

In the reversible second-order case the equilibrium composition was first solved by numerical means. The kinetic problem was treated as above, using as rate law: rate = $k_{\text{org}}^f c_{\text{org}}^{\text{RX}} c_{\text{org}}^{\text{Y}^-} - k_{\text{org}}^r c_{\text{org}}^{\text{RY}} c_{\text{org}}^{\text{X}^-}$.

References and Notes

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- (2) C. M. Starks, *J. Am. Chem. Soc.*, **93**, 195 (1971).
- (3) The number of possible models increases substantially if one includes ancillary equilibria (ion-association, micelle-formation, ion-solvation equilibria). While it is true that some of these equilibria undoubtedly perturb the selective distribution of anions between the phases,⁴ data do not exist to parametrize them for the PTC systems of interest. These effects, if present, are however included in the experimental liquid ion-exchange selectivity coefficients whose use in correlating PTC is advocated in this paper. Consequently, omission of ion-association equilibria, etc., may be expected to limit the ranges of concentrations for accurate application of the expressions derived, but to have little effect on qualitative differences in behavior of individual ions as predicted via $K_{Y/X}^{\text{org}}$.
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$$\begin{array}{c} \text{RX} + \text{Q}^+\text{Y}^- \longrightarrow \text{RY} + \text{Q}^+\text{X}^- \text{ (organic phase)} \\ \text{-----} \uparrow \qquad \qquad \qquad \downarrow \text{-----} \\ \text{M}^+\text{X}^- + \text{Q}^+\text{Y}^- \rightleftharpoons \text{M}^+\text{Y}^- + \text{Q}^+\text{X}^- \text{ (aqueous phase)} \end{array}$$
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Symmetry Considerations and Correlation Diagrammatic Analyses of Certain Photochemical Reactions with and without Spin Inversion

Tieh-sheng Lee

Contribution from the Chemistry Department, National Chung Hsing University, Taichung, Taiwan, Republic of China. Received April 2, 1976

Abstract: When studying the electronic radiationless transitions of molecular systems in general, Lin obtained a set of symmetry selection rules in 1966 by considering the symmetry features of the set of promoting modes involved. The rules read: $\Gamma(\phi_a^0)\Gamma(Q_i)\Gamma(\phi_b^0) = A$; $\Gamma(\phi_a^0)\Gamma((\partial h_{so}/\partial Q_i)_0)\Gamma(\phi_b^0) = A$; $\{\Gamma(\phi_a^0)\Gamma((\partial h_0/\partial Q_i)_0)\Gamma(\phi_c^0)\}\Gamma(\phi_c^0)\Gamma(h_{so}^0)\Gamma(\phi_b^0) = A$; $\{\Gamma(\phi_a^0)\Gamma(h_{so}^0)\Gamma(\phi_c^0)\}\Gamma(\phi_c^0)\Gamma((\partial h_0/\partial Q_i)_0)\Gamma(\phi_b^0) = A$; where the letter A stands for the phrase, "the totally symmetric species of the point group of interest" and $\Gamma(\xi)$ denotes the symmetry representation of the argument ξ , which may either be a function or an operator. It has been demonstrated in this article that the rules of Lin can be applied equally well to a large body of chemical reactions if certain slight modifications of the rules are introduced. In dealing with chemical reactions, if molecular systems are described by wave functions in the Born–Oppenheimer approximation, the wave function of the reacting system may take the form of the superposition of various such adiabatic wave functions with time-dependent coefficients. Chemical reactions can then be viewed as the transitions from the initial molecular systems to the final ones due to the breakdown of the Born–Oppenheimer approximation. This enables one to treat chemical reactions just the same way as Lin did for radiationless transitions and the same set of symmetry selection rules must be applicable. The verification of the applicability of this set of rules is explicitly demonstrated by studying a number of photochemical reactions. A systematic procedure for the symmetry analysis for chemical reactions in general is thus developed. This involves the examination of the orbital symmetries based on the newly proposed rules, the construction of the orbital correlation diagram, and the detection of the presence of a particular diagrammatic topology associated with the orbital avoided crossing. Results are promising. The Woodward–Hoffmann type symmetry conservation rules are found to be merely special cases. Reactions involving spin inversion can likewise be systematically analyzed so that the different behavior of the photochemically excited singlet and triplet states of various organic compounds can be better understood. Most importantly, the avoided surface crossing concept Salem originally discussed has been investigated by using the promoting mode concept of Lin. It has been found that when dealing with transitions involving open-shell states, the use of the MO energies obtained by the unrestricted Hartree–Fock wave function approach gives results different from those of Salem's in certain cases.

