

THERMAL CHEMISTRY AS AN EXERCISE IN PHOTOCHEMISTRY!

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Abstract - The Linear Combination of Fragment Configurations approach is used to generate qualitative potential energy surfaces. The theory is applied to "forbidden" cycloadditions, solvolysis, and electrophilic aromatic substitution. It is also used to illuminate principles of chemical selectivity and the electronic structure of diradicals. It is argued that chemical intermediates in thermal reactions arise from excited surfaces under the influence of perturbations such as substituent effects and solvation.

INTRODUCTION

In the last few years, qualitative theoretical chemistry has emerged as a new and distinct branch of science. It differs from classical physical organic chemistry to the extent that concepts are formulated on a quantum mechanical rather than an intuitive basis. For example, "steric effects" are discussed in terms of coulomb and overlap repulsion (1), "hyperconjugation", "aromaticity", and "antiaromaticity" are viewed as manifestations of exchange stabilization and overlap repulsion (1), "polarizability" is associated with low lying reactant mono- and di-excited configurations (2), etc. This new discipline also differs from classical theoretical chemistry to the extent that computations are used for testing predictive models rather than generating theoretical numbers to be compared with experimental numbers (1). By its nature, the qualitative theoretical approach presupposes a knowledge of experimental facts for the purpose of making sensible approximations, necessary in any treatment of large organic molecules or reaction complexes. In addition, a feeling for the "physical" significance of mathematical equations is needed for the formulation of new indices which can be used by the experimentalist in his search for new synthetic routes, mechanistic schemes, etc. For certain types of problems, e.g., chemical reactivity of large organic molecules, computations of model systems are, as we shall see, ill-advised and calculations of the actual reaction systems are technically impossible. In such areas, qualitative theory plays a leading role. Our recent treatises of structure (1) and reactivity (2) and past works by Streitwieser (3), Dewar (4), Zimmerman (5), Salem (6), Fukui (7), Oosterhof (8), Klopman (9), Herndon (10), Pearson (11), Lowe (12), Gimarc (13), Woodward and Hoffmann (14), and others, constitute the foundation of this new scientific domain.

Theoreticians can be grouped in two broad categories. One includes those who prefer to refine essentially worked-out problems. They seem to be concerned with exactly how large or small is a singlet-triplet energy gap, how much more "aromatic" or "antiaromatic" a molecule is relative to another, etc. The other includes those who have a penchant for exciting adventure, treading dangerous grounds in an attempt to develop new general concepts or computational procedures. My taste is along the latter lines. Thus, in keeping with such a philosophy, I have chosen to present in this lecture some proposed solutions of "hard" reactivity problems which at the present remain outside the range of "quantitative" ab initio calculations. The intent is to be illustrative and, in cases, even speculative rather than rigorous and exhaustive. The presentation is mainly aimed at the experimentalist. However, problems of interest to theoreticians involved in the study of polyatomic molecules do inevitably enter.

A casual perusal of the ground and excited two dimensional Potential Energy (P.E.) surfaces of H_2 (15) and NaCl (16) reveals the following:

(a) The P.E. surfaces are not straight lines. Rather, they are curves having maxima and minima, the latter housing isolable or spectroscopically observable entities.

(b) The ground surface of H_2 is mainly "covalent" while that of NaCl is made up of "covalent" and "ionic" parts. The latter situation is a result of the avoided crossing of

two different surfaces, one of the "covalent" and one of the "ionic" type.

The P.E. surfaces of H_2 , NaCl and many diatomics have been studied and reviewed extensively (17). From the organic chemist's standpoint, they are not very interesting in themselves. However, they do provide the stimulus for some thoughts regarding how one must proceed in order to formulate a general qualitative theory of chemical reactivity. In addition, they help bring into focus the deficiencies of currently popular models.

THE NEED FOR A NEW THEORY OF CHEMICAL REACTIVITY

A satisfactory treatment of (thermal and photochemical) chemical reactions tantamounts to the construction of the P.E. surfaces (ground and excited) for the case of interest. This means that we must reject the following methods or notions:

(a) The static approach, according to which the relative merits of two reaction paths are assessed by calculating the Stabilization Energies (SE's) of the corresponding reaction complexes at some arbitrary interfragmental distance, r . The difference, ΔSE , is taken to reflect a difference in slopes in a manner such that a greater stabilization energy is associated with a lower barrier height as illustrated in Figure 1. It is implicitly

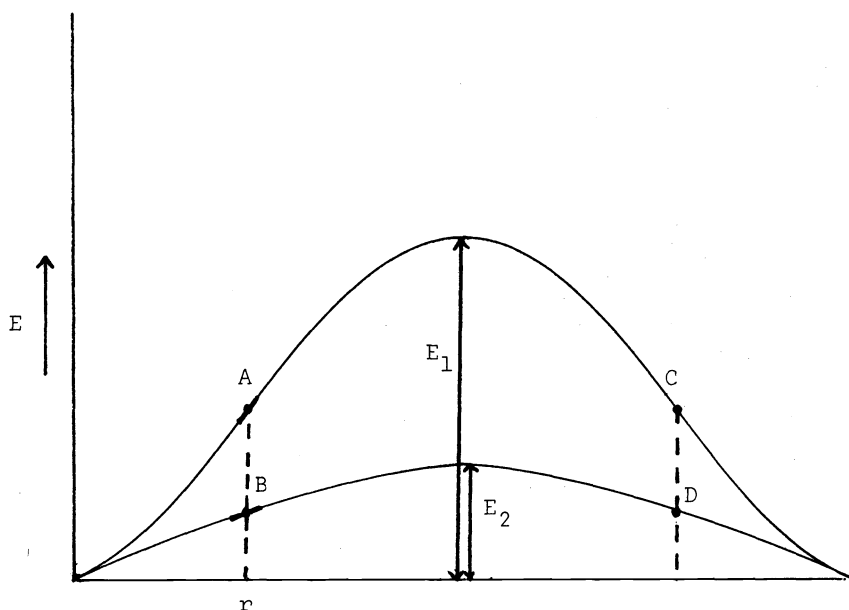


Figure 1. The assumptions of the static model. The stabilization energy for complex A at distance r , $SE(A,r)$ is taken to reflect the slope at A,r which, in turn, is assumed to be a measure of the barrier height E_1 . In our example, $SE(B,r) > SE(A,r)$ implies $E_1 > E_2$.

assumed that the corresponding transition states occur at the same (or, very similar) r . Furthermore, chemical intuition plays a great role insofar as a proper selection of the arbitrary r is concerned. For example, a comparison of points A and B is acceptable while a comparison of points C and D is inappropriate though it could accidentally lead to the right conclusions.

The most successful applications have made use of one electron Perturbation MO (PMO) theory for calculating SE's (4). Since two electron effects are ignored, one cannot differentiate among states which are spatially degenerate in a Hückel sense. As we shall see, this shortcoming can be very serious even at the qualitative level. The criticism, which partly amounts to self-criticism, should not obscure the fact that the static approach has been and still is an immensely useful qualitative tool.

(b) The correlation diagram approach, according to which initial and final states are joined by straight lines. Variants of this approach range from the original united atom model to the all important Woodward-Hoffmann (14a) and Longuet-Higgins and Abrahamson (14b) MO and state correlation diagrams.

The key drawbacks of this approach are the following:

1. It fails to reveal explicitly how certain barriers and chemical intermediates arise. There are two main reasons for this key failure:

i) Neglect of electron repulsion effects. As an example, consider the state correlation diagrams for $2\pi_s + 2\pi_s$ cycloaddition shown in Figure 2.

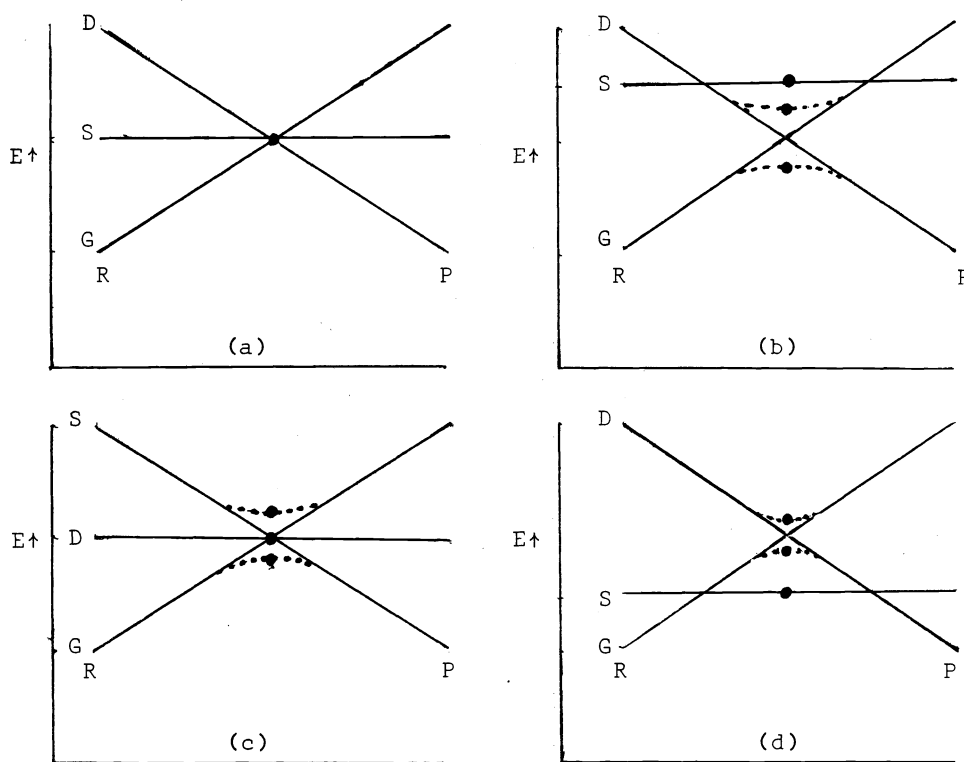


Figure 2. Possible state correlation diagrams for $2\pi_s + 2\pi_s$ cycloaddition.

G = Ground State, S = Singly Excited State, D = Doubly Excited State, R = Reactants, P = Products. All states are defined with respect to reactants. Dots indicate singlet diradical states.

If electron repulsion effects are neglected, we have the situation depicted in (a). If they are explicitly treated, we can have any of situations (b)-(d) depending on the nature of reactants. Note that (a)-(d) represent different mechanisms. As a result, what naively seems a simple affair turns out to be quite a complicated story. This ambiguity of correlation diagrams is the origin of the current confusion regarding the nature of "diradicals", the real meaning of the terms "forbidden" and "allowed", etc.

(ii) Neglect of MO interaction effects. This deficiency has been discussed recently by Devaquet et al (18). We note that the problem is much more general than these authors suggest. As an example, consider a simple chemical problem: Union of two radicals to form a molecule. The orbital correlation diagram (Figure 3a) fails to make explicit how the orbital interaction, which varies along the reaction coordinate, and two electron effects become ultimately responsible for a possible barrier on the ground and a zwitterionic intermediate on the excited surface (Figure 3b). Diabatic surfaces are indicated by solid and adiabatic surfaces by dashed curves.

