

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 94, NUMBER 24

NOVEMBER 29, 1972

## Orbital Symmetry Rules for Unimolecular Reactions

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Evanston, Illinois. Received March 24, 1972

**Abstract:** The rigorous symmetry rules of perturbation theory are reduced to simple, easily used rules for unimolecular reactions. The symmetry of the bonds that are to be broken must be the same as that of the bonds to be made, the symmetry being related only to those elements of symmetry which are conserved. This simple rule also applies to other concerted reactions of any molecularity. If the full symmetry of the reactant molecule is used, however, additional details of unimolecular mechanisms may be unveiled. An example is given for the metal ion catalyzed olefin disproportionation reaction. Reactions in which bonds are broken, but none made, are free of orbital symmetry restrictions, except those of the Wigner-Witmer variety.

Recently perturbation theory has been extensively applied for predicting the course of chemical reactions.<sup>1</sup> This has led to the development of orbital symmetry rules similar to those obtained by Woodward and Hoffmann using the orbital correlation method.<sup>2</sup>

Unimolecular reactions have been included in the examples discussed in the literature. Nevertheless the rules developed so far are incomplete and, in some respects, misleading. For example, it is difficult to formulate a clear statement as to when a unimolecular reaction is allowed and when it is forbidden by orbital symmetry.

One general approach is that pioneered by Bader<sup>3</sup> and elaborated by Salem and Wright.<sup>4</sup> This method relates the symmetries of the ground electronic state, the lowest excited state, and the reaction coordinate, considered as one of the normal modes of vibration of the reacting molecule. Movement along the reaction coordinate mixes in the excited state wave function with the ground state wave function to produce a changed electron distribution, given by the transition density,  $\rho$ . To be effective,  $\rho$  must be concentrated in the region of nuclear motion; the excited state must be close in energy to the ground state and become closer as the reaction proceeds.

The difficulty is that, especially for reactions which have an appreciable activation energy, it is not always

the first excited state which is important.<sup>5</sup> In searching among higher excited states of the correct symmetry, it becomes necessary to make subjective estimates of how effective the transition density might be, and what the excitation energy is. No sharp distinction between a forbidden and an allowed reaction exists, contrary to the results of the orbital correlation method.<sup>2</sup>

Another general method is due to Fukui.<sup>1a</sup> While based on perturbation theory, in the case of unimolecular reactions it becomes a largely intuitive method. The molecule is arbitrarily divided into two parts in which the bordering surface is crossed by the bonds to be formed in the reaction. One part is considered to contain a high energy occupied molecular orbital (HOMO), and the other part a low energy unoccupied orbital (LUMO). The symmetry rule is that reaction proceeds in such a direction as to increase the overlap, and the interaction, between the HOMO and the LUMO.

The method is simple and works well in a number of examples. However, it is by no means clear how to apply it in the general case. The minimum use made of symmetry properties suggests that restrictions due to symmetry may often be overlooked. A preliminary account of a third method has been given.<sup>6</sup> This combines the theoretical rigor of Bader's method and the convenience of Fukui's method. Furthermore, it gives an unambiguous answer as to whether or not a particular reaction path is allowed or forbidden.

The basic idea again is that of a transition density,  $\rho$ , which in molecular orbital theory is proportional to  $\varphi_i \times \varphi_f$ , where  $\varphi_i$  is an MO initially occupied in the ground state, and  $\varphi_f$  is an MO finally occupied in

(1) For general references, see (a) K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971); (b) R. G. Pearson, *ibid.*, **4**, 152 (1971); (c) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

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

(4) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

(5) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969).

(6) R. G. Pearson, *Theor. Chim. Acta*, **16**, 107 (1970).

its place in the excited state. All of the MO's derived from the valence shell AO's are considered as possible  $\varphi_i$  and  $\varphi_f$ .

Chemical reactions usually occur by the breaking of bonds between certain atoms, and the making of new bonds between other atoms. Also molecular orbitals are bonding between certain atoms, antibonding for other atoms, and nonbonding for the remaining atoms. Thus  $\varphi_i$  and  $\varphi_f$  in a reaction should be picked so that they correspond to the bonds that must be made and broken. Such selected orbitals then pick the reaction coordinate,  $Q$ , by the symmetry requirement that the symmetry of  $Q$  is the same as the symmetry of  $\varphi_i \times \varphi_f$ . After reaction begins,  $Q$  must be totally symmetric and  $\varphi_f$  must have the same symmetry as  $\varphi_i$ .

