A Perturbation Molecular Orbital Treatment of Photochemical Reactivity. The Nonconservation of Orbital Symmetry in Photochemical Pericyclic Reactions

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Abstract: Photochemical reactions can be conveniently described as one of three general types. X-Type reactions occur entirely on an excited-state surface and result in luminescent products. N-Type reactions start from an excited state and proceed to a nonbonding (intermediate) ground state. G-Type reactions start on an excited surface and proceed directly to a bonding ground-state configuration. PMO theory and a qualitative view of the breakdown of the Born–Oppenheimer approximation have been used to develop qualitative procedure for examining the topography of excited-state reaction surfaces and their connections with ground-state surfaces. A specific type of BO breakdown will destroy the state symmetries in the orbitally degenerate intermediates in photochemical pericyclic processes. By an extension of Dewar's PMO treatment of aromaticity to cases of delocalized excited states it is clear that all pericyclic reactions follow one rule. Pericyclic reactions take place *via* aromatic transition states. The analysis of each of the three reaction types has been illustated with examples from the literature. This analysis is necessary if photochemical transition states are to be described in the same detail as their thermochemical counterparts.

Photochemical reactions convert electronic excitation energy to chemical potential either in the form of thermal energy or through the formation of "high-energy" substances or intermediates. The general mechanisms by which these conversions occur have been known for many years. In this paper, we will attempt to show how an appreciation of the mechanism for energy conversion coupled with a qualitative potential surface analysis based on first-order perturbation theory[1] (PMO theory) can be used to develop a moderately detailed picture of photochemical transition states. This treatment depends upon the facts that PMO theory can be used to qualitatively describe the reaction coordinate for thermochemical reactions while it also provides a remarkably reasonable accounting of the energy separation between the first excited states and the ground states for a large number of conjugated systems.[2] When these facts are taken together it is logical to use PMO theory to construct qualitative reaction coordinates for excited-state processes.

Although there are a very large number of excited states available to any polyatomic system, rapid radiationless transitions virtually depopulate all upper states prior to the onset of chemical processes,[3] so the only states that generally need to be considered are the lowest excited states (the first excited singlet, S_1, and triplet, T_1, of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ types). There are exceptions to this generalization, one of which will be mentioned in section 6. PMO theory makes no allowance for electron correlation, so within the confines of this qualitative view S_1 and T_1 states are treated as equivalent. This means that the energies of triplet states will always be overestimated in this theory; however, this should have little effect on the qualitative results obtained.

In the following sections of this paper we will develop the concepts that are necessary for direct and general application of PMO theory to photochemical reactions. We have used several examples of photochemical pericyclic reactions to illustrate a number of the features of the PMO approach.

Our discussion of photochemical pericyclic reaction should not be interpreted as an attack on the Woodward–Hoffmann rules.[4] The predictions based on our modified form of Dewar's PMO approach to this subject[5,6] will be essentially the same as those of Woodward and Hoffmann with the major exceptions of the predicted electronic state of the products when first formed, and predictions regarding the thermal reversibility of photochemical processes.

1. The PMO Description of Excited States

The PMO description of ground-state structure and reactivity in organic chemistry has been clearly established as the most reliable of the available qualitative theories,[1,2,5–8] resonance theory being the only alternative of comparable simplicity. The PMO treatment of ground-state reactivity examines the "first-order" energy differences between the reactants and transition states, or products, by comparing the energies of nonbonding molecular orbital (NBMO) interactions between odd alternant π-electron systems (odd AH's). The first-order equation for the energy of interaction (1) contains

$$\Delta E_\pi = 2(\Sigma a_{0r}b_{0s})\beta_{rs} \qquad (1)$$

only NBMO coefficients (a_{0r} and b_{0s}) at the sites of union, atoms r and s. The NBMO coefficients can be very rapidly determined by a procedure first introduced by Longuet-Higgins.[9,10]

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[1] M. J. S. Dewar, "Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

[2] M. J. S. Dewar, (a) *J. Chem. Soc.*, 2329 (1950); (b) *ibid.*, 3532, 3544 (1952).

[3] B. R. Henry and M. Kasha, *Annu. Rev. Phys. Chem.* 161 (1968).

[4] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969), and papers cited therein.

[5] M. J. S. Dewar, *ibid.*, in press.

[6] M. J. S. Dewar, *Tetrahedron, Suppl.*, **8**, 75 (1966).

[7] M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3341, 3345, 3350, 3353, 3355, 3557 (1952).

[8] R. C. Dougherty, *ibid.*, **90**, 5780 (1968).

[9] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 275 (1950).

[10] If alternant atoms in an odd-alternant hydrocarbon are starred in such a way that the starred set is more numerous, the NBMO coefficients of the unstarred atoms are zero, and the sum of the NBMO coeffi-

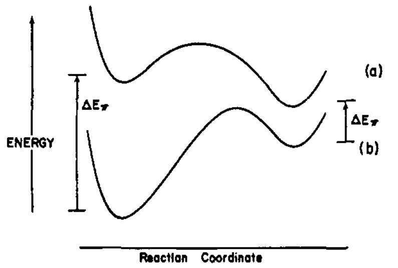

Figure 1. Construction of a zero-order surface for the first excited state: (a) ground-state reaction coordinate, (b) zero-order first excited state reaction coordinate. This figure also illustrates the mirroring of relative stabilities on the ground state and first excited state.

Dewar has shown that the first-order energy splittings given by eq 1 can be used to calculate the frequency of the first $\pi \rightarrow \pi^*$ absorption band for a very wide variety of aromatic hydrocarbons.[2] The frequency of the first absorption band represents the energy gap between the ground state and the first excited state. Approximate $n \rightarrow \pi^*$ excitation energies may be obtained by a simple extension of the $\pi \rightarrow \pi^*$ treatment. The success of the PMO analysis of absorption spectra makes it clear that relative π-electron energies of stable structures, which can be formed from the same pair of odd AH's on the ground state, will be approximately reversed on the excited-state surface.

The analysis of absorption spectra deals exclusively with regions on the excited-state surface which correspond to regions of stability on the ground-state surface. In order to develop a description of photochemical reactivity we must qualitatively map the areas on the ground- and excited-state surfaces between these regions of stability. This is not as simple as it would first appear. The difficulties occur in the region corresponding to the transition state between two stable ground-state structures. The next section is devoted to the development of the concept of the photochemical transition states for large molecules and simple MO procedures that may be employed to qualitatively map the excited-state reaction surface in the regions of the transition state.

2. The Born–Oppenheimer Approximation and the PMO Description of Photochemical Transition States

The Born–Oppenheimer (BO) approximation,[11,12] the separation of the quantum mechanical description of electronic and nuclear motions, is based on the fact that nuclei behave as if they were fixed in space in the time scale of electronic motions (*cf.* the Franck–Condon principle). If the nuclear motions are truly independent of electronic motions, then the reverse is also true and the potential curves for the first excited electronic state should be roughly parallel to the curves on the ground-state surface. In this case it is possible to qualitatively examine excited-state reactions by using a zero-order approximation to the excited-state contour (*i.e.* that individual coordinates parallel their ground-state counterparts), and a first-order analysis of relative energies on the excited surface (see section 1). We must use a theoretical approach to the structure of the excited-state surface because spectroscopic data are not available for structures which correspond to transition states on the ground-state surface. Figure 1 illustrates a cross section of a surface constructed in this way. The cross section of the excited-state surface in the reaction coordinate parallels the curves for the ground-state surface because the BO approximation holds and the electronic and vibronic motions are "independent." The relative energies of the bonding wells are reversed on the excited surface and consequently the transition state moves from one side of the reaction coordinate to the other in changing from the ground to the first excited state.

Photochemical processes which fit the analysis above can be analyzed in the same terms as conventional ground-state reactions. Methods for distinguishing these reactions and completing the analysis will be outlined in sections 3 and 6. The next questions are (1) what happens when the BO approximation fails and the excited state and ground state are no longer distinct entities, and (2) can PMO theory be used to qualitatively map the regions of the potential surfaces which lead to BO breakdown?

The consequences of BO breakdown are not easy to visualize because it is the BO approximation which permits us to draw molecules in the first place. When the energy gap between two electronic surfaces is of the order of one vibrational quantum it is possible for nuclear motion to mix the two states. When this happens it is no longer possible to say that the system is in one state or the other for a given total energy and nuclear q. It is impossible to draw single molecular structures in these cases because there is no valence bond method for indicating the mixing of the states. Structural representations of molecules in the regions where the BO approximation breaks down must involve the plotting of isopleths for the integrated squares of the electronic-nuclear wave function, just as we plot representations of p orbitals, etc., in descriptions of atomic structure. Fortunately, it is very seldom necessary to discuss the precise structure of molecules in regions where the BO approximation breaks down. It is sufficient to know that the breakdown will occur with a certain probability and that the states in question will mix with that probability.

If a BO breakdown occurs in the course of a photochemical reaction the ground state and first excited state of the system will be indistinguishable at that point. And the system can radiationlessly slip into the ground state through that geometry. This is very important because it provides the mechanism for converting electronic excitation energy to chemical potential on the ground-state surface.

It is well known that most photochemical reactions do not follow pathways which have direct thermal analogs. For these reactions the zero-order analysis given at the beginning of this section does not apply, because the BO approximation fails somewhere along the reaction pathway. In the zero-order analysis above we

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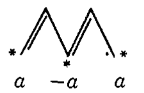
cients on the starred atoms attached to a given unstarred atom will be zero. Thus, for a linear odd AH, such as pentadienyl, the coefficients will be



where a is a normalization factor, since the sum of the squares of the NBMO coefficients must be equal to 1; thus $a^2 + a^2 + a^2 = 1$; $a = 1/\sqrt{3}$.

(11) M. Born and J. R. Oppenheimer, *Ann. Phys.*, **84**, 457 (1927).

(12) M. Bixon and J. Jortner, *J. Phys.*, **48**, 715 (1965).