Orbital Correlations

(a)

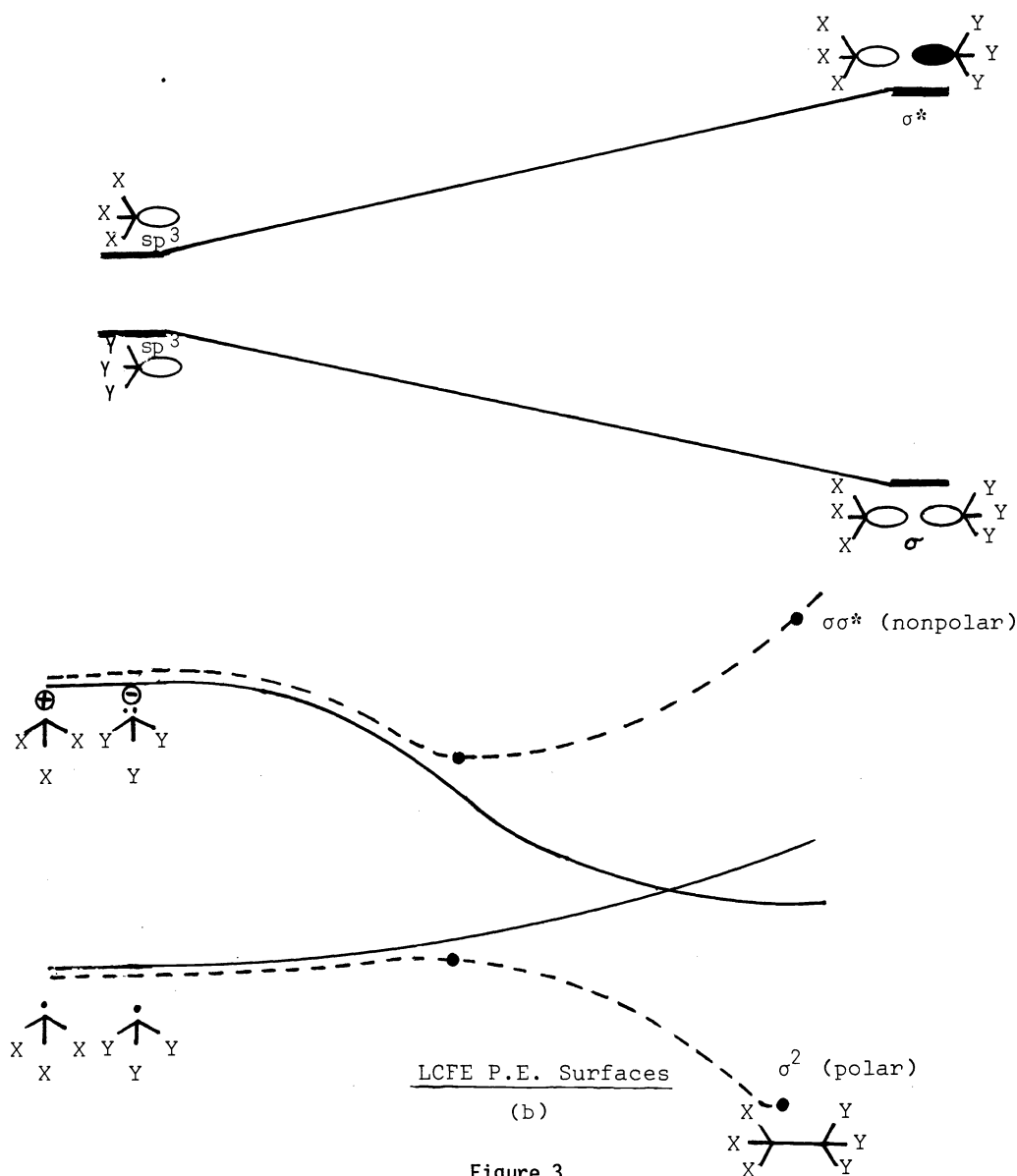


Figure 3

2. Since one must be able to classify MO's or states by reference to some symmetry element which is preserved in the course of the reaction, this method cannot be used for treating bicentric reactions.

(c) The notion of an across-the-board theory of chemical reactions based on gas phase unperturbed model systems. As revealed by the H_2 versus NaCl comparison, a change of the electronic nature of a component of a molecular or supermolecular system can produce surface crossings which alter the original picture in a drastic manner. To put it crudely, we must not expect that which is valid for ethylene + ethylene will be valid for tetramethoxyethylene + tetracyanoethylene. Strangely, many organic chemists, seduced by the esthetic beauty of orbital symmetry arguments, came to view reactions as "allowed" or "forbidden" depending upon the symmetry correlation or lack thereof of the orbitals and/or states of reactants and products. Furthermore, these symmetry correlations were frequently assumed to be independent of the electronic nature of reactants. As a result, unwarranted overextensions have been made only to lead to a current state of utter confusion. A dramatic evidence of this are the often asked questions as to how intermediates may or may not be compatible with "allowed" reactions, why a "forbidden" reaction is stereospecific, etc.

Our thesis is that qualitative P.E. surfaces, even at a primitive level, constitute the best hope for achieving, among others, the following goals:

- (a) An understanding of the mechanisms of thermal and photochemical multicentric reactions of molecules.
- (b) An understanding of thermal heterolytic reactions, the mainstay of organic chemistry (19), and the associated solvent effects.
- (c) As a by-product of (a) and (b), a unification of ground and excited state chemistry.

In a recently published treatise (2), we have shown that these objectives can be realized and we have advanced a viewpoint which is substantially different from the "accepted" one. In the space below, I present only some interesting applications of our approach.

THE LINEAR COMBINATION OF FRAGMENT CONFIGURATIONS THEORY AND QUALITATIVE POTENTIAL ENERGY SURFACES.

The theoretical formalism which we employ in order to generate qualitative P.E. surfaces is the Linear Combination of Fragment Configurations (LCFC) method. This is a "molecules in molecules" approach (20) and leads to the construction of states from configurations built from the MO manifolds of the two reacting molecules. A simple procedure for the development of the qualitative P.E. surfaces can be developed if the LCFC treatment is implemented at the level of the Zero Interfragment Differential Overlap (ZIDO) or Zero Interfragment Overlap (ZIO) approximation. Maximum simplicity is achieved with the former; on the other hand, only the latter makes a proper analysis of singlet-triplet differences possible. In such case, two electron repulsive integrals of the type $\langle ab\ cd \rangle$ ($a=b$ and/or $c=d$), which vanish at the ZIDO-LCFC level, play an important role. We shall adopt the ZIDO-LCFC method while keeping in mind that rejection of the ZIDO in favor of the ZIO approximation becomes necessary for problems of the type mentioned above.

We now outline the basic steps necessary for the construction of qualitative P.E. surfaces using the LCFC method. The first task is the specification of the basis configurations and this can be done as follows:

- (a) The two reactants are classified as donor (D) and acceptor (A) using familiar criteria (2). In general, a donor has a low ionization potential and a low electron affinity. The reverse holds true for an acceptor.
- (b) The number of "reacting" electrons is identified. In general, these electrons can be regarded as the "valence" electrons of the two uniting molecules or fragments and they are contained in the Frontier Orbitals (FO's). In the case of two closed shell reactants, the FO's are the Highest Occupied MO's (HO's) and the Lowest Unoccupied MO's (LU's). In the case of two open shell reactants, the FO's are defined as the singly occupied Non Bonding MO (NB) as well as the Highest Doubly Occupied MO's (HDO's) and the LU's.
- (c) Configurations are constructed by permuting the "reacting" electrons among the FO's of the two reactants. These are subdivided into ground, monoexcited, and diexcited configurations. All three types are necessary for the construction of the P.E. surfaces although simplifications can and will be made.

Diabatic surfaces, i.e., P.E. surfaces in the hypothetical case of no CI, can be generated

by the following procedure:

(a) Each configuration wavefunction is written as a Slater determinant or a linear combination of Slater determinants depending upon the number of open shell electrons.

(b) A complete nonrelativistic Hamiltonian, \hat{H} , is assumed.

(c) The energy, E , of each normalized wavefunction is evaluated. A plot of E versus q , the reaction coordinate, yields the desired diabatic surface.

At the level of ZIDO-LCFC treatment, there are only two different shapes of diabatic surfaces. Namely, a repulsive (R) and an attractive-repulsive (AR) shape. The former is associated with all configurations which do not involve positive-negative charge separations, e.g., DA; the latter with those which do, e.g., D^+A^- and D^-A^+ (Figure 4).

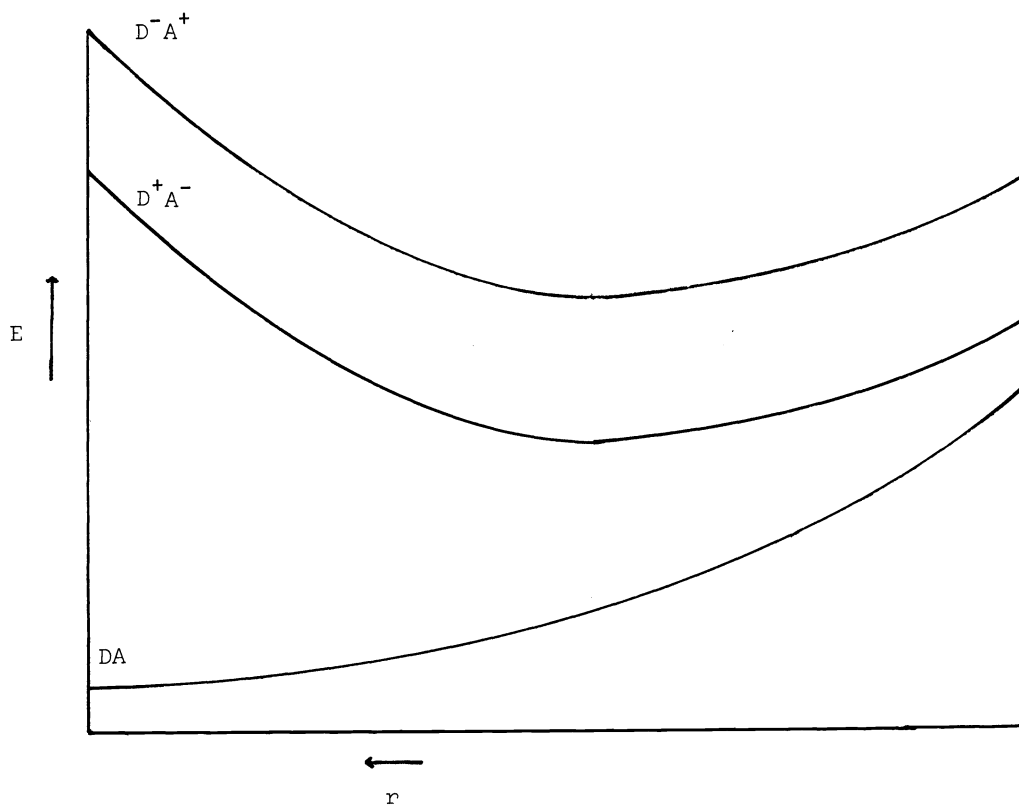


Figure 4

Having discussed the shapes of diabatic surfaces, we turn our attention to the question of their relative energy ranking. A good anchor is at infinite intermolecular distance, r , where all intermolecular integrals can be set equal to zero. At this limit, we obtain the terms which are independent of r . Having isolated them, we can deduce the factors which will cause an entire diabatic surface to move upward or downward in energy relative to a suitably chosen reference diabatic surface. The latter is taken to be the lowest energy diabatic surface; for most problems, this is DA. For the charge transfer, D^+A^- , and locally excited, D^*A , diabatic surfaces, the following predictions are made:

(a) The D^+A^- diabatic surface will be translated downwards in energy as the ionization potential of the donor, I_D , decreases and the electron affinity of the acceptor, A_A ,

increases. This arises because at $r=\alpha$ the following equation holds:

$$E(D^+A^-) - E(DA) = I_D - A_A$$

This discussion leads us to the definition of the term polarity, P . This is defined as the inverse of the quantity $I_D - A_A$. As we shall see, polarity exerts a profound influence on the shapes of P.E. surfaces.

(b) The D^*A diabatic surface will be translated downwards in energy as the excitation energy of D , G , decreases. This arises because at $r=\alpha$ the following equation holds:

$$E(D^*A) - E(DA) = G$$

The above discussion suggests that there is a very simple recipe for writing down the equations of all pertinent diabatic surfaces for a given reaction. Specifically, one can evaluate the energies of DA , D^+A^- , and D^-A^+ and generate all higher surfaces by appropriate electron promotions. In a qualitative sense we can write the energy expressions of the diabatic surfaces as follows:

$$E(DA) = S$$

$$E(D^+A^-) = I_D - A_A + C + S'$$

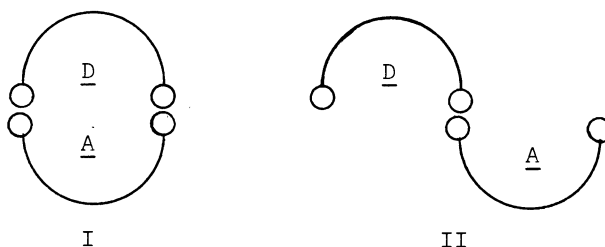
$$E(D^-A^+) = I_A - A_D + C' + S''$$

Recognizing that reactants do not combine in their "frozen" equilibrium geometry, but, rather distort and rehybridize on their way to becoming products, we can define the following terms:

C = Coulomb attraction of positive hole and excess electron.