At the start of a unimolecular reaction, when the molecule is at the minimum of its potential energy well, the reaction coordinate can be of any symmetry appropriate to the point group of the molecule. As soon as the molecule begins to move up the potential barrier, the reaction coordinate *must* become totally symmetric.<sup>6</sup> That is, elements of symmetry can only be created or destroyed at maxima or minima of potential energy surfaces. During the course of a concerted chemical reaction, certain elements of symmetry will be conserved. These elements are the important ones in determining symmetry rules. For example, they are the basis for correlation diagrams of the Woodward-Hoffmann type.

The statement that  $\varphi_i$  and  $\varphi_f$  should correspond to the bonds that are made and broken seems intuitively correct. Also it is quite common<sup>2,4</sup> to identify bonds with semilocalized MO's of a definite symmetry. Nevertheless, a more formal proof is desirable. The valence shell AO's of the reactant generate a set of canonical MO's, some of which are occupied and some of which are empty. The division between occupied and empty orbitals determines the bonding in the molecule.

As reaction occurs to form products, the same valence shell AO's are used to form a new set of MO's, exactly the same number as before, but differing in composition and in bonding characteristics. By perturbation theory the new MO's are formed from the old by a mixing of the originally empty MO's with the originally filled ones. Perturbation theory can be applied at each point along the reaction coordinate to make this process continuous. Only orbitals of the same symmetry can mix continuously.

Some of the new MO's will differ but little from the original MO's because they correspond to similar bonding situations. The greatest changes will occur in the orbitals that correspond most closely to the changes in bonding. While often these orbitals can be identified, it is convenient to transform the canonical MO's of reactant and products into more localized MO's corresponding to definite bonds between a limited number of atoms or to lone pairs isolated on a single atom. Such bonding orbitals are formed by linear combinations of the canonical orbitals of the same symmetry. Only the occupied MO's of each molecule can be combined to give the occupied bonding orbitals. The empty MO's combine to give the antibonding partners.

These bonding orbitals are not the same as the localized orbitals usually considered as equivalent to chem-

ical bonds,<sup>7</sup> since the latter are mixtures of MO's of different symmetries. However, they can be directly related to the usual chemical bonds of the molecule. Thompson<sup>8</sup> has shown how the bonds and lone pairs of a molecule can be used as a basis set for symmetry classification. Thus each unique bond in a molecule has a definite symmetry label. In the case of two or more identical bonds, symmetry adapted linear combinations of the bonds must be formed. Each of the symmetry adapted bonds will correspond to one of the bonding orbitals described above.

Motion along the reaction coordinate again mixes the occupied and empty MO's of the same symmetry. We can now focus our attention on the bonds to be broken which clearly select certain  $\varphi_i$ . The bonds to be made select the orbitals  $\varphi_f$ , since the only way we can create *new* bonds is by mixing  $\varphi_i$  and  $\varphi_f$ . With respect to the elements of symmetry that are conserved,  $\varphi_i$  and  $\varphi_f$  must be of the same symmetry. More important, the new bonding orbital that is formed *must* be of the same symmetry as the bonding orbital that was destroyed.

We can reach the same conclusion by using orbital correlation arguments. If the symmetries of the bonds that are broken and the bonds that are made always match up in pairs, the noncrossing rule will then guarantee that none of these orbitals will cross. If they do not cross, leading to a hypothetical excited state product, the reaction is allowed by the correlation diagram procedure.<sup>9</sup>

We have accordingly derived a simple and generally applicable symmetry rule: *a reaction is allowed if the symmetry of the bonds that are made is the same as the symmetry of the bonds that are broken.* The symmetry is related only to those symmetry elements that are conserved in going from reactants to products.

### Classification of Unimolecular Reactions

At this point it is convenient to classify unimolecular reactions into three categories of increasing complexity.

