

TOWARDS A UNITED THEORETICAL TREATMENT OF THE TRANSITION STATE IN THE REACTIONS OF UNSATURATED MOLECULES—I GENERAL THEORY

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Abstract.—An attempt is made to develop a unified theoretical treatment of the transition state in the reactions of unsaturated molecules. By careful choice of parameters, this treatment is shown to encompass both the Wheland and the delocalized models of the transition state.

INTRODUCTION

NUMEROUS attempts to apply quantum chemistry to the chemical reactivity of conjugated molecules have been made with varying degrees of success. These attempts can be divided into two basic methods: one static, the other dynamic.

The static method is based upon static indices such as bond order, free valence, charge density and frontier orbital coefficients. The successes of this method have been the subject of several reviews.¹⁻⁴ Despite these successes there have been numerous failures particularly when applied to substitution reactions of heterocyclic compounds. For example, the nucleophilic substitution of pyridinium ion occurs at position 4 for cyanide ion and at position 2 for hydroxide ion. Charge densities predict reaction at position 2 while frontier orbital coefficients predict reaction at position 4 for both ions. Since the use of static indices to predict chemical reactivity is based upon properties of the ground state of the molecule being attacked, and neither the attacking reagent nor the transition state is taken into account, this method has little chance of succeeding when applied to a wide range of chemical reactions.

A logical improvement in the static method is to take into account the transition state of the reaction. This is the basis of the dynamic method. In order to calculate any of the properties of the transition state, however, it is necessary to know its geometry. Unfortunately, this information is rarely available. Therefore calculations based upon this method have usually adopted the Hückel approximations and applied them to one of two models of the transition state. These two models are the Wheland and the delocalized model.

The Wheland model⁵ proposes a transition state in which there is a decrease in the extent of the delocalization of the π electrons relative to the starting molecule. The energy lost, which is the energy needed to localize two electrons at the center of reaction, is called the localization energy. This model is illustrated in Fig. 1 for an electrophilic substitution reaction on naphthalene.

Several theoretical calculations have been made using this model.¹ However, the attacking reagent is removed from the π -system being used to calculate the localization energy and as a result the localization energy is invariant to the nature of the

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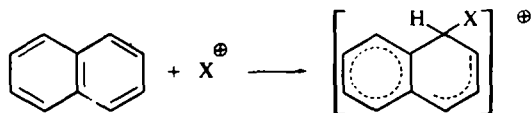


FIG. 1 Wheland model of the transition state for an electrophilic substitution reaction on naphthalene.

reagent in a series of isoelectronic reactions. An attempt to improve this model to include the nature of the reagent by allowing hyperconjugation between the tetrahedral center and the remaining cationic π -system was made by Müller *et al.*⁶ However, it has been shown⁷ in a series of alternant hydrocarbons that inclusion of hyperconjugation does not significantly improve the correlations between chemical reactivity and localization energy.

The second type of transition state that has been used successfully to explain certain substitution and addition reactions in conjugated molecules is the delocalized model, which corresponds to an extension of the delocalization of the ground state molecule to include the attacking reagent. This model was originally proposed by Evans,⁸ and is illustrated in Fig. 2 for the reaction of acrolein with 1-phenylbutadiene.

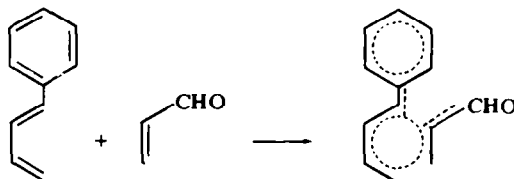


FIG. 2 The delocalized transition state for the reaction of 1-phenylbutadiene and acrolein.

This model has been used only infrequently. Streitwieser¹ proposed such a model for the transition state of the Diels-Alder reaction, as did Simonetta and Carra⁹ for nucleophilic reactions on nitro derivatives. More recently, Daudel and Chalvet¹⁰ have used this model to interpret the orientation effects of OH and NO₂ groups, in the photodeuteration of aromatic molecules. Similarly, Chalvet, *et al.*¹¹ have used this model to explain the orientation effect of electron donating groups in the photo-oxidation of substituted anthracene. Fukui¹² has used a delocalization model as the basis of the superdelocalization explanation of chemical reactivity.

