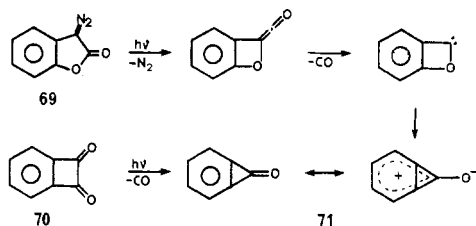
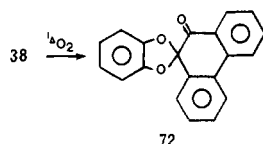


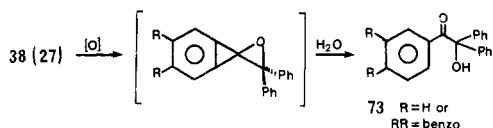
Scheme VI



isolated^{3,48} in a matrix at 8 K from photolysis of **69** and **70** (Scheme VI). While reaction of **27** with singlet oxygen gives benzophenone (20%), the isolation of methyl 2-naphthoate (25%) and 2-methoxynaphthalene (7%) confirms the intervention of 1-oxocyclopropa[b]naphthalene.⁴⁶ The benzene homologue **38** gives the unusual spirocycle **72** (identified by X-ray analysis⁴⁹) in low (6%) yield. Analogous studies with inorganic



oxidizing agents, e.g. osmium tetroxide, have also failed⁵⁰ to provide **71**. With peracids α -hydroxy ketones **73** are formed⁴⁶ and it is presumed that these arise from epoxidation and the subsequent nucleophilic addition of water to the epoxide. However, the site of attack



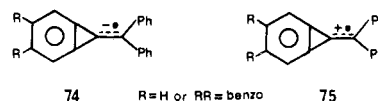
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on the epoxide (C1 vs C6) is not known. Unlike the epoxidation sequence, there is no reaction of **27** with carbenes under a variety of conditions which include those known⁵¹ to be effective for bicyclopopylidene.

Electrochemical and spectroelectrochemical investigations⁵² of **27** (and **38**⁵³) have shown that a stable radical anion (λ_{max} : **27**, 519; **38**, 587 nm) and a quasi-stable radical cation can be formed. The reduction and oxidation steps are reversible, which implies retention of the ring system and formation of the corresponding radical anion **74** and radical cation **75**.



Conclusion

Despite their recent availability the alkylidenecycloproprenes have obvious interest as the first, simple, stable, and polar hydrocarbons to contain a three-membered carbocycle with trigonal-planar hybridization at each center. The comparative ease of synthesis provides the potential for a wide range of derivatives and encourages alternative approaches to the as yet unknown parent hydrocarbon. Much of the chemistry of this intriguing class of compounds remains to be explored.

We are indebted to our co-workers, whose names appear in the citations. This research has been supported in New Zealand by The Universities Grants Committee and Victoria University and in Utah by the National Science Foundation (CHE-8419099). A travel grant from the NZ-US Educational Foundation (to B.H.) is also gratefully acknowledged.

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Paired Interacting Orbitals: A Way of Looking at Chemical Interactions

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Introduction

Molecular orbital calculations provide us with useful information about the structures and the physical properties of organic and inorganic molecules.¹ For instance, it is possible to find the transition-state structure of a chemical reaction and trace the reaction path on the potential surface.² As theoretical calculations become more available and more reliable, it will

be more important to have powerful methods for analyzing the results. It is helpful to know some of the factors that will control the stability of bonds and selectivity of reactions.

In fact, we already have a very useful way of generalizing the nature of chemical interactions and chemical bonds called the concept of "orbital interactions".³⁻⁵

(1) See for example: *Applications of Electronic Structure Theory*; Schaefer III, H. F., Ed.; Plenum: New York, 1977.

(2) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161.

(3) Fukui, K. *Theory of Orientation and Stereoselection*; Springer-Verlag: West Berlin, 1975.