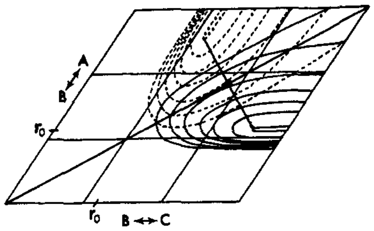


Figure 2. Intersection of AB and BC surfaces in ABC space with no first-order PMO stabilization of the ABC transition state. BC isopleths are dashed; AB isopleths are solid.

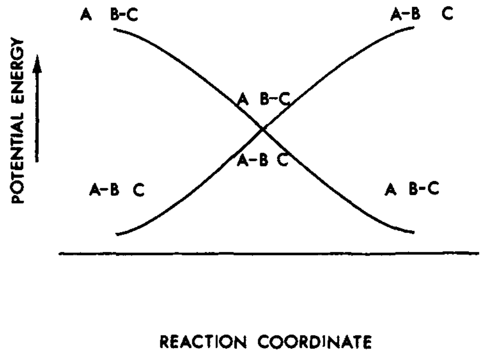


Figure 3. A Bell-Evans-Polanyi plot of the hypothetical reaction surface in Figure 2. Valence structures for the system at each of the points are illustrated.

treated the bonding potential wells in Figure 1, as if they were independent. This treatment follows the analytic approach which was introduced simultaneously by Bell,[13] and by Evans and Polanyi[14] (BEP), and has been reviewed by Dewar.[1] The major distinction between the treatment in Figure 1 and the classical BEP analysis is that the situation in Figure 1 is one in which the BEP analysis would fail for the ground-state reaction; that is, the first-order perturbation (E_{12} of eq 2[14])

$$\delta\Delta E^{\pm} = \delta\Delta G_0 + E_{12} \tag{2}$$

between the bond-forming and bond-breaking elements of the reaction is large so $\delta\Delta E^{\pm}$ will not be a linear function of $\delta\Delta G_0$. This perturbation energy will keep the energy gap between the ground state and first excited state large throughout the reaction course so the BO approximation will hold throughout the reaction course. The dissection of the reaction coordinate into two half-reaction coordinates can also be used to examine the cases where the BO approximation will break down.

The probability of breakdown of the BO approximation is a function of the reciprocal of the energy gap between the two states that are to be vibronically coupled.[12] When we find regions on the reaction surface where the energy gap between the ground state and first excited state(s) is minimal, we will have found places where the probability of breakdown of the BO approximation is the highest. When these points are mapped into the rest of the photosurface, it should be possible to describe the course of photochemical reactions.

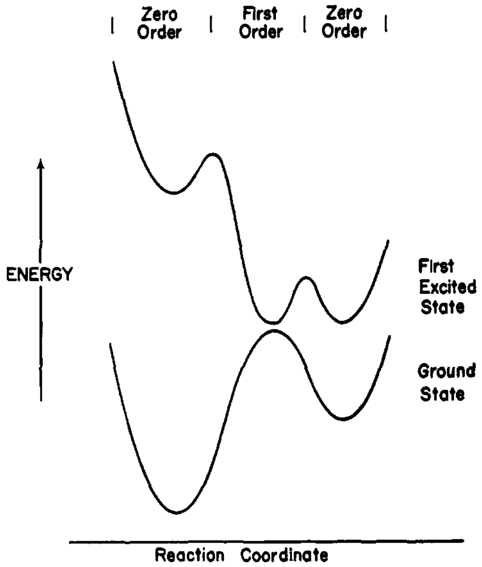


Figure 4. Convolution of zero-order and first-order approximations to the excited-state surface for a case when the BO approximation breaks down.

We will use the medium of a hypothetical bond-breaking–bond-forming reaction and the BEP analytic approach to illustrate the way in which PMO theory can be used to anticipate the regions where the BO approximation will break down.

$$\text{A–B} + \text{C} \longrightarrow \text{A} + \text{B–C} \tag{3}$$

The independent BEP surfaces for reaction 3 are the AB and BC disassociation surfaces in ABC space. If there is no first-order PMO interaction between the bond-breaking and bond-forming halves of the reaction (*i.e.*, there is no first-order stabilization of the transition state, E_{12} in eq 2 = 0) the two surfaces will mesh as indicated in Figures 2 and 3[15] and form two new surfaces. The new surfaces are the ground-state and first excited-state surfaces for reaction 3. In general, the two surfaces will not touch at the high-energy point on the ground-state surface because spin-orbit and spin-spin interactions will move the surfaces apart by a small amount.[16] The interactions which will move the surfaces apart will be substantially smaller than first-order electronic effects.

The formation of two new surfaces by the intersection of the two BEP half-reaction surfaces follows directly from the BEP analysis. The valence bond structures on the excited-state surface are those you would expect, namely eq 4. The antibonding MO for the AB bond

$$\text{A–B}\cdots\cdot\text{C} \xrightarrow{h\nu} \text{A}\cdot\cdot\text{B}\text{——C} \tag{4}$$

will have the proper phase for forming a B–C bond which gives the excited valence structure at the right of eq 4. The reason for redrawing Figures 2 and 3, which can be found in one form or another in most introductory theory texts (*e.g.*, ref 1), is that the information which these diagrams give about the first excited state is generally ignored, and it is this information that we are presently seeking. The first thing that is obvious from an analysis of Figures 2 and 3 is that they illustrate a BO breakdown. The excited-state surface in Figure 1

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[13] R. P. Bell, *Proc. Roy. Soc., Ser. A*, 154, 414 (1936).

[14] (a) M. G. Evans, and M. Polanyi, *Trans. Faraday Soc.*, 34, 11 (1938); (b) *ibid.*, 32, 1333 (1936); (c) R. A. Ogg, Jr., and M. Polanyi, *ibid.*, 31, 604 (1935).

[15] The surfaces in Figure 2 have included a repulsion potential because even in the absence of bonding or antibonding interactions between the components of the reaction of three hypothetical atoms must occupy space.

[16] K. J. Laidler and K. E. Shuler, *Chem. Rev.*, 48, 153 (1951).

where electronic and nuclear motions can be treated independently is substantially different from the surfaces in Figures 3 and 4. The latter figure illustrates the convolution of the zero-order and first-order excited surfaces for a hypothetical reaction. The zero-order parts of the surface in Figure 4 correspond to regions where the BO approximation holds and the ground-state and first excited-state energy contours are roughly parallel, as the interaction between the bond-breaking and bond-forming elements increases on the excited state whenever there is no first-order stabilization of the ground state. Thus in cases where the classical BEP analysis is directly applicable there will be a first-order depression in the excited-state surface near the nuclear configurations of the ground-state transition state.

If there is a depression in the excited-state surface, as indicated in Figure 4, reactions on that surface will tend to proceed *via* paths through that depression. The rate-limiting step in the reactions will generally be the crossing from the excited surface to the ground-state surface. These rates can be calculated in principle by analyzing the breakdown of the BO approximation.[12,17] The rates of crossing of two surfaces can also be calculated classically using a procedure developed by Teller[18] following Zener's treatment of surface crossing in diatomic molecules. We prefer the formalism which is based on the breakdown of the BO approximation[12,17] because it is directly adaptable to the BEP analysis, which shows vibronic energy levels on electronic surfaces. If the rate-limiting step in the reaction is the rate of crossing, the central well on the excited-state surface in Figure 4 represents the transition state for this type of photochemical reaction.

For photochemical reactions in which the reaction rate is determined by the rate of surface crossing, the temperature dependence of the reaction rate will be vastly different than that observed for thermal reactions. Lin's treatment[17] assumes a Boltzmann distribution of vibrational levels on the excited-state surface, and since the rate of crossing is a function of the population of the lowest vibrational level on the excited-state surface, the reaction rates for this type of reaction should show a modest inverse temperature dependence, for intermediate temperatures. For very low temperatures the rate of crossing to the intermediate well on the excited surface will be rate determining.

The photochemical transition state represented in Figure 4 must relax *via* vibronic coupling because the transition probability for radiative relaxation will be nearly zero. The transition probability for radiative relaxation is proportional to the absorption coefficient for the ground-state structure;[19] for a transition-state structure on the ground-state surface, the absorption coefficient will be effectively zero. The competition between radiationless relaxation to the product side or the reactant side will effect both the rate and quantum yield of the reaction. Jortner, Rice, and Hochstrasser have given a detailed mathematical discussion of this problem for the general case of photoisomerism and in particular cis–trans isomerism of olefins.[20]

The results which follow from the discussion above may be summarized by the following series of statements.

2.1. Reactions in which there is no first-order stabilization of the (ground state) transition state will be susceptible to a breakdown in the BO approximation in the region of that nuclear configuration. If there is a first-order (PMO) stabilization of the transition state, the ground-state and excited-state surfaces will move apart by twice the energy of stabilization of the ground transition state. Since first-order stabilization energies are large with reference to vibrational energies,[1] first-order stabilized transition states will be adequate.

2.2. Photochemical reactions which proceed by paths with no first-order PMO stabilization of the ground state will result in ground-state products. This statement follows directly from 2.1. The region in which the BO approximation breaks down is the hole through which excited-state reactants reach the product ground state. With the analysis of section 1, PMO theory can be used to anticipate the product electronic state for a given photochemical reaction.

There are two corollary statements to 2.2.

2.3. Chemiluminescent processes which involve bond formation and bond breaking will occur through transition states that have no first-order stabilization. This statement simply records the microscopic reversal of the situations mentioned in 2.2.

2.4. Photochemical reactions which proceed by paths which would be continuously stabilized on the ground-state surface by a first-order splitting will result in excited-state products. The last statement follows from the fact that the rate of surface crossing should be small for the entire reaction course because the gap between the ground state and the excited state should be relatively large for the entire reaction course.

In the following section we will use the results of the analysis above to develop a phenomenological classification for photochemical reactions, since it is clear that understanding the electronic-vibronic nature of a given reaction is an essential key to the mechanistic description of the process.