**Class I.** Reactions in which no bonds are made or broken, but the direction of the bonds in space are changed. Examples include conformational changes and the interconversion of polytopal isomers,<sup>10</sup> such as tetrahedral, square-planar interconversions. A large number of such reactions have already been considered from the viewpoint of perturbation theory.<sup>11</sup> For molecules of formulas  $XY_n$  and  $X_2Y_n$ , the valence orbitals of one structure always transform smoothly into the valence orbitals of another. No symmetry barriers seem to exist for these examples. In principle, there is no reason why cases of forbidden structural conversions should not be found for more complicated molecules, but they will be rare.<sup>12</sup>

It is interesting to note that some structural changes of transition metal complexes necessitate the formation

(7) For a discussion see W. England, L. S. Salmon, and K. Reudenberg, *Fortschr. Chem. Forsch.*, **23**, 31 (1971).

(8) H. B. Thompson, *Inorg. Chem.*, **7**, 604 (1968).

(9) It should perhaps be emphasized again that the crossing implied by the orbital correlation method is only an intended crossing. Configuration interaction will prevent an actual crossing.

(10) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).

(11) R. G. Pearson, *ibid.*, **91**, 1252, 4947 (1969); *J. Chem. Phys.*, **52**, 2167 (1970).

(12) A possible example is given by W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

of products in excited electronic states.<sup>13</sup> This results from the many low-lying excited states resulting from the d-orbital manifold. Such reactions are formally forbidden by the orbital correlation procedure.<sup>2</sup> Nevertheless it is known in many cases that they occur rapidly, even on the nmr time scale. An example would be the square-planar-tetrahedral interconversion of Ni(II) complexes.<sup>14</sup> Other cases where the orbital correlation method would fail have been discussed.<sup>15</sup>

**Class II.** Reactions in which bonds are broken, but no bonds are made. These include dissociation of a molecule into free radicals and atoms. Consider the reverse process, the recombination of radicals and atoms. The Wigner-Witmer rules<sup>16</sup> state that there are restrictions on the changes in spin-multiplicity and, for linear products, restrictions on the orbital angular momentum. However, these restrictions do not create energy barriers, and such free radical recombinations usually occur with near zero activation energy. That is, they are allowed by orbital symmetry.

Microscopic reversibility then tells us that dissociation reactions must also be allowed, except for spin and angular momentum restrictions on the products. The activation energy is essentially the endothermicity of the reaction, as shown in Figure 1a.

Consider the dissociation of a homonuclear diatomic molecule such as H<sub>2</sub>.



The valence shell orbitals are of  $\sigma_g$  (bonding) and  $\sigma_u$  (antibonding) symmetry. The reaction coordinate is totally symmetric, or  $\Sigma_g^+$ . Dissociation must involve movement of electrons from the  $\sigma_g$  to  $\sigma_u$  orbitals. The symmetry rule then requires that the excited state which mixes into the ground state is the doubly excited configuration,  $(\sigma_u)^2$ .

Normally such doubly excited states are too high in energy to be important.<sup>3</sup> The reason is that they contribute chiefly to changes in interelectronic repulsion which are second-order effects in perturbation theory. Nevertheless, in a dissociation reaction such as (1), it is just such configuration interaction which is needed.

It has been known for some time<sup>17</sup> that as H<sub>2</sub> dissociates, more of the  $(\sigma_u)^2$  configuration is mixed in with the ground state wave function, mainly  $(\sigma_g)^2$ . In the limit of complete dissociation  $(\sigma_g)^2$  and  $(\sigma_u)^2$  appear with equal weights. This assures that only one electron is on each atom at any one time, the wave function becoming identical with the valence bond wave function. Thus configuration interaction has lowered the interelectronic repulsion or improved the correlation energy.

The situation is somewhat different for a heteronuclear molecule, such as HCl. Both the bonding and antibonding orbitals are of  $\sigma$  symmetry, and the reaction coordinate is  $\Sigma$ .



(13) D. R. Eaton, *J. Amer. Chem. Soc.*, **90**, 4272 (1968); G. L. Caldow and R. A. MacGregor, *J. Chem. Soc. A*, 1654 (1971).

(14) L. H. Pignolet, W. D. Horrocks, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 1855 (1970).

(15) R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, *ibid.*, **93**, 5005 (1971).

(16) E. Wigner and E. Witmer, *Z. Phys.*, **51**, 859 (1928).

(17) C. A. Coulson and L. Fischer, *Phil. Mag.*, **40**, 386 (1949).