S = Steric function describing repulsion, distortion and rehybridization energy requirement, and, parametrically, overlap repulsion (neglected at the LCFC-ZIDO level).

In general, distortion and rehybridization is more difficult the more bonding electrons a given configuration involves. Furthermore, both C and S are path dependent. The former makes a greater negative and the latter a greater positive contribution as accumulation of nuclei within unit volume increases. To put it crudely, C favors a congested geometry, e.g., I, while S favors an uncongested one, e.g. II. At loose geometries, C dominates. The reverse is true at very tight geometries.



Our next task is to consider the interactions of the basis configurations. The corresponding interaction matrix elements contain terms which are functions of r . In conjunction with the diabatic surfaces, these interaction matrix elements can be used to generate the final adiabatic surfaces. At the ZIDO-LCFC level configurations differing by one electron in terms of MO occupancy can interact. If the MO's which differ in occupancy by one electron are ϕ_a and ϕ_b , the mono-electronic term is set proportional to the MO overlap integral, S_{ab} . In most, but not all, cases, the bielectronic terms vanish.

Once the basis configurations are defined and the equations for the diagonal and off diagonal elements of the energy matrix are written, one can proceed to solve the secular equations for a sequence of r values and obtain the adiabatic P.E. surfaces. Since we are interested in qualitative trends, we shall not seek to diagonalize the energy matrix in order to get exact solutions for the energies of the adiabatic P.E. surfaces. Rather, we shall make use of perturbation theory and rely on the cardinal rule that the interaction of two nondegenerate configurations is directly proportional to the interaction matrix element and inversely proportional to the energy separation.

At this point, it should be emphasized that the ZIO or ZIDO approximations are actually mandatory for two reasons:

- a) An unambiguous definition of ground and higher excited states of a system. This is possible only when orthogonal functions are used.
- b) An unambiguous description of bonding. For example, the bonding of ground hydrogen molecule is attributed to CI at the ZIO or ZIDO level. By contrast, if overlap is included, it is ascribed to CI at $r \gg r_{eq}$ and exchange stabilization of H^+H^- near r_{eq} where H^+H^- becomes identical to $H^+H^- + H^-H^+$, appropriately normalized (21).

In general, we can distinguish between interactions of crossing and noncrossing diabatic surfaces. The two different situations are illustrated in Figure 5. The resulting maxima on the lower and minima on the higher adiabatic surfaces are noteworthy.

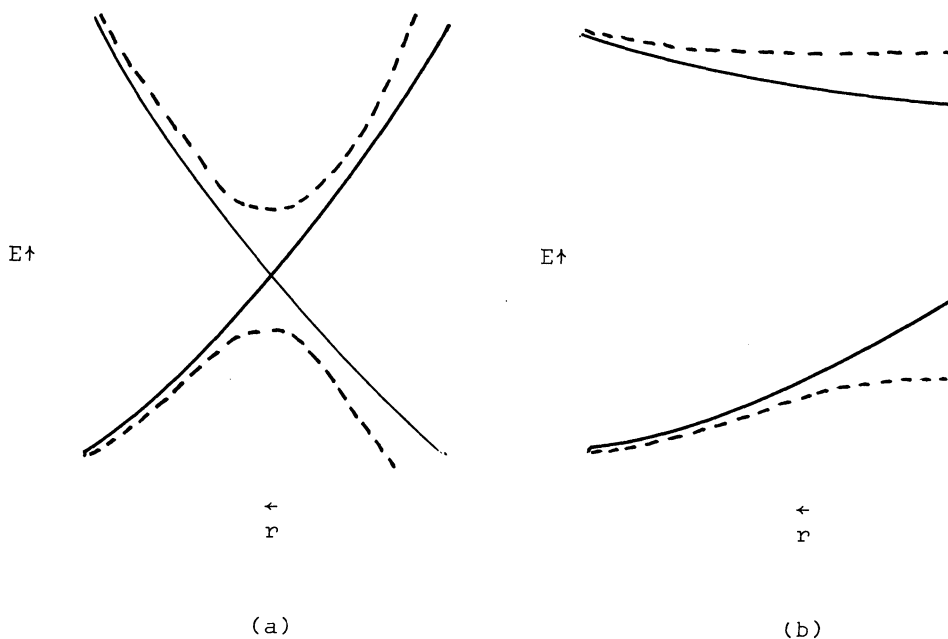


Figure 5. (a) Interaction of crossing diabatic surfaces. (b) Interaction of noncrossing diabatic surfaces. Note that as r decreases, spatial overlap and, hence, interaction increases. —: Diabatic surfaces. ----: Adiabatic surfaces.

A CLASSIFICATION OF CHEMICAL REACTIONS

The energetic interrelationships of DA and D^+A^- in thermal reactions and D^*A (or, DA^*) and D^+A^- in photochemical reactions provide the basis for a reaction classification scheme. For example, consider the four basic patterns shown in Figure 6, where it is assumed that DA and D^+A^- interact. As polarity increases, i.e., as I_{D-A} decreases, we are led from

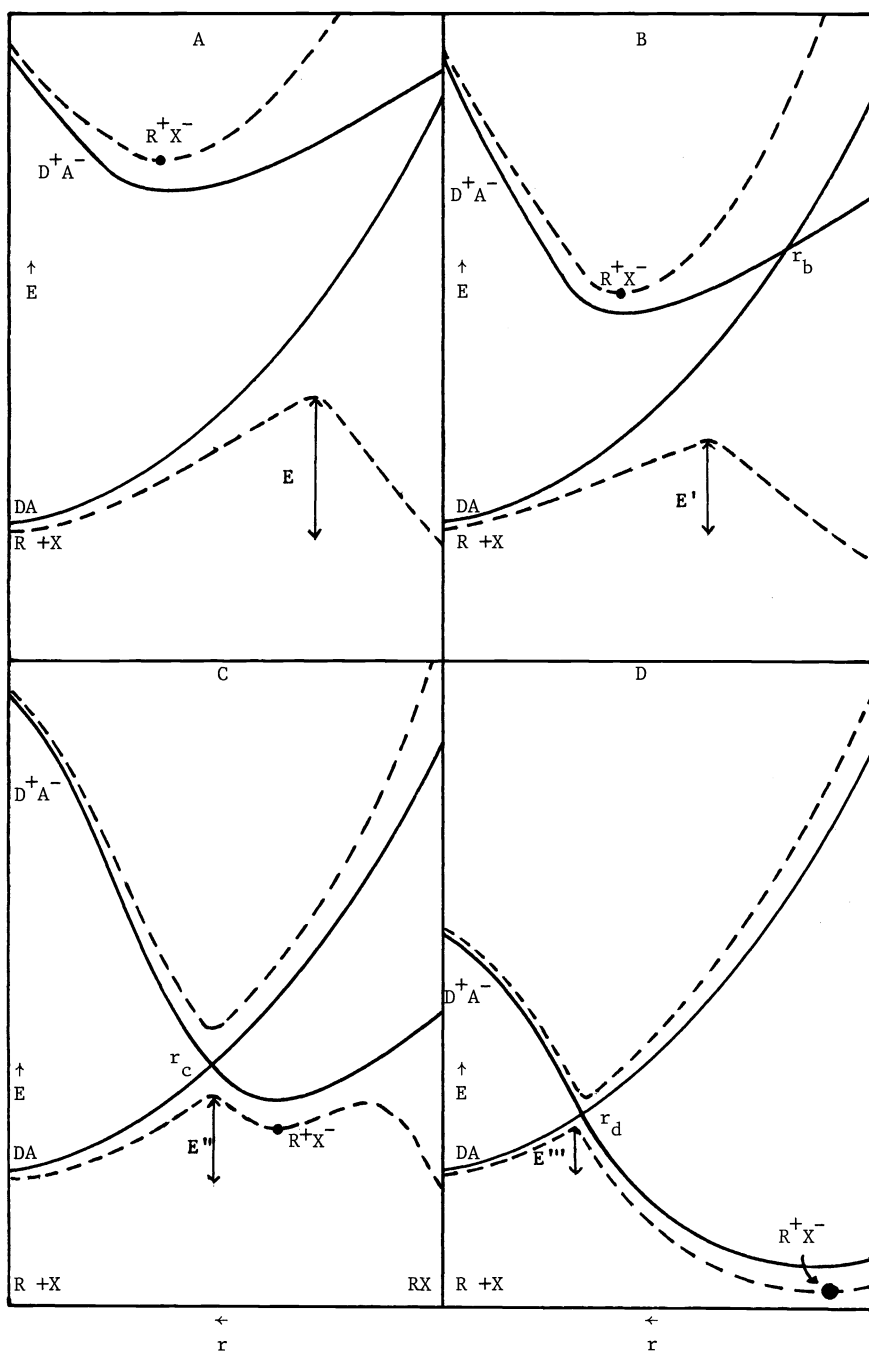


Figure 6. Classification of thermal "allowed" reactions by reference to the $DA-D^+A^-$ interrelationship. Type B $DA-D^+A^-$ late crossing is "invisible" due to strong interaction. ---: adiabatic surfaces, —: diabatic surfaces. $r_d > r_c > r_f > r_a$, $E > E' > E'' > E'''$.

situation A to situation D. In A, the ground surface has only a maximum. The same is true to B due to the fact that the $DA-D^+A^-$ crossing occurs late on the reaction coordinate where spatial overlap and, hence, interaction is still large. By contrast, in C and D this crossing comes early on the reaction coordinate and the original D^+A^- minimum is preserved, albeit modified. In the limiting case, D, the formation of a third well is prevented if R and X are "large" and repulsion is very strong.

Figure 6 amounts to a pictorial classification of thermal "allowed" reactions. A similar classification of "allowed" photochemical reactions is possible by replacing DA by D^+A^* (or DA^*). In a more general sense, we can differentiate between nonionic and ionic reactions, the former encompassing all cases where DA and D^+A^- do not cross at all or cross at relatively "tight" geometries (Figure 6 A and B) and the latter including all cases where crossing occurs at "loose" geometries (Figure 6 C and D). These definitions are operationally more useful than the ones offered before (2). Note that it is extremely hard to differentiate between type A and B nonionic situations. If the reaction is followed to the final equilibrium product geometry, a distinction should be attempted. Calculations show that, in most systems, D^+A^- has crossed DA at such geometry. For qualitative purposes, we trace the reaction to some short preequilibrium product geometry where a distinction cannot be easily made. In any event, at the level of LCFC theory, a diabatic surface touching or crossing is required for bond reorganization in "allowed" reactions. As we shall see, packet boundary crossing is responsible for the same phenomenon in "forbidden" reactions.

A COMMON LINK OF GROUND AND EXCITED STATE CHEMISTRY

As we have already discussed, appropriate substitution of a parent substrate can translate an entire diabatic surface and, hence, the corresponding adiabatic surface, upwards or downwards in energy. Solvation provides yet another mechanism for achieving a similar goal. Specifically, solvent can modify the gas phase P.E. surfaces in the following three ways:

- (a) By coordination (e.g., hydrogen bonding). This changes the intrinsic reaction polarity, intrinsic reactant excitation energies, etc. (e.g., protic solvent).
- (b) By dipolar interaction with the reactant(s) and product(s) (e.g., dipolar solvent).

All subsequent discussions apply to protic dipolar and aprotic dipolar solvents which cause a downwards translation of all adiabatic surfaces or segments thereof which involve appreciable charge separation, i.e., they selectively affect all adiabatic surfaces derived from charge transfer type diabatic surfaces. Henceforth, we group substituent and solvation effects under the heading "environmental perturbations". These are crucial for establishing a conceptual link between thermal and photochemical reactivity. One possible origin of this interrelationship is exemplified by the schematic diagram of Figure 7.

