlap with the bonding pair of orbitals in order not to increase drastically the energy in the transition region.[13] As a result, this orbital is *ungerade* in the transition region and the phase of this orbital changes sign as we proceed from the reactant to the product states. In this case we see that the phase relations between the nonbonding and the bonding orbitals change continuously from the reactant limit through the transition region to the product limit.

Similar results are obtained for other simple reactions (*e.g.*, $LiH + H \rightleftarrows Li + H_2$),[10] and we can expect these points to characterize a number of reactions. In particular: (i) bonding pairs of orbitals should remain strongly overlapping during reactions; (ii) when bonding and nonbonding orbitals must delocalize over the same region, they will tend to become orthogonal at the transition state,[13] and hence they will exhibit opposite phase-change characteristics; (iii) the phase relations among the orbitals should change continuously during the reaction.[15] When these conditions are satisfied, we expect low-activation energies; for simplicity we will denote such cases as "*favored reactions.*" Reactions that cannot retain the appropriate orbital phase continuity will generally require higher activation energies and will be referred to as "*unfavored reactions.*" We will denote the use of the above rules as the *orbital phase continuity principle* (OPCP).

In reaction 2 the bonding orbital on the central atom becomes *gerade* in the transition region and the bonding orbitals do not change phase in the reaction. There are also allowed reactions in which the bonding orbitals change phase during the reaction and the nonbonding orbital does not (still satisfying i, ii, and iii above). Consider, for example, $D + H_3CH \rightleftarrows DCH_3 + H$ through the Walden inversion reaction path. In this case (see the sketch in Figure 3)[16] because the central bonding orbital is an ungerade orbital in the transition region, the other bonding orbital must also be ungerade here (to keep high overlap between the bonding orbitals) and the nonbonding orbital must be gerade (to keep low overlap with the bonding pair). Thus the bonding orbitals change phase and the nonbonding orbital does not. This type of path is occasionally used to avoid what otherwise would have been a forbidden reaction.

## II. Selection Rules for Reactions

**(a) The $H_2 + D_2 \rightleftarrows 2HD$ Exchange Reaction.** We will now the consider the simplest reaction involving two bonds, the (four-center) exchange reaction (eq 3).

$$H_2 + D_2 \rightleftarrows 2HD \qquad (3)$$

First, we will ignore the second D and reconsider eq 2 for a nonlinear geometry, as in Figure 4a. [Here each orbital is schematically indicated by a simple contour line, and the symmetric coupling (singlet pairing) of $\phi_{1a}$ and $\phi_{1b}$ is indicated by a line connecting the appro-

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[13] We will denote as the *reaction path* the sequence of geometries leading from the reactants to the products but requiring always the smallest forces. The maximum (or maxima) along this path will be referred to as the *saddle point* for the reaction or else (loosely) as the *transition state*. When speaking of geometries close to the saddle point or transition state, we will refer to the *transition region*.

[14] For simplicity we refer to this third orbital of $H_2D$ as the nonbonding orbital. It *is* nonbonding in the reactant and product states, but one might argue that it is slightly antibonding in the transition region and responsible for the energy barrier. In any case it is neither strongly bonding nor strongly antibonding.

[15] These phase relations between the orbitals can also be approximately expressed in terms of continuity in the spin coupling angles $\Xi$ of ref 7b.

[16] The sketches in Figure 3 are based on calculations by R. C. Ladner and W. A. Goddard III, unpublished.

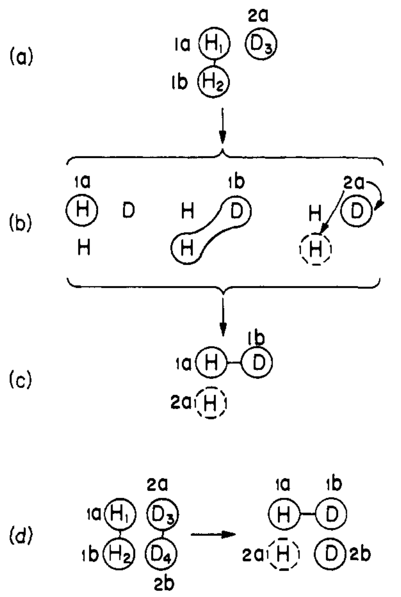

Figure 4. The changes in the orbitals for the $H_2 + D_2 \rightarrow 2HD$ exchange reaction: (a) shows the orbitals for the reactant $H_2$ + D; (b) shows the orbitals for a noncollinear transition state of $H_2 + D \rightarrow H + HD$; (c) shows the orbitals for the product H + HD; and (d) shows the reactant and product orbitals of $H_2 + D_2 \rightarrow 2HD$.

priate contours; the actual shapes of the orbitals are similar to those in Figure 2.] In the transition region for the triangular geometry, these orbitals should be as in Figure 4b. Here $\phi_{1a}$ and $\phi_{1b}$ retain high overlap with each other and remain a strongly bonding pair, while $\phi_{2a}$ is ungerade[17] in order to retain the low overlap with the bonding pair necessary to keep the energy low. The product orbitals are then as in Figure 4c.

Now consider the second D so that the reactant orbitals are as in the left part of Figure 4d, with $\phi_{2a}$ and $\phi_{2b}$ a bonding pair. As above, if the pair $[\phi_{1a}, \phi_{1b}]$ shifts to become an HD bond, then in order to avoid disrupting this bond the orbital starting off on the D at center 3 must delocalize onto the diagonally opposite H (center 2) and in the transition region must again be ungerade,[17] as in Figure 4b. But this means that, in the transition region, $\phi_{2a}$ is orthogonal to $\phi_{2b}$ and the 2a–2b bond must be broken.[18,19] Conversely we can allow $\phi_{2a}$ and $\phi_{2b}$ to adjust in the transition region so as to form a strongly bonding pair, but then $\phi_{1b}$ would have to be ungerade and the 1a–1b bond would be broken. The inability of the system to retain these phase-continuity requirements without breaking a bond indicates that the barrier height for the $H_2 + D_2 \rightarrow 2HD$ reaction should be comparable to the $H_2$ bond energy. Indeed a number of accurate independent *ab initio* quantum mechanical calculations[19] have shown that the barrier height for this reaction is about 120 kcal. In addition, a detailed consideration of the wave functions[19a] shows that the orbitals stay localized as in the left-hand side of Figure 4d until the geometry is nearly that of the saddle point. Then as the orbitals are forced to overlap significantly, the energy rises sharply, passing above the energy required to break one bond. Here all of the orbitals delocalize such as to decrease the energy as much as possible, but the barrier height remains greater than the $H_2$ bond energy.

The above discussion of phase relationships does *not* require a symmetrical (*e.g.*, square) geometry in the transition region, and the $H_2 + D_2 \rightarrow 2DH$ reaction should be unfavored regardless of the geometry of approach. Indeed many geometries have been examined[19b] and the reaction was found to be unfavored for all of them.

It may be helpful for understanding the above results to interpret the above results in terms of VB configurations. Let $\{\chi_1, \chi_2, \chi_3, \chi_4\}$ be localized H orbitals on the various centers, so that $\phi_{1a} \approx \chi_1$ along the reaction path, while $\phi_{1b} \approx \chi_2$ for the reactants, $\phi_{1b} \approx \chi_2 + \chi_3$ for the transition state, and $\chi_{1b} \approx \chi_3$ for the products. For $H_2D$ in the transition region if 1a and 1b are singlet paired (eq 4) then $\phi_{2a} \approx \chi_3 - \chi_2$ in order to be orthogonal to $\phi_{1a}$ and $\phi_{1b}$. Thus expanding eq 4 in terms of the $\chi$'s we get

$$\begin{array}{|c|c|}\hline 1a & 1b \\ \hline 2a & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \qquad (4)$$

$$\begin{array}{|c|c|}\hline \chi_1 & (\chi_2 + \chi_3) \\ \hline \chi_3 - \chi_2 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \approx \begin{array}{|c|c|}\hline \chi_1 & \chi_2 \\ \hline \chi_3 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} - \begin{array}{|c|c|}\hline \chi_1 & \chi_3 \\ \hline \chi_2 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \qquad (5)$$

where ionic configurations have been ignored. [In fact, the GVB wave function in addition to eq 4 also involves the other coupling

$$\begin{array}{|c|c|}\hline 1a & 2a \\ \hline 1b & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

in just such a way as to reduce the ionic components of eq 5.] In the transition state of eq 3 the corresponding wave function is[20]

$$\begin{array}{|c|c|}\hline \chi_1 & (\chi_2 + \chi_3) \\ \hline (\chi_3 - \chi_2) & \chi_4 \\ \hline \end{array} \approx \begin{array}{|c|c|}\hline \chi_1 & \chi_2 \\ \hline \chi_3 & \chi_4 \\ \hline \end{array} - \begin{array}{|c|c|}\hline \chi_1 & \chi_3 \\ \hline \chi_2 & \chi_4 \\ \hline \end{array} \qquad (6)$$

(ignoring ionic terms). This antisymmetric combination of VB configurations is only suited for describing one bonding pair as can be seen from the left side of

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(17) Generally the term *gerade* is used to denote a function that is invariant (does not change sign) under *inversion* (*ungerade* indicates the opposite). We will occasionally also use these terms to denote the symmetry with respect to a reflection that *inverts* the reaction. The reason is that the more general terms symmetric and antisymmetric are herein used to denote permutational symmetry.

(18) In examining the conditions necessary to shift bond $[\phi_{1a}, \phi_{1b}]$ from centers 1–2 to 2–3, we first impose as few restrictions as possible upon the other orbitals. As $\phi_{1b}$ moves from 2 to 3 it is necessary that $\phi_{2a}$ move from 3 and that an orbital move to 2. Leaving $\phi_{2b}$ on center 4, the other orbitals change as for $H_2 + D \rightleftharpoons H + HD$, and we find that $\phi_{2a}$ distorts in such a way as to essentially break the $[\phi_{2a}, \phi_{2b}]$ bond.