A unified treatment of the transition state

The object of this paper is to present a unified treatment of the transition state which encompasses both the Wheland and the delocalized models.

In the first few articles, all calculations will be carried out by a generalization of the Hückel method which can be derived in terms of a self consistent field (SCF) theory. Accordingly the molecular orbitals Φ_j of our molecule must be solutions of the wave equation:

$$H^{SCF} \Phi_j = E_{jj} \Phi_j$$

In the Hückel method the molecular orbitals Φ_j are approximated by ϕ_j which are formed by the linear combination of atomic orbitals χ_i .

$$\Phi_j = \sum C_{ij} \chi_i$$

Assuming that the operator H^{SCF} is known exactly, the coefficient C_{ij} can be obtained, according to the theorem of MacDonald,¹³ from the following secular equations:

$$\sum_j C_{ij} [H_{ij}^{\text{SCF}} - E_i S_{ij}] = 0$$

$$S_{ij} = \langle \chi_i | \chi_j \rangle$$

$$H_{ij}^{\text{SCF}} = \langle \chi_i | H^{\text{SCF}} | \chi_j \rangle$$

If the molecule belongs to the symmetry group G , the operator H^{SCF} can be formed in such a way that it will commute with the group operator. By means of a unitary transformation, it is possible to transform the basis set of atomic orbitals into a basis set of orbitals of symmetry χ which belongs to a linear irreducible representation of group G . It is in the case of a conjugated molecule containing a plane of symmetry that it is possible to construct a basis set with π and σ orbitals. Because the π and σ orbitals constitute spatial basis sets for different linear irreducible representations; we have:

$$\langle \pi | H^{\text{SCF}} | \sigma \rangle = 0$$

and

$$\langle \pi | \sigma \rangle = 0$$

where H^{SCF} has been built with functions that form a representation (not necessarily irreducible) of the same symmetry group. In this case there will be non zero matrix elements only between functions belonging to the same representation.¹⁴ Since the unit operator commutes with the operators of group G , the integrals which are products of a σ and π orbital vanish.

Therefore the molecular orbitals ϕ can be separated into two groups: those that contain only orbitals of symmetry π and those that contain only orbitals of symmetry σ which can be called ϕ_π and ϕ_σ respectively.

Let us now examine a transition state with extension of delocalization as illustrated in Fig. 3 for the reaction of X with a benzene molecule shown in profile.

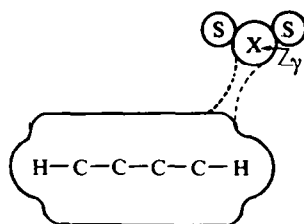


FIG. 3. A transition state with extension of delocalization.
S represents solvent molecules

As the two reactants approach, the interaction between them will be small and the situation can be represented by the introduction of a pseudo atomic orbital γ for the attacking specie.

In this picture of the transition state, the orbital plane of symmetry of the benzene ring is no longer a symmetry element for the entire activated complex. This introduces the following problem: is the separation of σ and π orbitals assumed in the simple

Hückel method, still valid in this case? We can examine this by considering the benzene portion of the activated complex and its corresponding local group. By doing so, it is possible to define the symmetry orbitals ϕ_π and ϕ_σ . Molecular orbitals Φ can again be formed in terms of the linear combination of the atomic orbital γ and the molecular orbitals ϕ_σ and ϕ_π . It is easy to imagine that the total wave function of the transition state contains a molecular orbital Φ , made up of the linear combination of ϕ_π , γ and ϕ_σ orbitals such that:

$$\Phi = \lambda\gamma + \sum_I U_I \phi_{\pi I} + \sum_{I'} V_{I'} \phi_{\sigma I'}$$