3. General Types of Photochemical Reactions

The analysis in the previous section clearly identifies two main types of photochemical processes from the point of view of PMO theory, *i.e.*, (1) those reactions for which the transition state on the ground-state surface is stabilized and for which the BO approximation will hold throughout, and (2) those reactions for which the ground-state transition state is not stabilized and for which the BO approximation breaks down. In this section we will define these processes from a phenomenological point of view and indicate again the application of PMO theory to each reaction type. In this section the second type above has been divided into concerted and nonconcerted subgroups.

X-Type Photochemical Reactions. X-Type reactions are those reactions which occur entirely on an excited electronic surface. In an X-type reaction the product must exhibit luminescence behavior similar to its luminescence when activated from its ground state. The

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(17) S. H. Lin, *J. Chem. Phys.*, 44, 3579 (1966).

(18) E. Teller, *J. Phys. Chem.*, 41, 109 (1937).

(19) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, Van Nostrand, New York, N. Y., 1966.

(20) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Advan. Photochem.*, 7, 149 (1969).

Table I. Characteristics of Photochemical Reaction Types

Reaction type	Product luminescence	Temperature dependence	Intermediates	PMO description of transition state	Examples (see section 6)
X	Yes	$\log K_r \alpha \frac{1}{T}$	No	Corresponding reaction on the ground-state surface will be stabilized to first order $\Delta E_{\pi\text{-GS.TS}} < 0$	Biprotonic phototautomerism[a]
N	No	$\log K_r \alpha \frac{1}{T}$ for steps after the formation of the intermediate	Yes (generally radicals)	The transition state for radical formation corresponds to a point of BO breakdown, no first-order stabilization of the ground state $\Delta E_{\pi\text{-GS.TS}} \sim 0$	Norrish type I cleavage of ketones
G	No	K_r variable function of T	No	Transition state corresponds to point of BO breakdown, no first-order stabilization of the ground state $\Delta E_{\pi\text{-GS.TS}} \sim 0$	Photochemical ring opening of cyclobutenes

[a] See ref 1.

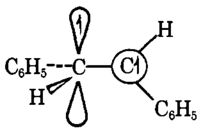
luminescence which is due to the product of an X-type reaction will generally be easy to detect,[21] so these reactions will be easy to identify.

The quantum yields for X-type reactions should show a temperature dependence indicating the competition between vibronic and luminescent relaxation in the structure corresponding to the starting materials and the rate of barrier crossing to the product state.

The PMO description of the transition state and reaction course for X-type reactions will be precisely analogous to the treatment of ground-state processes. This is because the BO approximation holds for these reactions, and the zero-order approximation to the excited-state surface is reasonable.

Table I and Figure 5 summarize the characteristics of X-type photoprocesses as well as those of the two other photochemical reaction types.

N-Type Photochemical Reactions. In N-type photochemical reactions the photochemical process is complete when the reagents reach a nonbonding ground state. These reactions are characterized by the presence of nonbonded (usually radical) intermediates. The detection of radical intermediates in a photochemical process is necessary and sufficient for classification of the reaction as N-type. For the purpose of classification of reactions, nonspectroscopic triplet states are considered to be radical ground states. For instance, the twisted triplet of stibene (1) and the biradical n→π* intermediate II are examples of the products of N-type reactions. It is obvious that the products of N-type photochemical reactions will be seldom isolated directly. These products will react either intra- or intermolecularly to form stable structures on the ground-state surface.



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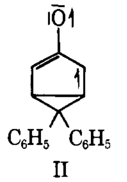

II

(5)

n→π* reactions which involve radical intermediates or nonspectroscopic triplets are also classed as N-type reactions even though only half a bond is "broken" in these reactions (the π* electron destabilizes the associated π bond by roughly half the bond dissociation energy).

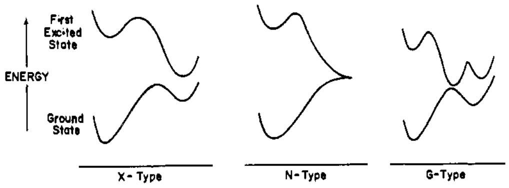

Figure 5. Hypothetical reaction coordinate profiles for the three major types of photochemical reactions.

The photochemical N-type reactions involve a breakdown in the BO approximation which is directly analogous to predissociation in small molecules. Photochemical N-type reactions will follow paths which minimize the energy gap between the ground state and first excited state (that is, minimize the PMO splitting which stabilizes the ground state). N-Type reactions are analogous to G-type reactions (see below) except in this case entropy effects separate the ground- and excited-state parts of the reaction into discrete steps. The temperature dependence of the rate of formation of the products of N-type photochemical reactions should be similar to the temperature dependence of X-type processes. The products of N-type reactions are intermediates in the overall reaction sequence (except in special cases, one of which will be discussed in section 6). The rate-limiting step in the overall reaction sequence will generally not be the rate of radical formation, so temperature effects on the overall reaction rate will be roughly the same as those for radical reactions in which some other means is used for radical generation.

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(21) C. A. Taylor, M. A. El-Bayoumi and M. Kasha, *Proc. Nat. Acad. Sci. U. S.*, **63**, 253 (1969).

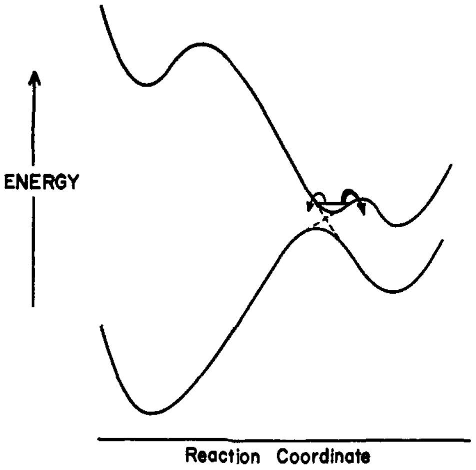

Figure 6. A BEP plot of a G-type reaction illustrating how changes in product stability can change the overlap of the excited-state transition state with a well on the ground-state surface.

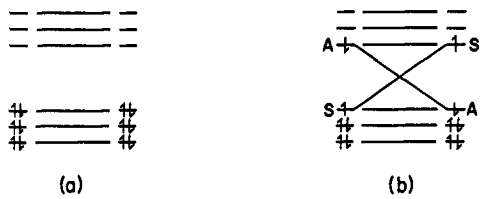

Figure 7. Hypothetical orbital correlation diagrams for (a) systems in which the bonding orbitals of the starting materials smoothly transform into those of the products and (b) systems in which a bonding orbital crosses in energy with an antibonding orbital.

Since the photochemical process in N-type reactions ends with a radical intermediate, the quantum yields for the entire reaction, which also includes thermal reactions of the radicals, may be larger than 1. Quantum yields larger than one, of course, indicate radical-chain processes occurring on the ground-state surface. Again Table I and Figure 5 illustrate the distinctive features of N-type photochemical reactions.

G-Type Photochemical Reactions. G-Type photochemical reactions either start or end in a *bonding ground-state* configuration. Photochemical reactions which start in the ground-state configuration are chemiluminescent processes. The distinguishing characteristics of G-type photochemical reactions, which start on the excited-state surface, are the absences of both radical intermediates and product luminescence. Furthermore, the temperature dependence of the rates of these reactions will be distinguishable from the previous two types.

At very low temperatures that rate-determining step for the reaction can be the rate of escape from the first valley on the excited-state surface. Under these conditions the reaction rate will increase with increasing temperature in the usual way.

The nonradiative and nonreactive decay of excited triplet states of hydrocarbons is an example of a G-type nonreaction. For very low temperatures the rates of radiationless decay increase dramatically with increasing temperature and may be characterized by Arrhenius kinetics.[22-24]

At temperatures above which the rate of getting out of the first well on the excited surface is no longer rate determining the rate of crossing to the ground-state surface will be rate determining. Since the rate of crossing is a function of the population of the lowest vibrational level on the excited surface[17] the reaction rate should show a slight negative temperature dependence in this temperature range (-50 to $+150°$).[19,22-24]

The quantum yields for G-type reactions will depend on the relative ground-state energies of the starting materials and products. The photochemical transition state will shift toward the high-energy side for G-type reactions, and the probability of crossing to a high-energy product will be correspondingly increased (see Figure 6).

The most common examples of the G-type photochemical reactions are found in photochemical pericyclic reactions. The next two sections of this paper are devoted to an analysis of the specific mode of BO breakdown in photochemical pericyclic reactions (section 4) and the PMO analysis of these reactions (section 5).

4. Orbital and State Correlation Diagrams for Photochemical Reactions

The Nonconservation of Orbital Symmetry. Orbital and state correlation diagrams are easily constructed without reference to symmetry for all cases in which the set of occupied orbitals of the starting materials smoothly transform into the occupied orbitals of the products (Figure 7a). If a pair of doubly occupied orbitals (or a pair of vacant orbitals) cross in the process, it will make no difference to any of the results because the orbital crossing in these cases does not lead to a change in the system which can be observed experimentally. In cases where orbitals that are, respectively, doubly occupied or vacant in the ground state cross, the orbitals must be distinguishable by symmetry or there would be no way of telling which orbital was which at the crossing point. If the symmetries of the states can be distingushed, antisymmetric states will correlate with antisymmetric states as shown in Figure 7b, as was first pointed out by Longuet-Higgins and Abrahamson.[25] In the following discussion, we will show that the symmetries of the states will be destroyed in real molecular systems. The destruction of the symmetry is caused by a specific breakdown in the BO approximation. Consequently, one-coordinate orbital or state correlation diagrams, *e.g.*, that in Figure 7b, are meaningless, and for photochemical reactions where there is a crossing of bonding and antibonding orbitals, these diagrams will not correspond to reality. The following statement summarizes these findings.

4.1. Orbital and electronic state symmetries will not be preserved in orbitally degenerate reacting systems. To prove statement 4.1 it is necessary and sufficient to show that either there will exist a vibrational mode which will destroy the appropriate elements of symmetry but not alter the energies of the degenerate orbitals or that alters their energies. Both of these conditions are met in the orbitally degenerate intermediates in pericyclic reactions. The general proof will be illustrated by considering the orbitally degenerate inter-

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(22) I. H. Leubner and J. E. Hodgkins, *J. Phys. Chem.*, **73**, 2545 (1969).

