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## Symmetry Rules for Chemical Reactions

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Recently there has been great interest in the devising of symmetry rules for predicting the course of chemical reactions. Much of this interest is due to the well-known work of Woodward and Hoffmann. Their method is based upon a correlation of the molecular orbitals of the reactant(s) with those of the product(s), and can be considered quite general. In this Account we present symmetry rules, derived in quite a different manner, whose predictions are not expected to differ from the most generalized application of the Woodward-Hoffmann rules but which are usually easier to apply.

Molecular orbital theory is still used as a basis, but the chemical reaction is considered as a perturbation on the reactant system. In particular, a small displacement along the reaction coordinate is taken as the perturbing influence. Using the quantum mechanical method of second-order perturbation theory, the symmetry rules for an elementary process of any molecularity can be stated in a rigorous way. This was first done by Bader<sup>1</sup> for the decomposition of an activated complex, a special example of a unimolecular reaction. The corresponding rules for bimolecular reactions have only recently been stated.<sup>2</sup> However the same conclusions can be drawn from a number of other perturbation theories of chemical reactivity.<sup>3</sup>

The mathematical language of group theory is useful in stating the symmetry rules in a concise way. Fortunately the conclusions can also be stated in a simple, pictorial manner. It is necessary to have some knowledge of the molecular orbitals of the system. In particular, the symmetry properties are needed. These are simply the changes in sign (plus or minus) of the

wave function, corresponding to the MO, at different parts of the molecule.

Chemical reactions consist of the breaking of certain bonds between atoms and the making of new bonds. All MO's correspond to the bonding together of certain atoms, the antibonding of other atoms, and the non-bonding of the remaining atoms. It follows that in a chemical reaction certain molecular orbitals must be vacated of electrons and others must be filled to create the new bonding situation.

The most important of these changes is a flow of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The importance of these orbitals has been stressed by Fukui, who in 1952 named them the frontier orbitals.

Electron movement between two orbitals cannot occur unless the orbitals meet the symmetry requirement. For a bimolecular reaction, the requirement is simply that the two have a net overlap. For a unimolecular reaction, the symmetries of the two must match up with the symmetry of the motion of the nuclei. The nuclear motion can be regarded as equivalent to one or more of the normal modes of vibration of the molecule.

### Theory

Consider an elementary process (concerted reaction) of any molecularity. The question is, how does symmetry enter into the variation of potential energy with changing nuclear coordinates? Group theory will first be used to obtain an exact answer to this question. The applications made later do not require the use of group theoretic language, but it is obvious that there are many reasons for chemists today to become familiar with the symbols used.

Figure 1 shows the usual adiabatic plot of potential energy vs. reaction coordinate. The points marked A, B, and C will be used to derive the symmetry rules since they represent characteristic features of such a plot. Any point on the diagram corresponds to some arrangement of the nuclei of the reactants. This ar-

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(1) (a) R. F. W. Bader, *Can. J. Chem.*, **40**, 1164 (1962); (b) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

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

(3) M. J. Dewar, *J. Amer. Chem. Soc.*, **74**, 3341 *et seq.* (1952); K. Fukui, *Bull. Chem. Soc. Jap.*, **39**, 498 (1966); K. Fukui and H. Fujimoto, *ibid.*, **41**, 1989 (1968); G. Klopman and R. F. Hudson, *Theor. Chim. Acta*, **7**, 165 (1967); L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

rangement will automatically generate a certain point group ( $T_d$ ,  $C_{3v}$ ,  $C_s$ , etc.). All of the symmetry properties are now contained in the irreducible representations or symmetry species of that point group.

The wave equation for the system is now assumed to be solved exactly. This gives rise to a number of eigenstates  $\psi_0, \psi_1, \dots, \psi_k$ , and corresponding eigenvalues  $E_0, E_1, \dots, E_k$ , where  $\psi_0$  and  $E_0$  refer to the ground electronic state. Now all the wave functions must belong to one of the symmetry species A, B, E, etc., of the point group. Indirectly then, each energy value has a symmetry label tied to it.

Any arbitrary small motion of the nuclei away from the original configuration can be analyzed as a sum of displacements corresponding to the normal modes of the pseudomolecule representing the reactants. Each of these normal modes (of vibration) belongs to one of the symmetry species of the point group.

We now use quantum mechanics in the form of perturbation theory to relate potential energy,  $E$ , to the reaction coordinate. First the Hamiltonian is expanded in a Taylor-Maclaurin series about the point  $Q_0$ , corresponding to the original configuration with Hamiltonian  $\mathcal{H}_0$  (eq 1). Here  $Q$  represents the reaction

$$\mathcal{H} = \mathcal{H}_0 + \left(\frac{\partial U}{\partial Q}\right) Q + \frac{1}{2} \left(\frac{\partial^2 U}{\partial Q^2}\right) Q^2 \dots \quad (1)$$

coordinate and also the magnitude of the small displacement from  $Q_0$ . For convenience, we consider only one normal mode at a time.

Since the Hamiltonian must be invariant to all the symmetry operations of the pseudomolecule, it follows that  $Q$  and  $(\partial U/\partial Q)$  have the same symmetry. Their direct product is totally symmetric. Since  $Q^2$  is symmetric, it follows next that  $(\partial^2 U/\partial Q^2)$  is also symmetric.  $U$  is the nuclear-electronic and nuclear-nuclear potential energy. The kinetic energy of the electrons and electron-electron potential energy are not functions of the nuclear coordinates, to the first order.

The last two terms in eq 1 represent the perturbation. Using standard second-order perturbation theory, we now solve for the new wave functions and energies. For the ground electronic state, the energy becomes

$$E = E_0 + Q \left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_0 \right\rangle + \frac{Q^2}{2} \left\langle \psi_0 \left| \frac{\partial^2 U}{\partial Q^2} \right| \psi_0 \right\rangle + Q^2 \sum_k \frac{\left[ \left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_k \right\rangle \right]^2}{E_0 - E_k} \quad (2)$$

$E_0$  is the energy at  $Q_0$ , the next two terms are the first-order perturbation energy, and the last term is the second-order perturbation energy. While eq 2 is valid only for  $Q$  very small, we can select  $Q_0$  anywhere on Figure 1. Hence eq 2 is general for the purpose of displaying symmetry properties.