However, the pseudo atomic orbital γ does not belong to the spatial basis set of the linear irreducible representation of the benzene molecule. It is assumed that the group X attacks the periphery of the π -electron cloud of the benzene ring as illustrated in Fig. 3. As a result, the interaction between X and the benzene ring is small and the *differential overlap* between an orbital ϕ_σ and the pseudo atomic orbital γ will also be small. Only the overlap between the pseudo atomic orbital γ and the ϕ_π orbitals will be appreciable since they are both situated at the periphery of the molecule. Thus, under these conditions, it is reasonable to neglect the integrals of the type:*

$$\langle \gamma | \phi_\sigma \rangle \text{ and } \langle \gamma | H^{\text{SCF}'} | \phi_\sigma \rangle$$

where $H^{\text{SCF}'}$ is slightly different from the original Hamiltonian operator used to develop the Hückel method. As a result, in the molecular orbital Φ containing γ the coefficients $V_{I'}$ will be negligible and consequently:

$$\Phi = \lambda\gamma + \sum_I U_I \phi_{\pi I}$$

The extension of the Hückel method to this case present no difficulty and the parameters α_x and β_x are defined by:

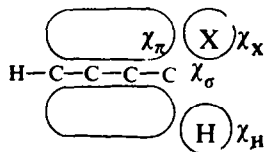
$$\alpha_x = \langle \gamma | H^{\text{SCF}'} | \gamma \rangle$$

and

$$\beta_x = \langle \gamma | H^{\text{SCF}'} | \chi_x \rangle$$

where χ_x represents the atomic orbital associated with the carbon atom at the reaction center. It is clear from this representation that a symmetry argument alone is insufficient to invalidate a separation of σ and π orbitals because the extent of orbital overlap must also be taken into account.

The model of the transition state containing a tetrahedral carbon atom at the reaction site, of which the Wheland model is but one example, can be incorporated into this unified representation of the transition state by applying the concept of hyperconjugation as illustrated in Fig. 4.



* Some precisions about the nature of this approximation are presented in the appendix.

The atomic orbitals of the attacking reagent X and the hydrogen, which is to be eventually displaced by X, can be linearly combined to form pseudo π and σ orbitals as follows:

$$\chi_{\pi_{X-H}} = N(\chi_X - \chi_H).$$

$$\chi_{\sigma_{X-H}} = N(\chi_X + \chi_H).$$

Again the total wave function of the transition state contains a molecular orbital such that:

$$\Phi = \Lambda\chi_{\pi_{X-H}} + S\chi_{\sigma_{X-H}} + \sum M\phi_{\pi_1} + \sum R\phi_{\sigma_1}$$

However, since the σ orbitals will not appreciably overlap with the π orbitals Φ reduces to:

$$\Phi = \Lambda\chi_{\pi_{X-H}} + \sum_1 M\phi_{\pi_1}$$

whereupon:

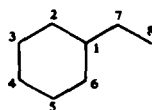
$$\alpha_{XH} = \langle \chi_{\pi_{XH}} | H^{\text{SCF}} | \chi_{\pi_{XH}} \rangle$$

and

$$\beta_{XH} = \langle \chi_{\pi_{XH}} | H^{\text{SCF}} | \chi_{\pi} \rangle$$

It is clear that this technique permits a description of both the Wheland and the delocalized models of a transition state by the same formalism. Only the values of the parameters will differ.

The resonance integral β_{C-X} between the attacking reagent and the C atom at the reaction site can be considered as a measure of the bonding between these two atoms in the transition state. In the delocalized model of the transition state where interaction between the two reactants is small, β_{C-X} will be considerably smaller than β_0 . This corresponds to a transition state that resembles the initial state with little bonding between the reactants. In the Wheland model described in terms of hyperconjugation on the other hand, there is considerable interaction between the two reactants and β_{CX} will be larger than β_0 . The Wheland model therefore corresponds to a transition state between the final and the initial state. In order to completely describe the Wheland model in this way, it is necessary not only to increase β_{C-X} but also to decrease the values of the resonance integrals of the reaction site with the adjacent neighbours. In this way, it is possible to account for both the increased bonding between the attacking reagent and the C atom at the reaction site and the decreased bonding between this same carbon C atom and its adjacent neighbours. Within the Hückel scheme there is a maximum value for the sum of the β 's of the bonds surrounding any one carbon atom in an unsaturated system.