Upon solving for the orbitals self-consistently,[19a] we find that they all readjust in such a way as to lead to lower energies, but still the optimum energy for the square geometry of $H_2D_2$ remains more than 120 kcal above the energy of $H_2 + D_2$. Since we are primarily concerned here with whether a reaction has a high- or low-energy barrier, we will continue to examine the orbitals of other reactions in this simplified way, even though solving to self-consistency may lead to modifications in the orbitals, especially for the unfavored reactions.

(19) (a) C. W. Wilson, Jr., and W. A. Goddard III, *J. Chem. Phys.*, in press; (b) C. W. Wilson, Jr., and W. A. Goddard III, *ibid.*, **51**, 716 (1969); (c) H. Conroy and G. Malli, *ibid.*, **50**, 5049 (1969); M. Rubenstein and I. Shavitt, *ibid.*, **51**, 2014 (1969).

(20) For convenience we consider the GVB wave function in terms of just one coupling scheme. The GVB wave function actually contains another coupling also, but this other term serves partly just to remove unfavorable ionic terms resulting from the main configuration.

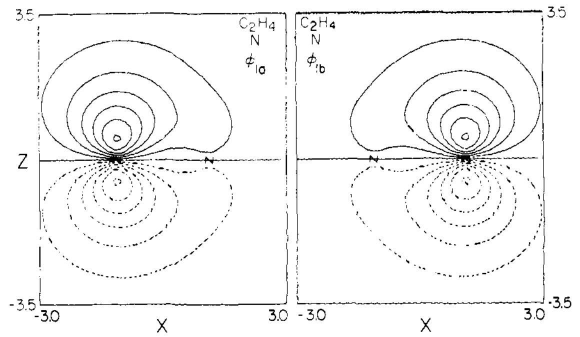

Figure 5. The two GVB $\pi$-bonding orbitals of ethylene (contour plots in the plane perpendicular to the molecule and passing through the C–C axis; negative amplitudes are denoted by dashed lines). The locations of the C nuclei are denoted by N. The outer solid contour represents an amplitude of 0.065, the other contours are separated by increments of 0.065.

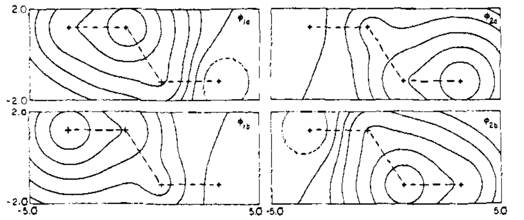

Figure 6. The GVB $\pi$-bonding orbitals of *s-trans*-1,3-butadiene (contour plots in the plane parallel to the molecule and $1.06a_0$ = 0.56 Å above the molecular plane). The dashed line represents negative amplitude and the first solid line is the nodal line; the other contours represent amplitudes of 0.01, 0.021, 0.0441, 0.0926, and 0.1945; thus, a purely exponential function would have equal spacings between the contours.

eq 6 and hence should involve a high energy. Note that the symmetric combination

$$\begin{array}{|cc|}\hline \chi_1 & \chi_2 \\ \hline \chi_3 & \chi_4 \\ \hline \end{array} + \begin{array}{|cc|}\hline \chi_1 & \chi_3 \\ \hline \chi_2 & \chi_4 \\ \hline \end{array} = \begin{array}{|cc|}\hline \chi_1 & (\chi_2 + \chi_3) \\ \hline (\chi_2 + \chi_3) & \chi_4 \\ \hline \end{array}$$

is even worse since orbitals of different pairs are highly overlapping.

In the discussions above we examined the forms of the orbitals in the transition region for eq 3 and concluded that it is an unfavorable reaction. We can obtain this same information by examining the orbitals of just the reactants and products, as indicated in Figure 4d. Allowing $[\phi_{1a}, \phi_{1b}]$ to shift from centers 1–2 to 1–3 with the resulting phase changes in $\phi_{2a}$ as it shifts from center 3 to center 2, the $[\phi_{2a}, \phi_{2b}]$ orbitals of the product would be out of phase. This indicates that the reaction involves an unfavorable relationship of the 2a–2b orbitals in the transition region as discussed above. In the following discussions we will generally take this short cut of examining the orbitals of the products (as in Figure 4c or 4d), using OPCP to establish the phases, rather than examining the orbitals in the transition region (as in Figure 4b).

**b. The GVB Orbitals of Conjugated Systems.** Before discussing reactions of conjugated systems in terms of the GVB description, we will examine the shapes of GVB orbitals of ethylene and butadiene.[21]

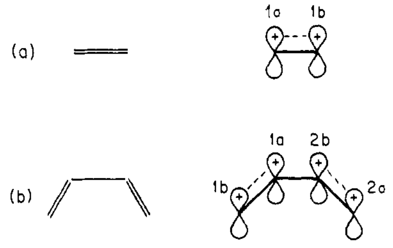

Figure 7. Sketches of the $\pi$ orbitals of ethylene and butadiene to be used in later figures.

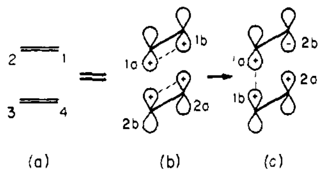

Figure 8. The 2 + 2 cycloaddition.

The two GVB $\pi$ orbitals of ethylene (this pair of orbitals corresponds to the Hartree–Fock doubly occupied $\pi$ orbital) are shown in Figure 5 (contour plots in the plane perpendicular to the molecular plane and passing through the carbon nuclei), where we see that one orbital is more localized on the left C and one more on the right C. Each orbital is qualitatively similar to a $p_z$ atomic orbital on the corresponding center and will be so represented in the following sections.

The four GVB $\pi$ orbitals of *s-trans*-1,3-butadiene are shown in Figure 6 (these are contour plots in the plane parallel to the molecule and passing 1.06 $a_0$ = 0.561 Å above the molecular plane). Although there is some delocalization of the orbitals, they can again be qualitatively described as $p_z$ orbitals on the respective centers. Orbitals $\phi_{1a}$ and $\phi_{1b}$ form one bonding pair, mainly around the left two carbons, and $\phi_{2a}$ and $\phi_{2b}$ form an equivalent bonding pair around the right two carbons.

In the following sections only the qualitative shapes of the GVB orbitals will be important, and we will schematically represent these orbitals of ethylene and butadiene as in Figure 7. Here the second column of Figure 7a represents *both* GVB $\pi$ orbitals of ethylene and the second column of Figure 7b represents *all four* GVB $\pi$ orbitals of *s-cis*-butadiene.

**c. Cycloaddition Reactions.** Consider now the cycloaddition of ethylene to ethylene to yield cyclobutane. As indicated in Figure 8, this is quite analogous to the $H_2 + D_2$ reaction. If we allow the bonding pair $[\phi_{1a}, \phi_{1b}]$ to move from centers 1–2 to centers 2–3, then the orbital $\phi_{2b}$ starting off on center 3 must move to center 1 and must change phase in order not to disrupt the $[\phi_{1a}, \phi_{1b}]$ bond. As a result, $\phi_{2b}$ must become nearly orthogonal to $\phi_{2a}$ in the transition region,[18] and hence the $[\phi_{2a}, \phi_{2b}]$ bond is essentially broken in the transition region. Thus, this 2 + 2 cycloaddition reaction is unfavored.

On the other hand, for the 4 + 2 cycloaddition of *cis*-1,3-butadiene and ethylene, the required phase changes are all consistent as shown in Figure 9, where the reaction is examined in terms of one bond shift at a time. Moving the $[\phi_{1a}, \phi_{1b}]$ pair from 1–2 to 1–6, we allow $\phi_{3b}$ to move from center 6 to center 1, changing phase in the process. (Note that the butadiene is in

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(21) G. Levin, W. A. Goddard III, W. J. Hunt, D. L. Heustis, and T. H. Dunning, unpublished work.

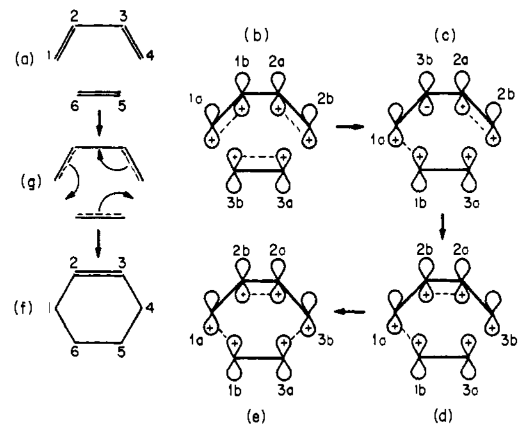

Figure 9. The 4 + 2 cycloaddition.

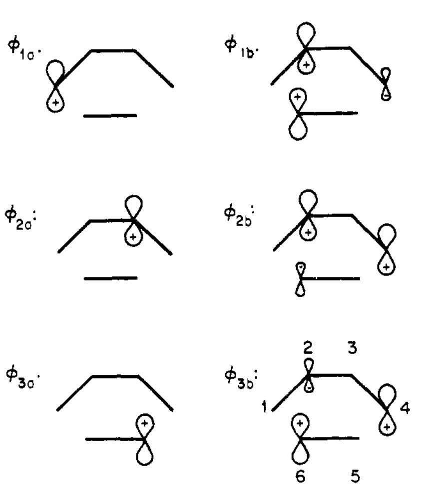

Figure 10. A sketch of the possible shapes of the orbitals for the transition state of the 4 + 2 cycloaddition.

a plane above the ethylene so that the upper lobes of the $C_2H_4$ $\pi$ orbitals are below the lower lobes of the $C_4H_6$ $\pi$ orbitals.) Next, we shift the $[\phi_{2a}, \phi_{2b}]$ bond from centers 3–4 to centers 2–3, allowing $\phi_{3b}$ to shift from center 2 to center 4, changing phase again in the process. The net result of the above shifts of the 1a–1b and 2a–2b bonds is to shift the pair of orbitals $[\phi_{3a}, \phi_{3b}]$ from 6–5 to 5–4; however, in this case the phase changes in $\phi_{3b}$ are consistent with the pair $[\phi_{3a}, \phi_{3b}]$ remaining strongly bonding during the reaction. Thus, this reaction is favored.