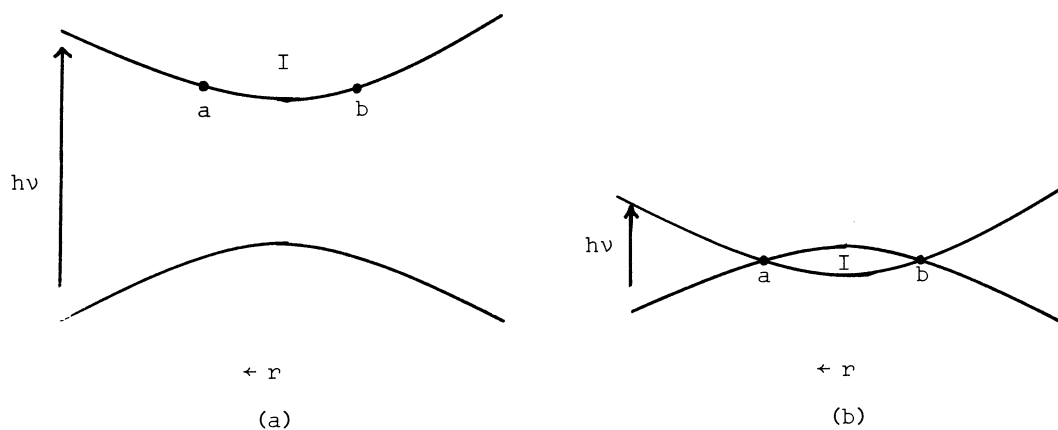
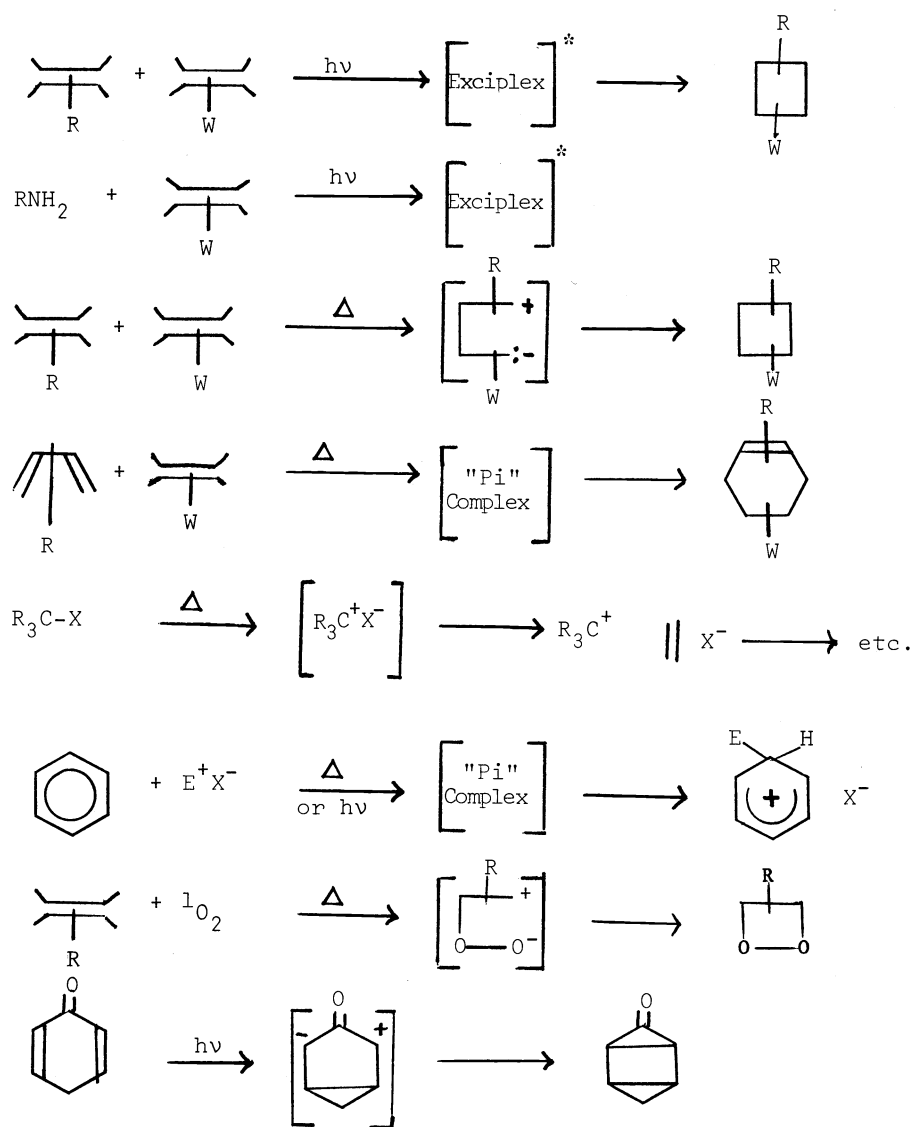


Figure 7.

In (a), the thermal reaction proceeds on the ground surface. By contrast, in (b), the reaction complex begins its sojourn on the original ground surface only to find itself eventually on an originally excited surface (segment ab) which has now become part of the ground surface under the influence of the environmental perturbation. Past b, the reaction complex returns to the original ground surface. We conclude that a photochemical study of (a) which tells us something about segment ab can also provide information about the thermal reaction (b), and conversely.

The thermal and photochemical reactions shown in Scheme 1 seem apparently unrelated. Nonetheless, they have one thing in common: They all involve an intermediate, I, whose progenitor is the D^+A^- diabatic surface modified by CI. The term "photochemical" merely conveys the fact that we approach I from "above" by excitation, while the term "thermal" means that we approach I from "below" by thermal activation. We now consider specific examples of surface crossings under the influence of environmental perturbations.

Scheme 1



$2\pi_s + 2\pi_s$ CYCLOADDITIONS

The necessary configurations grouped in three packets are shown in Figure 8. Only one electron intrapacket interactions of the $\text{HO}^{\text{D}}-\text{HO}^{\text{A}}$ and $\text{LU}^{\text{D}}-\text{LU}^{\text{A}}$ type are possible.

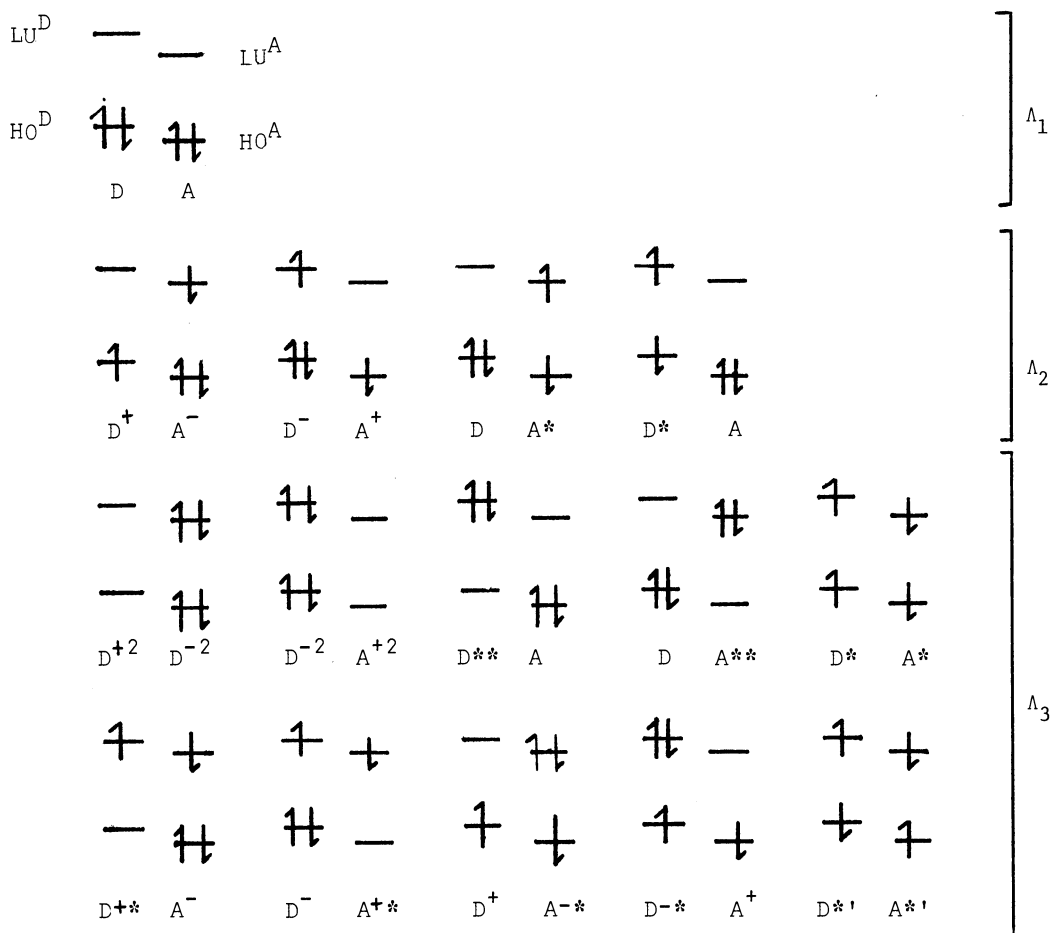


Figure 8.

The final crucial adiabatic surfaces are the boundaries of the three packets, Λ'_1 , Λ'_2 and Λ'_3 . In a typical nonpolar case, Λ'_2 is made up primarily of D^+A^- , D^*A^* , while Λ'_3 receives a dominant contribution from D^*A^* . In all cases, Λ'_1 is made up only of DA . It follows that increasing the donor ability of one reactant and the acceptor ability of the second will primarily affect Λ'_2 . Ultimately, we make a transition from the situation depicted in Figure 9a to the one depicted in Figure 9d. The same can be achieved by increasing the solvent polarity.

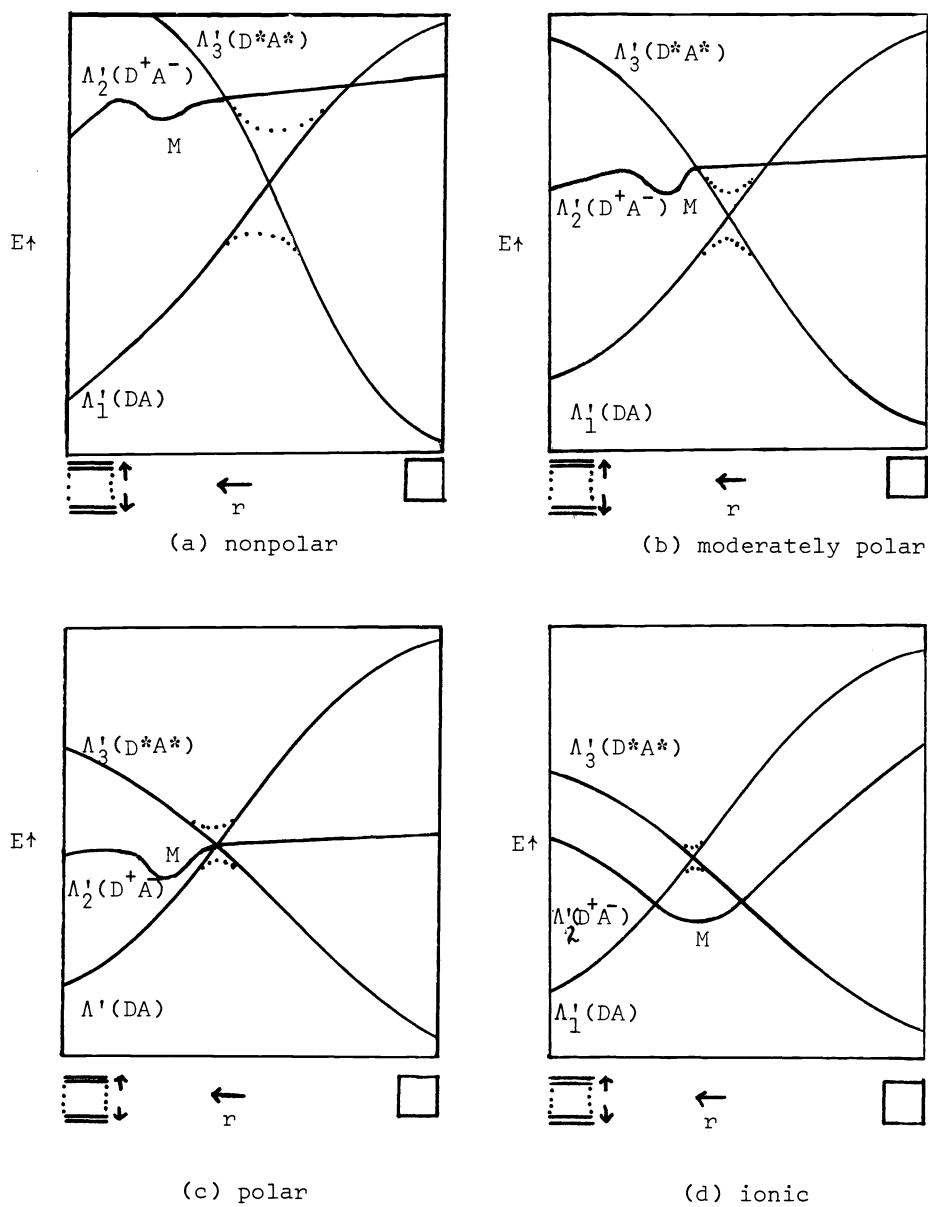
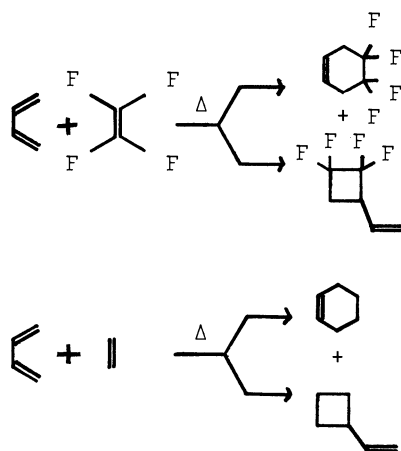


Figure 9

The P.E. surface manifolds for nonionic and ionic $2\pi_s + 2\pi_s$ cycloadditions suggest points of common interest for investigations of thermal and photochemical reactions. I will only provide two examples.

