

# ORBITAL SYMMETRY RULES AND THE MECHANISM OF INORGANIC REACTIONS

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## ABSTRACT

In the last few years symmetry arguments have been used very effectively to predict the course of chemical reactions. The Woodward–Hoffmann rules are famous examples. A complete, but simple, theory of how symmetry enters into a chemical process can be given. Use is made of group theory and second-order quantum mechanical perturbation theory.

The resulting simple equations can be reduced even further to a consideration of the symmetry of the molecular orbitals of the reactants. The relevant orbitals are the highest filled (HOMO) and the lowest empty (LUMO) with the correct symmetries to match the symmetry of the reaction coordinate. The closer in energy these orbitals are, the lower the activation energy. An orbital symmetry forbidden reaction is one where no orbitals of the right symmetry exist within a reasonable energy range of each other. In the usual case it is unnecessary to know the molecular orbital scheme of the products.

For bimolecular and trimolecular reactions, the reaction coordinate must be totally symmetrical, therefore the symmetry requirement for the HOMO and LUMO is that they have a net positive overlap. For unimolecular reactions, the reaction path need not be totally symmetrical. The direct product of the HOMO and LUMO symmetries determines the symmetry of the reaction coordinate.

The HOMO and LUMO also must correspond to bonds that are to be broken and bonds that are to be made; if they are bonding MOs the reverse statement holds true for antibonding MOs. Examples are given for all of these rules.

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The development of so-called orbital symmetry rules for chemical reactions has had a great impact on organic chemistry<sup>1</sup>. Corresponding rules for inorganic reactions have not been extensively presented or used up to now. The attempts in the literature<sup>2</sup> have dealt only with the *d* orbitals of transition metal complexes. The conclusions have been neither definitive nor consistent.

While *d* orbitals are of great importance in coordination chemistry, it is unlikely that these are the only important orbitals in chemical reactions. Also much of inorganic chemistry deals with the non-transition elements. It is necessary to include molecular orbitals made up of *s* and *p* atomic orbitals to have a complete understanding. In this article we will show in the most general way how symmetry rules for all chemical reactions can be derived<sup>3</sup>.

The procedure used is to consider the variation of potential energy with

changing nuclear coordinates and how symmetry enters into this relationship. Since any number of nuclei and electrons can be taken, the conclusions will be valid for a concerted reaction (elementary process) of any molecularity. While group theory can be used to get an elegant answer to the question of symmetry effects, rather simple considerations such as orbital overlap can also be used.

## THE THEORY

Figure 1 shows the usual adiabatic plot of potential energy versus 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 arrangement 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 eigen states  $\psi_0, \psi_1 \dots \psi_k$ , and corresponding eigen values  $E_0, E_1 \dots E_k$ , 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 analysed as a sum of displacements corresponding to the normal modes of the pseudo-molecule representing the reactants. Each of these normal modes (of vibration) belongs to one of the symmetry species of the point group. Hence the reaction coordinate can also be classified as having a symmetry label depending on which nuclei are moved, and in what direction.

We now use quantum-mechanics in the form of perturbation theory to relate potential energy,  $E$ , to the reaction coordinate. For the ground electronic state, the energy becomes

$$E = E_0 + Q \langle \psi_0 | \partial U / \partial Q | \psi_0 \rangle + \frac{1}{2} Q^2 \langle \psi_0 | \partial^2 U / \partial Q^2 | \psi_0 \rangle + Q^2 \sum_k [\langle \psi_0 | \partial U / \partial Q | \psi_k \rangle]^2 / (E_0 - E_k) \quad (1)$$

where  $Q$  represents the reaction coordinate and also the magnitude of the small displacement from the original point on the diagram,  $Q_0$ , for which  $E = E_0$ . While equation 1 is valid only for  $Q$  very small, we can select  $Q_0$  anywhere on Figure 1. Hence equation 1 is general for the purpose of displaying symmetry properties.  $Q$  and  $(\partial U / \partial Q)$  have the same symmetry, where  $U$  is the nuclear-nuclear and electron-nuclear potential energy.

The bracket 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 in equation 1 are exactly zero or not. The rule is that the direct product of three functions must contain the totally symmetrical species, or the integral over all space is zero.