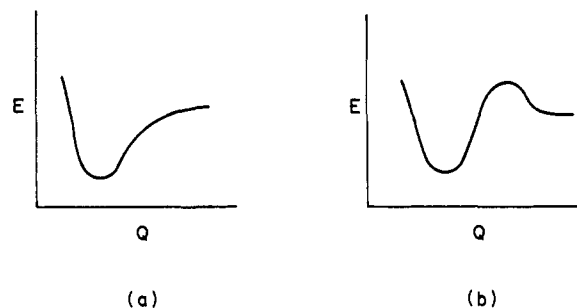
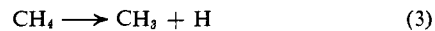


Figure 1. Potential energy vs. reaction coordinate plots for unimolecular reactions (a) allowed and (b) forbidden, by orbital symmetry.

Now dissociation is accompanied by mixing in of singly excited configurations,  $(\sigma)(\sigma^*)$ , as well as doubly excited configurations. The role of the singly excited states is to shift the overall valence electron density from being concentrated on chlorine in the molecule, to evenly distributed between H and Cl in the products. The bonding MO, of course, is concentrated on Cl, whereas  $\sigma^*$  is concentrated on H.

In the dissociation of a polyatomic molecule, the situation is only slightly different. The reaction coordinate may initially be nontotally symmetric. For example, the dissociation of methane



requires a  $T_2$  vibration to break the  $T_d$  point group. This can occur most easily by a  $(t_2) \rightarrow (a_1^*)$  excitation. After a short extension of the carbon-hydrogen bond, the point group becomes  $C_{3v}$ , the reaction coordinate becomes  $A_1$ , and the remaining process is that for a heteronuclear diatomic molecule. We can conclude that there is no orbital symmetry barrier to reactions of class II. The required electron redistribution can be achieved by symmetry compatible excitations that are always available within the valence shell. This analysis leaves unanswered the question as to which of several possible bonds in a molecule will break most readily. The answer to this usually requires much more detailed information.

**Class III.** Reactions in which bonds are both made and broken in a concerted process. These are the reactions most likely to be restricted by orbital symmetry considerations. Electrons must be transferred from certain regions of the molecule to other regions. This is in contrast with class II reactions, where the electrons stay on the same atoms, even as the bonds break, and class I, where the same atoms remain bonded.

A reaction which is forbidden by orbital symmetry will have an energy profile such as shown in Figure 1b. It must also be appreciated that even reactions which are completely allowed may have profiles resembling 1b. That is, large activation energies for reactions may exist for other reasons than those of orbital symmetry.

The symmetry rules will be illustrated by taking several examples. In some cases it will be found that the symmetries of the bonds that are broken and the bonds that are made are compatible with the selected reaction path. The reactions are allowed. For forbidden reactions, there is a basic incompatibility with the symmetries of the bonds and the selected reaction path. The path must necessarily lead to a high energy transition state.

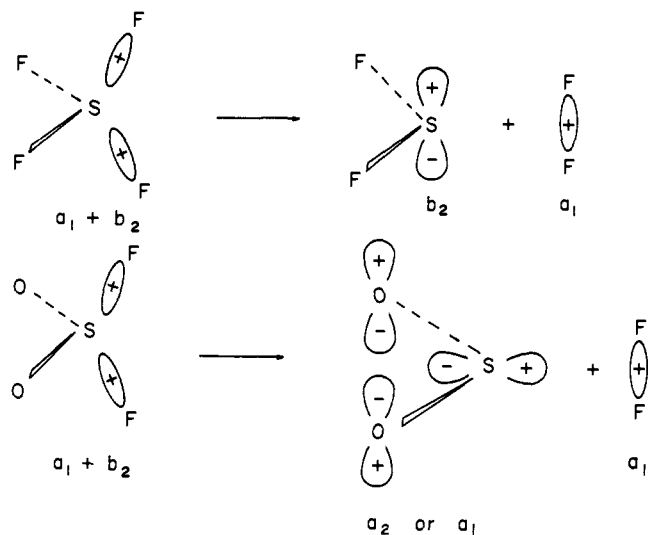
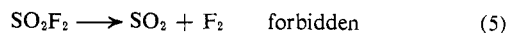
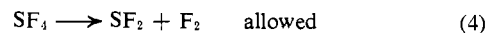


Figure 2. Symmetry of bond orbitals that correspond to bonds made and broken in decomposition of SF<sub>4</sub> and SO<sub>2</sub>F<sub>2</sub>. The point group is C<sub>2v</sub>.

The first two examples appear very similar, but one is allowed and the other forbidden.



