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Frontier Molecular Orbitals

A link between kinetics and bonding theory

There has been a significant resurgence of interest in molecular orbital theory recently due largely to the successes achieved with it in the understanding of pericyclic reactions (*1, 2*). Indeed, Pearson has said (*3*): "There will be a great displacement of valence bond theory, resonance theory, electrostatic theory and the like by molecular orbital theory as a way of looking at chemical reactions." In our view, the implications of Pearson's statement touch not only on our research thinking but also on our elementary teaching, foreshadowing a new unity to chemical understanding at this level.

In the last few years the simple concepts of MO theory have been applied to the elementary interpretation of static structure (*4*). In this way a weak link between bonding theory and thermodynamics has been forged. However, kinetics appeared isolated from bonding theory. Certainly, it could be claimed that all natural phenomena could be explained through quantum theory, but it seemed impossible to demonstrate this with regard to dynamic phenomena. Such a situation need no longer obtain since a particular form of MO theory, called frontier molecular orbital (FMO) theory, allows the linking of these dynamic (kinetic) phenomena with bonding theory. In this paper we aim to exemplify the use of FMO theory for elementary university chemistry teaching.

Frontier Orbitals and Their Interaction

FMO theory originated twenty years ago in publications by Fukui (*5*), and since then he (*6, 7*) and others, notably Salem (*8*), Klopman (*9*), Pearson (*10*), Dewar (*11*), and Woodward and Hoffmann (*1*), have developed these ideas in various directions. Basically, all species (atoms, ions, molecules) are considered to have frontier orbitals which are simply the highest energy occupied (HO) and lowest energy unoccupied (LU) orbitals. Where molecular orbitals are involved the abbreviations HOMO and LUMO are used. The kinetic characteristics of reactants and reactions are assessed by considering only FMO interactions. These are likely to be the major initial interactions as reactants approach since, at distances somewhat greater than typical bond lengths, the greatest orbital overlap is between FMO's. If this proposition is to be relevant to the assessment of kinetic behavior, then it must be presumed that the changes initiated by FMO interactions are not deflected into new directions by additional interactions which develop as molecular changes occur. This is a reasonable but not inexorable presumption (*6*).

The frontier interactions between reactants may be either repulsive or attractive: with different sites of contact and different relative orientations, different resultant interactions will occur. *The course, mechanism, and stereochemistry of reaction are then considered to be controlled by the maximizing of attractive interactions and the minimizing of repulsive interactions.*

Figure 1 illustrates how net attractive or repulsive interactions arise. The analysis proceeds by considering what intermolecular orbitals may be formed from FMO perturbations and what their occupancy might be, bearing in mind that the strongest perturbations occur between orbitals of comparable energy (*8*). In case I the strongest perturbations [1] will occur between the HOMO of B and the LUMO of A, resulting in the intermolecular orbitals shown in Figure 2, interaction [1]. An attractive interaction occurs since the two electrons of the HOMO of B pass into a lower energy intermolecular orbital. A weaker perturbation [2] (Fig. 1, case I) between the two HOMO's results in repulsion since four electrons pass into intermolecular orbitals (Fig. 2, interaction [2]) and the energy raising of one pair will outweigh the energy lowering of the other pair (*8*). The resultant in case I is attractive in view of the attractive nature of the stronger perturbation [1].

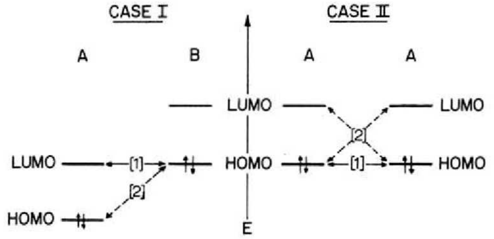
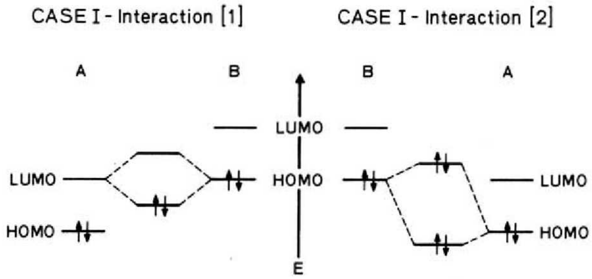


Figure 1. Schematic representation of FMO interactions between reactant molecules.