The symbol  $\langle \dots \rangle$  represents integration over the electron coordinates, covering all space. We can now use a group theory rule to decide whether the integrals

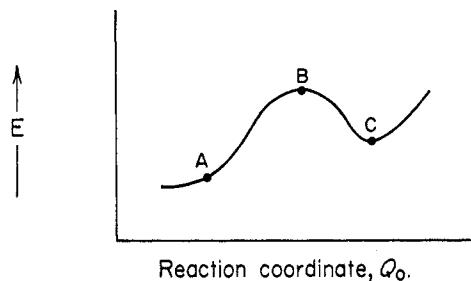


Figure 1. Points A, B, and C are discussed in the text.

in eq 2 are exactly zero or not. The rule is that the direct product of three functions must contain the totally symmetric species, or the integral over all space is zero.

Let us consider the term in (2) which is linear in  $Q$ . At any maximum or minimum in the potential energy curve,  $\partial E/\partial Q = 0$  and therefore the integral must be identically zero, independent of symmetry. At all other points this term must be the dominant one, since  $Q$  is small. If  $\psi_0$  belongs to a degenerate symmetry species (E or T), the term usually leads to the first-order Jahn-Teller effect,<sup>4</sup> which removes the degeneracy. Since this is not important in the present context, we will assume that  $\psi_0$  is nondegenerate.

Since the direct product of a nondegenerate species with itself is always totally symmetric, we derive our first symmetry rule: *all reaction coordinates belong to the totally symmetric representation.* That is,  $(\partial U/\partial Q)$ , and also  $Q$ , must be totally symmetric, otherwise its product with  $\psi_0^2$  will not be symmetric and the integral will be zero. However, it *must* be nonzero for all of the rising and falling parts of Figure 1. This means that once a reaction embarks on a particular reaction path it must stay within the same point group until it reaches an energy maximum or minimum. A totally symmetric set of nuclear motions can change bond angles and distances, but it cannot change the point group.<sup>5</sup>

We now consider point A on Figure 1. The integral  $\langle \psi_0 | \partial U/\partial Q | \psi_0 \rangle$  has a positive value since the reaction has a positive activation energy. Instead of trying to evaluate the integral we accept that its value is the slope of Figure 1 at the point A. The terms in  $Q^2$  in eq 2 now become important. Their sum determines the curvature of the potential energy plot. For a reaction with a small activation energy, the curvature should be as small as possible (or negative).

The integral  $\langle \psi_0 | \partial^2 U/\partial Q^2 | \psi_0 \rangle$  has a nonzero value by symmetry since  $(\partial^2 U/\partial Q^2)$  is totally symmetric. Furthermore, it will be positive for all molecules. It represents the force constant which resists the move of any set of nuclei away from an original configuration for which  $\psi_0^2$  is the electron density distribution. The last term in eq 2 represents the change in energy that

(4) H. A. Jahn and E. Teller, *Proc. Roy. Soc., Ser. A*, **161**, 220 (1937).

(5) This restriction on the point group is not as absolute as it sounds since an energy maximum may also be encountered in a normal mode orthogonal to the reaction coordinate. This then allows a nonsymmetric nuclear motion to change the point group.

results from changing the electron distribution to one more suited to the new nuclear positions determined by  $Q$ . Its value is always negative since  $E_0 - E_k$  is a negative number.

This can be seen more easily if the equation for the wave function is written down from perturbation theory

$$\psi = \psi_0 + \sum_k \frac{\langle \psi_0 | \frac{\partial U}{\partial Q} | \psi_k \rangle}{E_0 - E_k} \psi_k \quad (3)$$

The summations in (2) and (3) are over all excited states. Each excited-state wave function is mixed into the ground-state wave function by an amount shown in eq 3. The wave function is changed *only* because the resulting electron distribution,  $\psi^2$ , is better suited to the new nuclear positions. Salem<sup>6</sup> calls the resulting decrease in energy the *relaxability* of the system along the coordinate  $Q$ .

Now we can use group theory to show that only excited-state wave functions,  $\psi_k$ , which have the same symmetry as  $\psi_0$  can mix in and lower the potential energy barrier. This follows because we have already shown that  $(\partial U/\partial Q)$  must be totally symmetric. Hence the direct product of  $\psi_0$  and  $\psi_k$  must be totally symmetric, but this requires that they have the same symmetry. We can conclude that, *for a chemical reaction to occur with a reasonable activation energy, there must be low-lying excited states for the reacting system of the same symmetry as the ground state.* Such a reaction is said to be symmetry allowed. A symmetry-forbidden reaction is simply one which has a very high activation energy because of the absence of suitable excited states.

Equations 2 and 3 are exact, as are the symmetry rules derived from them. For practical applications, some rather drastic assumptions must now be made. One is that LCAO-MO theory will be used in place of the exact wave functions,  $\psi_0$  and  $\psi_k$ . Since we are interested only in the symmetry properties, this creates no serious error, since MO theory has the great virtue of accurately showing the symmetries of the various electronic states.

The second assumption is more serious, since we will replace the infinite sum of excited states in (1) and (2) by only a few lowest lying states. This procedure will work because we are not trying to evaluate the sum but only to decide if it has a substantial value. It can be shown<sup>1a</sup> that the various states contributing to (1) and (2) fall off very rapidly as the difference,  $|E_0 - E_k|$ , becomes large. This is because the integral  $\langle \psi_0 | \partial U / \partial Q | \psi_k \rangle$  decreases very rapidly for two wave functions of quite different energy.