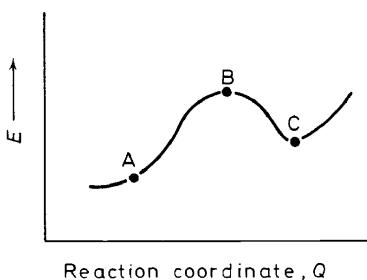
Let us consider the term in equation 1 which is linear in  $Q$ . At any maximum or minimum in the potential energy curve the integral must be identically

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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 non-degenerate.

Since the direct product of a non-degenerate species with itself is always totally symmetric, we derive our first symmetry rule: *all reaction coordinates belong to the totally symmetrical representation*. That is,  $(\partial U/\partial Q)$ , and also  $Q$ , must be totally symmetrical, otherwise its product with  $\psi_0^2$  will not be symmetric and the integral will be zero. But it *must* be non-zero 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



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

or minimum. A totally symmetrical set of nuclear motions can change bond angles and distances, but it cannot change the point group. 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 non-symmetrical nuclear motion to change the point group.

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 equation 1 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 non-zero value by symmetry since  $(\partial^2 U/\partial Q^2)$  is totally symmetrical. Furthermore it will be positive for all molecules. It represents the force constant which resists moving any set of nuclei away from an original configuration for which  $\psi_0^2$  is the electron density distribution. The last term in equation 1 represents the change in energy that 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.

$$\psi = \psi_0 + Q \sum \langle \psi_0 | \partial U / \partial Q | \psi_k \rangle \psi_k / (E_0 - E_k) \quad (2)$$

The summations in equations 1 and 2 are over all excited states. Each excited state wave function is mixed into the ground state wave function by an amount shown in equation 2. The wave function is changed because the resulting electron distribution,  $\psi^2$ , is better suited to the new nuclear positions.

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 1 and 2 are exact, as are the symmetry rules derived from them. For practical applications, some rather drastic assumption 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 equations 1 and 2 by only a few lowest lying states.

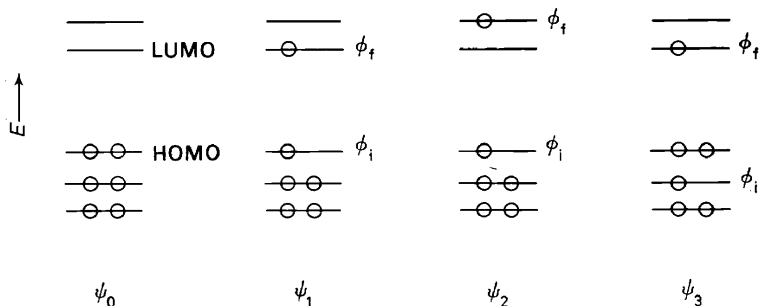


Figure 2. Molecular orbital description of ground state and first few excited states.

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>5</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 occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, since excitation of an electron from HOMO to LUMO defines the lowest excited state.

These two orbitals are called frontier orbitals by Fukui<sup>6</sup>. At this time 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 MOs 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 MOs will be produced.

For the reaction to be allowed by symmetry, we must have transfer of electrons from high energy occupied MOs ( $\phi_i$ ) to low energy empty MOs ( $\phi_f$ ) which have positive overlap. This will lower the energy of the system via the last term in equation 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.

All chemical reactions consist of the breaking of certain bonds and the making of new bonds. All MOs correspond to the bonding together of certain atoms, anti-bonding of other atoms, and non-bonding of the remaining atoms. It follows 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 anti-bonding 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 movement will be large. Conversely electron movement from an occupied MO in a halogen molecule to an empty MO in an alkali metal molecule, for example, would correspond to a large value of  $|E_0 - E_k|$ .

Reactions of hydrogen are particularly easy to describe. The only MOs of reasonable energy are the bonding  $\sigma_g$ , which is occupied and the anti-bonding  $\sigma_u^*$ , which is empty. One of the simplest of chemical reactions would be isotope exchange between hydrogen and deuterium.

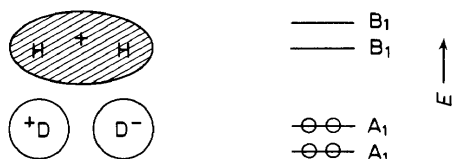


Let us assume that reaction 3 occurs by a bimolecular mechanism in which  $H_2$  and  $D_2$  collide broadside, giving rise to a four-centre transition state.