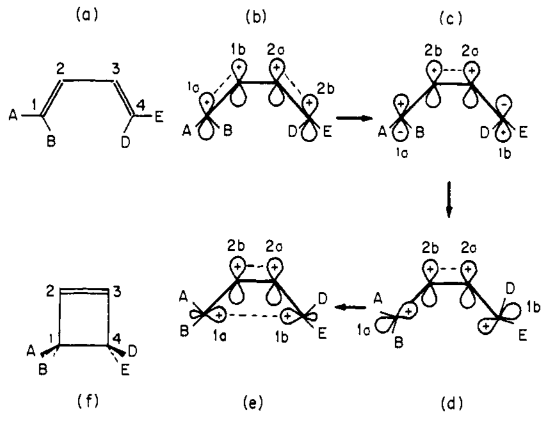

Figure 11. Electrocyclization involving two pairs of orbitals.

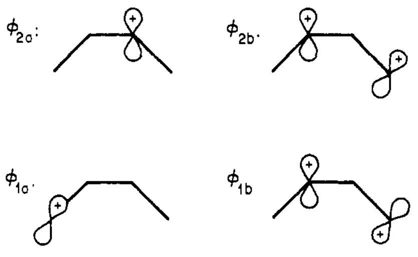

Figure 12. Sketch of the possible shapes of the orbitals for the transition state of the electrocyclic reaction of Figure 11.

In determining whether the phases of all the orbitals change consistently during the reaction, we have analyzed the reaction one step at a time, following the phase changes in one orbital, called the test orbital ($\phi_{3b}$ here). Of course, in the real reaction these changes may all occur simultaneously. In particular, in the transition region the orbitals might look something like those in Figure 10. For example, $\phi_{3b}$ is mainly concentrated near centers 4, 5, and 6, possessing a large overlap with $\phi_{3a}$, but because of the opposite phase near center 2, $\phi_{3b}$ would have a small overlap with the orbitals of bonds 1a–1b and 2a–2b. Thus, all phase conditions are consistent with the orbitals shifting in concert as indicated by the arrows of Figure 9g. On the other hand, although the orbital phases are consistent with the bonds all shifting simultaneously, it is quite possible that the minimum energy reaction path would involve the nuclei changing in such a way that some bonds would shift more rapidly than others (according to Woodward and Katz,[22] this probably is the case for the 4 + 2 cycloaddition).

Considering the general case of $p + q$ cycloadditions, we see from phase considerations that the reactions are favored when $p + q = 4n + 2$ and are unfavored when $p + q = 4n$. This is also the conclusion of Hoffmann and Woodward[2a] from considerations of molecular orbital (MO) correlation diagrams and is consistent with numerous experimental results.

**d. Electrocyclic Reactions.** Consider now the electrocyclic reactions, such as cyclobutene $\rightleftharpoons$ *s-cis*-1,3-butadiene, as indicated in Figure 11. Starting with a substituted butadiene, if bond $[\phi_{2a}, \phi_{2b}]$ moves from centers 3–4 to centers 2–3, then orbital $\phi_{1b}$ should move from center 2 to center 4, changing phase. In order to keep the barrier height low, a bond must concomitantly be forming between centers 1 and 4. Thus, rather than the (substituted) methylenes at centers 1 and 4 remaining fixed as the 2a–2b orbitals shift, they should rotate in such a way as to allow formation of a bond between 1 and 4; that is, they must rotate such that $\phi_{1a}$ and $\phi_{1b}$ retain their original phase relations (*e.g.*, plus lobe with plus lobe). This requires that the rotations at 1 and 4 be in the same direction, and hence the conrotatory mode is favored.

We should emphasize here that the sequence of orbital shifts indicated in Figure 11 is only of analytic significance in order to ascertain the influence of orbital phase conditions. The form of the self-consistent orbitals in the transition region might well be more as shown in Figure 12.

Similarly for the electrocyclization of 1,3,5-hexatriene, we see in Figure 13 that orbital $\phi_{1b}$ (starting on center 2)

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(22) R. B. Woodward and R. J. Katz, *Tetrahedron*, 5, 70 (1959).

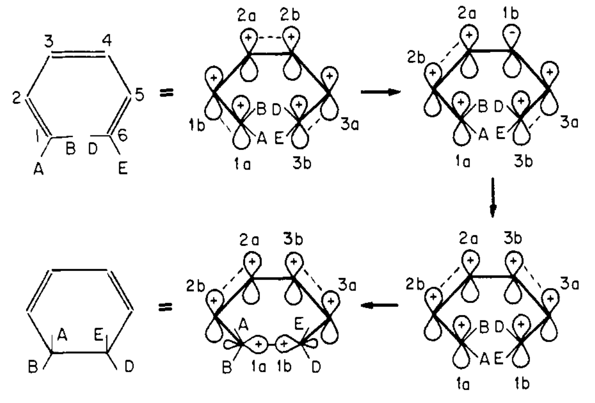

Figure 13. Electrocyclization involving three pairs of orbitals.

changes phase twice as the bonds on 3-4 and 5-6 shift to 2-3 and 4-5, respectively. Thus, for the orbitals starting on 1-2 to remain in phase and retain bonding character as they shift to 1-6, the methylenes on centers 1 and 6 must rotate in opposite directions. That is, only the disrotatory mode is favored.

For electrocyclic reactions of larger systems, similar considerations of orbital phases indicate that the conrotatory mode is favored for reactions involving shifts of an even number of bonding pairs and the disrotatory mode is favored for systems involving shifts of an odd number of pairs. This again is just the rule found by Woodward and Hoffmann[2b] from consideration of the change in symmetry of the highest occupied MO, and by Hoffmann and Woodward[2a] from consideration of the full MO correlation diagrams, and is consistent with numerous experimental results.[23]

It might be helpful here to examine the GVB orbitals (Figure 12) of the butadiene cyclization in terms of the approximate VB configurations. In terms of localized $\pi$ orbitals on each center the GVB wave function is approximately[20]

$$\begin{array}{|cc|}\hline \phi_{2a} & \phi_{2b} \\ \hline \phi_{1a} & \phi_{1b} \\ \hline\end{array} \cong \begin{array}{|cc|}\hline \chi_3 & (\chi_4+\chi_2) \\ \hline \chi_1 & (\chi_2-\chi_4) \\ \hline\end{array} \simeq \begin{array}{|cc|}\hline \chi_3 & \chi_4 \\ \hline \chi_1 & \chi_2 \\ \hline\end{array} - \begin{array}{|cc|}\hline \chi_3 & \chi_2 \\ \hline \chi_1 & \chi_4 \\ \hline\end{array} \qquad (7)$$

However, although $\phi_{1b} \approx \chi_2 - \chi_4$ is approximately orthogonal to $\phi_{2a}$ and $\phi_{2b}$, it need *not* be orthogonal to $\chi_1$ if the $CH_2$ at center 1 twists in the conrotatory direction. What distinguishes this reaction from the $H_2 + D_2$ reaction is that since the basic orbitals are $\pi$-like, it is possible for $\phi_{1b}$ to be orthogonal to the bonding pair $\phi_{2a}$ and $\phi_{2b}$ while retaining overlap with its bonding partner $\phi_{1a}$.

e. **Unfavored Cycloadditions.** We have considered the favorable reaction paths to be those for which each bond could be retained as a relatively strong bond at all points along the reaction path.[18] Now we will consider one of the unfavored cases, ethylene plus ethylene to yield cyclobutane. As we shift bond $[\phi_{1a}, \phi_{1b}]$ from centers 1-2 to 2-3 (see Figures 8 and 14), orbital $\phi_{2b}$ moves from 3 to 1 and in the transition region would have the shape indicated in Figure 14a. Thus in the transition region $\phi_{2a}$ is nearly orthogonal to $\phi_{2b}$ and we have essentially broken the 2a-2b bond. That is, the transition state could be considered as a biradical.[24] On the other hand, if we rotate the $CH_2$ group at center 4 by about 90° and displace center 4 out of the $C_1$-$C_2$-$C_3$ plane as in Figure 14c, then orbital $\phi_{2b}$ would retain a larger overlap with $\phi_{2a}$ as $\phi_{2b}$ is shifted between centers 3 and 1. Proceeding from Figure 14b to 14c to the product state, 14d, some bonding in the $[\phi_{2a}, \phi_{2b}]$ pair could be retained by continuing to rotate the $CH_2$ at 4 by another 90°. Thus this concerted process would lead to suprafacial addition to one ethylene and antarafacial addition to the other ethylene, whereas the biradical path would be expected to lead to roughly equal probabilities of suprafacial or antarafacial addition to either ethylene. The reaction path for the concerted reaction would probably involve a nonplanar approach (say, a $C_1$-$C_2$-$C_3$ angle of 90° and 30-60° angle between the planes of the $\pi$ orbitals) and would lead to a somewhat tighter transition state than the biradical path. This concerted path requires that a $CH_2$ group must rotate in a very specific way as the molecules approach—a requirement that would probably not be met in most collisions. Thus the concerted path might lead to a lower barrier height but should also lead to a smaller *A* factor. As a result, the biradical paths might well compete with or even dominate the concerted paths. The same considerations apply, of course, to the cycloreversion of cyclobutane to two ethylenes.