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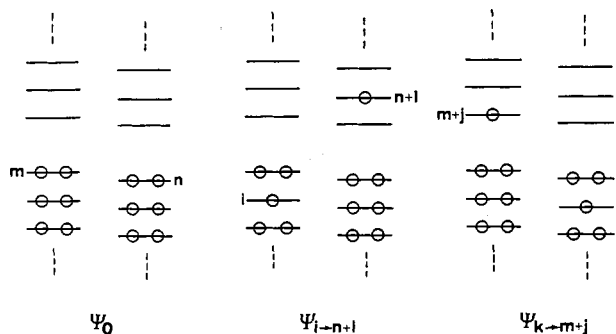


Figure 1. Schematic illustration of electron delocalization. Ψ_0 represents the initial configuration.

The delocalized molecular orbitals (MO's) of the reagent and reactant are used to construct interaction diagrams by applying perturbation theory.⁶⁻⁸ The evaluation of the matrix elements requires tedious calculations of integrals,⁹ and usually only the leading terms are taken into consideration. Consequently, it is difficult to represent local characteristics of chemical interactions. We have recently shown that chemical interactions are local by nature and are represented practically by means of several pairs of localized orbitals of the reagent and reactant. The pairwise interaction scheme appears to provide a useful tool for the interpretation of chemical interactions that allows delocalized orbitals to be transformed into concepts that are more familiar to us.

In the following, we clarify first the active regions of molecules. Pairs of interacting orbitals of fragments are generated by analyzing the wave function of a composite interacting system. These orbitals are shown to be localized specifically around the reaction sites, and they yield a succinct expression for functional groups in chemical interactions. We then show that orbitals that are similar to those obtained by the paired transformations are defined for an isolated reactant molecule by assuming an interaction with an imaginary reagent. We present an example in which reactivities are related to the electron-donating or -accepting ability of the active structural unit. These arguments require extra computations to be performed in addition to the ordinary MO calculations.

Orbital Interactions

Let us consider first the interaction between two molecular systems A and B. The electronic structure of the composite interacting system A-B is represented here by a combination of electron configurations of A and B as illustrated schematically in Figure 1.^{7,10} We assume here that both A and B have closed-shell electronic structures. When system A enters into an interaction with system B, the electrons in the occupied MO's ϕ_i of A ($i = 1, 2, \dots, m$) become delocalized between A and B by utilizing the unoccupied MO's ψ_{n+l} of B ($l = 1, 2, \dots, N - n$). Similarly, the electrons of B

are delocalized by means of the overlap between the occupied MO's ψ_k ($k = 1, 2, \dots, n$) of B and the unoccupied MO's ϕ_{m+j} of A ($j = 1, 2, \dots, M - m$). Electron delocalization is represented primarily by the one-electron-transferred configurations, $\Psi_{i \rightarrow n+l}$ and $\Psi_{k \rightarrow m+j}$. The coefficients C_0 , $C_{i \rightarrow n+l}$, $C_{k \rightarrow m+j}$, ..., of these electron configurations are obtained by carrying out a configuration analysis of the wave function or a perturbation calculation.⁷

Among the occupied MO's, the highest occupied (HO) MO shows the largest potential for electron donation, and among the unoccupied MO's, the lowest unoccupied (LU) MO possesses the largest potential for electron acceptance. Thus, the frontier orbital theory emphasizes that the interaction between the HOMO of A and the LUMO of B and that between the HOMO of B and the LUMO of A govern selectivities of reactions.^{3,11,12} It was assumed that electron delocalization controls the reaction paths.^{7,13} The change in the electron density due to the mixing of $\Psi_{i \rightarrow n+l}$ with Ψ_0 is given approximately by

$$\Delta\rho \approx C_{i \rightarrow n+l}^2(\psi_{n+l}^2 - \phi_i^2) + 2\sqrt{2}C_0C_{i \rightarrow n+l}(\phi_i\psi_{n+l} - S_{i,n+l}\phi_i^2) \quad (1)$$

where $S_{i,n+l}$ is the overlap between ϕ_i and ψ_{n+l} . Of these, the first term is well-known; it represents the transfer of electronic charge from A to B.¹⁴ On the other hand, the second term indicates that a part of the electron population donated by the orbital ϕ_i of A is retained in the region between A and B through the overlap between ϕ_i and ψ_{n+l} . This portion of electron population is utilized to generate new chemical bonds between the reaction centers of the two systems.

