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Symmetry Rules for Predicting the Course of Chemical Reactions

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Rules are given for a reaction of any molecularity which show whether it is allowed or forbidden by orbital symmetry properties. The rules are based on a rigorous treatment, but correspond to simple concepts in practice. A rough MO sequence for the reactants is all that is needed.

Für Reaktionen beliebiger Molekularität werden Regeln dafür angegeben, ob die Reaktion aus Symmetriegründen erlaubt oder verboten ist. Diese Regeln werden streng hergeleitet, sind jedoch in der Praxis einfach anwendbar. Benötigt wird lediglich die Reihenfolge der MO der Reaktionen.

On donne des règles de sélection pour une réaction de molécularité arbitraire selon les propriétés de symétrie orbitale. Les règles sont basées sur un traitement rigoureux mais correspondent en practique à des concepts simples. On a seulement besoin de connaître l'ordre des orbitales moléculaires des réactants.

Recently there has been great interest in the devising of symmetry rules for predicting whether a concerted chemical reaction can occur with relatively low activation energy (symmetry allowed) or would require excessive activation energy (symmetry forbidden). The most general method of using symmetry properties to predict the course of a chemical reaction is to apply group theory to the variation of potential energy with changing nuclear coordinates.

Fig. 1 shows the usual adiabatic plot of potential energy *vs.* reaction coordinate, showing possible features. The reactant molecules at each point generate a certain point group and the possible nuclear motions can be classified as the normal modes of vibration of a pseudo-molecule of that symmetry. For the ground electronic state the energy may be written as [1]

$$\begin{aligned} E = E_0 + Q\left\langle \Psi_0 \left| \frac{\partial U}{\partial Q} \right| \Psi_0 \right\rangle + \frac{Q^2}{2}\left\langle \Psi_0 \left| \frac{\partial^2 U}{\partial Q^2} \right| \Psi_0 \right\rangle \\ + Q^2 \sum_k \frac{\left[\left\langle \Psi_0 \left| \frac{\partial U}{\partial Q} \right| \Psi_k \right\rangle\right]^2}{E_0 - E_k} . \end{aligned} \tag{1}$$

Here Q represents the normal mode representing the reaction coordinate and also the magnitude of the displacement from *any* arbitrary point on the diagram, Q_0, for which $E = E_0$. While (1) is valid only for Q small, the point $Q = 0$ can be selected anywhere and hence (1) is general for the purpose of displaying symmetry properties. The wave functions, Ψ_0 and Ψ_k, must belong to one of the symmetry

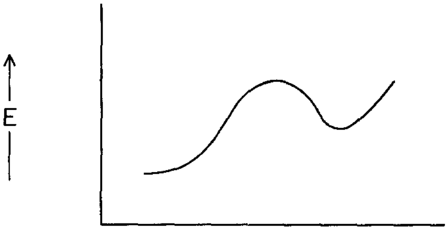

Fig. 1. Reaction coordinate, Q_0

species of the group. Q and $(\partial U/\partial Q)$ have the same symmetry, where U is potential energy.

If Ψ_0 is non-degenerate, the usual case, we can immediately conclude that the reaction coordinate *must* belong to the totally symmetric representation for all points which are not on a maximum or minimum. Furthermore, since the wave function corresponding to (1) is

$$\Psi = \Psi_0 + Q \sum_k \frac{\left\langle \Psi_0 \left| \frac{\partial U}{\partial Q} \right| \Psi_k \right\rangle}{E_0 - E_k} \Psi_k \qquad (2)$$

only excited state wave functions of the same symmetry as Ψ_0 can mix in under the influence of changing Q. It is essential to have efficient mixing in order to have a reaction of low activation energy. It has been shown in a number of examples that the infinite sums of (1) and (2) may be replaced by one or two terms corresponding to the lowest excited states [2, 3].

In molecular orbital theory $\Psi_0 \Psi_k$ has the same symmetry as $\Phi_i \Phi_j$, where Φ_i is the MO occupied in Ψ_0 and Φ_j is the MO occupied in its stead in Ψ_k. Thus Φ_i and Φ_j will usually, but not always, be the highest occupied MO and the lowest empty MO of the system. The requirements are (a) that they belong to the same symmetry species in the point group of the reacting system; (b) that they be close in energy; (c) Φ_i must represent bonds that are broken during the reaction and Φ_j bonds to be made, assuming both are bonding MO's, the reverse if anti-bonding.

It may happen that the highest occupied MO and the lowest empty MO of the system do not correspond to bonds that must be broken or made during the reaction. In this case it is necessary to examine the next lower and higher MO's. However, the symmetry rule must still be obeyed. Also as the energy gap increases, the activation energy will obviously increase.