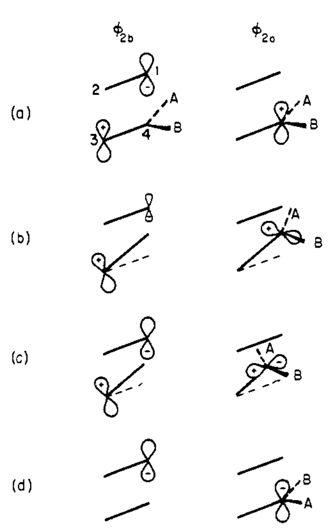

Figure 14. A concerted path for the 2 + 2 cycloaddition.

Woodward and Hoffmann[2c] have also considered the possibility of concerted 2 + 2 cycloadditions and also conclude that to be concerted, addition to one ethylene must be antarafacial. They suggest[2c] that the reaction path may have a geometry such that the C-C axes of the ethylene are perpendicular, with one ethylene having its plane parallel to the direction of approach and one perpendicular (however, their generalized rules do not necessarily require such a geometry). As we saw above, GVB considerations lead one to expect a rather different geometry.

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(23) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

(24) By a biradical we mean here a singlet state in which one pair involves orbitals that are nearly orthogonal and localized in different regions of the molecule and hence cannot contribute significantly to the bonding. Not a great deal of quantitative theoretical information is available about such states because they generally cannot be well described in terms of the Hartree-Fock framework

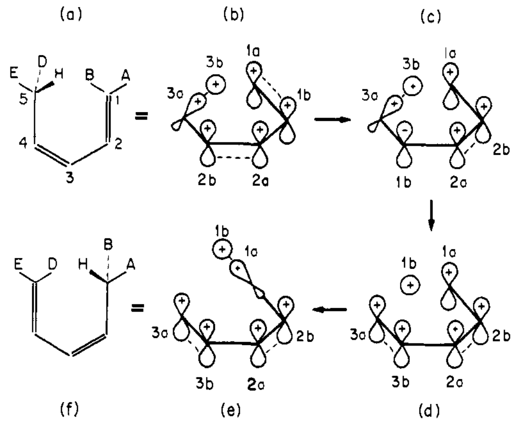


Figure 15. [1,5] H migration.

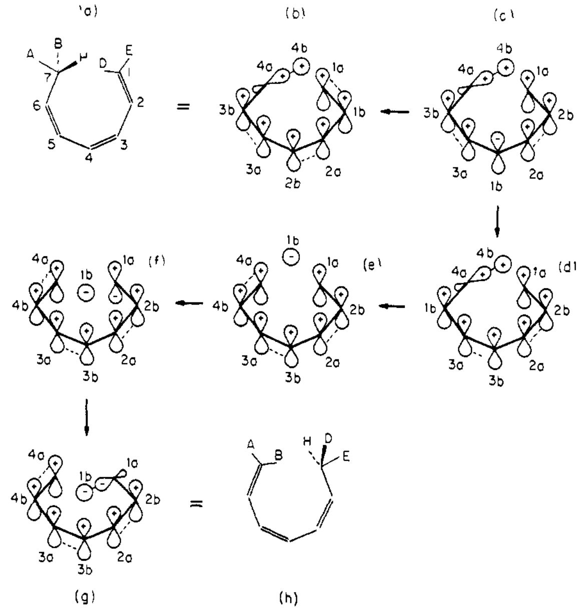
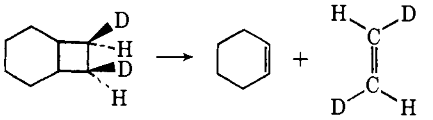


Figure 16. [1,7] H migration.

Baldwin and Ford[25] have examined the pyrolysis and



find that 57% *trans*-dideuterioethylene is formed. This result could be interpreted as indicating a competition between the concerted path (leading to trans) and biradical paths.

The pyrolysis of cyclobutane has been studied by Genaux, *et al.*,[26] and found to lead to two ethylenes with Arrhenius parameters of $E_a = 62.5$ kcal/mol and log $A = 15.6$, values quite close to those (log $A = 15.6$ and $E_a = 63.3$ kcal/mol) obtained by O'Neal and Benson[27a] from a thermochemical analysis assuming a biradical-activated complex. Based on the above experimental $E_a$, the cycloaddition of two ethylenes would be expected to involve an activation energy of about 44 kcal.

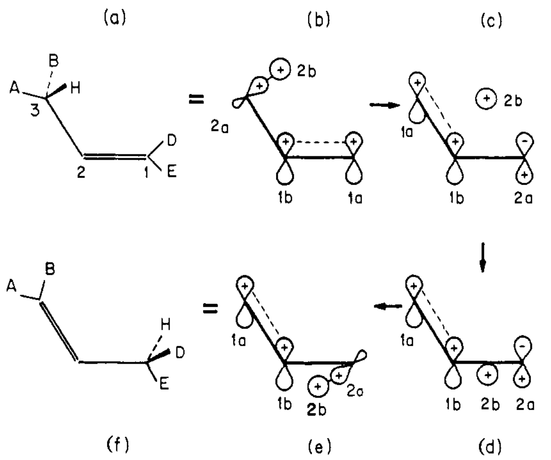
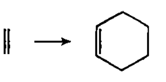


Figure 17. [1,3] H migration.

In comparison, the 2 + 4 cycloaddition of ethylene and 1,3-butadiene involves an activation energy of about 27.5 kcal/mol.[27b] Thus the experimental results are consistent with the biradical mechanism being dominant for the 2 + 2 cycloreversion. Extended Hückel calculations[28] also lead to the conclusion that, in the saddle point geometry, the reaction intermediate is of biradical form.



Thus, for the 2 + 2 cycloaddition it would appear that the concerted path is in competition with various biradical paths.

The point of this section is to indicate how GVB orbitals and phase relationships may be used to help indicate the most favorable geometry of transition states and to estimate activation energies. It should be clear that an unfavored reaction, which might normally be expected to be stepwise, might conceivably have a concerted mechanism if appropriate geometry changes were to occur. However, concerted mechanisms of this kind need not be competitive with those alternative nonconcerted reaction mechanisms that do not involve drastic geometric restrictions in the formation of the transition state.

**f. Sigmatropic Reactions.** Next, we consider the hydrogen migration in a system such as 1,3-pentadiene, as illustrated in Figure 15. Here we see that the [1,5] migration is allowed and that the H would be expected to stay on one side of the plane (suprafacial) during the reaction. Of course in the actual reaction of Figure 15, all bonds would be shifting at the same time along with rotation of the groups at centers 1 and 5 and some twisting of the carbon framework. All in all the geometries and orbital phases involved in 1,3-pentadiene are favorable for the suprafacial H migration, and a number of examples are known. On the other hand, in Figure 16 we consider a [1,7] H migration. Here Figure 16e is analogous to Figure 15d, but now $\phi_{1b}$ does not have the proper phase to bond to $\phi_{1a}$ unless the H passes through the molecular plane, as shown in Figure 16f. Considering the geometry of *cis,cis*-1,3,5-heptatriene, we see that the carbon framework must be non-

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[25] J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, 91, 7192 (1969).

[26] C. T. Genaux, F. Kern, and W. D. Walters, *ibid.*, 75, 6196 (1953).

[27] (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968); (b) D. Rowley and H. Steiner, *Discuss. Faraday Soc.*, 10, 198 (1951).

[28] R. Hoffmann, S. Swaminathan, B.-G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, 92, 7091 (1970).

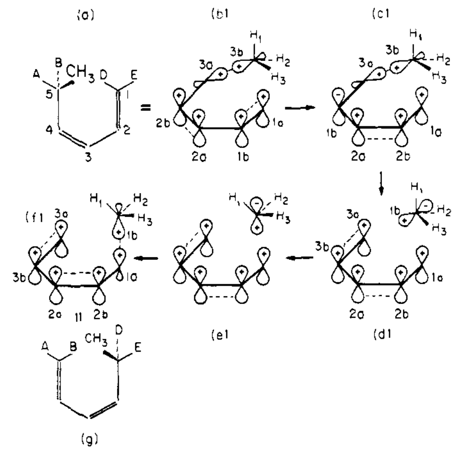

Figure 18. [1,5] $CH_3$ migration.

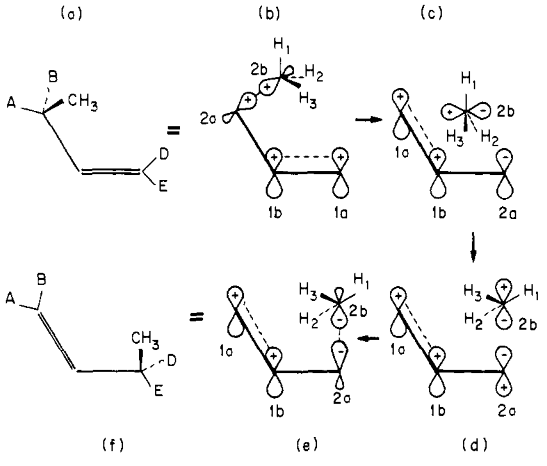

Figure 19. [1,3] $CH_3$ migration.

planar with center 1 over center 7. Thus, both the geometry and orbital phases favor an antarafacial H migration in this system.

Whether the reaction is suprafacial or antarafacial is determined by the number of phase changes in the test orbital ($\phi_{1b}$). Hence, we would expect $[i,j]$ H migrations to be suprafacial for $j + i = 4n + 2$ and antarafacial for $j + i = 4n$. In fact, these are just the predictions obtained by Woodward and Hoffmann[2] from consideration of the symmetry of the highest occupied molecular orbital of the carbon framework. However, H migrations other than those cases discussed in Figures 15 and 16 seem to have less favorable geometries. For example, the [1,3] H migration is pictured in Figure 17. For orbital $\phi_{2b}$ to remain bonding to $\phi_{2a}$, the H must pass through the plane of the molecule (antarafacial), as expected. However, in this case orbital $\phi_{2a}$ is antisymmetric with respect to the plane throughout the transition region and thus $\phi_{2a}$ becomes orthogonal to its bonding partner in the transition region. Hence, even forgetting about such geometric factors as the initial distance of the H from center 1, we expect the 2a-2b bond to be broken in the transition region and even the antarafacial [1,3] H migration should be unfavored. This problem did not occur in the [1,7] migration because of the necessarily nonplanar geometry.