It is assumed that a concerted process is followed and that the symmetry elements of the original C<sub>2v</sub> point group are conserved. Figure 2 shows the course of the two reactions. The MO's of the bonds to be broken are shown only as localized bonding MO's. However, as long as they are symmetry adapted, they take the place of the more complete MO's of the molecule, as already discussed.

The S-F bonds to be broken in both cases are of a<sub>1</sub> and b<sub>2</sub> symmetry in the C<sub>2v</sub> point group. The F-F bond to be made is of a<sub>1</sub> symmetry. In the case of SF<sub>2</sub>, the remaining new bonds are actually antibonding, since a π\* orbital of b<sub>2</sub> symmetry is filled. This orbital is chiefly concentrated on sulfur and it is sufficient to think of it as a p orbital on S, containing an unshared pair, Figure 2.

In this case, the reaction coordinate is A<sub>1</sub> throughout, mixing of a<sub>1</sub> and a<sub>1</sub>\* and of b<sub>2</sub> and b<sub>2</sub>\* orbitals is allowed, and the new bonds are formed as the old ones break. The conclusion that the reaction is allowed is quite consistent with an orbital correlation diagram, as it always will be if the symmetries of the bonds that are broken and the bonds that are made match up in pairs.

In the case of SO<sub>2</sub>, which has two fewer electrons than SF<sub>2</sub>, the new orbital that is filled is either an antibonding σ\* orbital of a<sub>1</sub> symmetry, or a π nonbonding MO of a<sub>2</sub> symmetry, Figure 2. These two orbitals appear to have rather similar energies.<sup>18</sup> At any rate, normally there are no electrons in the higher energy π\* orbital of b<sub>2</sub> symmetry. This is a fatal lack, since under the influence of an A<sub>1</sub> perturbation (the changing reaction coordinate), electrons cannot move from a b<sub>2</sub> orbital (S-F bonding) into either an a<sub>1</sub>\* or a<sub>2</sub>\* orbital. The symmetries of the bonds and the reaction

(18) S. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **47**, 1953 (1967).

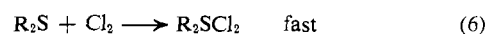
coordinate do not match up. The reaction is forbidden. In terms of orbital correlation, the SO<sub>2</sub> formed in reaction 5 would be formed in a doubly excited state.

The MO sequence for SF<sub>4</sub> has been calculated semi-empirically to be

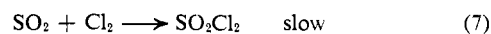
$$(a_1)^2(b_2)^2(b_1)^2(2a_1)^2(3a_1)^2(2b_1)^0(2b_2)^0(4a_1)^0$$

considering only σ bonds.<sup>19</sup> SO<sub>2</sub>F<sub>2</sub> would differ only in having the 3a<sub>1</sub> orbital empty. Excitation from filled to empty orbitals of a<sub>1</sub> and b<sub>2</sub> symmetry would be needed as the molecules moved along the reaction coordinate. It is by no means obvious from the MO sequence that SO<sub>2</sub>F<sub>2</sub> would be much less reactive than SF<sub>4</sub>. Indeed the opposite conclusion might easily be drawn.

The experimental evidence for these reactions is indirect. Orbital symmetry rules for the reverse reactions show that (4) is allowed and (5) forbidden.<sup>1b</sup> This is exemplified by the rapid reactions of halogens with organic sulfides to form products with the SF<sub>4</sub> structure.<sup>20</sup>

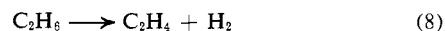


In sharp contrast, the reaction of SO<sub>2</sub> with chlorine is extremely slow in the absence of a catalyst.



Reaction in the gas phase occurs only at temperatures above 250° by a chlorine atom chain reaction.<sup>21</sup>

As another example of a forbidden reaction, consider the concerted suprafacial loss of hydrogen from ethane.



Since the reverse reaction is forbidden by orbital symmetry, the forward reaction (8) must also be (Figure 1b).