CASE I - Interaction [1]

CASE I - Interaction [2]

Figure 2. Schematic representation of intermolecular orbital formation in case I of Figure 1.

A similar analysis of case II (Fig. 1) reveals that the repulsive interaction [1] is likely to predominate because the strongest perturbations arise between the HOMO's. However, if the HOMO-LUMO separation is relatively small, the combined attractive interactions [2] could outweigh the intrinsically stronger repulsive interaction [1].

In this connection it is important to recognize a characteristic difference between repulsive and attractive interactions with respect to the magnitude of the corresponding electronic energy changes. For a given degree of mutual perturbation the electronic energy changes are greater for attractive interactions than for repulsive interactions. This arises because the repulsive interaction is a resultant of a two-electron energy lowering and a two-electron energy raising, while the attractive interaction is a consequence of two-electron energy lowering only.

FMO Interactions and Activation Energy

The nature and magnitude of FMO interactions are postulated to be an indication of the activation energy of a reaction step to which they are relevant (*6*). If a repulsive interaction is dominant the implication is that whatever net change might follow from pressing the interaction through, such a net change, even if thermodynamically allowed, will not occur because of a high activation energy. If an attractive interaction is found it does not mean necessarily that a negative activation energy should be expected. Rather it implies usually a moderate activation energy.

In FMO terms, we may say that if one reactant is to undergo bond breaking the relevant FMO's must correspond to bonding (HOMO) and antibonding (LUMO) orbitals. Bond breaking is initiated by removal of electron density from the bonding (HOMO) orbitals and/or accession of electron density into the antibonding (LUMO) orbital. These electron density changes arise from perturbation by the LUMO and/or HOMO respectively of the other reactant. This energy-increasing trend offsets the energy-decreasing trend indicated by simple FMO considerations, and indeed the former evidently generally outweighs the latter.[1] Similarly, a net attractive FMO interaction is no guarantee of reaction. If the frontier interactions lead in principle to the formation of products which are thermodynamically disfavored, these products will not form, of course, no matter how favorable the frontier interactions appear to be.

Where the participating FMO's of both reactants are non-bonding the conclusions concerning the activation energy follow readily: if attractive FMO interactions occur, zero activation energy is anticipated and seems to be found.

FMO Interactions, Electrophiles, Nucleophiles, and Radicals

At this stage of development of FMO concepts some revealing light can be shed on these familiar aspects of chemistry. Thus the concepts of nucleophile and electrophile and their characteristic attributes (e.g., their tendency to react with species or sites having opposite character) find a ready interpretation. Similarly, the typical features of radicals (e.g., their propensity for reacting with one another and their generally indiscriminate reactivity) can be readily understood. (SHAB concepts have also been considered by Klopman (*9*)).

The nucleophile-electrophile concept makes it possible to identify a direction of net electron "flow" accompanying the relevant bonding changes. Case I (Fig. 1) corresponds to a situation in which B is a nucleophile and A is an electrophile. The dominant interaction [1] corresponds to a transfer of electron density away from B and towards A.

Such an analysis is of value in showing the relative nature of the electrophile-nucleophile terminology. Thus although B functions as a nucleophile towards A in case I, B will not necessarily do so with other reactants. Another reagent C with comparatively high energy FMO's may cause B to act as an electrophile. In general, powerful nucleophiles should have high energy HOMO's and powerful electrophiles low energy LUMO's. Frontier interaction between such species is most likely to be attractive: the HOMO's of the two reactants are likely to be well-separated in energy while the HOMO of the nucleophile and the LUMO of the electrophile are likely to be reasonably close in energy. Moderate activation energies are thus predicted for these situations.

An advantage which flows from considering electrophilic and nucleophilic attributes in this way is that reactions in which no clearly-defined direction of electron "flow" can be recognized, do not appear unusual. They are examples in which the reactants have a close or identical match of FMO energies. It is common for such reactions to occur by a mechanism involving concerted bonding changes at several centers. By such mechanisms the activation energy barrier commonly encountered in a less concerted mode of reaction (c.f., Fig. 1, case II) can in favorable cases be circumvented (see Symmetry Considerations below).