The point-group of this transition state is  $C_{2v}$ . Also, at point A in *Figure 1* the point group is  $C_{2v}$ . The MOs of  $H_2$  and  $D_2$  should now be classified as  $A_1$  for the bonding  $\sigma_g$  and  $B_1$  for the anti-bonding  $\sigma_u^*$ .

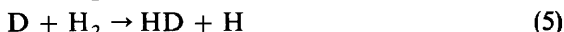
As *Figure 3* shows, the filled MO of one hydrogen or deuterium molecule has zero overlap with the empty MO of the other. This is the same as showing



*Figure 3.* Molecular orbitals in  $H_2 + D_2$  reaction. Occupied orbitals are shaded. Symmetry labels are for  $C_{2v}$  point group.

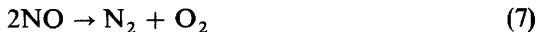
that there is no low-flying excited state of the same symmetry as that of the ground state. Hence the exchange reaction 3 is forbidden by orbital symmetry. This simply means that the selected mechanism and transition state would have an excessively high energy barrier.

Indeed reaction 3 does not occur in a single elementary step. Instead a series of allowed steps occurs:



Reactions of free radicals and atoms rarely have serious symmetry restrictions and are often found. Four-centre reactions of diatomic molecules, on the other hand, are almost always symmetry forbidden and either do not occur, or occur with high activation energies<sup>7</sup>.

An important example of a forbidden reaction is the decomposition of nitric oxide.



Since this reaction is highly exothermic (by 43 kcal), one would expect it to occur rapidly. In fact it is extremely slow, having an activation energy of 50 kcal. This is a symmetry imposed barrier.

This can be seen most readily by looking at the reverse reaction, since a symmetry barrier which exists for a forward reaction must also exist for the reverse. *Figure 4* shows the important MOs of  $N_2$  and  $O_2$ . The  $\pi_g^*$  anti-bonding MO of  $O_2$  is half-filled. It can act either as an electron acceptor or

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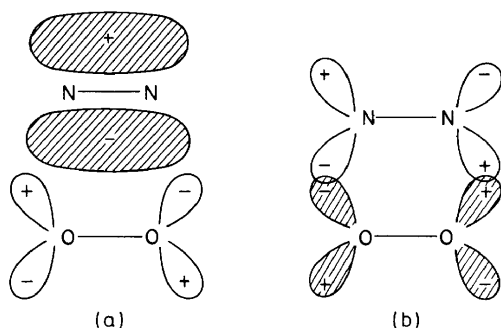


Figure 4. Molecular orbitals in  $N_2 + O_2$  reaction. Occupied orbitals are shaded.

donor. By symmetry, electrons cannot flow from the filled  $\pi_u$  MO of  $N_2$  into the  $\pi_g^*$  of  $O_2$ , since the overlap is zero. Electrons could flow from  $O_2$  to  $N_2$  by symmetry, since the  $\pi_g^*$  MO of  $N_2$  is empty. However, this is chemically unacceptable, since  $O_2$  is more electronegative than  $N_2$ . In addition, the O—O bond would be strengthened rather than weakened by emptying the  $\pi_g^*$  anti-bonding MO of  $O_2$ .

Orbital symmetry arguments can be used to decide between two proposed mechanisms for the oxidation of NO to  $NO_2$ .



This reaction, while third-order in kinetic behaviour, is believed to occur by a series of bimolecular steps<sup>8</sup>.



or

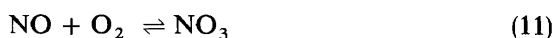


Figure 5(a) shows the relevant MOs for the reaction of the  $N_2O_2$  dimer with  $O_2$ . Flow of electrons from the filled  $B_1$  orbital of  $N_2O_2$  to the half-empty  $B_1$  orbital of  $O_2$  results in the breaking of the  $O_2$  bond by filling up

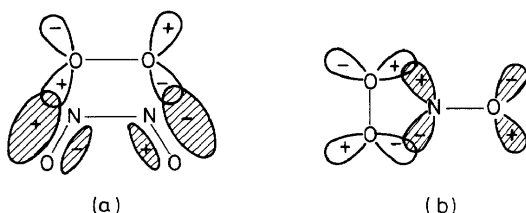


Figure 5(a). Molecular orbitals in  $O_2 + N_2O_2$  reaction. Product is  $N_2O_4$ . (b). Molecular orbitals in  $NO + O_2$  reaction.

an anti-bonding MO of  $O_2$ . The N—N bond is strengthened in  $N_2O_2$  because an anti-bonding MO is emptied. Two new N—O bonds are formed by positive overlap between the  $B_1$  orbitals.