The height of the thermal barrier of a $2\pi_s + 2\pi_s$ cycloaddition depends on the energy of D^*A^* , i.e., the triplet energies of the two reactants, as a function of the reaction coordinate. As the two reactants approach each other there is progressive pyramidalization of the union sites. Realizing that a planar $3\pi\pi^*$ olefin amounts to two coupled pi radicals, we can ask how substituents will affect the tendency for pyramidalization. It is known that increasing fluorination tends to make the preferred conformation of a methyl radical approach a tetrahedral geometry (22). Thus, we can predict that $3\pi\pi^*$ ethylene will be disposed towards pyramidalization much less than $3\pi\pi^*$ tetrafluoroethylene.

In the reactions shown below polarity remains relatively constant.

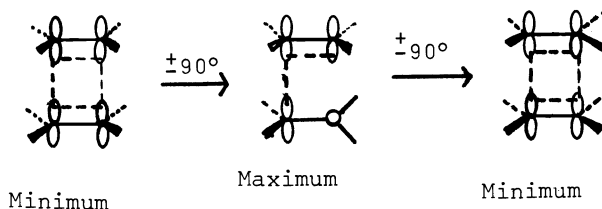


However, Λ^3 descends much faster in the $2\pi_s + 2\pi_s$ addition of $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ and $\text{CF}_2=\text{CF}_2$ than in the $2\pi_s + 2\pi_s$ addition of $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ and $\text{CH}_2=\text{CH}_2$. Thus, it is not surprising to find that, in the former case, the symmetry "forbidden" path is actually more favorable than the symmetry "allowed" one, in contrast to the latter case where normal expectations are met (23).

A comparison of Figures 9a and 9d shows that the "exciplex" of the "allowed" $2\pi_s + 2\pi_s$ photoaddition has become the "dipolar intermediate" of the "forbidden" $2\pi_s + 2\pi_s$ thermal addition. 4N pi electron nonionic photocycloadditions can lead to s+s stereoselective product formation via the intermediacy of exciplexes. The important work of Huisgen has illuminated the features of thermal ionic $2\pi + 2\pi$ cycloadditions (24,25). These reactions also proceed in a stereoselective or even stereospecific s+s manner (26). The reason for this is threefold.

(a) The noninteracting diradical D^+A^- has higher energy than the $D^+A^- + \lambda DA^* + \lambda'D^*A$ $2\pi_s + 2\pi_s$ complex. Put in different language, the M intermediate involves pericyclic bonding.

(b) Since the intermediate M materializes early on the reaction coordinate, the barrier to internal rotation is high.



This is due to the fact that the barrier height depends on the $DA-D^+A^-$ interaction which tends to zero as spatial overlap goes to zero.

(c) The cisoid M intermediate is formed faster than the TB intermediate (2) due to coulombic effects which can dominate orbital overlap effects whenever the transition state preceding the M intermediate occurs at long intermolecular distance. In our case, the early crossing of DA and D^+A^- is responsible for a loose transition state. As a result, the energy gaps separating various stereochemical paths due to orbital overlap effects are small and coulombic effects can take over.

The difference in stereoselectivity between nonionic and ionic thermal $2\pi + 2\pi$ cycloadditions can be appreciated by reference to Figure 10. Heavy lines indicate the preferred path and "classical" structures are used rather than the more appropriate delocalized ones (*vide infra*).

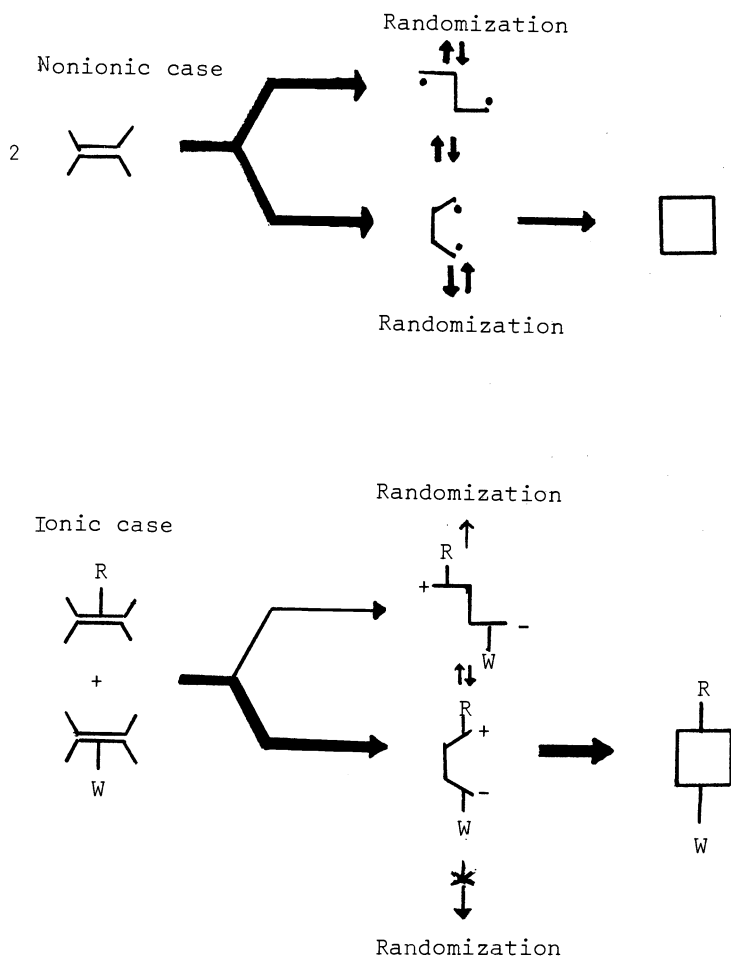


Figure 10

Of the three arguments (a), (b) and (c) presented above, only one, namely (a), can be formulated using a static theoretical model; (b) has to do with transition state and intermediate structure and (c) is a statement of the selectivity-polarity interrelationship in ionic reactions. Both of these arguments cannot be developed on the basis of any theory which does not involve at some stage the construction of P.E. surfaces. Argument (c) will be better understood when we return after a small detour to the all important problem of selectivity.

Photocycloadditions of appreciable polarity and ionic thermal cycloadditions have a common important characteristic which is, in fact, peculiar to any reaction where the rate determining step involves surmounting a barrier which is created by the early crossing of

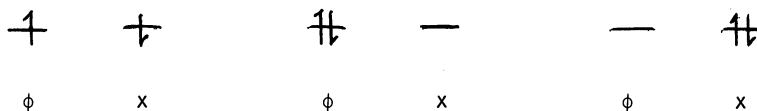
an ascending curve of the no bond or local excitation type and a descending curve of the charge transfer type. In reactions of this type, the transition state involves a very loose association of the reactants. As polarity increases and spatial overlap at the transition state tends to zero, the rate ratio for any two regiochemical or stereochemical union modes approaches unity. How fast this limit is achieved depends on differences in overlap, coulombic attraction, and steric repulsion between the two modes which are being compared. The latter two effects (and energy wastage in polar photoreactions) may, in fact, cause a reversal of normal selectivity (2).

At this point I make a brief digression in order to point out that Figure 9 shows how Hückel diradical states (26) are reordered under the influence of environmental perturbation. Since this is central to the understanding of the mechanism of "forbidden" reactions, I translate the LCFC theory to the more familiar MO language.

THEORY OF DIRADICALS (27)

Consider the $2\pi + 2\pi$ cycloaddition of two ethylenes. At some point along the reaction coordinate, two MO's (ϕ and x) become degenerate. At precisely this stage, we have a diradical for which three singlet states can be defined using the following configurations:

Configurations



$$\text{States: } K = \frac{1}{\sqrt{2}} [|\phi\bar{x}| - |\bar{\phi}x|]$$

$$L = \frac{1}{\sqrt{2}} [|\phi\phi| - |x\bar{x}|]$$

$$M = \frac{1}{\sqrt{2}} [|\phi\phi| + |x\bar{x}|]$$

All three states have the same one electron energy and are differentiated by their relative two electron repulsive energies. A consideration of the shapes of the MO's shown schematically in Figure 11a leads to the conclusion that the singlet state order is $K > M > L$. The lowest singlet diradical state has the appearance of a diradical structure (III).

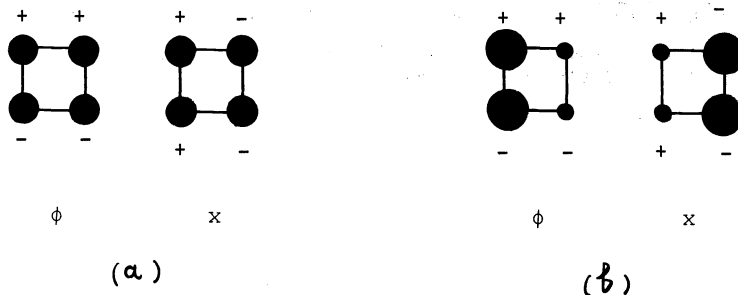
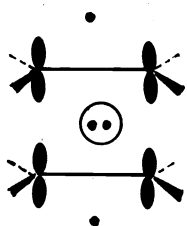


Figure 11

Once one ethylene is transformed to a strong donor and the other to a strong acceptor by appropriate substitution, the degenerate MO's, ϕ and x , assume a different look (Figure 11b). When the condition $0.5(J_{\phi\phi} + J_{xx}) - J_{\phi x} > 2K_{\phi x}$ is fulfilled the singlet state order

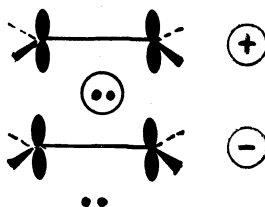
becomes $M \gg L > K$. The lowest singlet state has now the appearance of a zwitterionic structure (IV). To put it crudely, we have made a transition from a type (b) to a type (c) state correlation diagram (Figure 2). This analysis predicts that $2\pi + 2\pi$ photocycloadditions of modest polarity conforming to a type (b) state correlation diagram are possible.

DIRADICAL



(III)

ZWITTERION



(IV)

The message of the above analysis is clear: the term diradical has no meaning unless the relevant state is specified. This is so because there is no universal state ordering. Rather, this depends crucially on the environmental perturbations. Parenthetically, we note that diradical state reordering can also be enforced by factors other than polarity such as differential steric strain of reactants and products.

$4\pi_s + 2\pi_s$ CYCLOADDITIONS.

$2\pi_s + 2\pi_s$ cycloadditions constitute the simplest general models of Hückel antiaromatic reactions. In the same vein, $4\pi_s + 2\pi_s$ cycloadditions are the simplest general models of Hückel aromatic reactions. The P.E. surfaces shown in Figure 12 show a second type of thermal-photochemical connection. In this case, the environmental perturbations translate the excited D^+A^- diabatic surface and subsequent interpacket interactions product totally different adiabatic surface manifolds for nonionic and ionic reactions. Note the similarity of figures 6A and 12d as well as figures 6C and 12b. The important lesson here is that perturbed thermal aromatic or nonaromatic reactions can occur via the intermediacy of dipolar species. If the perturbation of D^+A^- is very large, formation of any ion pair devoid of any pericyclic bonding is expected.