Assume a D<sub>3h</sub> eclipsed conformation initially. If two eclipsed hydrogen atoms begin to leave, the point group changes to C<sub>2v</sub>. We can easily find the symmetry of the required reaction coordinate by looking at correlation tables for descent in symmetry. The rule is that the active mode must become totally symmetric in the lower symmetry. Table I shows that

Table I. Correlation Table for Reduction in Symmetry of Group D<sub>3h</sub>

D <sub>3h</sub> <sup>a</sup>	C <sub>3h</sub>	D <sub>3</sub>	C <sub>3v</sub>	C <sub>2v</sub>	C <sub>2</sub>	C <sub>s</sub>
A <sub>1</sub> '	A'	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A	A'
A <sub>2</sub> '	A'	A <sub>2</sub>	A <sub>2</sub>	B <sub>2</sub>	B	A''
E'	E'	E	E	A <sub>1</sub> + B <sub>2</sub>	A + B	A' + A''
A <sub>1</sub> ''	A''	A <sub>1</sub>	A <sub>2</sub>	A <sub>2</sub>	A	A''
A <sub>2</sub> ''	A''	A <sub>2</sub>	A <sub>1</sub>	B <sub>1</sub>	B	A'
E''	E''	E	E	A <sub>2</sub> + B <sub>1</sub>	A + B	A' + A''

<sup>a</sup> The vibrational modes listed under D<sub>3h</sub> will convert a molecular structure into that of lower symmetry in which the mode becomes totally symmetric.

an E' vibration converts D<sub>3h</sub> into C<sub>2v</sub>; also A<sub>2</sub>'' converts D<sub>3h</sub> into C<sub>3v</sub>, A<sub>1</sub>'' into D<sub>3</sub>, etc.

The MO configuration for eclipsed ethane is<sup>22</sup>

$$\dots(1e')^4(3a_1')^2(1e'')^4(3a_2'')^0(2e'')^0$$

(19) R. D. Willert, *Theor. Chim. Acta*, **2**, 393 (1964).

(20) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5749 (1969).

(21) Z. G. Szabo and T. Berces, *Z. Phys. Chem.*, **12**, 168 (1957).

(22) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967).

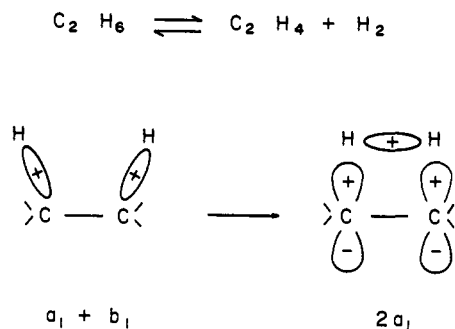


Figure 3. Symmetry of bonds that are made and broken in forbidden pyrolysis of  $\text{C}_2\text{H}_6$ . The point group is  $C_{2v}$ .

The lowest energy transition ( $1e'' \rightarrow 3a_2''$ ) gives a transition density of  $E'$  symmetry, as required. However, this transition cannot be effective in causing reaction 8 to occur, as both MO's are C-H bonding and C-C antibonding.

Using the  $C_{2v}$  point group, where the reaction coordinate is  $A_1$ , Figure 3 shows that the bonds to be broken are of  $a_1$  and  $b_1$  symmetry. The bonds to be made are both of  $a_1$  symmetry. Either the olefin or hydrogen would have to be formed in its excited state.

The Diels-Alder retrogression of cyclohexene is allowed. The point group is  $C_s$ .



As Figure 4 shows, the bonds that are broken (the 3-4  $\pi$  bond and the 1-2 and 5-6  $\sigma$  bonds) are of  $2A' + A''$  symmetry. The bonds to be made (the 1-6, 4-5, and 2-3  $\pi$  bonds) are of the same symmetry. All of the bonds are interconvertible. A disrotatory twist of the hydrogen atoms on carbon atoms 2 and 5 will preserve the  $C_s$  point group.

The forbidden concerted suprafacial cleavage of cyclobutane has been discussed in detail by Wright and Salem.<sup>23</sup> In the  $D_{2h}$  point group, the bonds to be broken are of  $A_{1g}$  and  $B_{2u}$  symmetry. The bonds to be made are of  $A_{1g}$  and  $B_{3u}$  symmetry. This is the feature which makes the reaction forbidden.

There are two allowed mechanisms, one being the dissociation into the biradical. As described above, this class II reaction is free of orbital symmetry restraints. Doubly excited configurations to reduce electronic repulsion are most important.