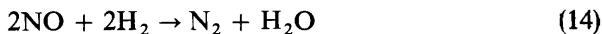
All of this seems reasonable except that clearly the reaction is



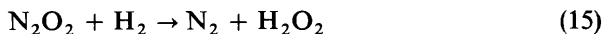
which is not the same as reaction 10. In fact, it is forbidden by spin conservation rules if the oxygen molecule is in the normal  ${}^3\Sigma_g^-$  ground state. It could only occur for the excited  ${}^1A_g$  state.

The alternative mechanism, shown in reactions 11 and 12, is allowed both by orbital symmetry and spin conservation. *Figure 5(b)* shows the MO situation for reaction 12 assuming a Y-shaped structure<sup>9</sup> for  $NO_3$ . There is some evidence that a peroxy structure exists<sup>10</sup> for  $NO_3$ , but its reaction with NO is also allowed.

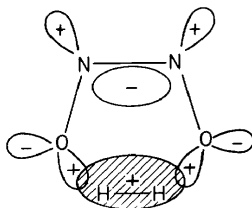
The third-order reaction of nitric oxide with hydrogen



is believed to go through a mechanism in which  $H_2O_2$  is formed as an intermediate,



followed by a rapid reaction of  $H_2O_2$  with  $H_2$  to give water. *Figure 6* shows that reaction 15 is symmetry allowed and is chemically reasonable. The

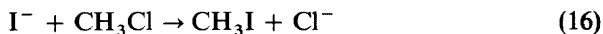


*Figure 6.* Molecular orbitals in  $H_2 + N_2O_2$  reaction. Products are  $N_2 + H_2O_2$  or  $N_2 + 2OH$ .

H—H bond is broken, two O—H bonds are formed, the weak N—N bond of  $N_2O_2$  is strengthened and two strong N—O bonds are weakened. While O—O bonding also is increased, it still remains questionable whether  $H_2O_2$  or two OH radicals would result from reaction 15.

## NUCLEOPHILIC SUBSTITUTION REACTIONS

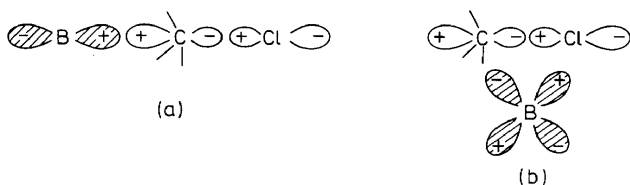
It is particularly instructive to look at old, well established mechanisms from the new viewpoint of orbital symmetry. A case in hand is the bimolecular nucleophilic substitution, or  $S_N2$  reaction. Clearly it is the HOMO of the nucleophile and the LUMO of the substrate which are the critical orbitals. *Figure 6* shows these orbitals for a typical case of organic chemistry, e.g.



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The anti-bonding  $\sigma^*$  orbital is a critical one in all molecules which can be regarded as X—Y, two groups joined together by a single bond. Filling this orbital will clearly break the bond between X and Y. Molecules of this type include  $H_2$ ,  $Cl_2$ ,  $HCl$ ,  $CH_3Cl$ ,  $CH_3CH_3$ ,  $CH_3H$ , etc. The symmetry of the  $\sigma^*$  orbital will always be roughly that shown in *Figure 6*.

We see in *Figure 7* the characteristic features of bond making between the nucleophile, B, and the carbon atom, as well as bond breaking between



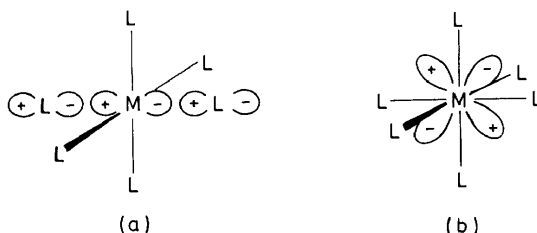
*Figure 7.* Nucleophilic displacement with (a) inversion of configuration, (b) retention of configuration at carbon atom.

carbon and halogen. Also inversion of configuration at the carbon atom is clearly indicated. This results from the easy availability of the  $\sigma^*$  orbital at this position. A similar situation would be found for many other four-coordinated central atoms of the non-transition elements.