Now we consider migration of a methyl group. The [1,5] case is examined in Figure 18. Here Figure 18d is analogous to Figure 15d and we see that the $CH_3$ should migrate in a suprafacial manner and without inversion. On the other hand, Figure 19 shows the [1,3] $CH_3$ migration. Here Figure 19c is analogous to Figure 17c, but now rather than the migrating species passing through the molecular plane (the only way to obtain the phase continuity in Figure 17), we may proceed from Figure 19c to Figure 19e with just a simple inversion at the migrating $CH_3$ and a slight rearrangement of the methyl hydrogens (*cf.* Figure 3). Thus, the [1,3] $CH_3$ migration is favored to be suprafacial but with inversion at the methyl. Experimental evidence for such a reaction has been presented by Berson and Nelson.[29]

In general, a consideration of the orbital phases implies that concerted suprafacial $[i,j]$ $CH_3$ migrations should proceed with inversion if $j - i = 4n + 2$ and without inversion if $j - i = 4n$. Similar considerations imply that concerted antarafacial $[i,j]$ $CH_3$ migrations would involve inversion if $j - i = 4n$ and no inversion if $j - i = 4n + 2$. Of course, in many systems geometric considerations rule out the reaction despite favorable orbital phases.

**g. Low Symmetry Reactions.** In the Hoffmann-Woodward approach of using correlation diagrams to obtain selection rules for reactions, it is important to have reaction paths with sufficiently high symmetry that could be used to establish the correlations among the orbitals. For reactions with low symmetry it is often very tedious or impossible to predict reliably whether a particular reaction path would be favored. However, since molecular symmetry is not involved in the use of OPCP, this approach should remain useful for low-symmetry reactions.

Woodward and Hoffmann showed that for the cyclooctatetraene to cubane reaction the occupied orbitals of the reactant correspond in symmetry to the occupied orbitals of the product.[2c] Although this might seem to imply that the reaction is allowed, Woodward and Hoffmann pointed out[2c] that a consideration of the changes in the orbitals as the reaction proceeds indicates that some of the occupied orbitals of the reactant correlate toward excited orbitals of the product and they conclude that the reaction is forbidden.

Figure 20 indicates how this reaction would be viewed with OPCP. To obtain cubane we may let bonds shift as 1-2 to 2-5, 5-6 to 1-2, 3-4 to 4-7, and 7-8 to 3-8. But as the bond $[\phi_{1a}, \phi_{1b}]$ shifts to 2-5, the orbital on 5, $\phi_{3a}$, moves to 1 and changes phase and hence does not remain in phase with the orbital on 6; thus we cannot have 5-6 shift to 1-6 and the reaction is unfavored (note that the orbital changes in this reaction are essentially the same as for two 2 + 2 cycloadditions).

Next we consider another low-symmetry reaction, two butadienes in the orientation given in Figure 21a reacting to give the product in Figure 21d. Shifting the bonds in the order 1-2 to 2-7, 5-6 to 1-6, and 3-4 to 4-5, we find that orbitals $[\phi_{4a}, \phi_{4b}]$ are not in phase for the shift of the bond on 8-7 to 3-8 (following orbital $\phi_{4a}$ we see that it shifts from 7 to 1 to 5 to 3 as the other bonds shift and hence changes phase three times, ending up at 3 with the wrong phase). Thus this reaction is unfavored.

In Figure 21e-h, we consider another orientation of the butadienes also yielding a boxlike structure after

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(29) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, 92, 1096 1970); J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968).

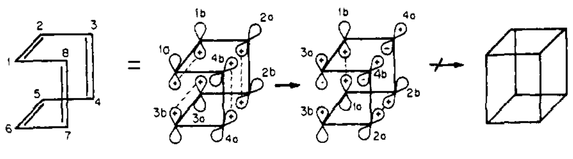

Figure 20. The cyclooctatetraene to cubane reaction.

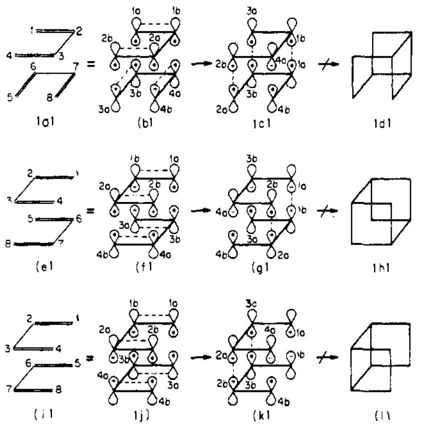

Figure 21. Addition of two *cis*-butadienes with removal of double bonds.

the bond shifts of 1–2 to 1–6, 5–6 to 2–5, 3–4 to 4–7, and 8–7 to 3–8. Moving 1–2 to 1–6, we see that the orbital $\phi_{8b}$ on 6 moves to 2 but with the wrong phase to remain bonded to the orbital on 5. In fact, this reaction is equivalent to two 2 + 2 cycloadditions and is (doubly) unfavored. The reaction for the other orientation of the butadienes is given in Figure 21i–l, where we see that it is also (doubly) unfavored, again equivalent to two 2 + 2 cycloadditions. Thus, using OPCP all three of these reactions are predicted to be unfavored.

Just as for the 2 + 2 cycloaddition of section e, we can obtain concerted paths for these reactions by rotating one or two $CH_2$ groups through 180° (for example, the $CH_2$ at center 8 in forming 21d, a similar rotation at both centers 5 and 8 in forming 21h, and similar rotations at, say, 1 and 4 in forming 21l). However, just as before, such concerted mechanisms for this reaction (or the reverse, the pyrolysis of 21d, 21h, or 21l to two butadienes) might be dominated by alternative biradical mechanisms and, indeed, by alternative concerted paths to different products (*e.g.*, 4 + 2 cycloaddition).

Miller[30] applied the original form of the Hoffmann–Woodward approach (making use of orbital symmetry and correlation diagrams) to these three reactions and concluded that the first two cases should be allowed. However, these cases have low-symmetry reaction paths with no symmetry planes bisecting bonds. This is just the sort of case for which the correlation diagram approach is expected to have trouble. No such problem occurs with OPCP since neither molecular symmetry nor correlation diagrams are used. However, the more recent inductive generalization[2c] of the Woodward–Hoffmann rules abandons the use of correlation diagrams and would immediately lead to the prediction that all three reactions of Figure 21 are forbidden (${}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s$).

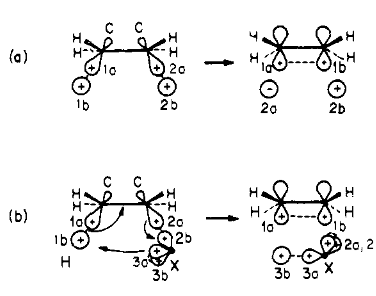

Figure 22. 1,2 eliminations.

From these examples we see that even for reactions involving low symmetry, OPCP has some advantages over the original formulation of the correlation diagram–orbital symmetry approach. However, the prediction of which reactions are favorable is made equally easily and accurately with OPCP or the generalized Woodward–Hoffmann rules.

**h. 1,2 HX Elimination from $C_2H_5X$.** Consider first the 1,2 elimination of $H_2$ from $C_2H_6$

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \tag{8}$$

The relevant orbitals are indicated in Figure 22a, which shows that the phases are not consistent with the reaction being concerted. Thus we would expect the activation energy for eq 8 to be comparable with the H abstraction energy, about 98 kcal. Similar considerations would apply to the 1,1 elimination of $H_2$ from $C_2H_6$ and to

$$CH_4 \longrightarrow CH_2 + H_2 \tag{9}$$

Now consider the 1,2 elimination of HX from $C_2H_5X$, $C_2H_5X \rightarrow C_2H_4 + HX$, where X is a halogen, as in Figure 22b (note that each orbital contains one electron, hence a nonbonding pair is indicated by two lobes connected by a dotted line). Besides the HC and XC bonding pairs, we have nonbonding pairs on the X. Thus, instead of shifting the XC bonding pair [$\phi_{2a}$, $\phi_{2b}$] to become an HX bonding pair, we can let the XC bonding pair shift over to become an X lone pair. Then another X lone pair [$\phi_{3a}$, $\phi_{3b}$] can shift to become an XH bonding pair while the HC bonding pair [$\phi_{1a}$, $\phi_{1b}$] shifts over to become a $\pi$ bonding pair. Now three pairs of orbitals are involved and the phases may be consistent. Thus the reaction is allowed to be concerted—the activation energy might be less than required to break one of the bonds. On the other hand, we should note here that the X is much more electronegative than the C and H. Since it is now less unfavorable for X to have an extra electron around, it may be that the transition state will not correspond to an even development of the new bonds (even if the reaction is concerted). For example, one might expect that the transition state would involve a stretched polar bond XC but little development of the X nonbonding pair toward the H.

The experimental activation energy for eq 4 with X = F is 58.2 ± 1.3 kcal/mol,[31] which is less than either the C–H or the C–F bond energies here [$D(C - F)$ = 107 kcal/mol]. On the other hand, the reverse reaction in eq 8 involves radicals so that the activation energy for eq 8 is probably of the order of 98 kcal/mol.[32,33]

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(30) S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968).

(31) M. Day and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 233, (1969); see also, H. W Chang and D. W. Setser, *J. Amer. Chem. Soc.*, **91**, 7648 (1969).

(32) A. Maccoll and P. J. Thomas, *Progr. React. Kinet.*, **4**, 119 (1967).