The occupied MO is usually a bonding orbital, and the unoccupied MO is an antibonding orbital between the reaction center and adjacent atoms. The old bonds begin to break both in the electron-donor part and in the electron-acceptor part as electron delocalization takes place. The antibonding nature of the unoccupied MO is usually stronger than the bonding nature of the occupied MO. In the case of the ethylene π bond, for instance, the C-C overlap population in the π MO is $2s/(1+s)$ and that in the π^* MO is $-2s/(1-s)$, where s is the overlap integral between the two 2p atomic orbitals ($0 < s < 1$). This shows that the bonds in B are weakened to the same extent as the bonds in A, though a part of electron population donated from A is not transferred to B but is utilized to form new bonds between the two systems.

Paired Interacting Orbitals

The most important outcome of electron delocalization is that electron density is accumulated in the region between the reagent and reactant molecules as mentioned above.¹⁵ This density change is characteristic of each chemical interaction because it is localized in the neighborhood of the reaction centers. Here we devise a method of representing this density change by

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a minimum number of orbitals. One way of doing this is to make pairs between the occupied MO's of A and the unoccupied MO's of B, that is, to find a new occupied orbital of A, ϕ'_i , which donates electronic charge only to its corresponding new unoccupied orbital of B, ψ'_{n+i} . This is similar in some respects to the use of hybrid atomic orbitals in specifying localized bonds in organic molecules; hybrid atomic orbitals are constructed under the symmetry constraint imposed upon the molecule.¹⁶ The problem is how to find hybrid molecular orbitals for various types of chemical interactions between sizable molecules.

Let us take a matrix **D**, the (i, l) element of which represents delocalization of an electron from the occupied MO ϕ_i of A to the unoccupied MO ψ_{n+l} of B.^{17,18} The order of the matrix **D** is $m(N-n)$, m being the number of occupied MO's of A and $(N-n)$ being the number of unoccupied MO's of B. By diagonalizing the square matrix **D[†]D**

$$\mathbf{D}^\dagger \mathbf{D} \mathbf{V} = \mathbf{V} \mathbf{T} \quad (2)$$

we obtain the transformation matrix **V**. Then, the occupied canonical MO's of A and the unoccupied canonical MO's of B are converted by a couple of unitary transformations¹⁹ into a set of paired interacting orbitals of the fragments

$$\phi'_f = \gamma_f^{-1/2} \sum_{i=1}^m \sum_{l=1}^{N-n} D_{i,l} V_{l,f} \phi_i \quad (3)$$

$$\psi'_f = \sum_{l=1}^{N-n} V_{l,f} \psi_l \quad (4)$$

where γ_f is the f th eigenvalue of **D[†]D**. Electron delocalization which was represented originally by $m(N-n)$ combinations of canonical MO's is now represented by μ pairs of the hybridized MO's of fragments; μ is the smaller of m and $(N-n)$. Similarly, another set of transformations can be found for combinations of the unoccupied MO's of A and the occupied MO's of B.

One advantage of this treatment is that reactivities of molecules of various sizes with the same reagent (normally having a smaller number of orbitals than the reactants) can be discussed by comparing the same number of hybridized reactive orbitals. As will be seen in the next section, these recombined MO's are localized in the frontier of the interactions. Hence, we called these specifically hybridized MO's the "interaction frontier orbitals".¹⁷ Usually, only a few pairs of orbitals contribute significantly to the delocalization interaction, and therefore it is feasible to understand interactions between large molecules. However, this simplification in the presentation of chemical interactions is done at the cost of having to do additional computations.