If we consider tetrahedral complexes of the transition elements, a general conclusion emerges. Filling up the  $d$  orbitals has the effect of decreasing the availability of the anti-bonding  $\sigma^*$  orbital. The most advantageous situation would be to have an empty  $e$  orbital. The next best would be to have an empty  $t_2^*$  orbital. Interestingly, using an  $e$  orbital corresponds to edge attack, and using the  $t_2^*$  orbital to face attack on the tetrahedron. Evaluating the relative rates of a series of  $d^n$  complexes would require assessing a number of different effects, including changes in crystal field stabilization energies.

A square planar complex offers a different situation. The LUMO now is ( $a_{2u}$ ), the  $p_z$  orbital perpendicular to the plane. It is a non-bonding, rather than an anti-bonding MO. This means that bond making will be considerably in excess of bond breaking. The reaction coordinate can lead directly to an intermediate of  $D_{3h}$  symmetry. Unlike the tetrahedral case, the entering and leaving groups will be equatorial, rather than axial.

*Figure 8(a)* shows a typical LUMO in an octahedral complex. This par-

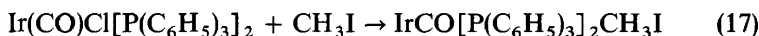


*Figure 8.* (a) Empty anti-bonding MO of  $T_{1u}$  symmetry in octahedral complex. (b) Non-bonding MO of  $T_{2g}$  symmetry in octahedral complex.

ticular one is of  $t_{1u}^*$  symmetry. Those of  $a_{1g}^*$  or  $e_g^*$  symmetry would have similar properties. The most significant feature is that the orbital is quite inaccessible to a nucleophilic reagent. The six ligands effectively block off access. Again, filling up the  $d$  orbitals would have an inhibiting effect. An empty  $t_{2g}$  orbital (Figure 8b) could be used as the LUMO and, if the ligands were not too bulky, would allow for an  $S_N2$  mechanism. It is a familiar fact that  $S_N2$  mechanisms are extremely rare for the substitution reactions of octahedral complexes. On the other hand, nucleophilic attack on a ligand, such as a CO group, can easily occur.

### OXIDATIVE-ADDITION REACTIONS

There has been much recent interest in the mechanism of oxidative-addition reactions such as (17)<sup>10</sup>.



Recently several observations<sup>11</sup> have been made which give detailed information on reactions such as this. These observations lead to the conclusions that (1) the reaction occurs in a one-step, concerted process without the formation of intermediates, and in the absence of solvents; (2) that *trans*

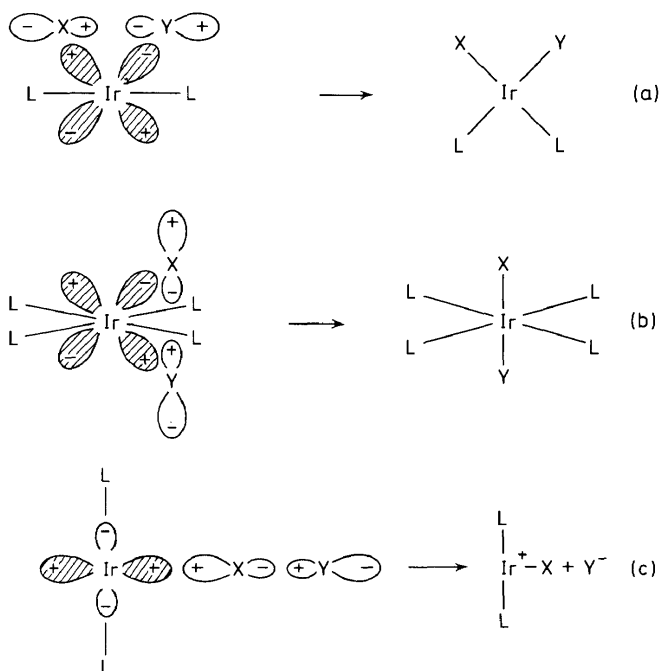
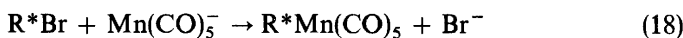


Figure 9. Mechanisms of oxidative addition: (a) one step *cis* addition of XY with retention at X, (b) one step *trans* addition with retention at X, (c) two step addition with inversion of configuration at X.

addition to the square plane can occur even with these restrictions; and (3) retention of configuration results at the carbon atom, when a more complex alkyl group than methyl is used.