Figure 2 shows how we use MO theory to represent the ground and excited states that are needed. The symmetry of  $\psi_0\psi_k$  is replaced by  $\phi_i\phi_f$ , where  $\phi_i$  is the occupied MO in the ground state and  $\phi_f$  is the MO occupied in its place in the excited state. Positions of special importance are occupied by the highest occu-

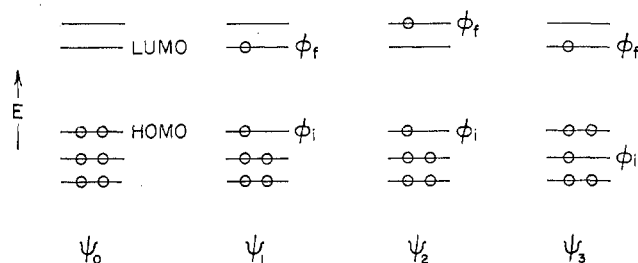


Figure 2. Molecular orbital description of ground state and first few excited states.

pled and lowest unoccupied molecular orbitals, since excitation of an electron from HOMO to LUMO defines the lowest excited state.

Before taking up examples, it is helpful to point out that the requirement that two orbitals,  $\phi_i$  and  $\phi_f$ , have the same symmetry is the same as saying that they must have a net positive overlap. Two molecular, or atomic, orbitals of different symmetry species have exactly zero overlap.

### Bimolecular Reactions

Let us consider a bimolecular reaction which has reached point A in Figure 1. Two molecules have approached each other with a definite orientation. They have started to interact with each other, but the interaction energy is still small. This means that the MO's of the two separate molecules are still a good starting point for considering the combined system. Those of the same symmetry (positive overlap) will interact more and more strongly as the reaction coordinate is traversed, and at the transition state (point B in Figure 1) quite different MO's will be produced.

For the reaction to be allowed by symmetry, we must have transfer of electrons from high-energy occupied MO's ( $\phi_i$ ) to low-energy empty MO's ( $\phi_f$ ) which have positive overlap. This will lower the energy of the system *via* the last term in eq 1 and prevent an excessive energy barrier. Now we can add an additional requirement on  $\phi_i$  and  $\phi_f$  using chemical knowledge rather than mathematical or quantum mechanical arguments. This is that  $\phi_i$  must represent bonds that are broken and  $\phi_f$  bonds that are made during the reaction, for their bonding parts. The reverse statement holds for their antibonding parts.

Also we know that some atoms are much more electronegative than other atoms. Therefore electrons will move more easily from  $\phi_i$  to  $\phi_f$  when they move in the direction of the more electronegative atoms. In such cases  $|E_0 - E_k|$  will be small and the stabilizing effect of electron excitation will be large.

To illustrate these principles Figure 3 shows the HOMO and LUMO of several diatomic molecules. Reactions of  $H_2$  are particularly easy to describe. The only MO's of reasonable energy are the bonding  $\sigma_g$ , which is occupied, and the antibonding  $\sigma_u^*$ , which is empty. The labels refer to the  $D_{\infty h}$  point group of the single molecule.

One of the simplest of chemical reactions would be

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

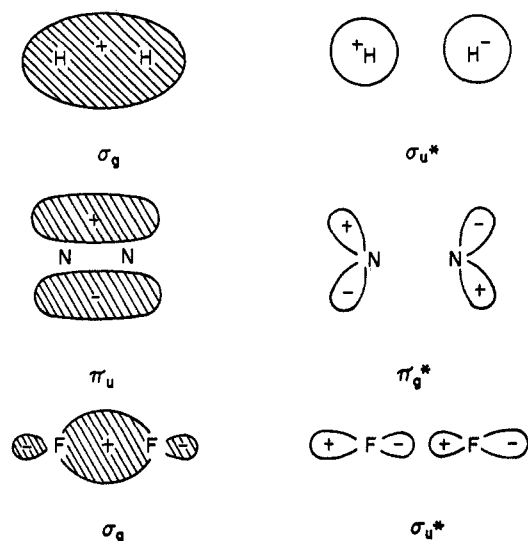


Figure 3. Molecular orbitals in some diatomic molecules. The drawings are schematic, intended to show only the symmetry properties. Occupied MO's are shaded here and elsewhere.

isotope exchange between  $\text{H}_2$  and  $\text{D}_2$  (eq 4). Let us

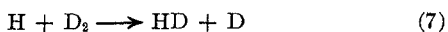
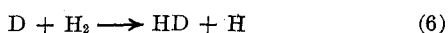
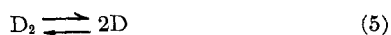


assume that (4) occurs by a bimolecular mechanism in which  $\text{H}_2$  and  $\text{D}_2$  collide broadside, giving rise to a four-center transition state



The point group of this transition state is  $C_{2v}$ . Also, at point A in Figure 1 the point group is  $C_{2v}$ . The MO's of  $\text{H}_2$  and  $\text{D}_2$  should now be classified as  $A_1$  for the bonding  $\sigma_g$  and  $B_1$  for the antibonding  $\sigma_u^*$ . As Figure 4 shows, there is no empty MO of the same symmetry as any of the filled MO's. Hence the reaction is forbidden by orbital symmetry. Figure 4 also shows that the requirement of same symmetry is simply that of nonzero overlap.

The statement that the reaction is forbidden, as stated earlier, is simply that of saying that the assumed mechanism has an excessive activation energy. Indeed the energy of the transition state in this case can be calculated quite accurately by *ab initio* quantum mechanical methods.<sup>7</sup> It lies 123 kcal above the energy of the reactants  $\text{H}_2 + \text{D}_2$ . The mechanism is impossible, for all practical purposes. Instead other allowed mechanisms take over for reaction 4.



The atom-molecule reactions 6 and 7 are symmetry allowed. Indeed, reactions of free atoms and radicals rarely have serious symmetry restrictions and are often found. Conversely, four-center reactions of diatomic molecules almost always turn out to be forbidden.