For example, in the molecule Styrene I the bonds surrounding C_1 have a total value of $3/\beta$ ($\beta_T = \beta_{1-2} + \beta_{1-6} + \beta_{1-7}$), while around C_7 the total value is 2β ($\beta_T = \beta_{1-7} + \beta_{7-8}$) and around C_8 merely 1β ($\beta_T = \beta_{7-8}$). For any atom in such a system, the maximum value will be 3β . It seems reasonable, therefore, that, in the Unified treatment of the Wheland model, the total value of β for the bonds associated with the reaction site should not exceed 3.

The unified Treatment represents the attacking species as a single orbital containing none, one or two electrons depending on whether the reagent is an electrophile, radical or nucleophile. A similar assumption has been made in the Polyelectron Perturbation Treatment described by Klopman¹⁵ and scales of relative hardness and softness of reagents have been derived. It cannot be denied, however, that such a representation is a gross over-simplification of the interactions occurring between the reagent and the substrate in a chemical reaction. It may be tempting to perform extensive calculations on the reagent and then consider the interaction of all the molecular orbitals of the reagent with the total substrate. Apart from the increasing complexity of such a treatment, it is questionable if much improvement in the correlation of the experimental observations would be obtained, since at no time in an aromatic substitution are we likely to be dealing with a "naked" attacking species. For instance, it is well known from mechanistic studies¹⁶ that in hydrogen exchange reactions, the nature of the H-atom carrier A is important in the transition state. The degree to which H and A are separated is not known but it would be certainly incorrect to consider that a proton was the species involved at the transition state. Equally, small changes in solvent can produce dramatic effects on the rates of reaction and it is quite likely that complexing between solvent and reagent is still a factor in the transition state. At the present state of knowledge it is dubious whether refined theoretical treatments can improve on the more empirical approach adopted towards the representation of the reagent in the present study. However, this is currently under study utilizing the more advanced CNDO method.

The Coulomb integral α_x , assigned to the attacking species, is expressed in the usual units of the standard α_0 and β_0 of benzene so that:

$$\alpha_x = \alpha_0 + h\beta_0.$$

Considering the molecular orbitals of an electrophilic species, the filled levels will be deep lying as a result of the positive (or partial positive) charge, and one might visualise the situation depicted in Fig. 5A. From simple perturbation concepts, in which only interactions between filled and unfilled levels produce a net lowering of energy, it can be seen that the principal contribution will be from the first unoccupied level of the reagent with the filled levels of the substrate. This analysis in part justifies the use of a single orbital to represent the attacking electrophile. In the case of nucleophilic attack reasoning indicates that the main perturbations will arise from the highest filled orbitals as shown in Fig. 5B. Since a free radical species will have an orbital singly occupied, interactions will occur between this orbital and both the filled and the unfilled levels of the substrate. It is also evident that, in the case of a free radical, variations in the reagent's orbital levels may produce significant contributions from the perturbations between completely filled levels and the antibonding levels of the substrate or the vacant levels of the reagent and the filled substrate orbitals.

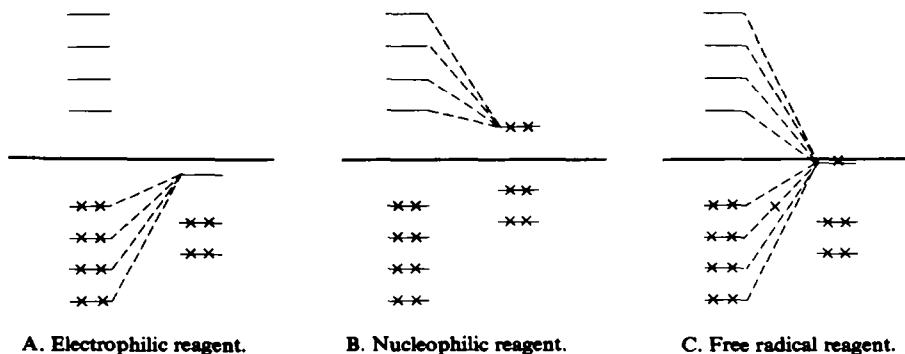


FIG. 5

It might be anticipated, therefore, that the Unified Treatment will be less successful in predicting or correlating experimental results for reactions involving free radicals. Another situation in which the present treatment would certainly fail is for a reagent which has several levels either degenerate or very close in energy and is hence not well represented by a single frontier orbital. The succeeding papers in this series hope to demonstrate that the approximate treatment of chemical reactions outlined above provide the organic chemist with a simple explanation of many of the imponderables persisting in the study of conjugated systems.