These results are completely in agreement with orbital symmetry considerations. *Figures 9(a)* and *(b)* show that the *d* orbitals of the metal which are of  $e_g$  symmetry constitute the HOMO. It is well known that soft metal atoms act as nucleophiles, or Lewis bases, in their reactions<sup>12</sup>. It is particularly important that in oxidative-addition, both the groups X and Y finish up bound to the metal. It can be seen that a metal complex using a *d* orbital as the HOMO could also react with an alkyl halide to give inversion of configuration, *Figure 9(c)*.

This mechanism is expected when only one group, X, is bound to the metal and Y is displaced. A number of examples of this type are known. For example, the reaction



occurs with inversion of configuration at the carbon atom of  $R^{13}$ . It is also possible that the group Y in *Figure 9(c)* could later add to the five-coordinated product first formed. This would be a two-step mechanism for oxidative-addition<sup>14</sup>. It appears that such a mechanism would be favoured in a polar solvent.

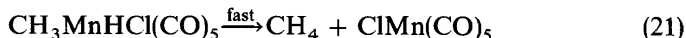
It is increasingly being realized that many examples of both homogeneous and heterogeneous catalysis on transition metals involve oxidative-addition, and its reverse, as key steps. These two processes, together with the ligand migration reaction, are the steps involved in most detailed mechanisms. In agreement with this concept, it has been found that silicon hydrides add to both metal complexes and to metal surfaces with retention of configuration at silicon<sup>15</sup>. Years ago it was shown that optically active hydrocarbons are adsorbed on metal surfaces with retention of configuration<sup>16</sup>.

Oxidative-addition reactions may occur more commonly than supposed with transition metal compounds. Many reactions with electrophilic reagents may proceed by prior addition of the reagent, followed rapidly by the reverse process. In such cases the product of the addition step need not be a stable species.

As an example, bromine cleavage of the optically active product formed in reaction 18 proceeds with retention of configuration<sup>13</sup>.



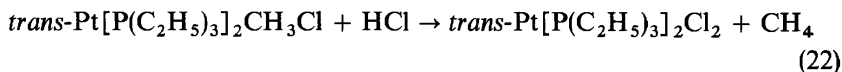
It is tempting to postulate that  $Br_2$  adds first to a filled *d* orbital of the manganese, and then that  $R^*Br$  splits out. In the same way cleavage by acid could follow the course



Such an oxidative-addition, reductive-elimination mechanism could account for the fact that molecular HCl is the cleaving agent<sup>17</sup>. Thus  $HClO_4$  is ineffective and  $H^+$  plus  $Cl^-$  in a polar solvent is not effective. A similar mechanism would also account for the well known retention of

configuration at carbon that results in the acid cleavage of organomercury compounds<sup>18</sup>. Other electrophilic reagents also give retention with the organomercurials.

In at least one case of a  $d^8$  planar complex, the addition-elimination mechanism for alkyl-metal bond cleavage seems well established<sup>19</sup>.



The intermediate would be a six-coordinated platinum(IV) complex. While not stable itself, certainly it would have many stable analogues. In methanol, the solvent where reaction 22 was studied, the solvated  $\text{H}^+$  can also cause cleavage. Apparently a one-step addition of HCl is not required.

### 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. For unimolecular processes, the theory is also called the second-order, or pseudo, Jahn-Teller effect.

The term linear in  $Q$  in equation 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 symmetry of the reaction coordinates. It need no longer be totally symmetrical. 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 symmetrical 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 asymmetric. 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. But this corresponds to a change in the point group, which can only come about by an asymmetric 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 MOs 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

## ORBITAL SYMMETRY RULES

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  $\phi_i \times \phi_f$ .

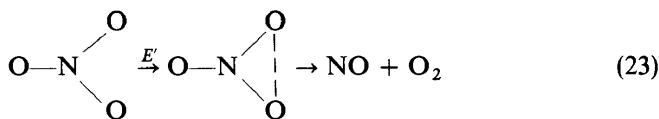
The size of the energy gap between  $\phi_i$  and  $\phi_f$  is critical. A small gap means an unstable structure, unless no vibrational mode of the right symmetry exists for the molecule capable of changing its structure. A large energy gap between the HOMO and the LUMO means a stable molecular structure. 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<sup>5</sup>. By the principle of microscopic reversibility, this can then be used to decide on the mechanism of formation of the activated complex.