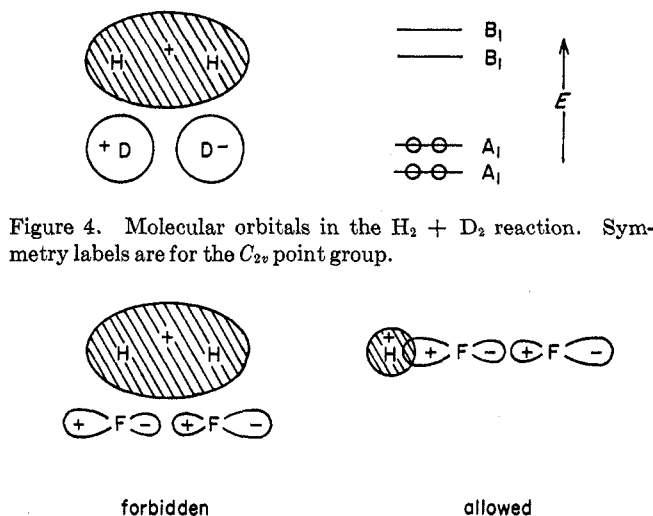


Figure 4. Molecular orbitals in the  $\text{H}_2 + \text{D}_2$  reaction. Symmetry labels are for the  $C_{2v}$  point group.

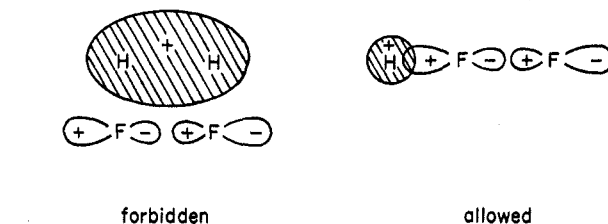


Figure 5. Forbidden four-center path and allowed free-atom path for the  $\text{H}_2 + \text{F}_2$  reaction.

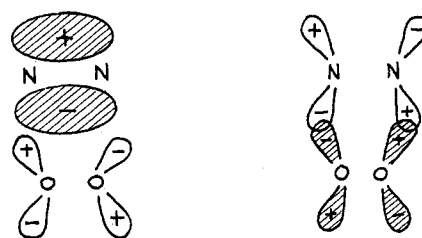
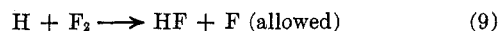
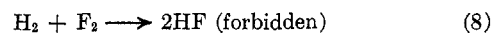


Figure 6. Electron flow from  $\text{N}_2$  to  $\text{O}_2$  forbidden by symmetry; opposite electron flow allowed by symmetry, but chemically forbidden.

Figure 5 shows the reaction intermediates in the case of reactions 8 and 9. Note that it clearly must be the



empty  $\sigma_u^*$  MO of  $\text{F}_2$  which accepts electrons in almost any reaction of  $\text{F}_2$ . This follows from the electronegativity of fluorine. Similar  $\sigma_u^*$  orbitals are the key LUMO's for the other halogen molecules as well.

For years it was considered that the hydrogen-iodine reaction occurred by a bimolecular process in which the two molecules collided broadside. In 1967 Sullivan showed that this was not so.<sup>8</sup> Instead there were mechanisms in which one (high temperature) or two (low temperature) iodine atoms reacted with a hydrogen molecule. These results are now completely understandable in terms of Figure 5.<sup>9</sup>

Figure 6 shows that the reaction of nitrogen with oxygen to form nitric oxide is forbidden by orbital symmetry. The important MO's are the filled  $\pi$  orbitals of  $\text{N}_2$  and the  $\pi^*$  MO's of  $\text{O}_2$ . These antibonding orbitals of oxygen are half-filled and can act as either the HOMO or the LUMO. By symmetry, flow of electrons from the  $\pi$  orbital of  $\text{N}_2$  to the  $\pi^*$  orbital of  $\text{O}_2$  is forbidden. Electrons could move from  $\text{O}_2$  to  $\text{N}_2$  (Figure 6) as far as symmetry is concerned. However, this is chemically unrealistic. Besides, such

(7) H. Conroy and G. Malli, *J. Chem. Phys.*, **50**, 5049 (1969).

(8) J. H. Sullivan, *ibid.*, **46**, 73 (1967); **47**, 1566 (1967).

(9) R. Hoffmann, *ibid.*, **49**, 3739 (1968).

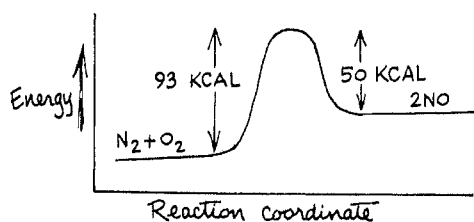
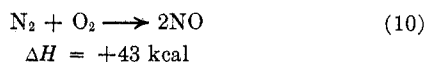


Figure 7. A symmetry-imposed barrier to a reaction automatically imposes a barrier for the reverse reaction.

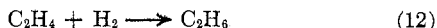
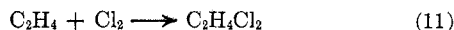
electron movement would convert the O-O double bond into a triple bond by emptying an antibonding orbital.

Since reaction 10 is strongly endothermic, the sym-

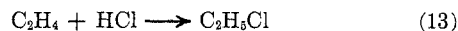


metry barrier is imposed in addition to a thermodynamic one. More important, the reverse of reaction 10, which is exothermic, is very slow, the activation energy being 50 kcal/mole. As Figure 7 shows, a symmetry barrier for a forward reaction automatically creates the same barrier for the reverse reaction.

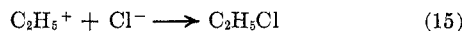
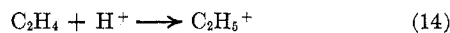
A number of other examples of forbidden reactions of diatomic molecules have been discussed.<sup>10</sup> The pattern also extends to otherwise saturated groups joined by bonds of any order. Thus reactions 11 and 12



are also forbidden as concerted processes (Figure 7). Reactions of lower symmetry, such as (13), are pre-

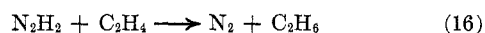


dicted to be partly forbidden by symmetry. This follows because the overlaps between the HOMO and LUMO orbitals of these systems are not identically zero, but can be seen to be small (Figure 8). A two-step mechanism (eq 14 and 15), which is not forbidden,



becomes the usual path for addition reactions to multiple bonds.