These conclusions are identical with those which could have been drawn from other perturbation theories of chemical reactivity [4]. Previously the perturbation operator used was the interaction Hamiltonian. Since this is also totally symmetric, as is $(\partial U/\partial Q)$, the same conclusions would follow about the rising and falling parts of Fig. 1. The approximation of using only the lowest excited state is the same as that of Fukui's frontier orbital theory [5]. The overall physical picture is that electrons will flow between orbitals when there is a positive overlap between them in the region where new bonds are to form.

Once a system starts on a given reaction path, it must maintain the same point group until a maximum or minimum in the potential energy is reached. This

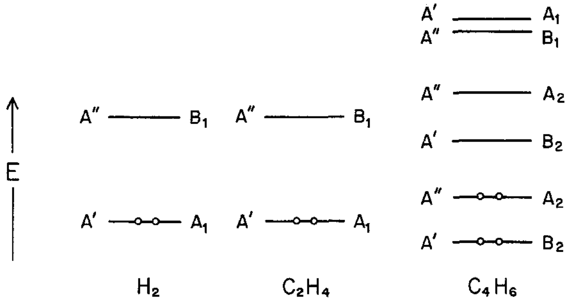

Fig. 2. MO sequences. C_s symmetry labels on left and C_{2v} labels on right

follows because a symmetric mode cannot change the point group. A non-adiabatic process involving a forbidden transition could change the point group, however. For a transition state (maximum in Fig. 1) the reaction coordinate will correspond to one of the normal modes of the activated complex, or combination of modes of the same symmetry. As shown by Bader [2], the symmetries of Ψ_0 and the lowest excited Ψ_k of the activated complex will determine which normal mode is selected. A number of examples have already been discussed [2, 3]. It should be noted that a number of point groups depend upon a unique value of Q_0. For example, a tetrahedral structure depends upon fixed bond angles. All such cases will correspond to either maxima or minima in plots such as Fig. 1. A non-symmetric mode will be needed for the reaction to proceed.

Unimolecular reactions start at a minimum in Fig. 1. For shallow wells, the lowest Ψ_k dominates, but this need not be true for deep wells (substantial activation energy). Instead the bonds to be made or broken select Φ_i and Φ_j, and these in turn select Q. The direct product of Φ_i and Φ_j must contain the symmetry species of Q.

Examples of the principles given above are shown in Fig. 2. The first refers to the *syn* addition of H_2 to ethylene and *cis*-butadiene. The mechanism is assumed such that the point groups become C_{2v} and C_s respectively. These point groups must be maintained until the transition state is reached.

The MO's of the separate reactants are shown with their symmetries in the combined point group. Those of the same symmetry will mix as Q_0 increases, but initially the mixing is small. The reaction of C_2H_4 with H_2 is seen to be forbidden since no Φ_i and Φ_j of the same symmetry lie near each other in energy. The 1,4-reaction of C_4H_6 with H_2 is symmetry allowed, as is the addition of C_2H_4 to C_4H_6.

Another example is the ring closing of *cis*-butadiene to give cyclobutene. The point group of the reactant is C_{2v} and the MO's in this symmetry are shown in Fig. 2. The π orbitals are of A_2 or B_2 symmetry, with A_2 defining the highest filled orbital. This orbital is bonding between carbon atoms 1 and 2, and 3 and 4; it is anti-bonding between 2 and 3. Clearly this is Φ_i, the orbital to be vacated. The lowest energy transition is $A_2 \rightarrow B_2$ giving a symmetry of B_1 for the product of $\Phi_i \Phi_j$. This vibrational mode does not correspond to the twisting motions needed to get ring closure. Furthermore it does not correspond to σ bonding between atoms 1 and 4, as needed in the final product. Only the anti-bonding MO's of A_1 symmetry have the property of being bonding between atoms 1 and 4.

The nuclear motion needed is of $A_2 \times A_1 = A_2$ symmetry. It can be seen that this is the symmetry of a conrotatory twisting of the end atoms. A disrotatory twist would be of B_2 symmetry and produce a B_1 anti-bonding orbital between atoms 1 and 4.

The Woodward-Hoffmann rules for electrocyclic and cycloaddition reactions can all be derived in this way [6]. It should be noted that the symmetry rules can be derived from the MO sequences of the reactants only. In no case is a detailed MO sequence for the products required. However some general information about the bonding in the products is still necessary.

In summary, some symmetry rules applicable to reactions of any molecularity have been given. In practice they correspond to rather simple concepts such as overlap of orbitals in bonding regions. Chemists should be quickly able to decide if a given reaction mechanism is allowed or forbidden by orbital symmetry considerations.

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