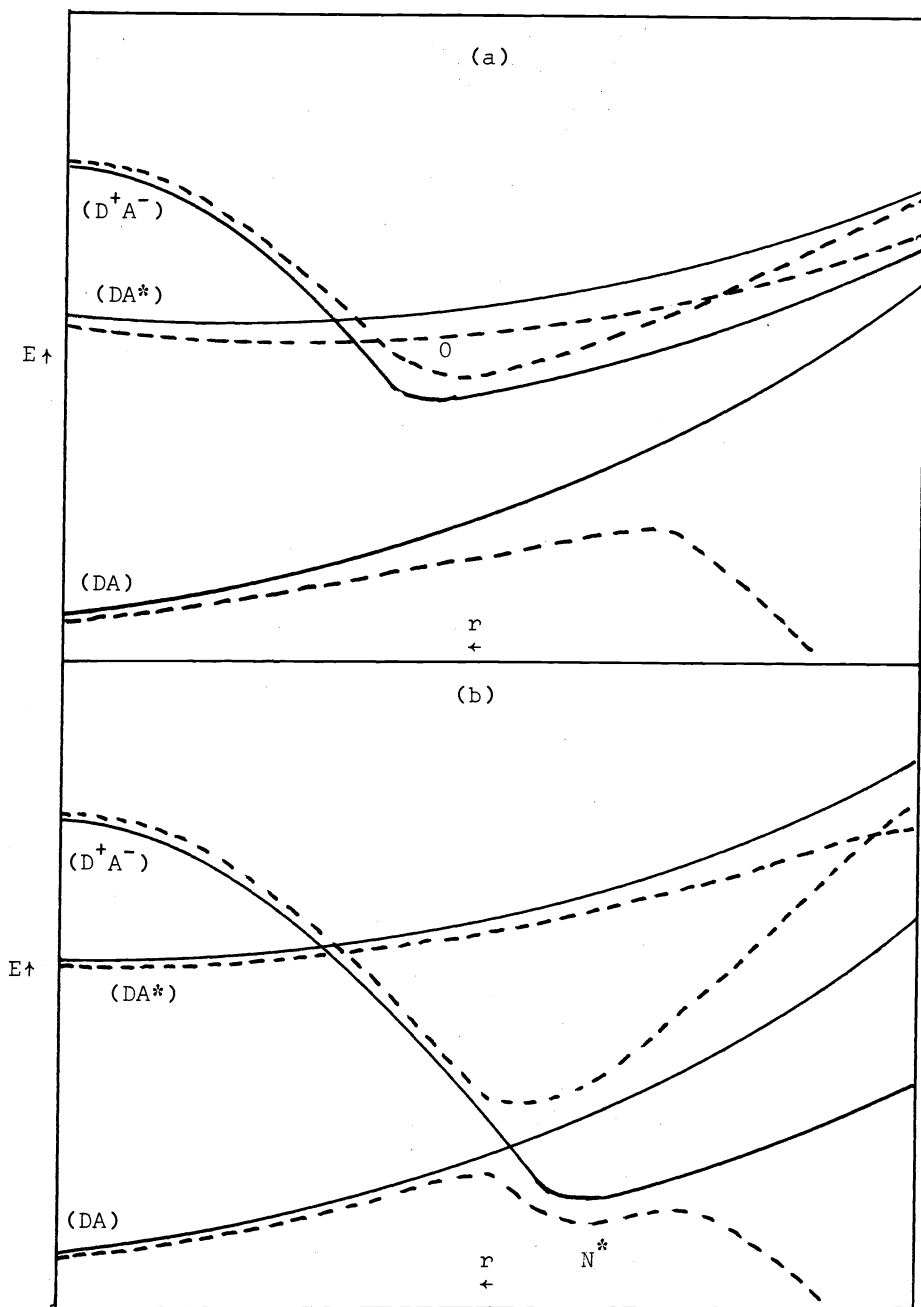


Figure 12

An important difference between the O and N^* dipolar intermediates derived from the D^+A^- diabatic surface merits attention. Specifically, the former involves an antibonding and the latter a bonding contribution of DA . Hence, a study of O can reveal important information regarding N^* (or, vice versa) only if the $DA-D^+A^-$ interaction is negligible.

By contrast, if the latter interaction is dominant, the electronic selection rules for maximization of the stability of O and N^* will be opposite.

CHEMICAL SELECTIVITY

With the background of the preceding sections, let us now attempt to answer the following often asked question:

- (a) Why does product distribution vary from reaction to reaction?
 (b) Why are "forbidden" reactions nonstereoselective in some instances and stereospecific in others?

These problems can now be tackled within the framework of the theory of chemical selectivity formulated on the basis of LCFC qualitative P.E. surfaces. The salient features of our approach are discussed below.

First, consider the case of two diabatic surfaces A (no bond or local excitation type) and B (charge transfer type) which describe a bimolecular reaction of two molecules D and A to yield product P . Furthermore, assume that this reaction can occur in two chemically distinct modes, one called F (Favored) and the other U (Unfavored) such that $S(F) > S(U)$ where $S(X)$ is the overlap integral of A and B for mode X . For example, D can be anisole, A an electrophile, A a DA surface, B a D^+A^- surface, F para attack, and U ortho attack since $S(\text{para}) > S(\text{ortho})$. In such a case, we deal with regioselectivity. Alternatively, D can be a donor olefin, A an acceptor olefin, A and B as above, F $2\pi_s + 2\pi_a$ union, and U $2\pi_s + 2\pi_s$ union since $S(2\pi_s + 2\pi_a) > S(2\pi_s + 2\pi_s)$. In such a case we deal with stereoselectivity. We can now examine two different situations.

- (a) A and B do not cross at all (Figure 6A) or they cross late (Figure 6B).

In such a case, selectivity is a function of $[S(F)^2 - S(U)^2] / \Delta E$, where $S(X)$ and ΔE are evaluated at a fixed intermolecular distance $r \gg r_{eq}$ since $S(X)^2 / \Delta E$ has the meaning of a slope (2). We predict that selectivity increases as polarity increases.

- (b) A and B cross early (Figure 6C). In such a case, selectivity is a function of $S(F) - S(U)$, where $S(X)$ is evaluated at the intermolecular distance at which crossing has occurred, i.e., $r = r_c$. Since $S(F) - S(U)$ is a function of spatial overlap and because increased polarity leads to earlier crossing, we predict that selectivity decreases as polarity increases.

The above predictions are valid if steric and coulombic attractive effects are comparable. The former are deemphasized and the latter become relatively more important when curves cross early. Stated in different language the attraction of an excess electron with a positive hole characteristic of a charge transfer diabatic surface is a second order effect when A and B do not cross and a first order effect when they cross early. Hence, in type (b) situations coulombic effects will operate so as to favor a "crowded" geometry.

Let us now consider what happens if F is a symmetry "allowed" and U a symmetry "forbidden" multicentric mode. The F mode will occur with high F stereoselectivity while the U stereoselectivity of the U mode will vary with polarity such that it will increase with increasing polarity. This occurs because the reactant bonds are less perturbed at the transition state which resembles (nonionic cases) or precedes (ionic cases) the diradical. The same is true of the diradical intermediate itself. As a result, a higher barrier to internal rotation will become responsible for greater U stereoselectivity.

We suggest that the above analysis constitutes the first realistic, though far from perfect, solution of the riddle of chemical selectivity. We can hardly overemphasize that this overview has been obtained by focusing on the entire reactivity range. In the past, claims have been made that single model theoretical treatments could, in principle, provide an understanding of chemical selectivity. We forcefully maintain that there is no such

possibility and that the only (computationally "painful") way to understand chemical selectivity is through a comparative study of P.E. surfaces.

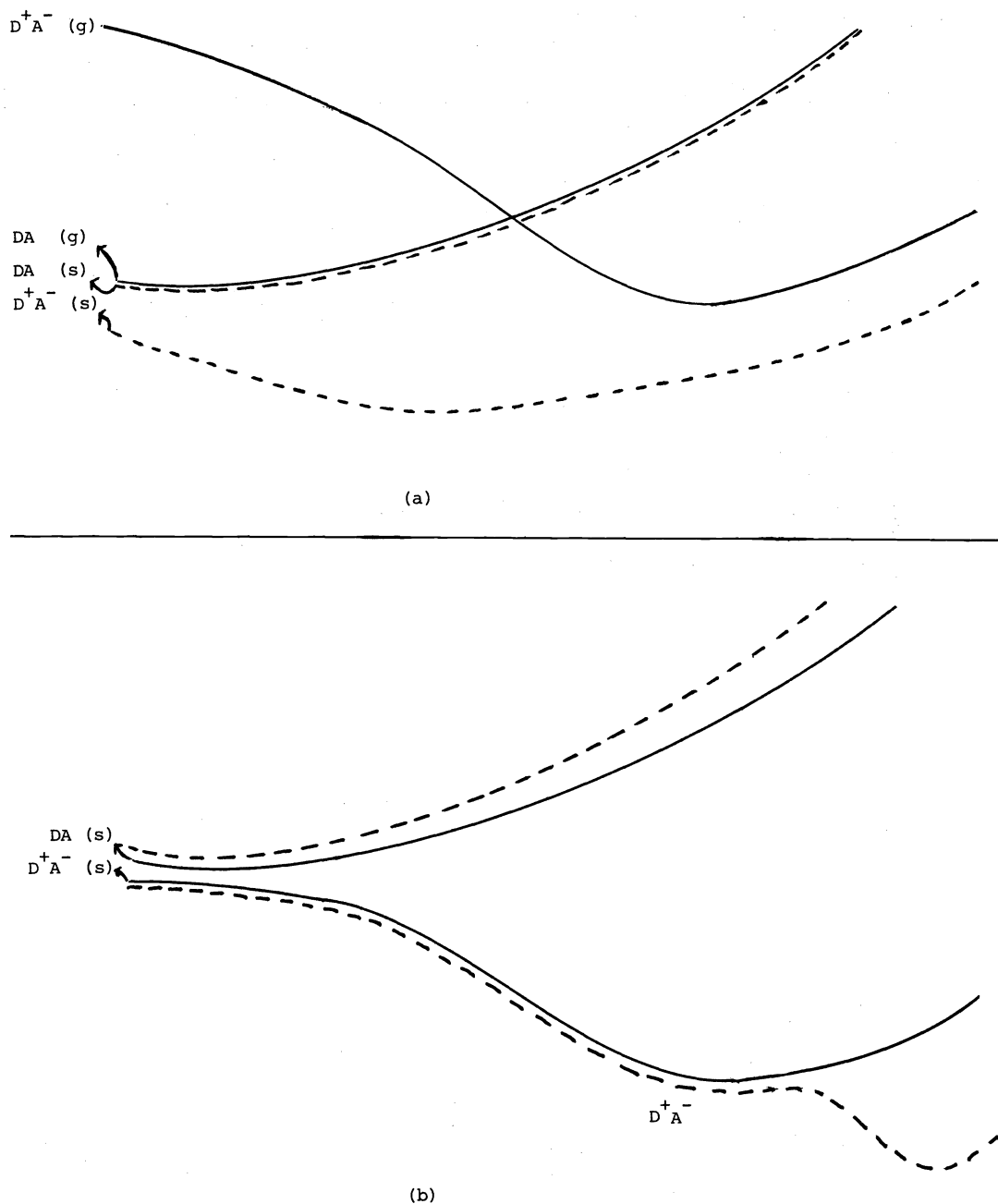


Figure 13

Figure 13. (a) Gas (g) and Solution (s) phase diabatic surfaces. (b) Diabatic (solid lines) and adiabatic (dashed lines) surfaces for solvolysis.

BOND HETEROLYSIS

Bond heterolysis is probably the most extensively studied chemical reaction; in a sense, it is the foundation of physical organic chemistry. On the other hand, it is the least understood subject. That is to say, many trends have been recognized, but recognition does not imply understanding. A bewildered student faced with "polarizability", "basicity", "hyperconjugation", "solvation", etc., finds that he can rationalize any single experimental fact without understanding why it is necessary to switch from one type of explanation (e.g., "basicity") to another (e.g., "polarizability") depending on the problem at hand. With the aid of qualitative P.E. surfaces, we have made a frontal attack on the complex problem of bond heterolysis. A preliminary report follows. This, taken in conjunction with our discussion of cycloadditions, should convince the reader that there is a cosmic simplicity in the trends of all chemical reactions.