The other allowed mode of decomposition is the puckering and twisting process leading to the reverse of antarafacial addition.<sup>2</sup> The point group becomes  $C_2$ . In this low symmetry the carbon-carbon  $\sigma$  bonds that are broken and the  $\pi$  bonds that are formed all have  $A$  symmetry. Obviously by sufficient distortion of any molecule, all symmetry can be lost and all molecular orbitals become of the same symmetry.

Since even small distortions can destroy the symmetry of a molecule, it would appear that here is a simple way to avoid symmetry restrictions. However, there is usually a very large price to pay. Saying that two orbitals have the same symmetry is the same as saying that they may have a nonzero overlap. A small distortion can only make a small overlap, which means very weak interaction. Large distortions are necessary to get substantial overlaps. Energetically one must

(23) J. S. Wright and L. Salem, *J. Amer. Chem. Soc.*, **94**, 322 (1972).

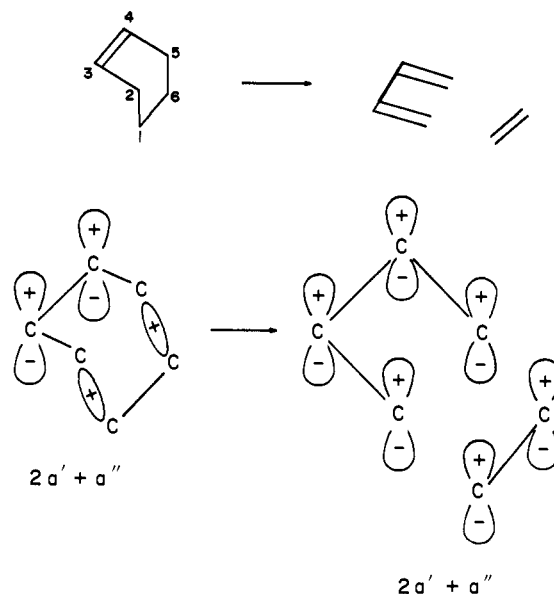


Figure 4. Symmetry of bonds made and broken in retrograde Diels-Alder reaction. The point group is  $C_s$ .

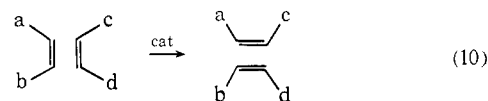
pay for serious departures from normal bond distances and bond angles.

There are other examples where symmetry rules will give the wrong answer, unless judgment is used. The conversion of cubane into cyclooctatetraene, maintaining the symmetry of the  $C_{2v}$  point group, seems to match up the symmetries of the bonds that are made and broken.<sup>2</sup> The matching is only formal, however, since there is nearly zero overlap between some orbitals of the same symmetry. They exist in two different parts of the cubane molecule and are essentially noninteracting.

Electrocyclic reactions have already been discussed from the present viewpoint.<sup>1b,6</sup> It should be added that two procedures are possible. One is to use the point group of the original reactant; the other is to use the (lower) point group after the reaction has begun.

For example, in the ring closure of *cis*-butadiene to give cyclobutene, an  $A_2$  reaction mode (conrotatory) is selected because the bond to be broken is of  $A_2$  symmetry, and the bond to be made corresponds to an originally antibonding orbital of  $A_1$  symmetry. The point group is  $C_{2v}$ , that of the original reactant. However, after twisting of the terminal methylene groups begins, the point group is  $C_2$ , since only the twofold axis is preserved. In this lower symmetry both  $A_1$  and  $A_2$  become of the same symmetry, namely  $A$ . A  $B_2$  reaction mode (disrotatory) would change  $A_1$  to  $A'$  and  $A_2$  to  $A''$ , and the reaction is forbidden.

As an example of the advantage of using the full symmetry of the reactant, let us try to predict the behavior of a molecule which has been postulated as an intermediate in the olefin disproportionation reaction catalyzed by transition metal complexes.<sup>24</sup>



(24) (a) W. B. Hughes, *ibid.*, **92**, 532 (1970); (b) F. D. Mango and J. H. Schachtschneider *ibid.*, **93**, 1123 (1971); (c) G. S. Lewandos and R. Pettit, *ibid.*, **93**, 7087 (1971).



and away from regions of negative overlap, or transition density.<sup>3</sup> An atom will migrate if a path of positive  $\rho$  is available from one site to another. Instead of forbidden and allowed processes, one would find favored and unfavored processes.