(23) S. H. Lin and R. Borsohn, *J. Chem. Phys.*, **48**, 2732 (1968).

(24) N. G. Kilmer and J. D. Spangler, *ibid.*, **54**, 604 (1971).

(25) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

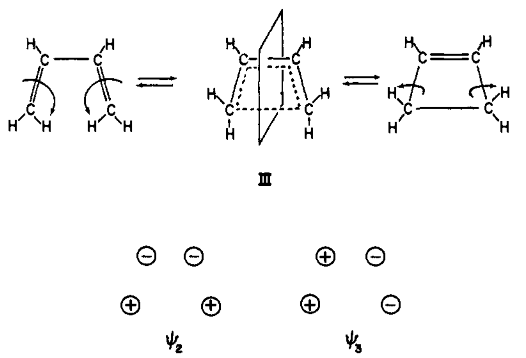
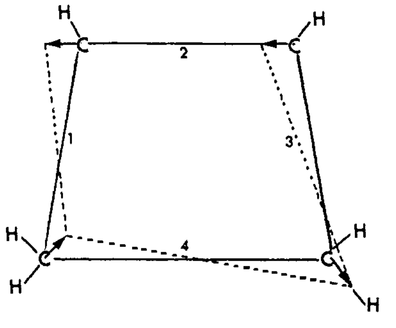


Figure 8. The disrotatory cyclobutene–1,3-butadiene transformation and the phases of the degenerate intermediate orbitals ψ_2 and ψ_3 with reference to the C_s plane.



III

Figure 9. A nontotally symmetric vibration in the cyclobutene–1,3-butadiene intermediate III.

mediate configuration in the disrotatory 1,3-butadiene–cyclobutene interconversion (Figures 8 and 9).

Orbitally degenerate intermediates, like III, are characteristic of photochemical pericyclic reactions.[4] In the case of the cyclobutene–1,3-butadiene intermediate, the degenerate orbitals, ψ_2 and ψ_3, are, respectively, symmetric and antisymmetric with respect to the mirror plane of the system. Although ψ_2 and ψ_3 have coefficients of the same magnitude, they are not pairs in a degenerate irreducible representation because the symmetry of the system is too low to have a degenerate irreducible representation. This means that III will not be subject to a specific Jahn–Teller distortion.[26,27] The potential function for III (V_0) as a function of any nontotally symmetric vibration in III, *e.g.*, that represented in Figure 9, will have to be a function of only even powers of the nontotally symmetric coordinate, q (eq 6). If V_0 were a function of odd powers of the nontotally symmetric coordinate, vibration in one sense with reference to the symmetry element would be distinguishable from vibration in the opposite sense, a situation which violates special relativity. The splitting between the two degenerate states that results from this orbital degeneracy must be a function of even powers of q (eq 7). This means that in first order (one nontotally symmetric vibrational quantum) the energies

$$V_0 = aq^2 + bq^4 \ldots \qquad (6)$$

$$V_* - V_0 = \alpha q^2 + \beta q^4 \ldots \qquad (7)$$

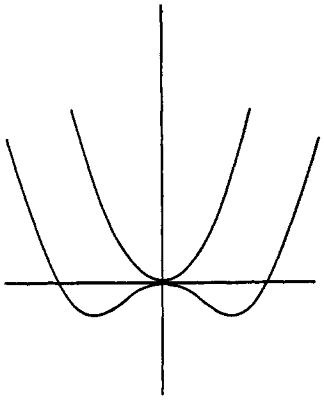
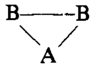


Figure 10. Cross section through the potential function along a nontotally symmetric coordinate for an orbitally degenerate system. The BO breakdown at the origin destroys the validity of this drawing for that region of the potential function.

of the orbitals and states will be unchanged but the symmetry distinction between them will vanish. In second order (two quanta) the states will both mix and split. The resulting potential functions must be very similar to Renner–Teller potentials, with considerable latitude in the depth of the wells and their proximity to the symmetry axis, Figure 10. The statement that the symmetric and antisymmetric states will mix and split under the influence of a nontotally symmetric vibration is equivalent to saying that the BO approximation will break down for that configuration of the molecule. The potential function in Figure 10 is thus "overdrawn" in the region of the origin. Statement 4.1 could be formulated equally well in Hellman–Feynman terms (HF) by analogy with the treatment of Jahn–Teller distortions.[27] In this case the driving force for electronic relaxation is clearly a second-order HF force. The situations covered by 4.1 are very closely related to the cases of nearly degenerate states described by the pseudo-Jahn–Teller effect.[28–31] The only difference is the energy gap between the excited state and the ground state and therefore the magnitude of the coupling. The pseudo-Jahn–Teller case, linear BAB, discussed by Öpik and Pryce,[28] is very closely related to the orbitally degenerate case triangular



which is the subject of 4.1. The degeneracy in this latter case has been recognized for the decomposition of H_2O or H_2S to H_2 and O or S, respectively.[19]

The cases covered by 4.1 are a subset of the general Jahn–Teller problem. The other two cases in which configurational instability of electronically degenerate systems can be understood in terms of symmetry are the original Jahn–Teller instability[18] and Renner–Teller instability in the excited states of linear triatomic (polyatomic) molecules.[19] The reason this situation did not previously come to the attention of spectroscopists is that orbitally degenerate systems, like III, are nonspectroscopic states.

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(26) H. A. Jahn and E. Teller, *Proc. Roy. Soc., Ser. A*, **161**, 220 (1937).
(27) W. L. Clinton and B. Rice, *J. Chem. Phys.*, 30, 542 (1959).
(28) U. Öpik and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **238**, 452 (1957).
(29) A. D. Liehr, *Ann. Phys.*, 1, 221 (1957).
(30) M. Gouterman, *J. Chem. Phys.*, 42, 351 (1965).
(31) W. D. Hobey, *ibid*, **43**, 2187 (1965).

It is relatively easy to confirm the result of 4.1 for the intermediate III. Figure 9 illustrates a nontotally symmetric vibration in III which would destroy the symmetry distinction but not the degeneracy of the orbitals. Under the influence of this vibration, the atomic interactions in bonds 2 and 4 will remain unchanged, and those in bonds 1 and 3 will increase and decrease, respectively, by equal amounts. By reference to the phase relationships for the degenerate orbitals in Figure 8, it is relatively easy to see that the orbitals will remain degenerate under the influence of this vibration. The phase relationships (coefficients determined by symmetry) in Figure 8 are valid only for the zero-order wave functions (no vibronic coupling). In the vibrationally perturbed state these phase relationships fail, and the second-order perturbations, due to the vibration of Figure 9, will be nonzero for the degenerate orbitals in III.

The discussion above indicates that reactions, which proceed from the excited state in such a way that bonding and antibonding orbitals with different symmetries cross, will result in ground-state products (G-type reactions). On the other hand, photochemical reactions which proceed by paths in which bonding and antibonding orbitals do not cross, will generally result in excited state products. By use of orbital and state symmetry correlations alone[4] one always anticipates a correlation of excited states with excited states or nonbonding states. The electronic state of the product is an important feature of photochemical processes, particularly pericyclic ones. The procedures above provide the basis for anticipating product electronic states. Examples which illustrate these points are discussed in section 6.

Statement 4.1 has direct consequences for theoretical attempts to calculate reaction surfaces, namely the following.

4.2. Calculations of reaction surfaces which proceed toward orbitally degenerate structures should use more than one coordinate, at least one of which is nontotally symmetric. The nontotally symmetric coordinate must be included in the calculation, otherwise the consequences of BO breakdown will not be reflected in the calculated energies, since none of the available semiempirical MO methods has provisions for directly accounting for a violation of the BO approximation. Dewar and Kirschner have recently shown this to be the case for the disrotatory opening of cyclobutene and other simple pericyclic reactions.[32]

The discussion in section 2 illustrated the fact that a BO violation will occur in a simultaneous bond breaking–bond forming reaction whenever there is no first-order bonding interaction among all of the components involved in the ground-state reaction. The state degeneracy at the transition state for these reactions has been called *accidental degeneracy*;[19] however, for these cases we prefer the term *coincidental degeneracy* because the point of intersection is determined by specific electronic features of the system. The orbitally degenerate intermediates in photochemical pericyclic reactions constitute a special case of *coincidental degeneracy* in which the crossing point is determined by symmetry. One of the distinguishing features of photochemical pericyclic reactions is the fact that an analogous ground-state process would proceed *via* an antiaromatic transition state[1,5,6] (that is, there is no first-order bonding perturbation among all of the elements involved in the reaction).

Coincidentally degenerate (or nearly so) intermediates will occur at the "holes" between excited-state and ground-state potential surfaces. These intermediates should be a key to understanding G-type photochemical reactions. The specific application of PMO theory to photochemical pericyclic reactions is the subject of the next section.

5. PMO Theory of the Aromaticity of Excited Electronic States

5.1. The General Analysis of Pericyclic Reactions. By definition, pericyclic reactions are simultaneous bond-forming–bond-breaking processes that occur with cyclic transition states. The requirement of simultaneity (within the time of one low frequency vibration) in bond forming and bond rupture for a cyclic reaction system implies electronic delocalization in the system at the transition state. Evans[33] was the first to recognize the importance of cyclic delocalization in the transition state for pericyclic processes (the Diels–Alder reaction). Evans' rule for thermal Diels-Alder reactions was generalized for pericyclic processes by Dewar on the basis of a PMO analysis of aromaticity.[1,5,6,34] Woodward and Hoffmann have recently stated the same rule in a slightly modified form by relating maximum bonding to transition-state stability.[4] Modifications of the thermal rule have been suggested for photochemical reactions.[1,4] The analysis above suggests the validity of only one rule for both thermal and photochemical pericyclic reactions. This fundamental rule for pericyclic reactions, the Dewar–Evans rule, follows—pericyclic reactions proceed *via* aromatic transition states—and if we accept Dewar's definition of aromaticity,[6] cyclic conjugated systems that have a higher bond energy than appropriate open-chain analogs are aromatic. The above rule is tautological for all pericyclic processes. The tautology follows from the third law of thermodynamics and the difference in entropy associated with open-chain and cyclic systems. This rule must apply equally well to both thermal and photochemical pericyclic reactions, since the formulation of the rule did not refer to the electronic state of reactants or products. The application of the Dewar–Evans rule to photochemical pericyclic reactions has been hampered by the lack of a generally reliable guide to the electronic state of reactants and intermediates in these transformations.