Examples of Interacting Orbitals

Figure 2 shows an example. We obtained the structure of a protonated formaldehyde by a minimal basis STO-3G calculation.²⁰ The proton is located at the

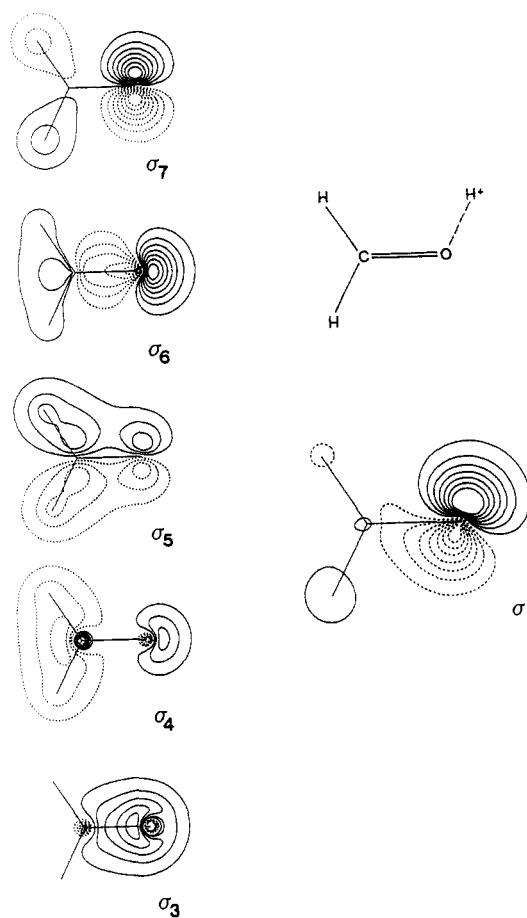


Figure 2. Occupied σ -type canonical MO's of formaldehyde (left) and the interaction frontier orbital for protonation (right).

position in the molecular plane at which we imagine that a sp^2 -like hybrid atomic orbital (AO) of oxygen is participating in electron donation. The wave function is given by

$$\begin{aligned} \Psi = & 0.517\Psi_0 + 0.005\Psi_{\sigma(1) \rightarrow H^+(1s)} + 0.001\Psi_{\sigma(2) \rightarrow H^+(1s)} + \\ & 0.022\Psi_{\sigma(3) \rightarrow H^+(1s)} + 0.066\Psi_{\sigma(4) \rightarrow H^+(1s)} + \\ & 0.119\Psi_{\sigma(5) \rightarrow H^+(1s)} + 0.185\Psi_{\sigma(6) \rightarrow H^+(1s)} + \\ & 0.375\Psi_{\sigma(7) \rightarrow H^+(1s)} + \dots \end{aligned}$$

Among the σ -type canonical MO's of formaldehyde, the HOMO σ_7 plays the dominant role in electron delocalization to the proton. However, it is a p-type orbital that has the direction of extension perpendicular to the C=O bond.

The orbital of formaldehyde that participates in electron delocalization by making a pair with the proton 1s AO is shown on the right-hand side. It is given by a combination of the canonical MO's, σ_1 – σ_7 . The orbital is shown to be well-localized around the oxygen atom and is directed toward the attached proton. Instead of seven electron-transferred configurations, now we have a single electron-transferred configuration:

$$\Psi = 0.517\Psi_0 + 0.440\Psi_{\sigma' \rightarrow H^+(1s)} + \dots$$

The contribution of the HOMO to the orbital σ' is calculated to have a weight of 72.5%. Inclusion of other MO's leads clearly to an expression of the interaction

(16) See for example: Maksić, Z. B. *Comp. Math. Appls.* 1986, 12B, 697 and the references cited therein.

(17) Delocalization stabilization was taken at first as the elements of the matrix **D**. See: Fukui, K.; Koga, N.; Fujimoto, H. *J. Am. Chem. Soc.* 1981, 103, 196.

(18) The coefficients of electron-transferred configurations were taken in the present calculation in place of the delocalization energy. Both calculations give essentially the same result. See: Fujimoto, H.; Koga, N.; Hataue, I. *J. Phys. Chem.* 1984, 88, 3539.