Although direct addition of H<sub>2</sub> to an olefin or acetylene is forbidden, it is possible to add simultaneously two atoms of hydrogen to an unsaturated linkage. All that is necessary is that the hydrogen first be bonded to one or two other atoms. For example, *cis*-diimide can act as a hydrogenating agent in a one-step, concerted process. The HOMO in diimide is one that is



bonding for both N-H bonds and antibonding for the N-N bond. Electron flow from this into the π\* orbital of C<sub>2</sub>H<sub>4</sub> (Figure 9) will break the carbon-carbon double bond and the two nitrogen-hydrogen bonds. At the same time the nitrogen-nitrogen bond will become a triple bond, and two new carbon-hydrogen bonds will be made.

(10) R. G. Pearson, *Chem. Eng. News*, **48**, 66 (Sept 28, 1970).

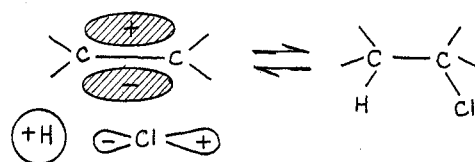


Figure 8. One-step addition of HCl to an olefin is partly forbidden by symmetry. Overlap is small, but is not zero.

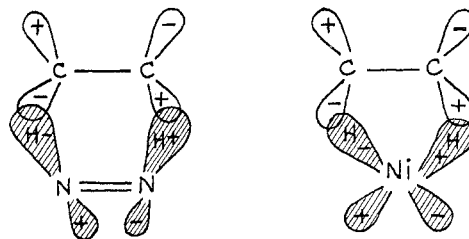


Figure 9. Concerted addition of two hydrogen atoms to a double bond is allowed in these cases.

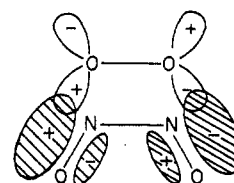
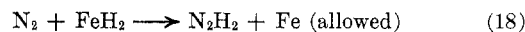
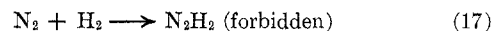


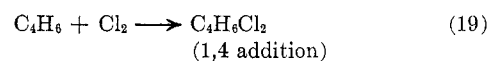
Figure 10. Molecular orbitals for the O<sub>2</sub> + N<sub>2</sub>O<sub>2</sub> reaction. The product must be N<sub>2</sub>O<sub>4</sub>, not 2NO<sub>2</sub>.

Another possibility is for the hydrogen molecule to first add to a transition metal. The d orbitals of such metals have the right symmetry to react directly with the H<sub>2</sub> molecule. Electron flow from the filled d orbital into the empty σ\* orbital of H<sub>2</sub> will break the H-H bond and create two new metal-H bonds. This metal hydride can now transfer two H atoms in one step to an olefin molecule (Figure 9). Similar addition of hydrogen atoms to other unsaturated molecules is also possible.



Many important examples of catalysis, in fact, involve just those diatomic, or pseudodiatomic, molecules whose reactions are forbidden by orbital symmetry: O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, etc. The role of the catalyst is largely to circumvent the symmetry restrictions in these cases.

If we have more extended π systems than found in O<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>, then four-center reactions again become possible (eq 19 and 20). This follows from the change



in symmetry of the HOMO and LUMO of the extended π systems. Figure 10 shows a possible mechanism for the oxidation of nitric oxide dimer to N<sub>2</sub>O<sub>4</sub>. Notice that a symmetry-allowed electron transfer from a filled B<sub>1</sub> orbital of N<sub>2</sub>O<sub>2</sub> to an empty or half-empty B<sub>1</sub> orbital of O<sub>2</sub> results in the breaking of the O<sub>2</sub> bond (by filling up an antibonding MO of O<sub>2</sub>), the strengthening of the

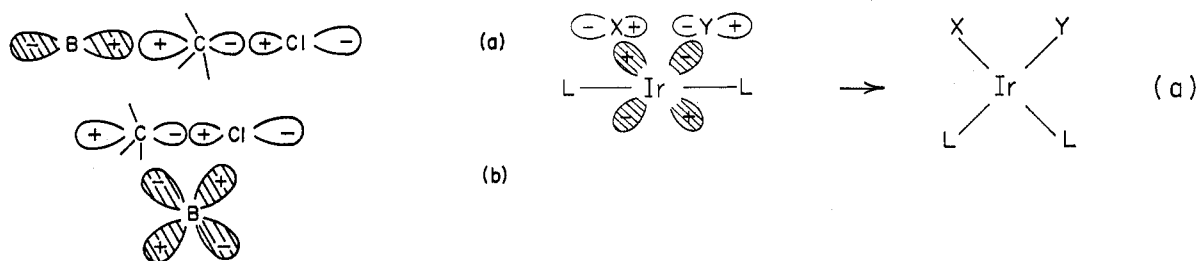


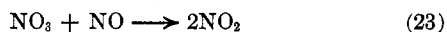
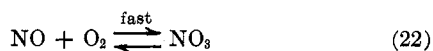
Figure 11. Nucleophilic displacement with (a) inversion of configuration, (b) retention of configuration at carbon.

N-N bond in  $N_2O_2$  (by emptying out an antibonding MO), and the formation of two new N-O bonds by positive overlap. The N-N bond strength in  $N_2O_4$  is obviously much greater than in  $N_2O_2$ , which has only a transitory existence.

Because of electron spin conservation rules it is only possible for the  ${}^1\Delta_g$  excited state of  $O_2$  to react in this fashion. The ground-state  ${}^3\Sigma_g^-$  state of  $O_2$  could only react if the products were  $NO_2$ , rather than  $N_2O_4$ .



From Figure 10 we can see that there is no way to transfer electrons from  $N_2O_2$  to  $O_2$  so that the N-N bond is weakened, allowing the formation of  $2NO_2$  molecules as the direct product of the reaction. We conclude that the mechanism of air oxidation of NO involving the dimer  $N_2O_2$  is forbidden by orbital symmetry and electron spin considerations. This leaves the alternative mechanism (eq 22 and 23) as the most

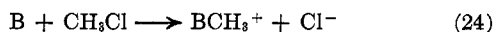


probable. Both (22) and (23) are fully allowed by symmetry and spin.