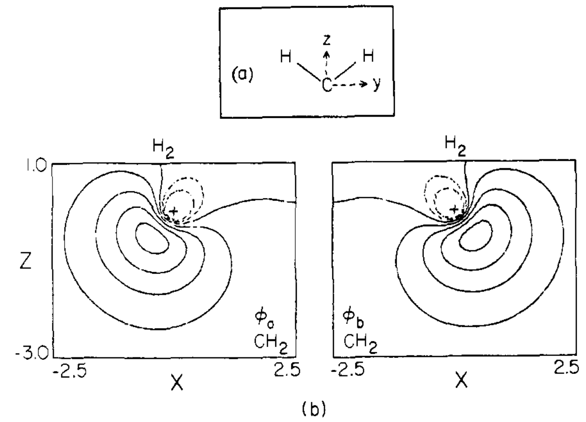
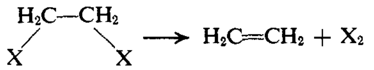


Figure 23. The GVB nonbonding orbitals of the $^1A_1$ state of $CH_2$ (contour plots in the plane perpendicular to the molecule, passing through the carbon and bisecting the HCH angle; the dashed lines indicate negative amplitude, the first solid line is the nodal plane; the contour increments are 0.10 au).

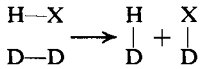
These experimental results are consistent with the predictions from OPCP.

In the reaction



$$\underset{X\quad\quad X}{H_2C{-}CH_2} \longrightarrow H_2C{=}CH_2 + X_2 \tag{10}$$

there is a lone pair on each X that must be considered so that eq 10 involves the shift of four pairs of orbitals and hence is unfavorable. Similarly the concerted reaction $H_2 + X_2 \rightarrow 2HX$ through a four-center transition state is unfavorable, whereas the exchange



$$\begin{array}{c} H{-}X \\ D{-}D \end{array} \longrightarrow \begin{array}{c} H \\ | \\ D \end{array} + \begin{array}{c} X \\ | \\ D \end{array}$$

is favorable (especially with HX vibrational excitation).

According to Miller,[30] Hoffmann–Woodward considerations would lead to all of the above reactions being forbidden, and hence this may be a case where the OPCP and Hoffmann–Woodward approaches would lead to different predictions.

**i. Addition of Carbene and Open-Shell Molecules to a Double Bond.** Consider first the cycloaddition of a carbene to an alkene. First a word about the orbitals of carbene or methylene. Two orbitals are involved in each CH bond, leaving two nonbonded valence orbitals. The ground state of $CH_2$ is a triplet state, $^3B_1$, with an HCH angle of about 140°.[34–36] The first singlet, $^1A_1$, is about 0.5[37a]–1 eV[34] higher with an HCH angle of 102.4°[36] and the second singlet, $^1B_1$, is at least another 1.36 eV higher[37a] with an HCH angle of about 144°.[34] The $^1B_1$ and $^3B_1$ states both involve one $\sigma$- and one $\pi$-nonbonding valence orbital, whereas the $^1A_1$ state involves the pair of nonbonding orbitals[37a] indicated in Figure 23. [The coordinate system is indicated in Figure 23a, while Figure 23b shows the orbitals in the *xz* plane.]

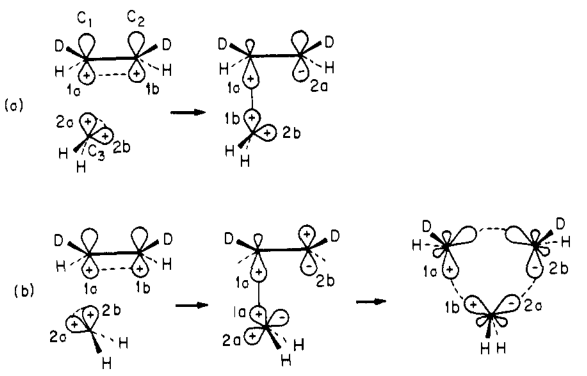


Figure 24. The addition of $^1A_1$ carbene to an alkene double bond.

In Figure 24 we consider the 1,2 cycloaddition of singlet carbene ($^1A_1$) onto an alkene. Just as for the 2 + 2 cycloaddition in Figure 14, the phases are not consistent and we might not expect both bonds to form simultaneously. However, Figure 24b shows how the $CH_2$ could be oriented in order to lead to phase continuity. In this case the transition-state geometry probably would be somewhat as shown and one would expect the bonding in the transition region to favor retention of configuration of the ethylene. In fact, Hoffmann,[37b] using the extended Hückel method, found that the $CH_2$ cycloaddition to ethylene involves a reaction path passing through geometries quite similar to those expected from Figure 24b. The Woodward–Hoffmann rules would suggest that carbene cycloaddition to ethylene is forbidden for the linear $C_{2v}$ approach and hence also suggest a nonlinear approach.[2c]

Experimental cases are known for which the cycloaddition of singlet carbene to an alkene is stereospecific and cis. For example, Doering and La Flamme[38] found that at −75 to −5° diazomethane plus *cis*-2-butene yield 99% 1,2-dimethylcyclopropane, exclusively cis.

From the standard heats of formation it is expected that the cyclopropane obtained by eq 11 would be

$$CH_2 + C_2H_4 \longrightarrow c\text{-}C_3H_6 \tag{11}$$

formed with 92 kcal/mol[39,40] of excess energy, which is 27 kcal[27] greater than the activation energy for the geometric and structural isomerization of cyclopropane. Thus, to obtain cis addition it would be necessary to have rapid collisional stabilization of the product cyclopropane.

With such an exothermic reaction we might expect the $CH_2$ to begin adding to a near alkene as soon as it is released from the $H_2CN_2$ and in fact the processes could occur simultaneously: $H_2CN_2 + H_2CCH_2 \rightarrow$

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[33] The alternative to the bond shifts in Figure 22a would be to shift [$\phi_{1a}$, $\phi_{1b}$] to the $H_2$, allowing the out-of-phase orbitals to move onto the ethylene. Because of the large separation of the appropriate H's, this should not be as favorable as Figure 22a.

[34] C. F. Bender and H. F. Schaefer III, *J. Amer. Chem. Soc.*, **92**, 4984 (1970); S. V. O'Neil, H. F. Schaefer III, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971). The calculated HCH angles are 133.3° for $^3B_1$, 104.4° for $^1A_1$, and 143.8° for $^1B_1$.

[35] E. Wasserman, W. A. Yager, and V. Kuck, *Chem. Phys. Lett.*, **7**, 409 (1970). The experimental HCH angle from this esr study is 136 ± 8°.

[36] (a) The original study of G. Herzberg [*Proc. Roy. Soc., Ser. A*, **262**, 291 (1961)] indicated the triplet state to have either the geometry $r_{CH}$ = 1.036 Å, $\theta$(HCH) = 180°, or $r_{CH}$ = 1.071 Å, $\theta$(HCH) = 140°. Herzberg favored the linear geometry, but from ref 34 and 35 it is clear now that the correct choice is the bent geometry; (b) G. Herzberg and J. W. C. Johns, *Proc. Roy. Soc. Ser. A*, **295**, 107 (1966); (c) in a recent publication [*J. Chem. Phys.*, **54**, 2276 (1971)] Herzberg and Johns reinterpret the spectroscopic data to obtain an HCH angle of 136 ± 10°.

[37] (a) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.* 12 (1971); (b) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

[38] W. V. E. Doering and P. La Flamme, *ibid.*, **78**, 5447 (1956).

[39] $\Delta H_f^\circ$ = 92 kcal for $CH_2$ fits experiments[40] and calculations[37a] for the $^3B_1$ state. The $^1A_1$ state is about 12 kcal higher and would lead to a greater exothermicity.

[40] W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968).

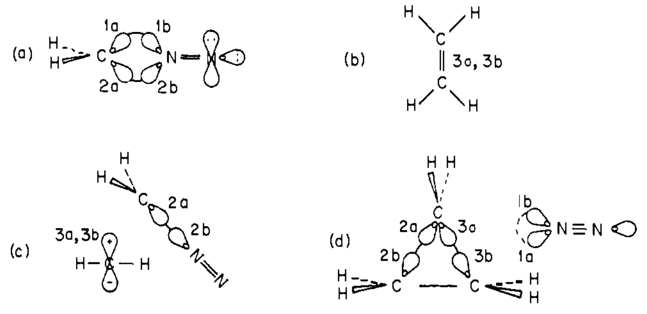
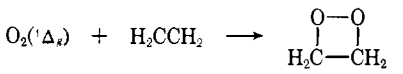


Figure 25. The diazomethane + ethylene → cyclopropane + $N_2$ reaction: (a) and (b) are top views of the reactants, (c) is a side view of the reactants, and (d) shows the products.

$c$-$C_3H_6$ + $N_2$. This reaction is examined in Figure 25 where we see that the orbital phases are consistent with a concerted $N_2$ elimination and cis addition of the $CH_2$ to the ethylene. In this case, since $\Delta H_f{}^\circ(H_2CH_2) = 71$ kcal and since some of the 71-kcal excess energy could go into translational energy of the products, the net excess energy might well not be sufficient to isomerize the product cyclopropane.

Reactions involving nitrene, NH, should be somewhat analogous to those of carbene. The ground state is again a triplet ($^3\Sigma^-$) while the lowest singlet state has $^1\Delta$ symmetry. The GVB wave function for NH($^1\Delta$) has one pair of the form $[x(1)y(2) + y(1)x(2)]$. Thus the orbitals of this pair are orthogonal for the reactant state; consequently considerations such as the possible differences between the geometries in Figure 24a and b need not be made. Given favorable energy differences it would appear that orbital phases could not forbid reactions involving $^1\Delta$ nitrene.