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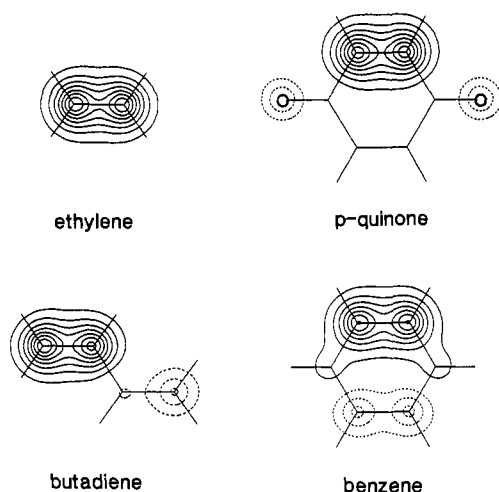


Figure 3. Orbitals of conjugated systems taking part in electron delocalization with a proton. The proton is located 1.5 Å above the midpoint of C-C bond in each system.

that appears to be much easier to understand. This orbital has greater p character than the lone-pair orbitals determined so as to represent the electronic structure of isolated aldehyde molecules.²¹ This orbital reflects the greater ability of the p orbital than the s orbital to donate electrons. This scheme has been found to be transferable to acetaldehyde and acrolein but not to an ether molecule; furan gives a somewhat different orbital for protonation. It is therefore necessary to carry out an analysis for each group of molecules. Incidentally, the proton 1s orbital is left unchanged in the paired orbital transformation.

Let us look at another example. Figure 3 illustrates the occupied MO's of ethylene, butadiene, *p*-quinone, and benzene that donate electronic charge to the attached proton. Other electrophiles induce similar interacting orbitals in these molecules. The orbitals are localized on the interaction site, indicating that the reactive unit is a C-C double bond in this type of interaction. These orbitals remind us of the important concept of "functional groups" which is the starting point of organic chemistry. The orbital of quinone looks like that of an olefinic double bond, but the benzene orbital is slightly more delocalized. The difference in the strength of conjugation has a certain effect in determining the region of the molecules involved directly in the interaction.

In addition to the formation and breaking of chemical bonds in interactions, electron delocalization has been shown above to play another important role in defining functional units in molecules. It is argued frequently that the delocalized MO's of a molecule are constructed by taking the combinations of the orbitals of its fragments.^{22,23} It is interesting to see that the delocalization interaction determines the localized orbitals in the fragments that are most suitable for the expression of the interaction. These orbitals illustrate which bonds are weakened and which bonds are strengthened.

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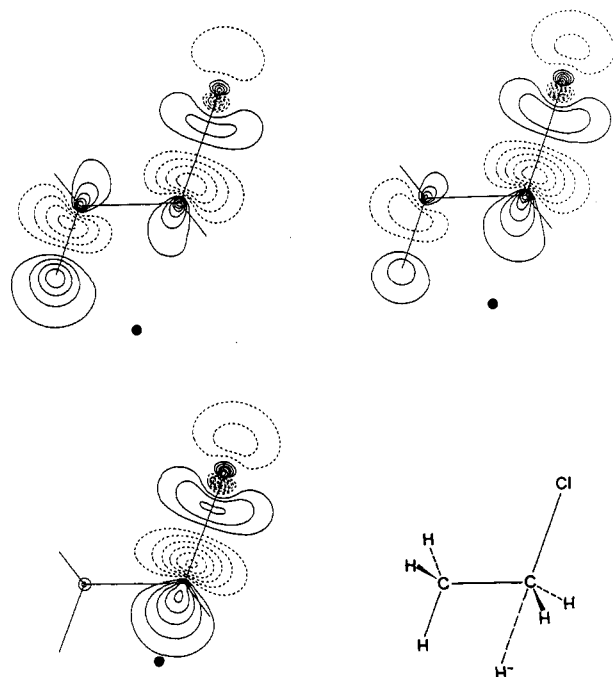


Figure 4. Unoccupied orbital of ethyl chloride. The location of the attacking hydride ion is indicated by a dot.