### Nucleophilic Displacement Reactions

All molecules X-Y in which a single bond connects two groups are somewhat equivalent to a halogen molecule as far as symmetry is concerned. The critical LUMO is an antibonding  $\sigma^*$  type. Electrons must flow into this orbital to break the X-Y bond (or electrons must be removed from the occupied  $\sigma$  orbital which corresponds to  $\sigma^*$ ). Consider that X-Y is an alkyl halide and that the reaction is a nucleophilic substitution occurring by an  $S_N2$  mechanism. Clearly electrons are transferred from the HOMO of the nucleophile to the  $\sigma^*$  orbital of the alkyl halide.

Figure 11 shows this reaction from the viewpoint of orbital symmetry.<sup>11</sup> The symbol B is used for the



nucleophile. It can be seen that the usual displacement mechanism with inversion of configuration at the carbon atom is symmetry allowed for a  $\sigma$ -type donor orbital. However, a  $\pi$ -type donor can also react in another way, at the front side of the carbon-chlorine

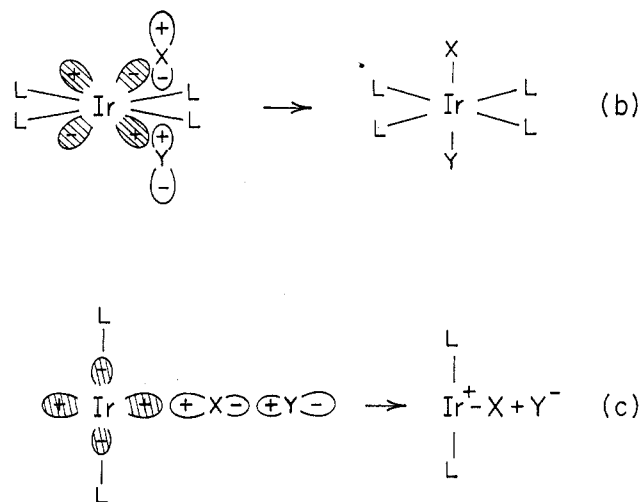
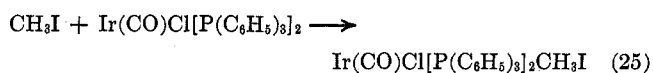


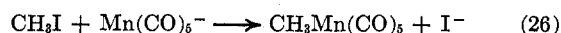
Figure 12. Mechanisms of oxidative addition: (a) one-step cis addition of XY with retention at X; (b) one-step trans addition with retention at X; (c) two-step addition with inversion of configuration at X.

bond. A d orbital on the nucleophile would be best for this kind of interaction, but a p orbital might also be effective.

For a  $\pi$  donor, electron transfer from the nucleophile to the alkyl halide will result in breaking the carbon-chlorine bond and in bonding both carbon and chlorine to B. The stereochemical result is now retention of configuration at the carbon atom. In the oxidative addition of alkyl halides to square-planar  $d^8$  metal complexes, both carbon and the halogen become bound to the metal atom.



Just as predicted in Figure 12, both cis and trans addition of  $CH_3I$  can occur. Furthermore, when an optically active alkyl halide is used, retention of configuration at the carbon atom is found in the product.<sup>12</sup> It should be noted that the iridium atom acts as the electron donor in these reactions. In other reactions of nucleophilic metal atoms with alkyl halides, inversion of configuration at carbon occurs.<sup>13</sup> These are cases where only the carbon atom binds to the metal. Figure



12 shows this is also allowed from the viewpoint of orbital symmetry.

(12) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970).

(13) R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1970).

(11) H. Kato, K. Morokuma, T. Yonezawa, and K. Fukui, *Bull. Chem. Soc. Jap.*, **38**, 1749 (1965).

### Unimolecular Reactions

We now go to a consideration of points B and C in Figure 1. B refers to an activated complex and C to a single molecular species, which is unstable with respect to isomerization, or breakdown to other products. In either case, the theory is changed somewhat from that of the bimolecular reactions discussed earlier.

The term linear in  $Q$  in eq 1 now vanishes, since we are at an extremum in the potential energy plot. As before, the first quadratic term is positive, and the second one is negative. Clearly at a maximum, point B, the second term is larger than the first. At a minimum, point C, the first term dominates, but the magnitude of the second term determines whether we lie in a deep potential well or a shallow one.

Again the existence of low-lying states,  $\psi_k$ , of the correct symmetry to match with  $\psi_0$  is critical. Now there is no restriction on the reaction coordinate which forces it to be totally symmetric. However,  $\psi_0$ ,  $(\partial U/\partial Q)$ , and  $\psi_k$  are still bound by the symmetry requirement that their direct product must contain the totally symmetric representation.

If we consider rather symmetrical molecules to begin with, it will usually be found that the reaction coordinate, and  $(\partial U/\partial Q)$ , are nonsymmetric. The reason for this is that maximum and minimum potential energies are usually found for nuclear arrangements with a high degree of symmetry. Any disturbance of the nuclear positions will now reduce the symmetry. However, this corresponds to a change in the point group, which can only come about by a nonsymmetric vibrational mode.

Conversely, it may be pointed out that a number of point groups depend upon a unique value of  $Q_0$  in Figure 1. For example, a tetrahedral molecule has uniquely determined bond angles. All such cases must correspond to either maxima or minima in Figure 1 if the reaction coordinate is taken either as the bond angles or relative bond distances.

In molecular orbital theory the product  $\psi_0\psi_k$  is again replaced by  $\phi_i\phi_f$ , where both the occupied and empty MO's must be in the same molecule. Electron transfer from  $\phi_i$  to  $\phi_f$  results in a shift in charge density in the molecule. Electron density increases in the regions where  $\phi_i$  and  $\phi_f$  have the same sign (positive overlap) and decreases where they have opposite signs (negative overlap). The positively charged nuclei then move in the direction of increased electron density. The motion of the nuclei defines a reaction coordinate. The symmetry of  $Q$  is the same as that of the product  $\phi_i \times \phi_f$ .