In such an analysis, it is important to keep proper phase relationships between the interacting orbitals. The phase of one orbital is not independent of that of the other, as implied by Fukui.<sup>1a</sup> In a recent paper Goddard has shown how favored and unfavored reaction paths can be predicted by following the orbital phases.<sup>2b</sup>

Accordingly, symmetry in a molecule is not necessary for making deductions about favorable reaction

(25) W. A. Goddard, *J. Amer. Chem. Soc.*, **94**, 793 (1972).

paths. Its presence does facilitate the task of analysis very markedly. Molecular orbitals built up of atomic s, p, and d orbitals will always have an inherent symmetry that can be used for prediction.

In conclusion, the rule that a reaction is allowed, if the symmetries of the bonds that are made match up with the symmetries of the bonds that are broken, seems to be unusually simple and reliable. While derived above for unimolecular reactions, it clearly is equally valid for ground state reactions of any molecularity. A requirement is that at least one element of symmetry be conserved over the reaction path.

**Acknowledgments.** The author is grateful to National Sciences Foundation Grant GP-31060X for support of this work.

## Generalized Valence Bond Description of Simple Alkanes, Ethylene, and Acetylene<sup>1a</sup>

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Received January 24, 1972

**Abstract:** Generalized valence bond wave functions are reported for CH, CH<sub>2</sub>, CH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>6</sub>. These wave functions have the form of valence bond wave functions except that the orbitals are solved for self-consistently (as with Hartree-Fock wave functions). General characteristics of these wave functions are discussed.

Considerable progress in the understanding of bonding and molecular structure has been made through the use of both valence bond<sup>2a</sup> and Hartree-Fock wave functions.<sup>2b</sup> In many respects these wave functions lead to different interpretations of the wave functions, but in recent years the emphasis has been on the Hartree-Fock or molecular orbital description, which has also yielded quantitatively useful wave functions. Recently the *ab initio* generalized valence bond (GVB) method<sup>3,4</sup> has been developed which takes the wave function to have the form of a VB function, but which allows all orbitals to be solved for self-consistently (as in Hartree-Fock). Thus in GVB no special hybridization is imposed on the orbitals, and, in addition, the orbitals are permitted to delocalize onto other centers. With this approach one would hope to combine quantitatively useful calculations with the convenient VB oriented interpretations to obtain useful conceptual ideas concerning similarities and differences in bonding for various states and reactions of molecules. Herein

are reported the results of GVB calculations on a number of related hydrocarbons (CH, CH<sub>2</sub>, CH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>6</sub>).

In the GVB approach the doubly occupied molecular orbitals  $\phi_i$  of the many-electron Hartree-Fock wave function are replaced by two-electron valence bond functions  $\phi_{ia}$  and  $\phi_{ib}$

$$\phi_i(1)\phi_i(1)\alpha(1)\beta(2) \rightarrow [\phi_{ia}(1)\phi_{ib}(2) + \phi_{ib}(1)\phi_{ia}(2)]\alpha(1)\beta(2)$$

and the optimum orbitals,  $\phi_{ia}$  and  $\phi_{ib}$ , of each pair are solved for variationally, subject only to the restriction that they be orthogonal<sup>5</sup> to the orbitals in other pairs. In addition to yielding an energy lower than the Hartree-Fock energy, this method offers two major conceptual advantages.

(1) The orbitals of each pair turn out to be localized hybrid atomic-like orbitals in close correspondence to chemists' "intuitive" ideas of bonds and lone pairs in molecules. (Note that each orbital contains *one* electron; thus a two-electron bond involves *two* different orbitals, generally one more concentrated on each of the two atoms involved in the bond.)

(5) The restriction that the orbitals of one pair are orthogonal to the orbitals of other pairs is called the strong orthogonality restriction. We have examined this restriction for a number of cases<sup>4b</sup> and find that for ground states of molecules of the type considered herein, this restriction should have only minor effects on the energies and their properties.

(1) (a) Partially supported by a grant (GP-15423) from the National Science Foundation; (b) National Science Foundation Predoctoral Fellow; (c) NDEA Predoctoral Fellow.

(2) (a) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960; (b) R. S. Mulliken, *Rev. Mod. Phys.*, **41**, (1932); A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

(3) W. A. Goddard and R. C. Ladner, *J. Amer. Chem. Soc.*, **93**, 6750 (1971).

(4) (a) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1971); (b) W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.*, **56**, 738 (1972).