Figure 4 illustrates the changes in the orbital of ethyl chloride that accepts a negative charge from a hydride ion, attacking from the carbon end of the C-Cl bond. When the anion is located far away from the substrate molecule, the orbital looks like the LUMO, showing its amplitude both in the C_α-Cl bond region and the C_β-H bond region. The anion interacts weakly with the hydrogen before attacking the C_α or will cause an E₂ elimination. As the anion comes closer to the C_α atom, the orbital begins to be localized on the C-Cl bond and finally shows its amplitude only in the C-Cl bond region. In other words, the orbital tends to bear a resemblance to the LUMO of methyl chloride. When two or three methyl groups are attached to the α carbon, it is suggested that the anion attacks a C-H bond more easily than the C-Cl bond.

The next example is a concerted cycloaddition.²⁴ As shown in Figure 5, two acrolein molecules give rise to interacting orbitals that are entirely different in shape, demonstrating that they play different roles in this reaction. In the molecule shown on the left-hand side, the orbitals are delocalized over the whole conjugated chain, but in the molecule on the right-hand side, the orbitals are localized in the terminal C-C bond region. This way of representing the interaction is in line with our empirical classification of reactants in this type of cycloadditions, i.e., diene and dienophile. This description of the reaction is generally more familiar than the orbital interactions utilizing the canonical MO's.^{25,26}

Isolated Molecule Orbitals

We have seen above that the orbitals that participate in electron delocalization between molecules are highly localized in a certain region of the reagent molecule and

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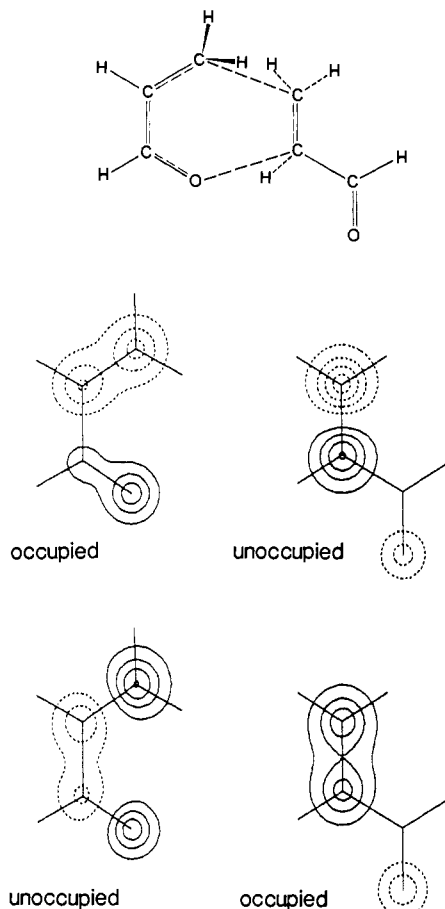


Figure 5. Two pairs of interacting orbitals in the dimerization of acrolein. Geometry was assumed with reference to the cycloaddition of ethylene to butadiene.

of the reactant molecule than the usual canonical MO's. Different molecules give similar orbitals in the same type of reaction, and the same molecule gives different orbitals for different types of reactions. The delocalization stabilization is analyzed by means of these interacting orbitals. Molecules do not produce localized interacting orbitals in unfavorable reactions. We examine next the physical significance of these orbitals with the aim of utilizing the results obtained above to yield a simple measure of predicting reactivities of molecules.

For a long time, maximum overlap has been a criterion, whether it is explicit or implicit, to measure the strength of chemical bonds and interactions.²⁷ The frontier orbital theory has suggested that the overlapping between some particular MO's is significant.³ We consider this principle in a somewhat specific manner by taking a combination of occupied MO's or unoccupied MO's of a molecule to construct an occupied orbital or an unoccupied orbital that has its maximum amplitude on the interaction center.