The size of the energy gap between  $\phi_i$  and  $\phi_f$  is critical. A small gap means an unstable structure, unless no vibrational mode of the right symmetry exists for the molecule capable of changing its structure. A large energy gap between the HOMO and the LUMO means a stable molecular structure. Reactions can occur, but only with a high activation energy.

For an activated complex (point B) there must

necessarily be at least one excited state of low energy. The symmetry of this state and the ground state then determines the mode of decomposition of the activated complex. This was the subject of the first application of eq 2 to chemical reactions by Bader.<sup>1</sup>

When a molecule lies in a shallow potential well (point C), the activation energy for unimolecular change is small. In this case we can again expect a low-lying excited state. The symmetry of this state and the ground state will determine the preferred reaction of the unstable molecule. For a series of similar molecules, we expect a correlation between the position of the absorption bands in the visible-uv spectrum and the stability.

As an example, consider the similar molecules ozone and sulfur dioxide. The former is blue in color and is highly unstable. Sulfur dioxide is colorless and is also



much more stable toward dissociation into SO and O. We correlate the instability of  $\text{O}_3$  with the fact that it absorbs light of lower energy than  $\text{SO}_2$  does.

An *ab initio* calculation gives the MO sequence<sup>14</sup>  $\dots(3b_1)^2(4b_1)^2(6a_1)^2(1a_2)^2(2b_2)^0$  for  $\text{O}_3$ , with  $\text{SO}_2$  probably having the same sequence. Both molecules have an angular structure and the point group is  $C_{2v}$ . The  $a_2$  and  $b_2$  MO's are  $\pi$  orbitals, while the  $a_1$  and  $b_1$  MO's are  $\sigma$  orbitals.

The lowest energy transition is expected to be between the nonbonding ( $a_2$ ) orbital and the antibonding ( $b_2$ ) orbital. The symmetry of the transition is  $A_2 \times B_2 = B_1$ . The  $B_1$  vibration is the unsymmetric stretch in which one O-O bond shortens and the other lengthens. It corresponds to the dissociation of eq 27.

The first absorption bands for  $\text{O}_3$  are at 1.5 and 2.1 eV, and those for  $\text{SO}_2$  are at 3.2 and 3.7 eV.<sup>15</sup> Unfortunately for the simple interpretation, these correspond to triplet and singlet excitations from the  $6a_1$  MO to the  $2b_2$  MO. Hence the symmetry of  $\phi_i \times \phi_f$  is  $B_2$ , which does not correspond to any vibration of these molecules. A higher pair of bands at 2.2 and 4.7 eV for  $\text{O}_3$  and at 3.7 and 5.3 eV for  $\text{SO}_2$  does correspond to the required  $a_2$  to  $2b_2$  transition.<sup>15</sup> For most molecules there is still considerable uncertainty in assigning the observed absorption bands to definite molecular orbital transitions.

For molecules which lie in deep potential wells, it may not be the LUMO which is important. The reason is that, since a high activation energy is required, higher lying states may be utilized. It is also difficult to place the higher excited states of a molecule in correct order. Nevertheless the symmetry rules may still be of great help in selecting the reaction path.

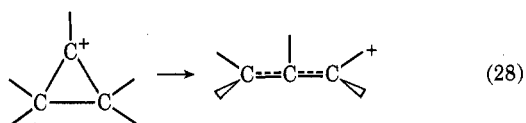
Suppose we know that a certain unimolecular reaction occurs, but do not know the detailed mechanism.

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

(15) H. J. Maria, P. Larson, M. E. McCarville, and S. P. McGlynn, *Accounts Chem. Res.*, **3**, 368 (1970).

Certain bonds must be made and broken during the reactions. The bonds can then select  $\phi_i$  and  $\phi_f$ . These MO's in turn will fix the symmetry of the reaction coordinate,  $Q$ . The only requirement is a knowledge of the symmetries of the MO's which relate to the bonds that are affected.

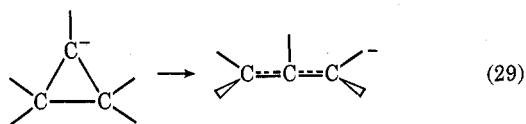
As an example we take the ring-opening reaction of the cyclopropyl cation (eq 28). The critical orbitals



are an empty, nonbonding  $\pi$  orbital on the cationic carbon and the filled  $\sigma$  bonding orbital connecting the two other carbon atoms. Transfer of electrons from the filled to the empty MO will break the carbon-carbon bond, as required, and start to form  $\pi$  bonds involving the central carbon.

The symmetry of the  $\pi$  orbital is  $B_2$  and that of the  $\sigma$  orbital is  $A_1$  in the  $C_{2v}$  point group. Their direct product is of  $B_2$  symmetry, and hence the reaction coordinate must be  $B_2$ . Figure 13a shows that a disrotatory movement of the methylene hydrogen atoms is  $B_2$ , and a conrotatory movement has  $A_2$  symmetry. Accordingly the ring opening will be disrotatory for the cyclopropyl cation.

If the cyclopropyl anion were considered, the  $\pi$  orbital would be filled. In that case, the other critical orbital would be the empty antibonding  $\sigma^*$  orbital involving the two carbon atoms. Electron transfer will now break the carbon-carbon bond and concentrate the negative charge on the two terminal carbon atoms.



In the new  $\pi$  system that is formed, the negative charge is indeed located on the terminal carbon atoms.

The symmetry of an antibonding  $\sigma^*$  orbital must be  $B_1$ , whereas the  $\pi$  orbital is still  $B_2$ . Since  $B_1 \times B_2 = A_2$ , we have just shown that ring opening in a cyclopropyl anion occurs by a conrotatory process. We could have arrived at these same conclusions by considering the ring-closing reactions of the alkyl cation and anion, respectively.