In bond heterolysis, the initial state is a covalently bound molecule $\underline{D-A}$ and the final states can be the "intimate" ion pair $\underline{D^+A^-}$ or the solvent separated ion pair $\underline{D^+} \quad \underline{A^-}$, whichever has lower energy. Solvent separated ion pairs can be treated satisfactorily in a classical manner. By contrast, the LCFC approach yields new insights regarding the electronic nature of "intimate" ion pairs and all heterolytic processes which involve formation of such intermediates in the rate determining step. Consequently, we focus attention on the rates of solvolytic reactions which typify heterolytic processes of the latter type.

Solvation must be treated as a strong perturbation of the charge transfer type diabatic surfaces as illustrated in Figure 13. Effectively, it causes a change from type B to type C reaction (Figure 6). Henceforth, we focus exclusive attention on the energetics of the "intimate" ion pair $\underline{D^+A^-}$ with the aid of LCFC interaction diagrams.

Figure 14 shows the gas and solution phase configurations as well as the final electronic states of the "intimate" ion pair described at the minimal basis set level. Under the assumption that the energetics of the $\underline{D^+A^-}$ intimate ion pair parallel the energetics of the transition state involved in the $\underline{D-A} \rightarrow \underline{D^+A^-}$ transformation, the following predictions can be made.

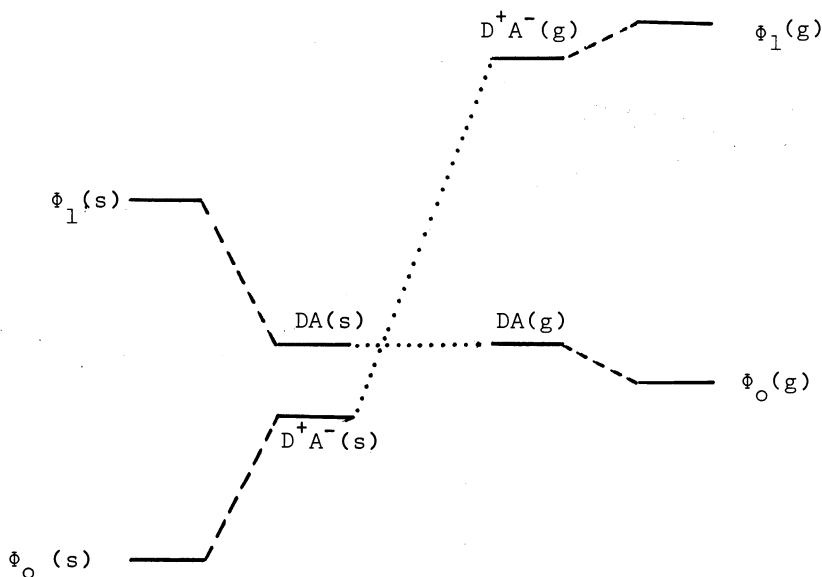


Figure 14

(a) The stability of the "intimate" ion pair depends principally on the $DA(s) - D^+A^-(s)$ interaction as well as the interaction of $D^+A^-(s)$ with higher lying configurations of the charge transfer [e.g., $D^-A^+(s)$], local excitation [e.g., $DA^*(s)$] or diexcitation [e.g., $D^*A^*(s)$] type. The key $DA(s) - D^+A^-(s)$ interaction decreases as the incipient carbenium ion becomes more stable and the $DA(s)-D^+A^-(s)$ energy gap, ΔE , increases. At the limit of very large E , the relative stability of two ion pairs will approximate that of the corresponding "naked" carbenium ions.

(b) If a substrate can yield two epimeric ion pairs, (e.g., exo and endo, syn and anti, etc.), their energy difference will tend to zero as the incipient carbenium ion becomes more stable and the $DA(s)-D^+A^-(s)$ energy gap increases. This is yet another application of the chemical selectivity concepts discussed before.

(c) If a substrate can yield "classical" and "nonclassical" (i.e., sigma bridged) cations of comparable stability [e.g., 2-norbornyl halide (28)], the energy difference of the corresponding ion pairs will be controlled principally by the $DA(s)-D^+A^-(s)$ interaction. This always favors the "classical" ion pair as illustrated in Figure 15.

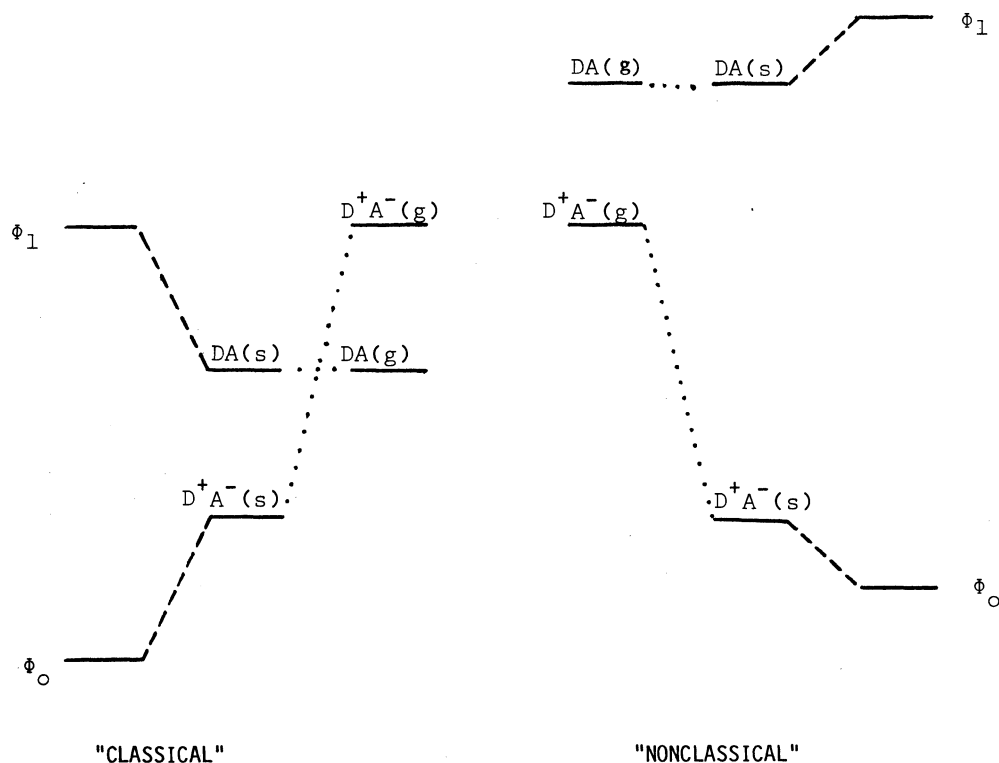


Figure 15. The difference between "classical" and "nonclassical" ion stabilization. The "classical" and "non classical" gas D^+A^- configurations are assigned equal energies [see ref.(28)]. It is assumed that solvation energies are also comparable.

(d) The geometry of the ion pair will depend on the strength of the $DA(s)-D^+A^-(s)$ interaction. In primary systems, ΔE is relatively small and interaction strong. The preferred geometry is the one which maximizes the interaction, i.e., a near tetrahedral geometry. In tertiary and stabilized systems, ΔE is relatively large and interaction weak. Hence, a number of different geometries have comparable energy.

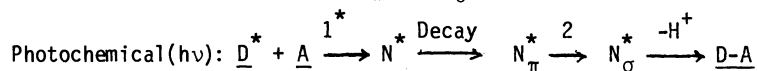
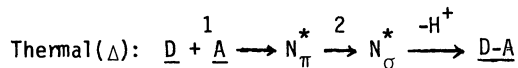
(e) As solvation power increases and the $DA(s)-D^+A^-(s)$ energy separation increases, the

relative stability of two ion pairs having a common counteranion tends to equal the relative stability of the two corresponding "naked" carbenium ions.

AROMATIC SUBSTITUTION

When the electrophilicity or nucleophilicity of a reagent is intrinsically high, ionic reactions occur. Aromatic substitution is a typical case.

The qualitative surfaces for Electrophilic Aromatic Substitution (EAS) have been published (2). The reaction mechanisms can be written as shown below.



\underline{D} = Aromatic Substrate, \underline{A} = Electrophile, TS = Transition State

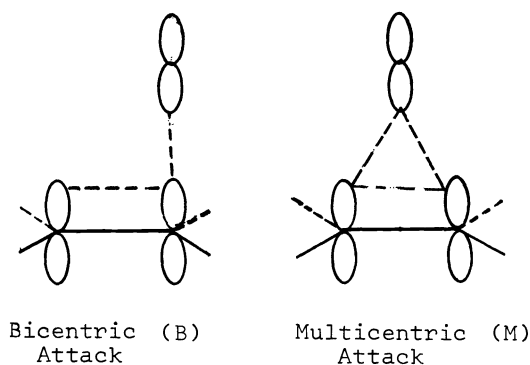
A similar mechanism can be written for Nucleophilic Aromatic Substitution (NAS) with D = Nucleophile and A = Aromatic Substrate.

The following regiochemical rules have been proposed:

Reaction	Barrier Optimization	Decay Optimization
EAS, Δ	HO Max.	-
EAS, $h\nu$	LU Max.	HO Min.
NAS, Δ	LU Max.	-
NAS, $h\nu$	HO Max.	LU Min.

The symbol Max. means that the corresponding overlap integral should be maximized. Min. stands for minimization. The rules have been applied to diverse thermal and photochemical reactions under the assumption that the initial formation of N_{π}^* involves bicentric attack.

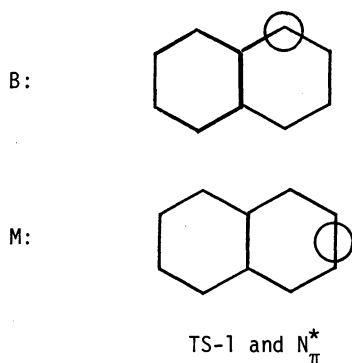
This is a reasonable assumption since a multicentric complex can achieve superiority over a bicentric complex only at tighter geometry due to differences in spatial overlap. As a result, steric effects may affect adversely the otherwise electronically favorable multicentric attack.



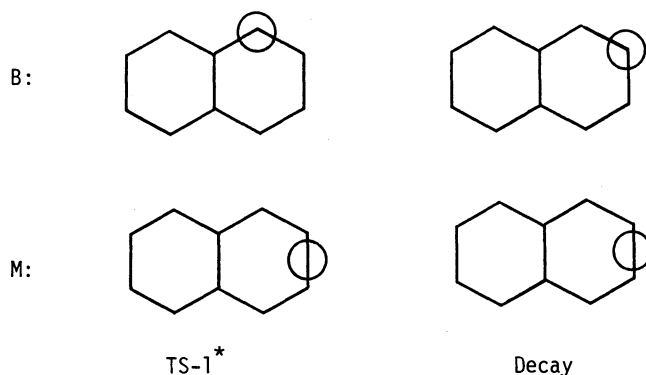
In the case of monosubstituted benzenes, both B and M models lead to identical predictions. Nonetheless, it is of interest to examine whether there are grounds for adopting the M model. In order to reach a decision, we must study the regiochemistry of aromatic substitution reactions where the B and M models lead to different predictions. Thermal nucleophilic and photochemical electrophilic aromatic substitution of naphthalene are critical cases. In the case of photoreaction, it is assumed that excitation is caused by a $HO \rightarrow LU$ transition and that only the singlet state is involved. The predictions of the B and M models regarding the AS orientational selectivity expressed at various critical points of the P.E. surfaces are shown in Scheme 2.

SCHEME 2

1. Thermal NAS



2. Photochemical EAS



A circle indicates the predicted position of the reagent attack. Furthermore, for illustrative purposes, it is assumed that formation of the N_{π}^* intermediate is rate determining.

Clearly, if the B model is adopted, α attack is predicted for thermal NAS, but the regiochemistry of the photochemical EAS will depend on whether traversing a barrier or decaying to the ground surface is the kinetically important step. By contrast, if the M model is adopted, β attack is predicted for thermal NAS and photochemical EAS. We suggest that the combined study of thermal NAS (EAS) and photochemical EAS (NAS) systems where the B and M models lead to different predictions will go a long way towards clarifying the controversial mechanisms of thermal aromatic substitutions and pinpointing the crucial event in photochemical aromatic substitution.