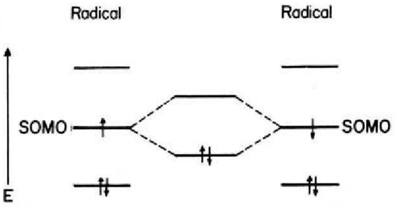


Figure 3. Schematic representation of intermolecular orbital formation between like radicals.

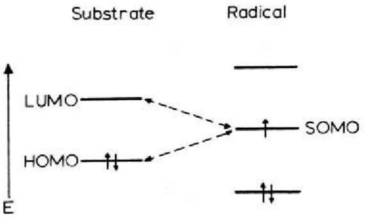


Figure 4. Schematic representation of FMO interactions between a radical and a non-radical substrate.

Unlike electrophiles and nucleophiles, radicals are rarely encountered in significant concentrations because they tend to be mutually destructive. Figure 3 shows that facile coupling of like radicals is to be expected.[2] Radicals usually have their odd electron in a non-bonding orbital so that zero activation energy for combination is anticipated and appears to be found. Where the odd electron is in a bonding or antibonding MO, the activation energy is moderate. Most "stable" radicals are in this category, although often they are dependent also on congestion for their stability.

The indiscriminate manner in which radicals often behave in reactions with non-radical substrates is implied by Figure 4. The SOMO may play the part of either a HOMO or LUMO, or both. Both interactions are weakly attractive (being either one electron or three electron situations) and thus both alternatives are characterized by moderate activation energies.

FMO Interactions, Stereoselectivity, and Frequency Factors

Because orbitals have specific spatial properties it is immediately clear within the framework of FMO theory how stereoselectivity may arise in reactions. The overriding demand for the maximizing of attractive FMO interactions and the minimizing of repulsive FMO interactions in order to minimize activation energy, will give rise to a preferred site for reaction. The occurrence of stereoselectivity is reflected in the magnitude of the Arrhenius factor, whose value decreases as the demands of stereoselectivity increase.

Qualitative stereoselectivity considerations often invoke the minimizing of interactions between bulky groups. Such considerations are readily incorporated within the FO framework and both attractive and repulsive interactions with groups near to a reaction site can be encompassed. Corresponding influences on activation energies are in effect considered at the same time.

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[1] This finding might be anticipated from the typical form of the *P.E.* curve for a diatomic molecule.

[2] SOMO = Singly occupied molecular orbital. For convenience the odd electrons of the two radicals are shown to be of opposite spin. If they are not, the net result is repulsive since they cannot both occupy the lower energy intermolecular orbital.

Symmetry Considerations

These aspects of FMO theory have been described frequently (*1-3, 10*). The point we shall emphasize is that multi-centered concerted mechanisms are adopted when, only by doing so, reactants may encounter a comparatively favorable activation barrier. Invariably, this arises because of the nodal properties of the FMO's, which are of less importance when fewer centers interact concertedly. Generally in favorable cases repulsive HOMO-HOMO interactions have no net result while attractive HOMO-LUMO interactions are maintained.

A comparison of the feasibility of reaction between two ethylene molecules and between one ethylene and one buta-1,3-diene molecule provides exemplification. FMO energies (*12*) indicate (Fig. 5) that repulsive HOMO-HOMO interactions should be dominant in both cases and render reaction unfeasible. This applies only if some multi-centric mode of reaction is not envisaged. Figures 6 and 7 reveal that if concerted cycle formation is considered different results are obtained. For the combination of two ethylene molecules (Fig. 6) HOMO-HOMO interactions remain repulsive while HOMO-LUMO attractive interactions have no net result. Conversely, for the combination of ethylene and butadiene (Fig. 7) the repulsive HOMO-HOMO interactions have no net result whereas the attractive HOMO-LUMO interactions persist. This latter pair of molecules thus may circumvent the formidable activation energy barrier encountered in any mode of reaction which is concerted at fewer centers by accepting the onus of a lower frequency factor.

FMO Interactions and Catalysis

Since catalysis is an essentially kinetic phenomenon, FMO considerations should shed some useful light on it. For a substance to function as a catalyst both its initial interaction with the substrate and the subsequent steps must be facile. It thus becomes clear why certain classes of substances, e.g., acids, bases, and transition metals, frequently feature as catalysts. Acids and bases are invariably quite strong electrophiles and nucleophiles, respectively, and typically they catalyze reactions of molecules having character of the opposite kind. The substrate will acquire a changed set of FMO's particularly at sites adjacent to that where interaction with the catalyst has occurred. The catalyst transfers some of its character to the substrate thereby activating the latter to reactants of the opposite character.