### Molecular Structure

One of the interesting applications that can be made of the symmetry rules is the prediction of the stable shapes of molecules.<sup>16</sup> Molecules with formulas  $XY_n$  or  $X_2Y_n$  usually are found with rather regular structures. A decision can be made as to which of several alternative structures is the most stable using eq 2. It is necessary to assume that the term linear in  $Q$  has

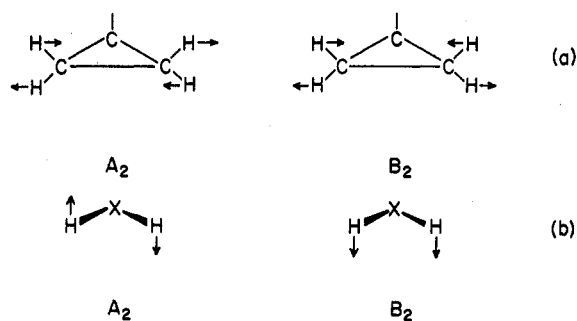


Figure 13. (a) Conrotatory ( $A_2$ ) and disrotatory ( $B_2$ ) twisting motions of methylene groups in cyclopropyl system. (b) Vibrations of planar  $H_2XY$  molecule ( $Y$  is in back of  $X$ ).  $A_2$  corresponds to simple rotation, and  $B_2$  to distortion to pyramidal structure.

a coefficient of zero. That is, we can only decide if a certain point group is stable for the molecule. We cannot find the best values for the bond angles and bond distances within the point group.

The procedure is to test a given molecule in two (or more) possible structures, *e.g.*, square planar and tetrahedral. One structure usually corresponds to a maximum in Figure 1 and the other to a minimum. The reaction coordinate is the normal mode which interconverts the two structures. The stable structure will have a large energy gap between the HOMO and LUMO that matches up with this transition. The unstable structure, conversely, must have a small energy gap. Occasionally both structures are unstable, indicating an intermediate structure, *e.g.*, of  $D_{2d}$  symmetry (squashed tetrahedron).

A complex molecule with many atoms will have many possible structures. If an accurate MO sequence is available for such a molecule in an unstable structure, it is possible to predict which normal mode is favored. This is actually a prediction of the stable structure into which the original configuration will distort.

As an illustration, molecules of the general formula  $H_2XY$  will be tested to see if they are stable in the planar form, or whether they will distort to a pyramidal form. The planar form has  $C_{2v}$  symmetry and the pyramidal form is  $C_s$ . Figure 13b shows that the motion of the hydrogen atoms which destroys the planarity is of  $B_2$  symmetry. The alternative motion of  $A_2$  symmetry simply rotates the molecule about the  $XY$  bond axis.

An *ab initio* MO sequence for formaldehyde,  $CH_2O$ , in  $C_{2v}$  symmetry is given by<sup>17</sup>  $\dots(4a_1)^2(1b_1)^2(5a_1)^2(1b_2)^2(2b_1)^2(2b_2)^0(6a_1)^0$ . The lowest energy transition is  $2b_1 \rightarrow 2b_2$ , also known as the  $n$  to  $\pi^*$  transition, since the  $2b_1$  orbital is rather nonbonding and localized on the oxygen atom. The absorption occurs at about 350 nm and corresponds to an energy gap of 3.5 eV.

This is not a large gap, but the direct product  $B_1 \times B_2 = A_2$  and there is no true vibration of  $A_2$  symmetry present in the  $CH_2O$  molecule. Since the next

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(17) M. D. Newton and W. E. Palke, *J. Chem. Phys.*, **45**, 2329 (1966).



excited state lies very high in energy ( $>7$  eV), we conclude that  $\text{CH}_2\text{O}$  is stable in the planar form.

An *ab initio* MO sequence has also been calculated for the free radical,  $\text{NH}_2\text{O}$ , assuming it to be planar ( $\dots(1b_2)^2(2b_1)^2(2b_2)^1(6a_1)^0$ ). The higher orbitals are in the same order as for  $\text{CH}_2\text{O}$ .<sup>18</sup> The lowest energy transition is now of  $B_2 \times A_1 = B_2$  symmetry. This is the right normal mode to make the planar form pyramidal. While the energy gap is not known, it must be fairly small, since both the  $b_2$  and  $6a_1$  orbitals are antibonding.

We conclude that  $\text{NH}_2\text{O}$  is nonplanar, in agreement with the detailed *ab initio* calculations.<sup>18</sup> In this connection, it is of interest to note that the first excited state of  $\text{CH}_2\text{O}$  is also nonplanar. The same transition of  $B_2$  symmetry ( $\dots(1b_2)^2(2b_1)^1(2b_2)^1(6a_1)^0$ ,  $\text{CH}_2\text{O}^*$ ) is also available to  $\text{CH}_2\text{O}^*$ .

The MO sequence for  $\text{BH}_2\text{F}$  is essentially the same as for the isoelectronic  $\text{CH}_2\text{O}$ .<sup>19</sup> It also is planar.  $\text{NH}_2\text{F}$

should have the electronic configuration  $\dots(1b_2)^2(2b_1)^2(2b_2)^2(6a_1)^0$  and is predicted to be pyramidal. The radical  $\text{CH}_2\text{F}$  is isoelectronic with  $\text{NH}_2\text{O}$  and is predicted to be pyramidal. Unlike the  $\text{CH}_3$  radical,  $\text{CH}_2\text{F}$ ,  $\text{CHF}_2$ , and  $\text{CF}_3$  are indeed pyramidal.<sup>20</sup>

Unfortunately it is not possible to test the pyramidal,  $C_s$ , structures for stability in the case of  $\text{H}_2\text{XY}$  molecules. The reason is that the normal mode which converts to the planar structure is a symmetric one. As explained earlier, we cannot say anything about totally symmetric distortions, since they are equivalent to optimizing the bond angles and lengths. For many other cases, however, it is possible to test two or more structures for stability.<sup>16</sup>

*I thank the National Science Foundation and the U. S. Atomic Energy Commission for financial support which made this work possible. Figures 6, 7, 8, and 9 are reproduced by permission from Chemical and Engineering News.*<sup>10</sup>

(19) M. E. Schwartz and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 1466 (1970).

(20) K. Morokuma, L. Pedersen, and M. Karplus, *J. Chem. Phys.*, **48**, 4801 (1968).

(18) A. W. Salotto and L. Burnelle, *J. Chem. Phys.*, **53**, 333 (1970).