Figure 6 illustrates an example. We assume that an electrophile attacks the C₁ atom of a benzene molecule. The interaction is most likely to be one-centered, and therefore we recombine the three occupied π MO's in such a way as to produce an occupied orbital that has its maximum amplitude on that carbon.²⁸ This orbital

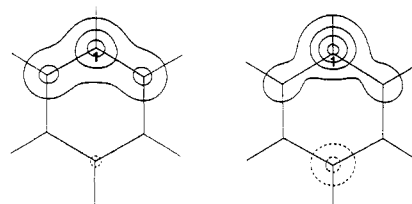


Figure 6. Occupied orbital of benzene having the maximum amplitude on C₁ (left) and the orbital participating in electron delocalization with a proton (right). The latter was obtained for the STO-3G optimized geometry by placing a proton 1.5 Å away from C₁.

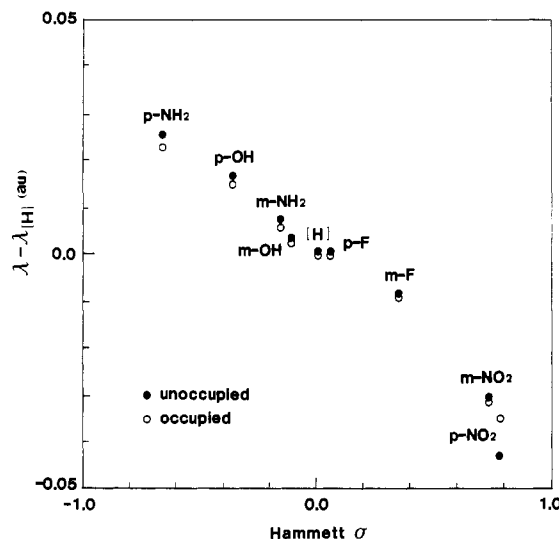


Figure 7. Correlation between the Hammett σ constant and the electron-donating potential λ of the orbital that has the maximum amplitude on C₁ of substituted benzenes. Benzene, indicated by H, was taken as the standard, and λ values were evaluated by a STO-3G calculation.

is assumed to make a pair with an unoccupied orbital of the imaginary electrophile. One sees a close resemblance between the occupied orbital that has the maximum amplitude at C₁ (left) and the orbital that represents electron delocalization by making a pair with the 1s AO of the attacking proton (right). A slight difference in the orbital shape is attributed to the fact that the orbital on the left is calculated for a planar benzene molecule, whereas the orbital on the right is obtained for a nonplanar geometry. This suggests that the maximum overlap criterion is reasonable so far as electron delocalization is concerned.

The orbital obtained by taking a linear combination of occupied MO's or unoccupied MO's shows a shape characteristic to the imagined interaction. The reactivity may be interpreted in terms of its potential for electron donation or electron acceptance for a series of molecules. The electron-donating potential λ of an orbital is estimated approximately by taking a sum of the energies of the constituent MO's multiplied by the square of the coefficients.²⁸ Figure 7 compares substituted benzenes with several kinds of electron-releasing and electron-withdrawing groups. The occupied orbital of a benzene molecule that has been substituted by a stronger electron-releasing group has a larger potential for electron donation. Figure 7 also shows that a benzene molecule that has been substituted by a stronger electron-withdrawing group has an unoccupied orbital with a larger potential for electron acceptance.

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(28) Fujimoto, H.; Mizutani, Y.; Iwase, K. *J. Phys. Chem.* 1986, 90, 2768.

Here, the unoccupied orbital is obtained in a similar manner, to give the maximum amplitude on C_1 , by taking a combination of the unoccupied π MO's. The correlation with the Hammett σ constants is beautiful.²⁹ In this case, unlike the discussion using canonical MO's,³⁰ one can compare in a unified manner not only the different substituent groups but also their effect at different positions. A similar argument was found also to be applicable to the Diels-Alder reaction.³¹

In this way, we can construct the occupied orbitals or unoccupied orbitals that have the largest amplitude around a certain structural unit. When the HOMO has a large amplitude at the interaction center, the HOMO will be the important component of the interacting orbital. The orbital will have a strong potential for electron donation. Similarly, if the LUMO has a large amplitude around the reaction center, the LUMO will be the dominant constituent of the unoccupied interacting orbital and it will have a strong potential for electron acceptance. Thus, our interacting orbital may be regarded in some respects as a general extension of the frontier orbital concept. By applying the present procedure to simple Hückel MO's, we obtain simple reactivity indexes which show better agreement with experiment than the frontier electron density does.²⁸