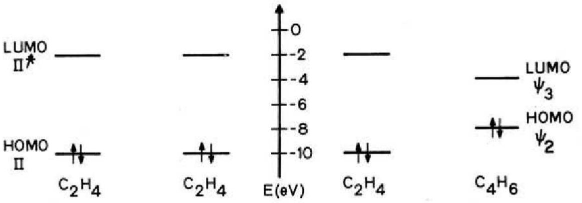

Figure 5. FMO's in ethylene and buta-1,3-diene, with approximate FMO energies (*12*).

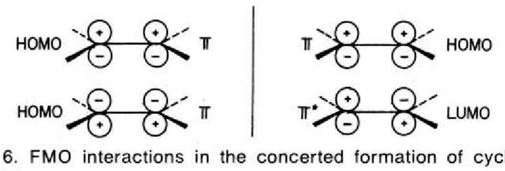

Figure 6. FMO interactions in the concerted formation of cyclobutane from ethylene.

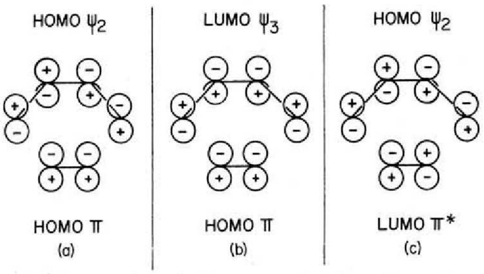

Figure 7. FMO interactions in the concerted formation of cyclohexene from ethylene and buta-1,3-diene.

Transition metals may function similarly but they also typify the situation of a reaction center having a number of orbitals of similar energy, some occupied and some vacant, with a multiplicity of lobes variously directed in space. Thus they can act on a substrate in a concerted manner at more than one point at a time, using a geometrical arrangement which by symmetry minimizes repulsive interactions. Reactions which otherwise would be "symmetry forbidden" thus may occur through a number of "symmetry allowed" steps (*13*).

Using FMO Concepts

There are a variety of ways in which these concepts may be used. The classification of reactants as electrophiles and nucleophiles and acids and bases is a useful one and the relationship to FO properties has been shown. Once this has been done, these labels can be used with confidence, and there is no particular virtue in discussing, say a proton transfer, in specific FMO terms. The occasions on which use of FMO concepts will be rewarding have to be judged at the time: two such occasions are exemplified.

Example 1: The Reaction between Hydrogen and Ethylene

Thermodynamically this reaction is favorable ($\Delta G^\circ = -24.14$ kcal mole^{-1}) but no reaction is observed unless a catalyst is present. To establish why there is no reaction, we can consider possible mechanisms. An obvious mechanism is the bimolecular combination of reactants in which the relative orientation in the transition state is consistent with the initial geometries of the reactants and the final geometry of the product. Figure 8 reveals that even with no knowledge of FMO energies, a high activation energy is anticipated since repulsive HOMO-HOMO interactions occur and there are no attractive HOMO-LUMO interactions.

The details of how transition metals catalyze the reaction are not proven, but it is probable that the catalyst interacts with both hydrogen and ethylene. The cleavage of the H—H bond by a transition metal may be conceived in terms of electron flow from the bonding σ orbital (HOMO) of H_2 into a non-bonding *d* orbital (LUMO) of

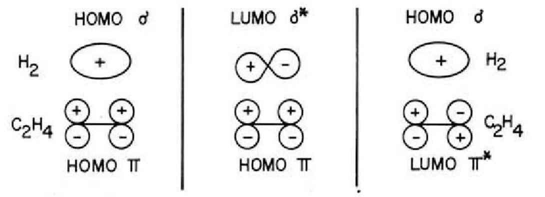

Figure 8. FMO interactions in the concerted formation of ethane from ethylene and hydrogen.