It has been established that photochemical pericyclic reactions proceed through transition states that would be antiaromatic for ground-state processes.[1,5,6] In the PMO treatment of antiaromatic alternant hydrocarbons, there is a larger π-bonding PMO interaction in the open-chain analog than there is in the cyclic hydrocarbon.[6] The perturbational stabilization is estimated by dividing the cyclic alternant hydrocarbon (AHC) into two fragments. Union of these fragments at one point gives the perturbational stabilization of the open-chain analog; union at two points gives stabilization of

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[32] M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 93, 4290 (1971).

[33] M. G. Evans, *Trans. Faraday Soc.*, 35, 824 (1939).

[34] See, *e.g.*, M. J. S. Dewar, *Annu. Rept. Chem. Soc.*, **48**, 132 (1951).

the cyclic hydrocarbon which topologically corresponds to the delocalized transition state.[6] It is precisely this dissection of a cyclic transition state that must be carried out to approximate the BEP separation of the bond-forming and bond-breaking parts of our hypothetical ABC system in section 2. Since an antiaromatic conjugated system has no first-order stabilization as compared to its open-chain analog, it is clear that a BO violation will occur in the antiaromatic configuration (see 2.1). Photochemical pericyclic reactions (or pseudoreactions) thus provide a general mechanism for the radiationless relaxation of electronic excitations. We will now show that the "intermediates" in photochemical pericyclic processes are indeed aromatic with reference to the appropriate reference state.

Development of theorems concerning the aromaticity of the first excited states of alternant hydrocarbons requires only a simple extension of Dewar's treatment of ground-state systems.[6] In discussing electronically excited states, we need concern ourselves only with first excited states, as higher excited states are virtually nonexistent on the time scale of normal chemistry,[3] *e.g.*, pericyclic reactions. PMO theory does not distinguish between singlet and triplet excited states. The energy of triplets will generally be different from that of singlets because of differences in electron correlation; however, along a single excited-state surface (either singlet or triplet) the PMO arguments should be valid. In triplet intermediates the rate of crossing to the ground state will be lower because of the required spin-orbit coupling; thus triplets will be generally less selective, and more susceptible to biradical pathways than corresponding singlet reactions.

Aromaticity is always defined by comparison of cyclic delocalized systems with either open-chain or bond-fixed analogs. The open-chain structures, which would be appropriate models for assessing the aromaticity of the first excited states of monocyclic AHC's, are the first excited states of the open-chain analogs of these molcules. Following Dewar's arguments, we assume that the conclusion derived from an analysis of the π-electron systems of AHC's will be applicable to the σ–π delocalized systems involved in pericyclic reactions. The validity of this argument depends on the fact that there is no first-order difference between a σ–π delocalized system and a pure π delocalized system.

5.2. The first excited singlet states of monocyclic alternant hydrocarbons will be antiaromatic with reference to the first excited singlet state of an appropriate open-chain analog. By use of the "pairing theorem"[1] and the approximate expression for the second-order energy difference between an open-chain and cyclic system[6]

$$\Delta E_{\pi \mathrm{RS}^{2+}} = \frac{-\beta_{\mathrm{rs}}^{2}}{2\tilde{E}} \tag{8}$$

where $\tilde{E}$ is the average energy of the bonding orbitals, you can show that 5.2 is always satisfied because ΔE_π in eq 8 is always positive. It is easy to show that union of the ends of a 4*n* electron polyene in its first excited state will give the ground state of a Hückel antiaromatic system. Mobius union of the ends of a 4*n* + 2 electron polyene in its first excited state will give the ground state of an anti-Hückel antiaromatic system.

5.3. The ground state of antiaromatic, monocyclic, conjugated AHC's will be aromatic *vis-á-vis* the first excited singlet states of their open-chain analogs. This statement may be easily verified by use of the expression for the first-order splitting obtained on union of the ends of a polyene chain (eq 9).[1] The extension to non-

$$\Delta E_\pi = 2P_{\mathrm{rs}}\beta_{\mathrm{rs}} \tag{9}$$

alternant systems is obvious.

5.4. Antiaromatic ground states of nonalternant monocyclic HC systems will be aromatic with reference to the excited singlet states of their open-chain analogs; nonaromatic (radical nonalternant systems) will be nonaromatic with reference to the excited singlet states of their open-chain analogs. One interesting feature of the discussion above is the fact that the antiaromatic ground state is obtained by union of the ends of either the ground state of the first excited state of the appropriate polyene. This argument is very similar to Oosterhoff's permutation symmetry discussion of pericyclic reactions.[35]

The statements above establish the fact that atomic configurations, which are antiaromatic with reference to ground-state open-chain structures, will be aromatic with reference to excited-state open-chain structures. These intermediates will lie on the pathways of G-type photochemical pericyclic reactions. The reversal of aromatic properties from ground state to excited state makes it possible to use only one set of "rules" for both states, the distinction between states being based on a reversal of *aromatic* and *antiaromatic*. Dewar was the first to present the full proof of the Hückel 4*n* + 2 electron rule for aromatic systems[6] at the time he proved the Heilbroner 4*n* electron rule for aromatic anti-Hückel systems.[6] Table II presents the full set of PMO-derived "rules" for pericyclic reactions.

Table II. Preferred Transition States for Monocyclic Pericyclic Reactions

	Ground state		Excited state	
	Hückel	Anti-Hückel	Hückel	Anti-Hückel
No. of electrons	4*n* + 2	4*n*	4*n*	4*n* + 2

Multicyclic reactions can be treated by the same methods used to examine the aromaticity of polycyclic hydrocarbon systems;[1] again the *aromatic* and *antiaromatic* labels should be exchanged on going from the ground-state to excited-state systems.

Finding phase inversions, that is, identifying anti-Hückel systems, often presents a problem to the analysis of pericyclic processes. The keys to this problem are the phase properties of carbon p orbitals and those of chemical bonds. Carbon p orbitals invert phase at the carbon nucleus so that conjugated bonding, which involves bonding of one atom to one side of a carbon and another atom to the other, will require a phase inversion. Atomic orbitals in chemical bonds must have the same (arbitrary) phase. It is obvious that the four carbon AO's in the intermediate in Figure 8 can all have the same phase. When the cyclobutene ring is opened

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(35) J. C. Mulder and L. J. Oosterhoff, *Chem. Commun.*, 305, 307 (1970).

with a *controtatory* motion, one of the σ-bonding orbitals will overlap with the top of the π bond and one will overlap with the bottom; since the σ orbital must have the same phase this requires a phase inversion, an anti-Hückel system. The energy barrier between "allowed" and "forbidden" reactions should be substantially smaller than the delocalization energy of the hydrocarbon which is analogous to the σ–π delocalized transition state. The magnitude of the decrease will of course depend on the overlap, etc., in the transition state. The estimated difference in energy between an "allowed" and a "forbidden" monocyclic pericyclic process of $\sim$15 kcal/mol[36] is roughly half of the delocalization energy of benzene, and thus is quite within the range of this discussion.

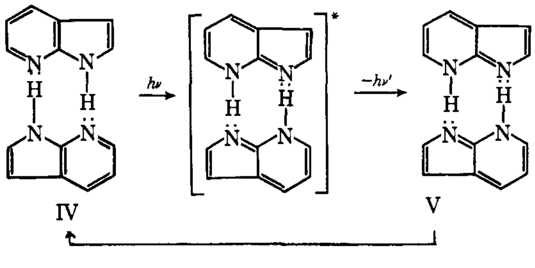
The electronic state of the products of any given pericyclic reaction can be anticipated by use of the considerations in section 2. Photochemical pericyclic reactions should belong to the G type and result in ground-state products because of the BO violation which will occur in the course of the reaction. When these reactions are carried out in the gas phase, vibronic–electronic coupling between the product ground and excited states may occur if there is little or no vibrational deactivation. Ground-state pericyclic reactions which proceed through antiaromatic intermediates should be chemiluminescent, again G-type reactions. The efficiency in chemiluminescence will depend on the energies of the state involved and the selection rules for emission.

In the following section we will illustrate the division of photochemical reactions into X, N, and G-types. In the discussion of all three types of reactions we will give particular attention to pericyclic processes, as there are examples of each kind in the literature.

6. Examples

If all of the pertinent data were recorded, it would be easy to classify photochemical reactions in the literature as X, N, or G-type; however, in most cases the luminescence data for the products have not been reported. There are, however, several cases where luminescence data are available, and others where the required information may be obtained by inference. In the following discussion, we have selected specific examples to illustrate the differences between the photochemical reaction types and the application of PMO reasoning to each type.

X-Type Photochemical Reactions. One example of an X-type photochemical pericyclic reaction is the biprotonic phototautomerism of the hydrogen-bonded dimers of 7-azaindole (eq 10). The observation of product luminescence for this reaction[21] classes it as an X-type process.



(10)

An orbital correlation for this reaction would show that all of the doubly occupied orbitals of the ground state of IV smoothly transfer into the doubly occupied orbitals of the ground-state V. The PMO description of the transition state in reaction 10 involves four distinct but coordinated elements, namely, reorganization of the electronic structures of the two π systems and two, three-atom proton-transfer systems in the σ framework. These coordinated electronic systems are very much like the phosphonitrile halides where true conjugation does not occur.[1] Each element in the transition state should be first-order stabilized on the ground-state surface. The σ systems are analogous to the allyl anion, and the π systems are analogous to the aromatic heterocycle.