Symmetry-based selection rules for chemical reactions have now become a research interest that receives an increasing popularity since the publication of a series of communications of Woodward and Hoffmann.^{1–3} Reactions analyzed by their

approach included the electrocyclic type, the sigmatropic type, and the concerted cycloaddition type. This well-known orbital-symmetry conservation concept was extended to deal with transition metal catalytic reactions first by Mango and

Schachtschneider.⁴ Eaton later studied the isomerization and substitution reactions of transition metal ion complexes by considering the symmetry properties of the atomic d orbitals of the central metal atom.⁵ On the other hand, Pearson investigated the symmetry feature of the isomerization of four-coordinated complexes of transition metal ions between tetrahedral (T_d) and square planar (D_{4h}) structures.^{6,7} His arguments were based on another type of selection rules originally proposed by Bader for analyzing the perturbation theory of the Jahn–Teller effect. In 1970, Pearson^{8–10} made an even more significant progress in this field by proposing that the true electronic Hamiltonian of the reacting system varies as the system moves along the reaction coordinate Q . He then expanded the Hamiltonian in a Taylor–Maclaurin series about Q_0 , the point corresponding to the original configuration,

$$H = H_0 + (\partial U/\partial Q)Q + \frac{1}{2}(\partial^2 U/\partial Q^2)Q^2 \dots \quad (1)$$

By considering the last two terms in eq 1 as the perturbation and carrying out the expansion to second order, he obtained a set of symmetry selection rules so versatile that a large body of reaction types such as the unimolecular, the bimolecular, and the nucleophilic displacement reactions can be better understood.

Although symmetry arguments can only provide qualitative information, the importance is now increasingly recognized by chemists working in almost all fields. For example, Salem^{11,12} recently observed one type of symmetry conservation involving a symmetry plane not related to any of the Woodward–Hoffmann type symmetry elements when studying the mechanistic details of certain photochemical reactions. In fact, the surface avoided crossing concept Salem introduced is here briefly reviewed and extensively applied to all reactions considered in this article. It is also observed that the diversity of most of the photochemical reaction pathways can be easily analyzed by symmetry considerations. The disallowedness of a pathway can almost always be predicted unambiguously by detecting the presence of any avoided crossing topology in the orbital correlation diagram. The chief objective of this paper is therefore to develop a systematic symmetry analysis procedure for studying certain photochemical reactions, either spin conserved or spin inverted.

Results and Discussion

Rules of Lin. In this paper, we are trying to look at chemical reactions from a different point of view. When studying the electronic radiationless transitions of molecular systems in general, Lin¹³ considered the expression

$$w(bv' \rightarrow av'') = (2\pi/\hbar) \sum_i |R_i(ab)|^2 |\langle X_{av''} | \partial/\partial Q_i | X_{bv'} \rangle|^2 \cdot \Pi_j |\langle X_{av''} | X_{bv'} \rangle|^2 \delta(E_{av''} - E_{bv'}) \quad (2)$$

In this expression, $w(bv' \rightarrow av'')$ is the transition probability of the transition $|bv' \rangle \rightarrow |av'' \rangle$. The initial and the final vibronic states are respectively specified by two sets of the electronic quantum numbers b and a , together with two sets of the vibrational quantum numbers v' and v'' . $|X_{bv'} \rangle$ and $|X_{av''} \rangle$ are to designate the wave functions of the clamped nuclei associated with the electronic wave functions $|\phi_b \rangle$ and $|\phi_a \rangle$, respectively. The matrix element $R_i(ab)$ is

$$R_i(ab) = -\hbar^2 \langle \phi_a | \partial/\partial Q_i | \phi_b \rangle \quad (3)$$

where Q_i stands for the normal coordinate of the i th vibrational mode. The energy conservation throughout the transition is ensured by including in eq 2 the factor $\delta(E_{av''} - E_{bv'})$. Lin then distinguished in eq 2 between the promoting modes i , responsible for the transition, and the accepting modes j , which form a sink for the excess electronic energy. Obviously, for any mode i to be a possible promoting mode, the matrix element $R_i(ab)$

is required to take a nonzero value. By writing the electronic Hamiltonian as

$$H_{elec} = h_0^0 + h_{so}^0 + \sum_i [(\partial h_0/\partial Q_i)_0 + (\partial h_{so}/\partial Q_i)_0] Q_i \quad (4)$$

and carrying out the perturbation to second order, Lin succeeded to obtain the set of selection rules for the processes known as internal conversion and intersystem crossing. In eq 4, all the operators are referred to the equilibrium nuclear configuration. The operator h_0^0 contains the usual kinetic and potential energies for the electrons and h_{so}^0 represents the spin–orbit coupling operator. The rule for the internal conversion is simply

$$(\phi_a^0) \cdot \Gamma[(\partial h_0/\partial Q_i)_0] \cdot \Gamma(\phi_b^0) = A \quad (5)$$

where $\Gamma(\xi)$ represents the symmetry species of the argument ξ , which may either be a function or an operator. The letter A stands for the phrase, “the totally symmetric species of the point group”. Equation 5 may be rewritten as

$$\text{Rule I. } \Gamma(\phi_a^0) \cdot \Gamma(Q_i) \cdot \Gamma(\phi_b^0) = A \quad (6)$$

since the operator H_{elec} is invariant with respect to any symmetry transformation and so is every term in eq 4. The direct product $\Gamma(Q_i) \cdot \Gamma[(\partial h_0/\partial Q_i)_0]$ therefore must be totally symmetric, or $\Gamma(Q_i)$ must be identical with $\Gamma[(\partial h_0/\partial Q_i)_0]$. This rule, eq 6, is valid not only for radiationless electronic transitions involving no spin multiplicity changes, but has also been used by Pearson,⁸ by interpreting only one Q as the reaction coordinate while ignoring the other Q_i 's, as a criterion for the determination of the allowedness of chemical reactions.