Other Orbital Effects

When the attacking reagent is an electron-rich species, the exchange repulsion plays an important role. For example, the Walden inversion in the S_N2 reactions of alkyl halides occurs to reduce the repulsion between the electron pairs in the attacking nucleophile and the electron pairs in the bonds of the alkyl group. The charge brought to the reaction center by the delocalization interaction is redistributed over the molecule by the polarization interaction. This interaction has another important effect for defining the reaction centers in the reactive structural unit. These interactions are included in the orbital transformations by using, for example, the intermolecular part of density matrix of the composite interacting system, in place of the matrix **D** to stand for the delocalization interaction.^{32,33}

Figure 8 illustrates the change in the interacting orbital along the intrinsic reaction coordinate² of the rearrangement of vinyl alcohol.³⁴ At the beginning, the orbital has a large amplitude on the oxygen atom. Then, the methylene group begins to rotate in order to receive the migrating proton. With the help of the polarization effect, the orbital shows a high amplitude only on the terminal carbon atom of the vinyl group at a later stage. The proton migrates to a low altitude above the plane of the C-C-O skeleton, and conse-

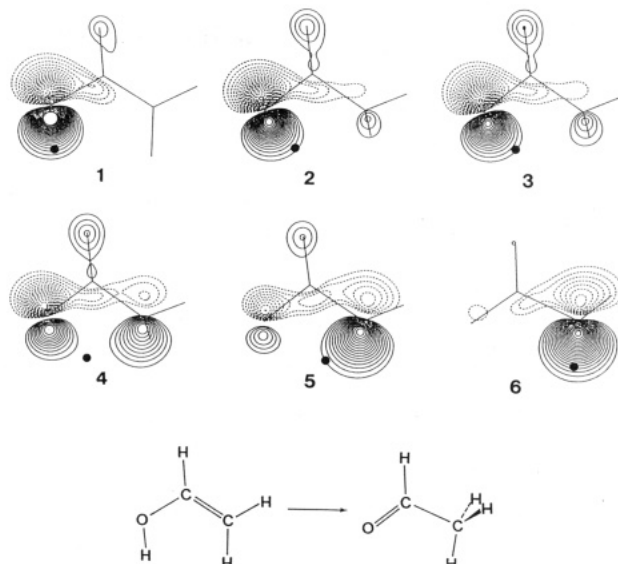


Figure 8. The orbital that makes a pair with the 1s AO of the migrating proton in a rearrangement of vinyl alcohol.

quently orbital symmetry arguments do not apply here. However, one can understand easily that this rearrangement in the gas phase would need a high activation energy to take place.³⁵ The proton is located "outside" of the orbital lobes of the remaining fragment at the transition state (stage 4).

Concluding Remarks

To try to simplify our discussion, we have chosen small species for the attacking reagent in the models presented above. This method has also been applied to interactions of sizable systems as well. For instance, the roles of transition-metal complexes in organic synthesis have been analyzed by the aid of these paired localized interacting orbitals.³⁶

The concept of orbital interactions has been used frequently as a simple way of interpreting chemical reactions and bonds. It has led to the discovery of important rules in chemistry⁴ and even to predictions of new reactions. On the other hand, theoretical calculations offer very accurate and reliable information on structures, heats of formation, and other physical properties. Calculations to predict what is possible can be used more confidently if we have methods to understand the way the results are linked with the simple concepts of interactions and chemical bondings. Empirical notions which have been refined in the long history of chemistry will also be of great use if they are connected with theoretical calculations and given a firm theoretical basis. Visualization of the local characteristics of chemical interactions may be utilized to make sense of theoretical calculations.

I am grateful to Prof. Kenichi Fukui for encouragement and to the Institute of Molecular Science for generous permission to use its Computer Center.

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