As an example of a molecule in a shallow potential well (point C), we will consider the molecule  $\text{NO}_3$ . Assuming a planar structure of  $D_{3h}$  symmetry, the MO sequence is<sup>20</sup>

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

The transition  $(3e') \rightarrow (1a_2')$  requires very little energy, according to the calculations. The direct product  $E' \times A_2' = E'$ , a normal mode which distorts the molecule into a Y-shaped structure, with two oxygen atoms close together. The predicted mode of dissociation of  $\text{NO}_3$  is therefore into  $\text{NO}$  and  $\text{O}_2$ , in agreement with the facts.



If we were to add one more electron, as in  $\text{NO}_3^-$  or  $\text{SO}_3$ , the easily available excited state would be blocked. Thus these molecules would be much more stable towards dissociation. The  $\text{NO}_3$  molecule absorbs visible light, with a maximum at 660 nm. The  $\text{NO}_3^-$  ion, however, does not absorb until 300 nm. Coloured molecules are less stable than colourless molecules, providing the symmetry rules can be obeyed.

Predicting the mode of decomposition of a molecule lying in a deep potential well is more difficult. Since the reaction requires much energy, quite high-lying excited states may be important. Nevertheless, the symmetry rules can be very useful.

Suppose we know that a unimolecular reaction occurs in which certain bonds are broken and some other bonds are made. These bonds can then select  $\phi_i$  and  $\phi_f$ , the relevant molecular orbitals. These MOs, in turn, can determine the symmetry of the reaction coordinate,  $Q$ . We need to know only the symmetries of  $\phi_i$  and  $\phi_f$ . Considerations of this kind have been of great importance in elucidating complex organic reactions<sup>21</sup>. Applications to inorganic chemistry are still unknown.

Alternatively, we can pick the symmetry of the reaction coordinate and then seek suitable molecular orbitals. For example, the unimolecular ( $S_N1$ ) dissociation of a tetrahedral complex requires a vibration of  $T_2$  symmetry<sup>22</sup>.

Hence we seek a HOMO and LUMO whose direct product is of this symmetry type. The MO sequence for  $\text{CH}_4$  is

$$(a_1)^2(t_2)^6(a_1^*)^0(t_2^*)^0$$

Excitation of an electron from a bonding ( $t_2$ ) to an anti-bonding ( $a_1^*$ ) orbital will promote dissociation into  $\text{CH}_3$  and H.

A transition metal complex inserts the  $d$  manifold between the above bonding and anti-bonding MOs.

$$|(e)^m(t_2^*)^n|$$

Since  $E \times T_2 = T_1 + T_2$ , it is possible that a hole in the  $d$  shell will promote unimolecular dissociation of tetrahedral complexes. At the moment there is little evidence one way or another on this point.

In an octahedral complex it is a  $T_{1u}$  vibration which corresponds to dissociation of one ligand<sup>22</sup>. We see that the  $d$  manifold

$$|(t_{2g})^m(e_g^*)^n|$$

cannot contribute excitations that will promote dissociation, since  $T_{2g} \times E_g = T_{1g} + T_{2g}$ . This raises the suspicion that, because of the inherent *gerade* properties of  $d$  orbitals,  $d-d$  transitions in general will not effectively promote the dissociation of even less symmetrical complexes.

## 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>23</sup>. Molecules with formulas  $\text{XY}_n$  or  $\text{X}_2\text{Y}_n$  usually are found with rather regular structures. A decision can be made as to which of several alternative structures is the most stable using equation 1. It is necessary to assume that the term linear in  $Q$  has 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, say, 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, say 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 favoured. This is actually a prediction of the stable structure into which the original configuration will distort.

The geometric isomers of  $\text{XY}_n$ , which can be interconverted without breaking bonds, have been called polytopal isomers<sup>24</sup>. More complex molecules, such as  $\text{X}_2\text{Y}_n$ , have many more structures possible, some of which can be interconverted only by the breaking of bonds.