Similar considerations apply to



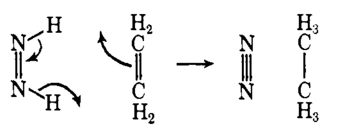
$$O_2(^1\Delta_g) + H_2CCH_2 \longrightarrow \begin{array}{c} O-O \\ |\quad\;\; | \\ H_2C-CH_2 \end{array}$$

where again the unpaired orbitals of the reactants are orthogonal ($\pi_{gx}\pi_{gy} + \pi_{gy}\pi_{gx}$). Thus again, such reactions would not be forbidden by orbital phase conditions.[41]

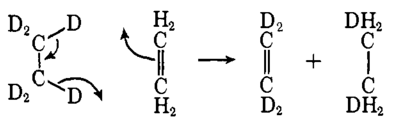
These predictions concerning the reactions of NH($^1\Delta$) and $O_2(^1\Delta_g)$ seem not to be in agreement with the Woodward–Hoffmann rules.

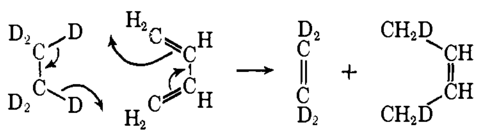
**j. Other Reactions.** We will now sketch out the implications of OPCP for several other reactions.

The orbital shifts for eq 12 are all in phase and thus this reaction should be favored.[42] Similarly is favored whereas eq 13 involves an odd number of phase changes in any test orbital and would be unfavored.



(12)





(13)

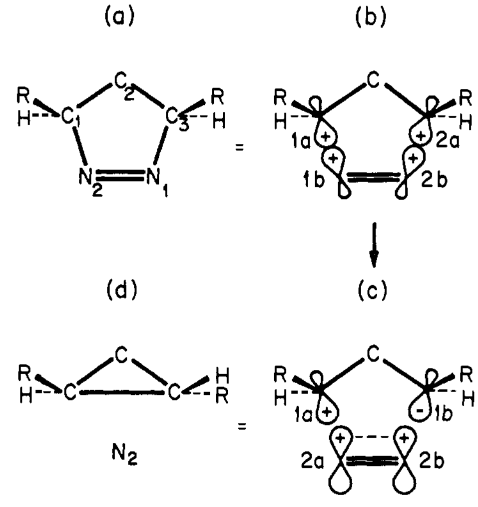


Figure 26. The pyrolysis of pyrazoline.

For the pyrolysis of pyrazoline, Figure 26c shows that, for cis elimination of the $N_2$, the orbitals of the product cyclopropane would be out of phase. As a result we expect the reaction path to be such that the groups on $C_1$ and $C_3$ rotate to lead to the product in Figure 26d. As discussed earlier, this concerted path may be only slightly favorable compared with various biradical paths and hence there should be competition. In fact, Crawford *et al.*,[43] find that a cis-substituted pyrazoline leads to 66% trans product (as in Figure 25d) and the *trans*-pyrazoline leads to 73% cis product.

The above predications are in general agreement with what could be expected from the Woodward–Hoffmann rules.

Considering "reactions" between the Kekule structures of an aromatic molecule, we find from OPCP that the structures are in phase for molecules (such as benzene) exhibiting aromaticity and are out of phase for molecules (such as pentalene) considered as antiaromatic.

**k. Comparison of OPCP with the Hoffmann–Woodward and Other Approaches.** As we have pointed out, the fundamental foundations of the Hoffmann–Woodward and OPCP approaches are different. The Hoffmann–Woodward approach is based upon the MO or Hartree–Fock method, whereas the OPCP approach is based on the GVB method (and involves orbitals and concepts closely related to valence-bond ideas). The MO method does not properly describe the process of breaking a single bond and should lead to a very poor and probably misleading description of reactions that involve biradical intermediates. The GVB method should lead to a good description of these intermediate states but the largest such system to which it has been applied is the trimethylene biradical.[44]

The Woodward–Hoffmann rules were originally derived by one of two procedures. One was to examine the highest occupied molecular orbital of the reactants and to use symmetry considerations to establish whether this orbital could correlate properly[2b] with an occupied orbital of the products. We will refer to this as the

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(41) I thank W. J. Hunt for a helpful discussion on this point.

(42) E. J. Corey, D. J. Pasto, and W. L. Mock, *J. Amer. Chem. Soc.*, **83**, 2957 (1961).

(43) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); D. E. McGreer, R. S. McDaniel, and M. G. Vinje, *Can. J. Chem.*, 43, 1389 (1965).

(44) P. J. Hay, W. J. Hunt, and W. A. Goddard III, in preparation.

Woodward–Hoffmann approach (it was used for the electrocyclic and sigmatropic reactions).[2b] The second approach was to construct a correlation diagram containing the bonding and antibonding orbitals of relevant bonds and to use orbital symmetries to establish the correlations.[2a] We will refer to this as the Hoffmann–Woodward approach (it was used for the cycloaddition and electrocyclic reactions).[2a] Of course the second approach includes the first as a special case. These methods can lead to difficulties for systems with low symmetry where the MO symmetries may not help in determining the effective correlation of the orbitals. Later Woodward and Hoffmann[2c] inductively generalized their rules in such a way that they could be applied to systems for which correlation diagrams would be difficult or impossible to construct.

There are several other theoretical approaches of obtaining selection rules for chemical reactions, nearly all based on the MO viewpoint. Longuet-Higgins[45] emphasized the use of both orbital and many-electron correlation diagrams (for electrocyclic reactions) and showed how the consideration of only the highest occupied MO can lead to incorrect predictions for systems with odd numbers of electrons. Fukui[46] has long emphasized the importance of the highest occupied MO and the lowest vacant MO, and Pearson[47] has used these orbitals and Bader's[48] rule to study selection rules for a number of different types of chemical reactions and also to predict geometries of molecules. Zimmerman[49] has established the correlations of orbitals in electrocyclic reactions using the Hückel formula for the cyclic form obtained from disrotatory motions and the Möbius formula for the cyclic form obtained from conrotatory motion. Trindle[50] has suggested an approach involving mapping the reactant MO's onto the product MO's in order to predict the reactions of low-symmetry systems. Dewar[51] has modified an earlier suggestion by Evans[52] to postulate that thermal reactions involving an aromatic transition state (*i.e.*, six electrons in a configuration analogous to that of benzene) should be preferred over those involving antiaromatic transition states (analogous four- or eight-membered rings).

Van der Lugt and Oosterhoff[53a] in discussing photoinduced electrocyclic reactions have viewed the cyclobutene–butadiene system from a valence-bond (VB) viewpoint and suggest an alternative explanation for the excited state reaction involving an opposite rotatory sense from that of the thermal reaction. Mulder and Oosterhoff[53b] have generalized this work to discuss the selection rules of electrocyclic reactions in terms of the VB orbitals of a cyclic system. With neglect of nonneighbor overlaps and with neglect of ionic structures, they find that the important exchange term is one involving a cyclic permutation of all orbitals. Such terms depend upon the signs of the overlap integrals and upon the number of electron pairs in the cycle, and Mulder and Oosterhoff find that such considerations lead to the Woodward–Hoffmann rules. The energy of the GVB wave function can also be analyzed into VB-like exchange terms, one of which is the term examined by Mulder and Oosterhoff (of course, the GVB orbitals are somewhat delocalized onto neighboring centers). Since the Oosterhoff and OPCP analyses are based on broadly similar wave functions, one should expect a correspondence between these analyses. Indeed, they lead to similar conclusions for cyclic systems.

The OPCP approach makes use only of the bonding orbitals of the reactants and products and does not involve orbital symmetry or correlation diagrams. Thus, this method is more generally applicable than the original Hoffmann–Woodward approach for systems with low symmetry. On the other hand, for thermal reactions the generalized Woodward–Hoffmann approach[2c] leads to predictions in general agreement with those from OPCP and can be applied easily to systems of low symmetry.

A disadvantage of the OPCP approach is that the wave function on which it is based is more complicated than the Hartree–Fock wave function, although the GVB orbitals are themselves just as easy to interpret as the Hartree–Fock orbitals. A further disadvantage is that computer programs for applying the GVB method to a detailed study of chemical reactions of large molecules are not in such a refined state of development as for Hartree–Fock. However, such calculations are feasible and should be much more useful for reactions involving excited states.

Since the Hartree–Fock method often leads to difficulties in treating open-shell systems whereas these problems are overcome in the GVB method, it may be that for reactants involving radicals or excited states [*e.g.*, $O_2(^1\Delta_g)$, $CH_2(^1A_1)$, or $NH(^1\Delta)$], the OPCP ideas would be more reliable than treatments based upon MO's.

**I. Summary.** The use of the orbital phase continuity principle (OPCP) along with simple ideas concerning the form of the (SOGI or valence-bondlike) orbitals of moleculeo permits simple, reliable predictions of the selection rules for chemical reactions. We have considered only thermal reactions here and found general agreement [possible exceptions are the 1,2 elimination of HF from $C_2H_5F$ and reactions involving $O_2(^1\Delta_g)$, $NH(^1\Delta)$, or $CH_2(^1A_1)$] with the predictions of Woodward and Hoffmann, who use a much different approach based molecular symmetry and Hartree–Fock molecular orbital correlation diagrams.

In the above discussions the changes in the orientation of all orbitals have been considered as though the reactions proceed in a stepwise manner involving one bond shift at a time. It should be emphasized that this was done only to make clear the considerations involved. The OPCP method can be employed in many cases by merely drawing in the arrows for the bond shifts, as in Figure 9g, and counting the phase changes. Thus, in Figure 9 there are three end-to-end shifts (and hence two phase changes in any given test orbital) and the reaction is allowed. Similarly, in Figure 21a–d we find four end-to-end shifts (*i.e.*, three phase changes in any given test orbital) and thus the reaction is not allowed (without a rotation about one of the C–C bonds).

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(45) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, 87, 2045 (1965).

(46) K. Fukui, *Tetrahedron Lett.*, 2009 (1965).