Parenthetically, it should be mentioned that the so-called "I. Repulsion Theory" provides a rationalization of the thermal β attack by nucleophiles (29).¹¹ It is argued that generating an electron pair next to fluorine is unfavorable and this is the major factor controlling orientational selectivity in thermal NAS. However, a casual perusal of the introductory section of a monograph on organic fluorine chemistry (30) reveals that "Whereas the chemistry of hydrocarbon aromatic compounds and olefins most frequently involves attack by electrophiles leading to carbonium ion-type transition states, fluorocarbon aromatic compounds and olefins more frequently undergo nucleophilic attack leading to carbanionic transition states". That is to say, while the kinetically beneficial effect of

fluorination is well-documented, " I_{π} Repulsion Theory" has as a cornerstone a kinetically adverse effect of fluorination!!! A recent scathing criticism of the Frontier Orbital method (31) can now be fully appreciated in the light of the above discussion and the following additional facts:

- (a) Burdon and Parsons (31a) fail to identify correctly frontier orbitals. As a result, an inflated number of failures is ascribed to the bicentric FO method.
- (b) Burdon and Parsons (31a) sweep conveniently under the rug cases where the " I Repulsion Theory" fails. For examples, see ref. (23), p. 284 and 241.
- (c) Proponents of the " I Repulsion Theory" have never offered theoretical justification of the so-called I_{π} Repulsion orders (e.g., F more repulsive than Cl, etc.).

We have examined this last problem and an example will suffice to illustrate the difficulties.

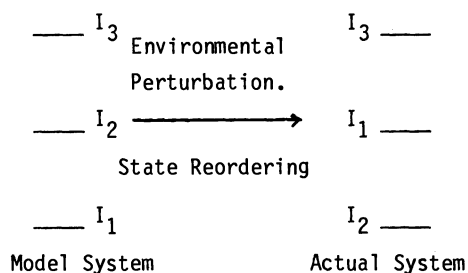
I_{π} repulsion can be thought of as the combined effect of coulomb and overlap repulsion. If one considers the F/Cl pair, it can be shown that coulomb repulsion is greater for F. By contrast, there is ambiguity insofar as overlap repulsion is concerned. Here, the ϵ_0 term favors F, but the k term works in an opposite direction (32). Clearly, the repulsive order will depend on the relative magnitudes of the various quantities.

THE SUPREME IMPORTANCE OF QUALITATIVE THEORY: A TOOL FOR
EXPERIMENTALISTS AND CLASSICAL THEORETICIANS ALIKE.

The experimentalist can use the results of qualitative theory to test new mechanistic schemes and design novel synthetic pathways. However, the classical theoretician who is primarily concerned with a "quantitative" prediction also stands to gain a lot. For qualitative theory can suggest that certain computations run a high degree of risk of being wrong, while others are irrelevant to the problem at hand, though they may lead accidentally to the "right" result. In the space below, I provide typical examples.

1. Wrong computations. We have shown that, in comparing two heteroatoms of a column of the Periodic Table, the relationship of the heteroatom energy levels and those of the substrate to which they are attached is critical (33). For example, in $\text{CH}_2=\text{CHX}$, we expect SH to be a weaker pi donor than OH with the trend reversing in the case of $\text{CH}_2\lambda$. For intermediate cases, "quantitative" calculations will yield the wrong answer unless they reproduce, in effect, the correct stacking of energy levels. Qualitative theory can warn against placing undue reliance on calculations of such systems.

2. Irrelevant calculations. Our discussion of singlet biradical states implies that one must calculate the actual system including any solvation effects rather than relying on model calculations. For example, the lowest energy diradical involved in the actual reaction is not necessarily the same as that involved in the model reaction, as illustrated below.



Predicting that I_1 should be the lowest energy intermediate through which the model reaction must go may be totally irrelevant to the actual reaction. Once again, qualitative theory can warn against inappropriate utilization of model systems.

3. Accidentally successful calculations. Our discussion of bond heterolysis suggests that computations of naked ions are pertinent for gas phase and, probably, strong acid solution studies. They can also be very useful in probing the effect of ion pairing in solvolysis. However, taken by themselves, they have no meaning insofar as solvolysis is concerned. Thus, any "successes" in predicting or correlating the solvolytic behavior by ab initio computations of naked ions must be regarded as accidental.

CONCLUSION

About seven years ago, I submitted a series of papers to the Journal of the American Chemical Society dealing with the stereochemistry of multicentric reactions (34). Three seminal ideas were contained in the first paper of this series:

- (a) The idea of surface crossing (D^+A^- below DA) resulting in reversal of stereoselectivity embodied in Figure 8 of ref. 34a.
- (b) The idea that a noninteracting diradical (D^+A^-) has a higher energy than the corresponding "forbidden" ($2\pi_s + 2\pi_s$) state also embodied in the same Figure.
- (c) The idea that solvent can primarily affect the transition state of the more polar ("forbidden") reaction thus causing unexpected shifts in stereoselectivity.

A general LCFC theory of organic reactions was proposed based to a large extent on these and other ideas (20g). From this base, we have launched what may well be our final attack on reactivity. In our work, the qualitative LCFC P.E. surfaces have replaced once and for all interaction and correlation diagrams. This has led to the crystallization of a viewpoint which I have attempted to project in this lecture: There are only artificial barriers separating "photochemists", "thermal chemists", "theoreticians", etc. For example, the photochemical hydrogen abstraction and the thermal S_N2 reaction seem totally unrelated. Nonetheless, the P.E. surfaces reveal interesting similarities (Figure 16). A comparative study of these two reactions will go a long way towards providing a better understanding of reactivity, in general. A superchemical approach of this type is what I envision to be the way of the future.

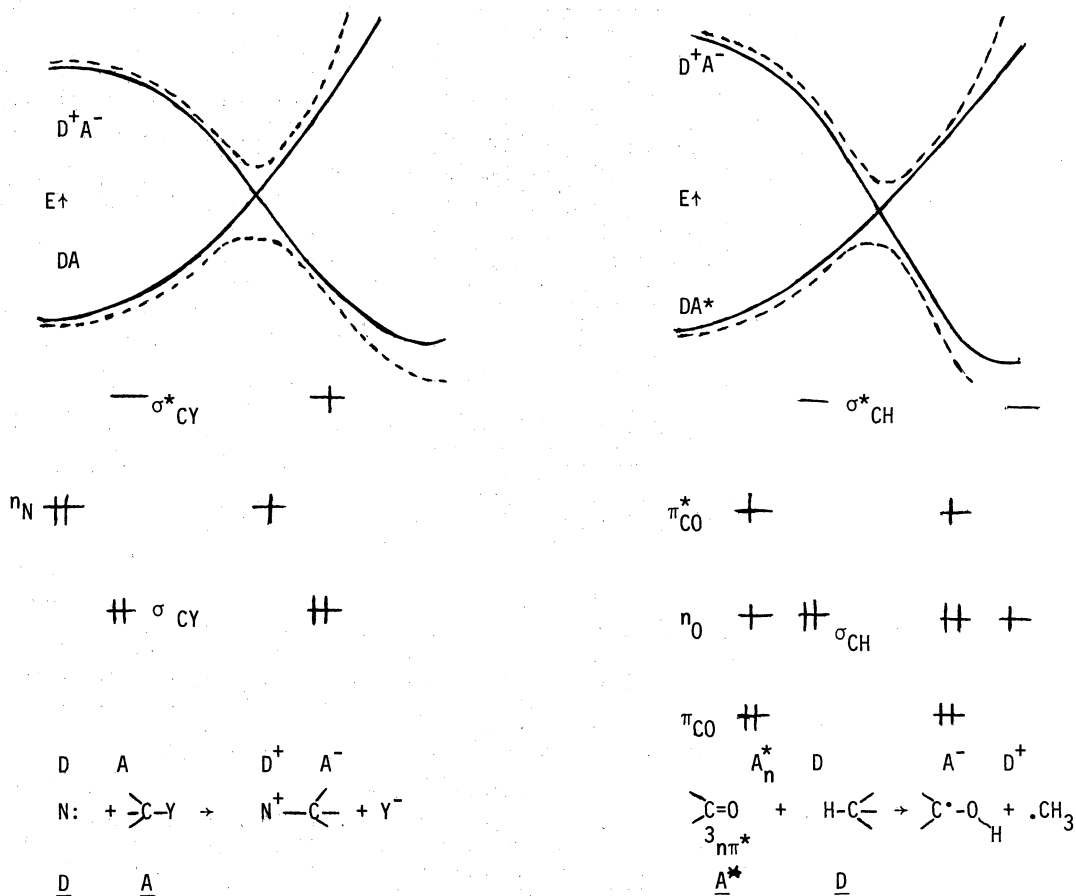
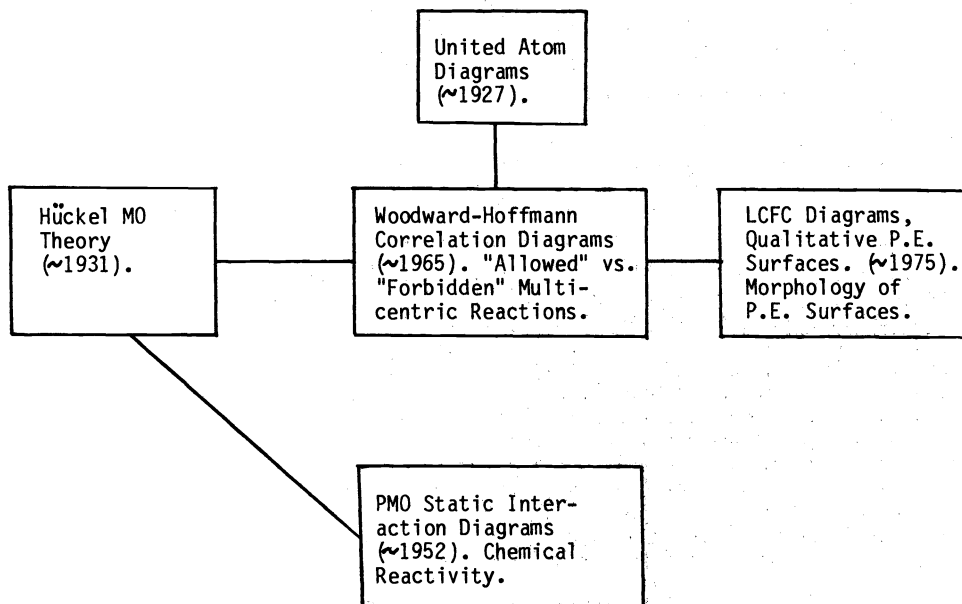


Figure 16. The similarity of thermal S_N2 and photochemical hydrogen abstraction is $3n\pi^*$ carbonyl. The barrier of the former is controlled by the $n-\sigma^*_{CY}$ interaction; the barrier of the latter by the $n-\sigma^*_{CH}$ interaction.

The theory of chemical reactivity has evolved in the manner schematically indicated below. Needless to say, this is only a gross outline of past and present theoretical



approaches which seem to have attracted the attention of the great majority of theoreticians and experimentalists. The transition from united atom to correlation diagrams was spurred by the realization that orbital symmetry is important in chemical reactions. The transition from correlation diagrams to LCFC diagrams espoused in our work is advocated on the basis that only the latter can provide information about the morphology of P.E. surfaces, i.e., the presence of barriers, intermediates, decay channels, etc. After all, these are the reactivity aspects which are most fascinating to the experimental chemist.

That this is only a beginning towards a better understanding of reactivity, I hold to be self evident. Clarification, refinements and even revisions are likely to follow. Is it possible that secondary minima (e.g., N^*) in "allowed" time reactions exist only due to solvent coordination? What is the magnitude of the ion pairing effect? etc. The situation is not unlike the one encountered in atomic and molecular electronic spectroscopy where the identification of an excited state can be a formidable problem: Is it $n\pi^*$ or $\pi\pi^*$? Is it $n\pi^*$ singlet or triplet? Is it valence or Rydberg? These are recurring worries of spectroscopists and theoreticians alike. Our work emphasizes the necessity for identification of the electronic state of a "transition state", a reactive intermediate, etc., and provides a general methodology for attacking the problem. We envision a fusion of thermal and excited state chemistry with the common purpose of pinpointing the molecular and supermolecular electronic state responsible for physical and chemical change.

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