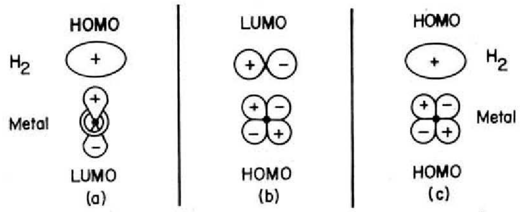

Figure 9. Possible transition metal-hydrogen molecule FMO interactions.

the metal (Fig. 9a), coupled with electron withdrawal from a non-bonding *d* orbital (HOMO) of the metal into the antibonding σ^* orbital (LUMO) of H_2 (Fig. 9b). These attractive HOMO-LUMO interactions and the fact that corresponding repulsive HOMO-HOMO interactions (Fig. 9c) have no net result suggest a moderate activation energy. A similar analysis may be made for ethylene. Provided that the bonding of the hydrogen and ethylene to the catalyst is not too strong, the subsequent transfer of hydrogen atoms to ethylene should be facile.

Other mechanisms concerted at fewer centers may be envisaged, but they are improbable since they usually involve a highly endothermic step. FMO interactions are not evaluated since other considerations ensure high activation energies.

Example 2: The S_N2 Reaction between an Alkyl Halide and a Nucleophile

Consideration of the polarity of the C-halogen bond indicates that the carbon atom is electrophilic. Nucleophiles would thus be expected to react at this atom. The LUMO of the alkyl halide is likely to be the σ^* MO of the C-halogen bond[3] and interaction of this orbital with the HOMO of the nucleophile will be attractive and will lead to accession of electron density into the LUMO. The fission of the C-halogen bond results from this frontier interaction. The nature of the reactants suggests that the other HOMO-LUMO interactions and the HOMO-HOMO interaction will be of lesser significance.

Interesting details of the reaction are revealed if the spatial properties of the LUMO of the alkyl halide are considered (Fig. 10). Because of the polarity of the C-halogen bond, the σ and σ^* MO's are not symmetrical (*8*). The amplitude of the σ MO is greater at the halogen atom than at the C atom, while the situation is reversed in the σ^* MO. Since C uses an sp^3 orbital we can represent the σ^* LUMO as shown in Figure 10. If the nucleophile, e.g., OH^-, NH_3 has non-bonding electrons in a *p* or sp^3 orbital, it will most likely approach the C atom from the rearside (Fig. 10a). Attack from the frontside (Fig. 10b) necessitates close approach to the other atoms bound to C in order to get overlap with the LUMO of the alkyl halide. Strong repulsive HOMO-HOMO interactions must be expected in this case. Other types of nucleophiles, e.g., with non-bonding electrons in *d* orbitals, will not be constrained in the same way and frontside attack (Fig. 10c) is sometimes observed (*3, 10*).

Thus, while simple electrophile/nucleophile considerations account for attack by nucleophiles at the electrophilic C atom, FMO considerations provide a satisfying account of the observed stereochemistry. As Breslow (*14*) has pointed out, electrostatic factors are not adequate to account for the stereochemical findings.

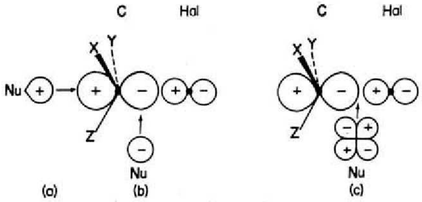

Figure 10. Possible alkyl halide-nucleophile (Nu) FMO interactions.

Conclusion

In anticipation of two principal criticisms, we conclude with the following observations. Firstly, it is reasonable to suggest that the application of these concepts is hampered by the lack of necessary data such as FMO energies. For some applications of FMO theory this is certainly true, but for many elementary applications it is not. Where such data are available (e.g., for ethylene and butadiene) they may be used to strengthen the argument, but in other cases a familiarity with elementary MO theory (*4*), coupled with a knowledge of electronegativity and bond strength trends, provide the necessary tools. As Fukui (*15*) has noted: " . . . the method . . . employs only the symmetry property of the highest occupied and lowest unoccupied molecular orbitals throughout."

Secondly, it might be said that all the effort is not worth it, there being no point in obscuring, by sophistication, simple concepts such as electrophiles and nucleophiles. Indeed, if this were the only point, we too would have doubts. However, we see the wider benefits that should flow from weaving together the interpretation of thermodynamic and kinetic phenomena in a conceptually uniform manner through MO theory. Each component thereby may achieve a new relevance and perspective.

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[3] This assignment is based on the electronegativity of the halogen and the relative weakness of the carbon-halogen bond (except when the halogen is fluorine).