Since the ground-state transition state is first-order stabilized the lack of a BO breakdown in the course of the reaction is very reasonable. The reaction occurs on the excited-state surface because of the inversion of the stabilities of the structures IV and V in the excited state, as first pointed out by Kasha and his coworkers.[21]

This kind of phototautomerism should be possible for hydrogen-bonded peptides as well. It is conceivable that phototautomerism is responsible for several enigmatic reports of phosphorescence from simple peptide systems.[37]

A large number of *eximer* formation reactions are X-type photochemical processes. For example, concentrated solutions of pyrene exhibit a fluorescence which is both delayed and shifted in wavelength from the monomer emission[38] (eq 11).

In the case of the π-bonded dimer formation in pyrene, all of the doubly occupied orbitals in the ground state of the monomers will smoothly transform into the doubly occupied orbitals of the π-associated dimers.

Figure 11 illustrates the first-order interaction of the highest occupied and lowest vacant orbitals in the dimer. The net stabilization of the excited dimer will be $(\delta E_{\pi_1} + \delta E_{\pi_2})$. In the ground state of the dimer, the first-order stabilization will be zero, and the second-order terms will destabilize the system with reference to the independent monomers. There will be no first-order stabilization of the transition state for dissociation on the ground-state surface, but the activation energy for dissociation must be very nearly zero. If the activation energy for the thermal reverse is very small, the zero-order approximation to the first excited state will be valid, and radiative and radiationless relaxation of the electronic excitation will be competitive as suggested in Figure 12. The competition between radiative and radiationless relaxation should be quite sensitive to structure. Structural changes which would stabilize the ground-state dimer should favor radiationless relaxation. Virtually all of the factors, which would stabilize the ground-state π complex, will favor charge-transfer phenomena. On the basis of the discussion above, and the fact that the transition state for disassociation of the π complex is not first-order stabilized, we would not expect to observe anomalous fluorescence in charge-transfer systems.[39] One specific example of

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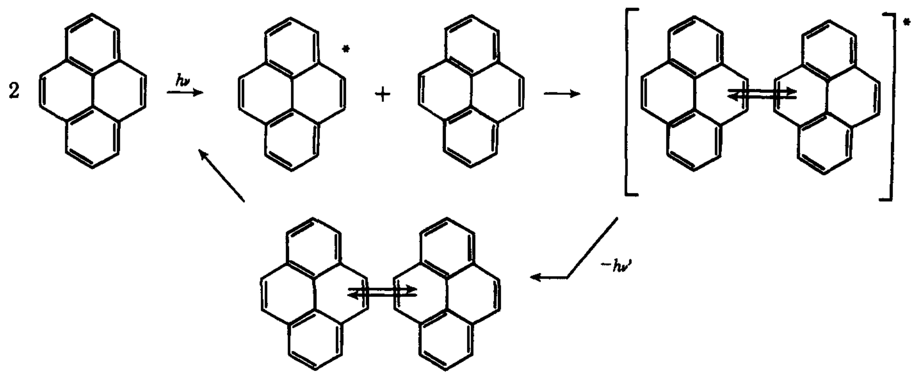
(36) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, 90, 1920 (1968).

(37) M. J. Maria, D. Larson, M. E. McCarville, and S. P. McGlynn, *Accounts Chem. Res.*, 3, 368 (1970).

(38) C. A. Parker, *Advan. Photochem.*, 2, 305 (1964).

(39) See, for example, (a) C. Reid and R. S. Mulliken, *J. Amer. Chem.*



(11)

the effect of stability of the loosely bonded ground-state associamer on radiationless relaxation from excited $\pi \rightarrow \pi^*$ states of aromatic systems has recently been reported by Hammond and coworkers.[40] The ground-state π complexes between methyl chloroacetate and electron-rich aromatics will certainly be more stable than an aromatic dimer complex although the difference should be slight. The small shift in the reaction coordinate is evidently quite enough to allow vibronic relaxation of the aromatic excited state without significantly populating the excited state corresponding to the π-complex structure.[40] This photochemical process would then be properly classed as a G-type photochemical pseudoreaction. Its reaction coordinate profile should look like that in Figure 6.

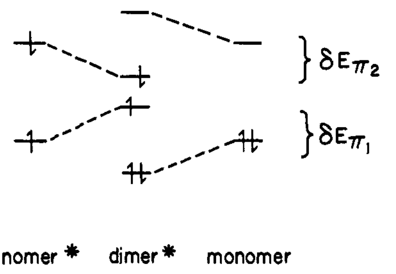
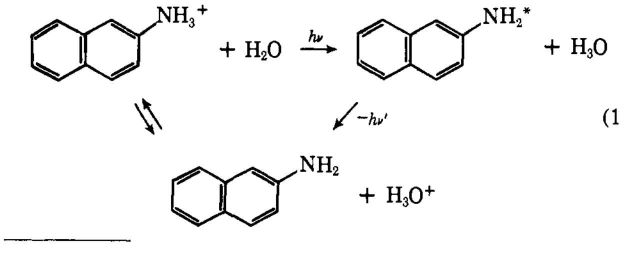


Figure 11. First-order splitting of orbital energies in an excited-state π complex.

There are a number of photochemical bond-breaking reactions that have luminescent products and are thus X-type reactions. A large number of the examples of this type of reaction are reactions from the upper excited states of small molecules in which the luminescent product is $OH(^2\Sigma)$, $NH_2(^2A_1)$, or some other small fragment.[19] The cases that are of interest to organic chemists involve acid–base behavior in the excited state, *e.g.*, eq 12.[41]



(12)

The transition state for proton transfer in an acid–base reaction is first-order stabilized. The orbital system is analogous to the allyl anion (see the discussion of reaction 10). The fact that the reaction is an X-type process is very reasonable on this basis. The inversion of stabilities on the excited surface (see section 2) explains the fact that the acidity constants for the conjugate acid of β-naphthylamine in its ground state and first excited singlet state differ by 10^6 ($pK_{S_0} = 4.1$, $pK_{S_1} = -2$).[41]

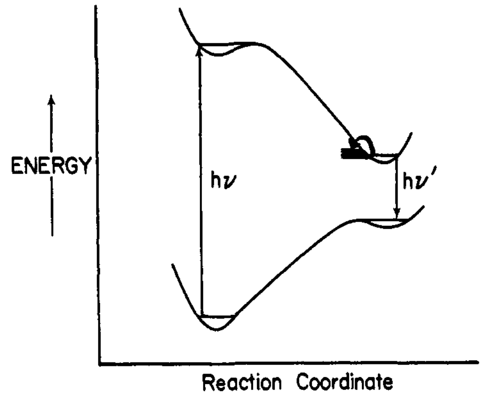
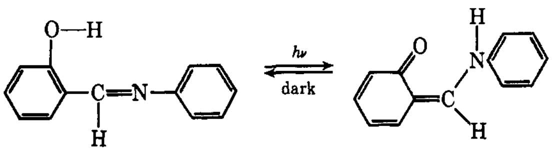
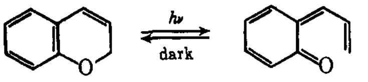


Figure 12. A hypothetical reaction coordinate cross section for eximer formation 11.

There are a large number of photochromic reactions that involve 1,5-phototropic shifts, *e.g.*, eq 13,[42] or 1,6 cyclizations, *e.g.*, eq 14.[43] Unfortunately, luminescence



(13)



(14)

spectra have not been recorded for these reactions, so it is not possible to identify them as to reaction type. It seems likely to us that some of these reactions will be found to be X-type reactions.

For reaction 13, the overlaps are substantially better for suprafacial proton transfer than for antarafacial transfer. For suprafacial transfer, the transition state will be topologically analogous to the cyclopentadienyl

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Soc., **76**, 3869 (1954); (b) M. J. S. Dewar and H. Rogers, *J. Amer. Chem. Soc.*, **84**, 395 (1962).

(40) M. T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *ibid.*, **92**, 6991 (1970).

(41) G. Jackson and G. Porter, *Proc. Roy. Soc., Ser. A*, **260**, 13 (1961), and papers cited therein.

(42) R. S. Becker and W. F. Richey, *J. Amer. Chem. Soc.*, **89**, 1289 (1967), and papers cited therein.

(43) R. S. Becker and J. Michl, *ibid.*, **88**, 5931 (1966).

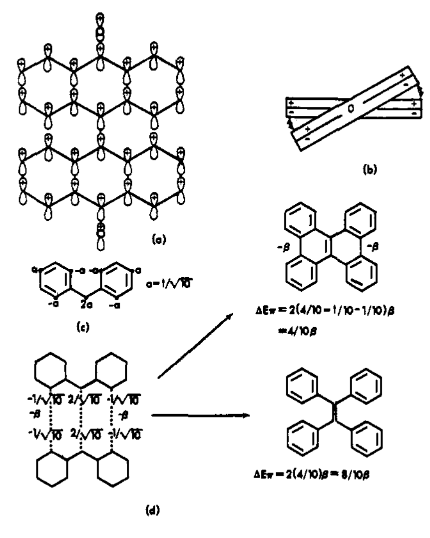
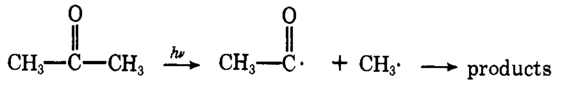


Figure 13. (a) Orbital phase relationships in the intermediate leading to VII; (b) the same system seen on edge, the signs indicate AO phases with reference to the carbon planes in the rings; (c) calculation of the NBMO coefficients for diphenylmethyl;[10] (d) union of two diphenylmethyl radicals to give a π system analogous to bianthrone ($\Delta E_\pi = 8/10\beta$) and one analogous to the delocalized intermediate leading to VII ($\Delta E_\pi = 4/10\beta$).