APPENDIX

The self consistent operator can be written as:

$$H^{\text{SCF}} = H^{\text{C}} + \sum_i (2J_i - K_i) \quad (1)$$

where H^{C} denotes the core operator and where J_i and K_i are constructed from the other molecular orbitals ϕ_i .

H^{C} will be made up of two parts; the core of the conjugated molecule H^{C} and the core of the reagent h^{C} :

$$H^{\text{C}} = H^{\text{C}} + h^{\text{C}} \quad (2)$$

We can write:

$$\langle \phi_n | H^{\text{SCF}} | \phi_n \rangle = \langle \phi_n | H^{\text{C}} | \phi_n \rangle + \langle \phi_n | h^{\text{C}} | \phi_n \rangle + \langle \phi_n | \sum_i (2J_i - K_i) | \phi_n \rangle \quad (3)$$

The model of the transition state under consideration is only valid if the interatomic distance between the reagent and the conjugated molecule is rather large. Therefore H^{C} will possess approximately the same symmetry properties as the isolated molecule and:

$$\langle \phi_n | H^{\text{C}} | \phi_n \rangle$$

can be neglected. Also:

$$\langle \phi_n | h^{\text{C}} | \phi_n \rangle$$

will be small.

Let us now consider a first iteration in which the ϕ_i 's are written as:

$$\phi_i = \alpha\Psi_i + \lambda\gamma \quad (4)$$

where:

$$\Psi_i = \sum_j C_{ij} 2p_{ji}$$

the $2p_{ji}$ being the p atomic orbitals of the conjugated molecule.

The Ψ_i 's will have approximately the same symmetry properties as the corresponding orbitals in the isolated molecule.

During such an iteration the J_i 's can be written as:

$$J_i = \int |\phi_i|^2 \frac{e^2}{r_{12}} dv_2 = |\alpha|^2 \int |\Psi_i|^2 \frac{e^2}{r_{12}} dv_2 + \alpha^* \lambda \int \Psi_i^* \gamma \frac{e^2}{r_{12}} dv_2 + \alpha \lambda^* \int \gamma^* \Psi_i \frac{e^2}{r_{12}} dv_2 + |\lambda|^2 \int |\gamma|^2 \frac{e^2}{r_{12}} dv_2 \quad (5)$$

Therefore an integral like $\langle \phi_n | J_i | \phi_n \rangle$ takes the form:

$$\langle \phi_n | J_i | \phi_n \rangle = |\alpha|^2 \langle \Psi_i | \phi_n \phi_n \rangle + \alpha^* \lambda \langle \Psi_i^* \gamma | \phi_n \phi_n \rangle + \langle \gamma^* \Psi_i | \phi_n | \phi_n \rangle + |\lambda|^2 \langle \gamma | \phi_n \phi_n \rangle \quad (6)$$

The generalized Hückel method we are describing can be considered to be a particular case of the CNDO approximation.

In this approximation all the terms in the second member of (6) vanish. The same result is found for:

$$\langle \phi_n | K_i | \phi_n \rangle$$

The third term in the second member of Eq. (3) also vanishes and:

$$\langle \phi_n | H^{\text{SCF}} | \phi_n \rangle$$

is negligible.

Therefore the ϕ_i obtained at the end of the first iteration will be of the form:

$$\phi_i' = \alpha'\Psi_i + \lambda'\gamma$$

which is identical to Eq. (4). The assumed separation of ϕ_i and ϕ_n is not destroyed by iteration. Thus neglecting $\langle \phi_n | H^{\text{SCF}} | \phi_n \rangle$ is reasonable and self consistent.

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