(47) R. G. Pearson, *J. Amer. Chem. Soc.*, 91, 1252, 4957 (1969).

(48) R. F. W. Bader, *Can. J. Chem.*, 40, 1164 (1962).

(49) H. E. Zimmermann, *J. Amer. Chem. Soc.*, 88, 1563, 1566 (1966).

(50) C. Trindle, *ibid.*, 92, 3251, 3255 (1969).

(51) M. J. S. Dewar, *Tetrahedron, Suppl.*, 8, 75 (1966).

(52) M. G. Evans, *Trans. Faraday Soc.*, 35, 824 (1939).

(53) (a) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); *J. Amer. Chem. Soc.*, 91, 6042 (1969); (b) J. J. Mulder and L. J. Oosterhoff, *Chem. Commun.*, 305, 307 (1970).

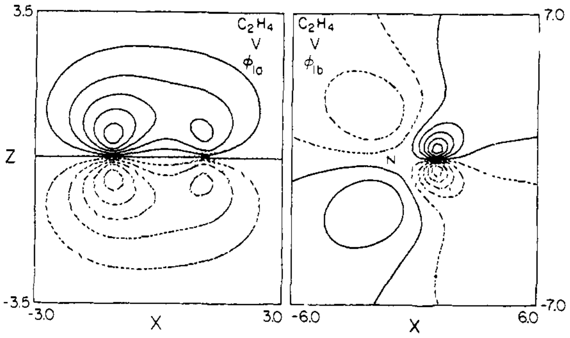

Figure 27. The GVB $\pi$ orbitals of the V state of ethylene (contour plots in the plane perpendicular to the molecule and passing through the C–C axis). The contour values for (a) are the same as in Figure 5; the outer contour and contour increments in (b) are both 0.018.

## III. Excited States

Excited states of molecules are often more complicated than would appear from the standard MO picture. For example, for planar ethylene in the $x$–$y$ plane, the MO method would use a $p_z$ atomic orbital on each carbon combined to yield two molecular orbitals

$$\begin{aligned}\pi &= pz_A + pz_B \\ \pi^* &= pz_A - pz_B\end{aligned} \tag{14}$$

From these one can construct the two-electron (spatial) wave functions

$$\begin{aligned}&N,\ \pi(1)\pi(2) \\ &T,\ \pi(1)\pi^*(2) - \pi^*(1)\pi(2) \\ &V,\ \pi(1)\pi^*(2) + \pi^*(1)\pi(2) \\ &Z,\ \pi^*(1)\pi^*(2)\end{aligned} \tag{15}$$

(these are to be combined with the $\sigma$ orbitals and appropriate spin functions and antisymmetrized to obtain the many-electron wave functions).

Here N refers to the ground state, T to the lowest triplet state, and V to the $\pi$–$\pi^*$ singlet state. The description of the N and T states by eq 15 is qualitatively reasonable; however, this is not the case for the V state. The fully optimized self-consistent field solutions[54] for the V state lead to a very diffuse $\pi^*$ orbital, with a scale (size) more like that of an $n = 3$ excited-state orbital of C rather than the scale of the 2p atomic orbital expected from eq 9.[55] In addition, a complete Hartree–Fock treatment leads to another excited singlet state *below* the V state.[54] This new state involves an excitation of one of the $\pi$ orbitals of the N state up to an excited $\pi$ orbital of the same symmetry and in the HF description is about 0.3 eV lower in energy than the V state.[54] However, to describe this $1\pi$–$2\pi$ excited state, we require more than one $\pi$ basis function per carbon; thus this state could not be described in the usual simple MO model.

In the GVB description, the V state of ethylene has two orbitals[21] as shown in Figure 27. Orbital $\phi_{1a}$ is somewhat similar to the corresponding orbital for the N state of ethylene (Figure 5), except that in the V state this orbital is more delocalized. The other orbital $\phi_{1b}$ is the excited orbital and has the size and shape of a carbon 3d orbital (except that it has a small component of tight $p_z$ character on the right carbon).[56] As the $CH_2$ groups of the molecule are rotated (about the C–C bond) with respect to each other, the diffuse orbital ($\phi_{1b}$) becomes more contracted until at 90° the unpaired orbitals ($\phi_{1a}$ and $\phi_{1b}$) are of comparable size.

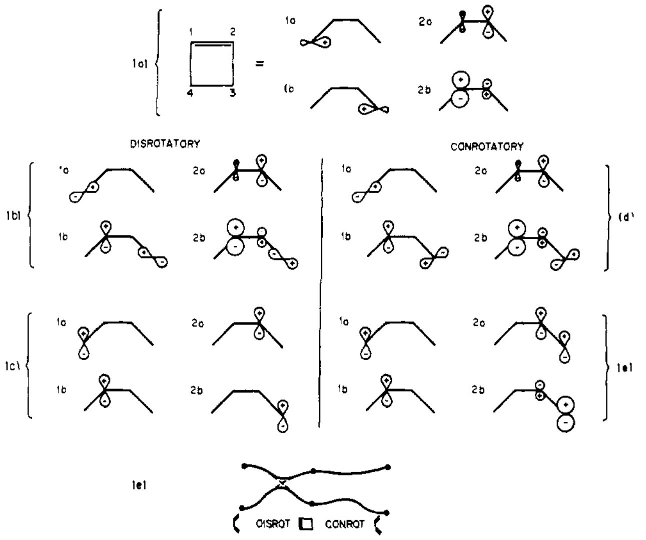

Figure 28. The photochemical cycloreversion of cyclobutene: abc represents the disrotatory path, ade represents the conrotatory path, and f is an approximate potential energy diagram.

For cyclobutene we expect the excited states to involve $\pi$ orbitals essentially the same as those of ethylene, as indicated in Figure 28a, where $\phi_{2a}$ and $\phi_{2b}$ denote orbitals like $\phi_{1a}$ and $\phi_{1b}$ of Figure 27.

Now consider the disrotatory opening of cyclobutene as in Figure 28a–c. As the bonding pair [$\phi_{1a}$, $\phi_{1b}$] moves from 4–3 to 4–1, orbital $\phi_{2a}$ (and $\phi_{2b}$) must shift away from center 1 in such a way as to stay nearly orthogonal to the pair [$\phi_{1a}$, $\phi_{1b}$]. Thus, as shown in Figure 28a–c, the orbital $\phi_{2b}$ changes in such a way as to lose its vertical nodal plane. That is, with disrotatory twisting, the orbitals [$\phi_{2a}$, $\phi_{2b}$] of Figure 28a correlate toward those of the *ground state* of butadiene. [Even so, we do not expect the potential curve for the excited state of cyclobutene to connect with the potential curve of the ground state of butadiene as the methylenes are disrotated; instead, as shown in Figure 28f, there should be an avoided crossing[57] with the excited state of butadiene that correlates toward the ground state of cyclobutene.] On the other hand, for the conrotatory path, the orbitals (see Figures 28a,d, and e) of the excited state of cyclobutene correlate directly with those of the excited state of butadiene.[58] As a result of these considerations, one would expect potential energy curves as in Figure 28f [for the ground state a small barrier for conrotatory twist but a large barrier for disrotatory twist; for the excited state a

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(54) T. H. Dunning, Jr., W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, 4, 231 (1969).

(55) However, as the molecule is twisted the $\pi^*$ orbital becomes much tighter and by 90° is just as tight as the $\pi$ orbital (these are $e_x$ and $e_y$ orbitals at 90°).

(56) The orbitals of Figure 26 are not symmetric and the full many-electron wave function for the V states involves[21] the product of the orbitals of Figure 26 plus the product of the reflected (in the $yz$ plane) orbitals.

(57) An avoided crossing usually refers to a pair of levels that cross in some simple approximation but actually mix and avoid crossing in the exact description.

(58) The orbitals of Figure 28e indicate an excited state of butadiene; however, the self-consistent orbitals may have somewhat different shapes and perhaps a modified spin coupling; see ref 21.

relatively flat curve for disrotatory twist but a well along the disrotatory path with a relatively large probability for crossing to the ground-state curve (nonadiabatic transition)]. Thus, given a molecule in the (symmetric) excited state of cyclobutene, there would be an appreciable probability of a nonadiabatic crossing over to the ground states of butadiene only if we proceed along the disrotatory path.

In fact, van der Lugt and Oosterhoff[53] have carried out a series of valence-bond calculations on this system and have found potential energy curves very much like those of Figure 28f. They suggest that the avoided crossing and nonadiabatic transitions discussed in the previous paragraph occur generally and are responsible for the stereochemistry of excited states being opposite to that for ground states.

This description seems reasonable but the ordering of excited states of various systems is dependent upon a number of factors, and it appears necessary to study carefully the excited states of several prototype systems before arriving at general selection rules for photochemical reactions.

## IV. Summary

The orbital phase continuity principle (OPCP) (derived from *ab initio* calculations on the reactions of some small molecules) leads directly to selection rules for a number of thermal reactions in good agreement with experiment and with the theoretical predictions of Woodward and Hoffmann. However, OPCP makes no use of molecular symmetry and treats open-shell systems consistently and hence should be more widely applicable, even to reactions with little or no molecular symmetry.

Application of the OPCP idea to excited states and hence to photochemical reactions is of great interest but is complicated by the variety of possible states and reactions. Indeed, this very variety leads to a number of possible alternatives depending upon the ordering of the excited states, their closeness in energy, and the changes in the ordering of excited states with geometry. For example, in the GVB approach, excited triplet states can behave differently from the corresponding singlet states. As a result, each system requires much more detailed consideration than was necessary for thermal reactions.

**Acknowledgments.** I thank Professors J. D. Roberts, R. G. Bergman, and J. H. Richards for many helpful suggestions and criticisms on the manuscript and R. Weiss, W. J. Hunt, George Levin, Tom Morton, R. C. Ladner, and Professor W. E. Palke for additional discussions and comments.