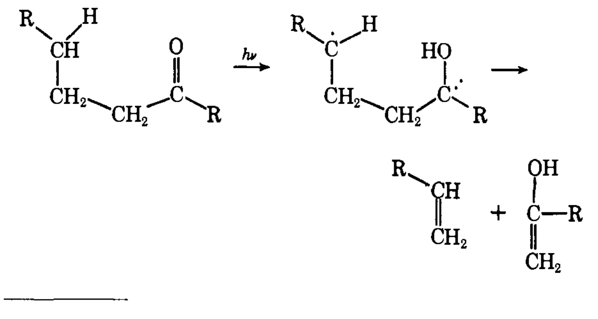
anion and it will be aromatic on the ground-state surface. Antarafacial transfer introduces one orbital phase inversion in the ring so the transition state will resemble the anti-Hückel cyclopentadienyl anion. An excited-state reaction proceeding with suprafacial transfer should be X type (ground-state transition state is first-order stabilized) and the antarafacial reaction should be G type (no first-order stabilization of the ground-state transition state). Similar factors will affect the course of reaction 14.

Since the differences between the two transition states are so small, it seems very likely that structural changes in the reactants could interconvert the reaction between X and G types. Just as in the π complexes discussed above, factors which destabilize the product ground states should favor X-type reactions.

N-Type Photochemical Reactions. The literature abounds with examples of N-type photochemical processes. The Norrish cleavage reactions of ketones are classic examples of N-type photoprocesses 15 and 16.[44] In both cases, the existence of radical intermediates has been clearly established.[44]

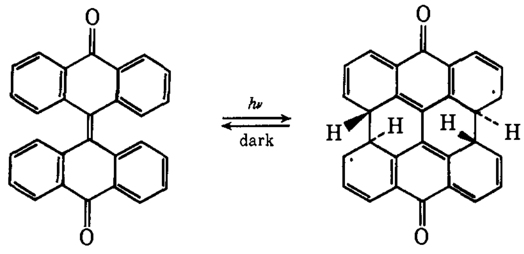


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{h\nu} CH_3-\overset{O}{\overset{\|}{C}}\cdot + CH_3\cdot \longrightarrow \text{products} \quad (15)$$



(16)

The intramolecular photochemical reaction of bianthrone[45] (VI) is an example of an N-type photoprocess which is also a pericyclic reaction (17).



VI VII (17)

Space-filling models indicate that bianthrone must be propeller shaped, so closure to VII must give the ring juncture stereochemistry as shown. Figure 13 indicates the orbital phase relationships for the ring closure and the topologically equivalent π structure. The analysis in Figure 13 indicates that the delocalized intermediate leading to VII should be antiaromatic with reference to bianthrone itself. Thus, the BO approximations should break down for the photochemical interconversion of VI and VII, and VII should be formed in its nonbonding ground state by the photochemical process. VI and VII may also be thermally interconverted. Microscopic reversibility requires that the thermal reverse of 17 be potentially chemiluminescent.

G-Type Photochemical Reactions. The luminescence spectra of photochemical reactions are not as available as one would like. There are, however, a large number of cases of photochemical reactions that must be G-type processes simply because the photoactivated reactants do not have the energy required to populate the first excited state of the products and the absence of radical intermediates can be rigorously established. This was first pointed out for the photochemical formation of cyclobutene from 1,3-butadienes by Dauben and coworkers.[46] There are many related cases, *e.g.*, the photochemical formation of Dewar benzene or the conversion of hexatrienes to bicyclohexenes. There are a large number of related cases where the relative stabilities on the excited-state surface follow the same order as those on the ground-state surface. In these cases, photoactivation of the low-energy side cannot lead to population of excited states on the high-energy side. This appears to be in direct conflict with the analysis in section 1, until the distinction between the π- and σ-electronic systems is established. The analysis in section 1 is devoted entirely to π-electronic systems of the same size. When the size of the π system changes in the reaction, the energy analysis of section 1 will, of course, be inadequate. In the following discussion, we have selected several cases of reactions that must be G type for energetic and stereochemical reasons. We will also discuss examples of chemiluminescent processes which are the reverse of G-type photoreactions.

The photochemical conversion of hexatrienes to bicyclo[3.1.0]hexenes (eq 18)[47] and related reactions in cyclooctatetraene photochemistry (eq 19)[48] are clearly

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[44] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

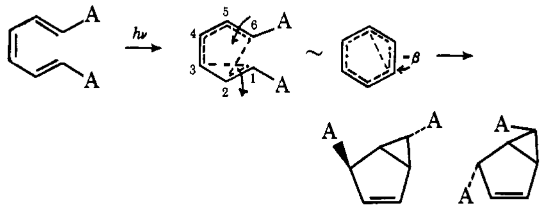
[45] (a) E. Wasserman, *J. Amer. Chem. Soc.*, **81**, 5006 (1959); (b) E. Wasserman and R. B. Woodward, *ibid.*, **81**, 5007 (1959).

[46] W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *ibid.*, **87**, 3996 (1965).

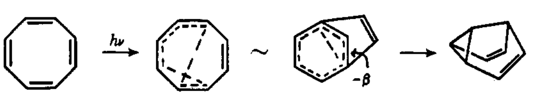
[47] J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 1775 (1967).

[48] H. E. Zimmerman and H. Iwamura, *ibid.*, **92**, 2015 (1970).

G-type reactions. The reactions are stereospecific which excludes N-type processes, and they occur at energies such that the excited states of the products are definitely not accessible. These reactions have been explained on an orbital symmetry basis by dividing the system into ethylene and butadiene fragments.[4,48] Although this procedure gives a proper rationalization of the observed results, considerations which deny delocalization in excited electronic states seem to be poorly founded in theory. Arguments which depend on the existence of unspecified higher excited states,[49] which may have proper symmetry properties for conversion to ground states, also lack a sense of rigor. Below we illustrate models for the orbitally degenerate states in each of the reactions, and their π-electronic analogs.



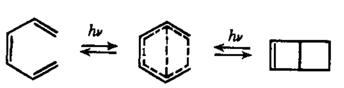
(18)



(19)

In the PMO formalism, the bond order between atoms of like parity is zero for alternant systems, so the 1–3 formal π bond in the systems above should neither stabilize nor destabilize the systems. It can thus be neglected, which explains why neglecting this bond works for the symmetry-based arguments. Dewar has shown that bonds, like the "extra" ethylenic unit in cyclooctatetraene, can be neglected for this same reason.[5]

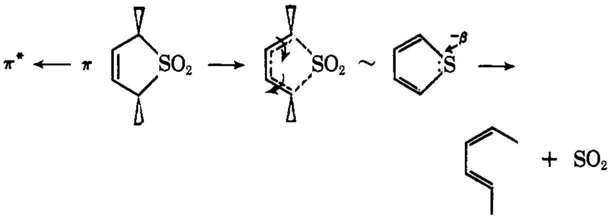
In contrast to the cases cited above, neglect of specific bonds is neither necessary nor desirable in considerations of the hexatriene–bicyclo[2.2.0]hexene interconversion (eq 20). In this case the π-electronic analog of the orbitally degenerate intermediate is the bicyclo[2.2.0]hexatriene system. Reaction 20 from left to right must be a G-type reaction on energetic grounds alone.



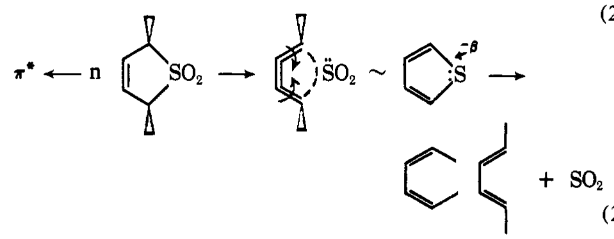
(20)

The formation and destruction of Dewar benzene involve an intermediate which is orbitally analogous to the π electrons of the bicyclo[2.2.0]hexatriene system. Both thermal and photochemical excitation of Dewar benzene should lead to formation of benzene. The thermal opening of Dewar benzene is a clear example of a reaction in which there is no first-order interaction between the bond-forming and bond-breaking elements, but the reaction should be concerted for entropic reasons. Detection of thermal population of a benzene triplet would not constitute proof of nonconcertedness since the ground-state and excited-state surfaces intersect at the intermediate. We expect the thermal opening of Dewar benzene to be a chemiluminescent process, although the efficiency may be low, because of the relatively large energy involved. The fact that this chemiluminescence has not been reported to date reflects both the low efficiency and high energy of the luminescence (uv detection will almost certainly be required).

A large number of stereospecific photochemical ring-opening reactions are known.[4] These reactions must be G-type processes for the following reason: if the product polyene were formed in its first excited state (which is generally energetically possible) it would be isomerized through an N-type process that is characteristic of the first excited state. The reaction stereospecificity suggests that the product excited states are not populated in the reactions. The apparently low stereospecificity in the photochemical elimination of SO_2 from a hexadiene sulfone,[50] which should be a G-type reaction by analogy, can be easily treated within the present framework. The $\pi\rightarrow\pi^*$ state of the sulfone requires one-phase inversion to get to an orbitally degenerate ground-state antiaromatic intermediate, and this should lead to a *cis,trans*-hexatriene from the *cis*-dimethylbutadiene sulfone (eq 21). Competitive population of the sulfone $n\rightarrow\pi^*$ state should produce the opposite result (eq 22) since the π^* orbital associated with the sulfone will have d orbital phase properties. The bond stretching which would be required in order to allow the sulfone π^* orbital to mix with the σ and π orbitals of the hydrocarbon system would account for the smaller than expected differences in the ratio of the *trans,trans*- to *cis,cis*-hexadiene product.[50] Since the *cis,cis*-hexadiene above arises, according to this view, from the $n\rightarrow\pi^*$ state of the sulfone, we would expect to observe a smaller amount of this product, relative to the abundance of the trans,trans product, if it were to come from the carbon $\pi\rightarrow\pi^*$ state as required for the *trans*-dimethylbutadiene sulfone. This was observed experimentally.[50] The clear prediction from this analysis is that factors which alter the relative energies of the two excited states, the ring $\pi\rightarrow\pi^*$ state and the sulfone $n\rightarrow\pi^*$ state, should substantially alter the product composition in these photoreactions.