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Consider the possible isomerization of four-coordinated complexes of the transition metal ions between tetrahedral ( $T_d$ ) and square-planar ( $D_{4h}$ ) structures. The normal mode which takes a tetrahedral structure into a planar one is of  $E$  symmetry<sup>22</sup>. The molecular orbital scheme (needed to express the symmetries) is generally agreed to be

$$(t_1) \text{ or } (t_2) \left| (e)(t_2^*) \right| (a_1)$$

with the  $d$  manifold separated by dashed lines.

Since  $T_1$  (or  $T_2$ )  $\times E = T_1 + T_2$ , there is no low-lying transition which causes a tetrahedral complex to rearrange to a planar complex. This is true for all systems from  $d^0$  to  $d^{10}$ .

However, first-order Jahn–Teller effects are important for many of these complexes. Only  $d^0$ ,  $d^2$ , high-spin  $d^5$ ,  $d^7$  and  $d^{10}$  complexes have  $A_1$  or  $A_2$  ground states and are stable. All others are  $E$ ,  $T_1$  or  $T_2$  states. Since  $E \times E = A_1 + A_2 + E$ , and  $T_1 \times T_1 = T_2 \times T_2 = A_1 + E + T_1 + T_2$ , all of these allow a distortion in the direction leading toward a planar structure.

Since a  $D_{2d}$ , or distorted tetrahedral structure, is sufficient to lift the orbital degeneracy in every case except low-spin  $d^3$ , we cannot tell whether the initial distortions will continue on to a planar structure. To get further information we must now look at the stability of the possible planar forms.

The generally agreed upon MO scheme for  $D_{4h}$  symmetry is<sup>25</sup>

$$(a_{2g})(b_{2u}) \left| (a_{1g})(e_g)(b_{2g})(b_{1g}) \right| (a_{2u})$$

The vibration which takes a planar complex into a tetrahedral one is of  $B_{2u}$  symmetry<sup>22</sup>. The transitions which can give the correct symmetry are  $(b_{2u}) \rightarrow (a_{1g})$  and  $(b_{1g}) \rightarrow (a_{2u})$ . It seems likely that the energy gap in both cases is only 2–3 eV.

This leads to the conclusion that low-spin  $d^2$ ,  $d^4$ ,  $d^5$ ,  $d^6$ ,  $d^7$  and  $d^8$  complexes are stable as square-planar structures. Low-spin  $d^3$  is orbitally degenerate. In all other cases an excitation is possible which favours the  $B_{2u}$  vibration. This means a low, or zero, activation energy for conversion into either  $D_{2d}$  or  $T_d$  symmetry. In combination with the conclusions from the first-order

Table 1. Stable structures for  $MX_4$  systems

	High spin	Low spin		High spin	Low spin
$d^0$	$T_d$	$T_d$	$d^6$	$D_{2d}$	$D_{4h}$
$d^1$	$D_{2d}$	$D_{2d}$	$d^7$	$T_d$	$D_{4h}$
$d^2$	$T_d$	$D_{4h}$	$d^8$	$D_{2d}^b$	$D_{4h}$
$d^3$	$D_{2d}$	<sup>a</sup>	$d^9$	$D_{2d}$	$D_{2d}$
$d^4$	$D_{2d}$	$D_{4h}$	$d^{10}$	$T_d$	$T_d$
$d^5$	$T_d$	$D_{4h}$			

<sup>a</sup> Less than  $D_{2d}$  symmetry. <sup>b</sup> Spin–orbit forces can remove the first-order Jahn–Teller effect.  $NiCl_4^{2-}$  has  $T_d$  symmetry.

Jahn–Teller effects, we can assign a most stable structure for each four-coordinate system according to the number of  $d$  electrons and the spin state. Table 1 summarizes the results for all systems.

The predictions are in accord with experimental facts where known. The

conclusions for  $D_{4h}$  are based on no interaction with other groups above and below the plane. Such interactions could raise the ( $a_{2u}$ ) level markedly and stabilize the planar form. Four simple ligands such as halide or cyanide lead to  $D_{2d}$  structures in solution for copper(II) complexes, so that axial solvent perturbations are not sufficient in these cases to create planarity. It appears that a combination of first-order and second-order Jahn–Teller effects can be used to predict the stable structures of molecules. In practice an MO scheme is required which need be only qualitatively correct. It also follows that an incorrect MO scheme may predict structures wrongly. It seems reasonable to apply a test for second-order Jahn–Teller distortions to MO calculations in general.

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