(21)



(22)

Reaction 23 is closely related to eq 22 and it also provides the basis for understanding eq 24.[51]

Sensitization of the sulfone $n\rightarrow\pi^*$ state would allow relaxation of the electronic excitation by a disrotatory ring opening with elimination of SO_2 (eq 23) like that indicated in eq 22. In the hydrocarbon, the lowest excited state in the benzocyclobutene portion of the mole-

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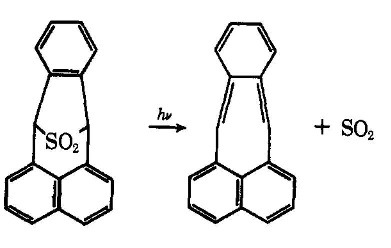
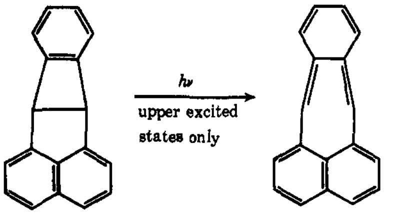
(49) W. Th. Am. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, 91, 6042 (1969).

(50) J. Saltiel and L. Metts, *ibid.*, 89, 2232 (1967).

(51) (a) J. Michl and J. Kolc, *ibid.*, 92, 4148 (1970); (b) J. Michl, *ibid.*, 93, 523 (1971).

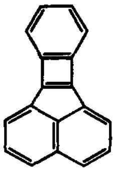


(23)



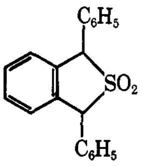
(24)

cule is considerably more energetic than the lowest excited state for naphthalene. The π-electronic analog of the σ–π delocalized intermediate in reaction 24 is VIII.

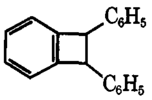


VIII

The bonds between the naphthalene and benzocyclobutadiene portions of VIII are essentially single bonds;[2] as far as PMO theory is concerned those bonds contribute nothing to the structure. Vibronic relaxation of the electronic excitation through ring opening (a G-type reaction) can only occur if it is the benzocyclobutene portion of the molecule that is excited. The analysis above predicts that naphthalene will sensitize ring opening in IX and not in X.

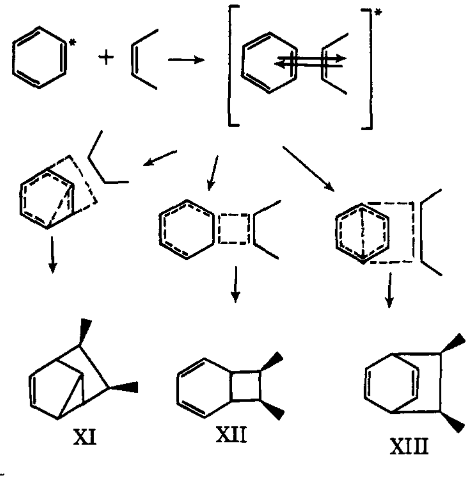


IX

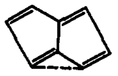


X

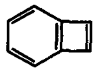
Wilzbach and Kaplan have recently reported the results of a study of the stereospecific addition reactions of olefins to photoexcited benzene[52] (eq 25). Once again the reaction energetics require this process to to be G type. The π-electronic analogs of the intermediate structures in reaction 25 are, respectively, XI′, XII′, and XIII′. Each of these systems is PMO anti-



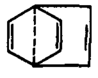
(25)



XI′



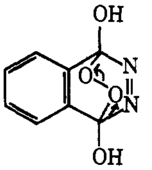
XII′



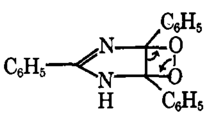
XIII′

aromatic[1] and should, therefore, be at a hole between the ground and excited states. Bryce-Smith's symmetry analysis of the olefin addition reactions to electronically excited benzene[53] requires different benzene electronic states for the production of XI, XII, and XIII. The mechanistic evidence[52] indicates that all three products are formed from a common precursor, presumably the *exiplex* shown in eq 25. Since all three products must reach the ground state by a BO violation, there is no reason to believe that the electronic state symmetries should be important in determining the product composition. Of the three structures a PMO analysis suggests that XI should be the most antiaromatic which may be one of the reasons why XI often dominates the product mixture.[52]

Chemiluminescent reactions are easily conceptualized as photochemical reactions run backward. The factor which controls the direction of the reaction is the relative energies of the starting and final states. Very few photochemical processes are reversible in the sense that the products can be converted into reactants with a resulting chemiluminescence. The ring opening of Dewar benzene may be an exception to this generalization (see above). Nonetheless, the description of concerted photochemical reactions which result in products in their ground electronic states (G-type reactions), must apply with equal force to the reverse reactions, namely chemiluminescent processes, reactions which proceed from the electronic ground state of the starting materials to an excited state(s) of the products. Chemiluminescent processes must involve the release of a large amount of chemical potential (equal to or in excess of the energy of the quantum of emitted radiation) roughly within the period of one vibration. This restriction essentially limits chemiluminescent processes to electron transfer, charge annihilation, and pericyclic reactions. The intermediates in pericyclic chemiluminescent reactions should correspond to antiaromatic ground-state structures just as for other G-type photochemical pericyclic reactions. The decomposition of proposed intermediates in the chemiluminescence of luminol (XIV) and lophine (XV)[54] is virtually certainly a pericyclic process which involves a six-electron state with one phase inversion for XIV and a four-electron four-orbital state for XV. Both of these transformations proceed through antiaromatic ground states. The phase



XIV



XV

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(52) (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **93**, 2073 (1971); (b) K. E. Wilzbach and L. Kaplan, *ibid.*, **88**, 20661 (1966).

(53) D. Bryce-Smith, *Chem. Commun.*, 806 (1969).

(54) F. McCapra, *Quart. Rev., Chem. Soc.*, **20**, 485 (1966).

inversion in XIV occurs in breaking an oxygen–oxygen single bond in a transoid fashion.

7. Conclusions

Because more than one electronic surface is inevitably involved in photochemical reactions, it is desirable to phenomenologically classify photochemical reactions prior to developing mechanistic interpretations. Our mechanistic understanding of a given reaction will depend to a considerable extent on whether the reaction (1) occurs entirely on an excited state surface, X type, (2) starts on an excited surface and results in bond breaking to give ground-state nonbonding radical intermediates which subsequently react, N type; or (3) starts on an excited surface and ends in a bonding ground state without the intervention of intermediates (or the reverse), G type. We have indicated the ways in which first-order perturbation theory and an analysis of the breakdown of the Born–Oppenheimer approximation can be used to develop a mechanistic understanding of the three types of photochemical reactions.

The PMO treatment offers a direct insight into the driving force for G-type photochemical pericyclic reactions, whereas an orbital symmetry analysis offers very little insight into the virtue of concertedness for these processes. Even Lewis's principle of maximum bonding in the transition state[55] is difficult to apply to photochemical processes in the absence of an electronic analysis coupled with an analysis of Born–Oppenheimer breakdown. The discussion in section 4 indicates that in reactions that proceed through orbitally degenerate structures, where there are significant symmetry elements, those elements will be destroyed by electronic–vibronic coupling. This is the specific mechanism for conversion of electronic excitation to chemical potential for those reactions.

Finally, it appears that chemical reactions generally might be usefully divided into two types: those for which the Bell–Evans–Polanyi analysis holds (BEP reactions) (see section 2) and those for which it does not (anti-BEP reactions). For the BEP reactions both thermal and photochemical processes will proceed by paths which minimize the energy gap between the ground state and the first excited state. The anti-BEP reactions will proceed by paths which maximize that same gap.

Acknowledgments. It is a pleasure to acknowledge the patient help and criticism of Professor William Rhodes in the development of this manuscript. I am also indebted to many of my colleagues, the editor, and referees for numerous helpful suggestions.

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(55) G. N. Lewis, "Valence and the Structures of Atoms and Molecules," Chemical Catalog Co., New York, N. Y., 1923.

Ground States of σ-Bonded Molecules. XIV.[1a] Application of Energy Partitioning to the MINDO/2 Method and a Study of the Cope Rearrangement[1b]

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Received April 23, 1971

Abstract: The technique of energy partitioning of Fischer and Kollmar has been extended to the MINDO/2 approximation and used in a detailed analysis of the Cope rearrangements of 1,5-hexadiene, bullvalene, barbaralane, and semibullvalene. The relationship between the quantities introduced in this treatment and bond lengths and bond energies is studied.

One of the problems that has arisen with the development of more sophisticated MO treatments[3] is the difficulty of relating the results of such calculations to the traditional picture of molecules in terms of localized bonds, resonance energy, etc. Correlations of this kind were well established in the HMO era;[4] however, SCF expressions for the total energy[5] are far more complex and it is very much harder to see their relationship[6] to traditional ideas.

Recently Fischer and Kollmar[7] have proposed a scheme for dissecting such expressions into contributions by individual atoms and bonds. Such a partitioning of the energy is clearly just what is needed to interpret and enlarge on the classical bond picture; it also provides an excellent basis for studying the effect of changes in the parameters in semiempirical SCF–MO treatments.

We have been applying this technique to the MINDO/2 approximation,[8,9] with both objects in view.

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(1) (a) Part XIII: Michael J. S. Dewar and Wolfgang W. Schoeller, *Tetrahedron*, 27, 4401 (1971). (b) This work was supported by the Air Force Office of Scientific Research through Contract No. F44620-70-C-0121.

(2) Robert A. Welch Postdoctoral Fellow.

(3) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 93, 289 (1971); S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, 49, 312 (1968).

(4) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(5) C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

(6) O. Sinanoglu and K. B. Wiberg, "Sigma Molecular Orbital Theory," Yale University Press, New Haven, Conn., 1970; R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971).

(7) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, 16, 163 (1970).