The rules, on the other hand, for intersystem crossing are much more complex. We first summarize some of the results of Lin. The transition matrix for intersystem crossing is given by

$$\langle \phi_a | \partial/\partial Q_i | \phi_b \rangle_{\text{int cross}} = \frac{\langle \phi_a^0 | (\partial h_{so}/\partial Q_i)_0 | \phi_b^0 \rangle (E_b^0 - E_a^0)}{(E_a^0 - E_c^0)(E_b^0 - E_a^0)} + \frac{\langle \phi_a^0 | h_{so}^0 | \phi_c^0 \rangle \langle \phi_c^0 | (\partial h_0/\partial Q_i)_0 | \phi_b^0 \rangle}{(E_a^0 - E_c^0)(E_b^0 - E_a^0)} + \frac{\langle \phi_a^0 | (\partial h_0/\partial Q_i)_0 | \phi_c^0 \rangle \langle \phi_c^0 | h_{so}^0 | \phi_b^0 \rangle}{(E_b^0 - E_a^0)(E_b^0 - E_c^0)} \quad (7)$$

It indicates that an intersystem crossing type transition may go through three distinct paths. It may go in one step through the perturbation of the operator $(\partial h_{so}/\partial Q_i)_0$; it may go first to one intermediate state ϕ_c^0 due to the perturbing operator h_{so}^0 followed by the coupling between ϕ_c^0 and ϕ_a^0 through the vibronic coupling operator $(\partial h_0/\partial Q_i)_0$; and it may involve an initial vibronic coupling between ϕ_b^0 and ϕ_c^0 and a final spin–orbit coupling between ϕ_c^0 and ϕ_a^0 . We are then concerned with the direct products,

$$\text{Rule II. } \Gamma(\phi_a^0) \cdot \Gamma[(\partial h_{so}/\partial Q_i)_0] \cdot \Gamma(\phi_b^0) = A \quad (8)$$

$$\text{Rule III. } \{\Gamma(\phi_a^0) \Gamma[(\partial h_0/\partial Q_i)_0] \Gamma(\phi_c^0)\} \times \{\Gamma(\phi_c^0) \Gamma(h_{so}^0) \Gamma(\phi_b^0)\} = A \quad (9)$$

$$\text{Rule IV. } \{\Gamma(\phi_a^0) \Gamma(h_{so}^0) \Gamma(\phi_c^0)\} \times \{\Gamma(\phi_c^0) \Gamma[(\partial h_0/\partial Q_i)_0] \Gamma(\phi_b^0)\} = A \quad (10)$$

where the explicit expression for h_{so}^0 is

$$h_{so} = (\frac{1}{2}m^2c^2) \sum_i \sigma_i \cdot (\nabla_i V \times \mathbf{P}_i) + (e/m^2c^2) \sum_i \sum_j \sigma_i \cdot (r_{ij} \times \mathbf{P}_j) / r_{ij}^3 \quad (11)$$

In developing this formulation, Lin argued from the physical point of view that although the eigenstates described by functions of the form

$$\Psi_{av} = \phi_a \Pi_i X_{av_i} \quad (12)$$

are to be regarded as good, they are, however, not stationary

in the exact sense, and the whole system oscillates to and fro among various good quantum states of almost the same energy. He then interpreted this as the transition from one electronic state to another, accompanied by a transition in the quantum states of nuclear motion. Such a mechanism of Lin for non-radiative electronic transitions is in spirit identical with the one proposed by Kubo in 1952 for rationalizing the processes called thermal ionization of trapped electrons in semiconductors.¹⁴ Now, the essential events occurring in a chemical reaction are simply the breaking and the making of chemical bonds. The bond-order change in chemical reaction is generally observed to be accompanied by a corresponding bond length change. In other words, the experimental fact is that an electronic transition of the reacting molecular system is always accompanied by a transition in the quantum states of nuclear motion. Thus, it seems reasonable to assume that chemical reactions also occur due to the breakdown of the Born-Oppenheimer approximation. Following the work of Kubo,¹⁴ or of Lin,¹³ we write

$$\Psi = \sum C_{av}(t) \Psi_{av}(r, R) \quad (13)$$

where Ψ is the time-dependent wave function describing the reacting system and the set of functions Ψ_{av} is obtained by the adiabatic approximation method. This set is not the eigenset of the true Hamiltonian H of the system, but satisfies

$$H \Psi_{av}(r, R) = E_{av} \Psi_{av} + H' \Psi_{av} \quad (14)$$

where

$$H' \Psi_{av} = T \phi_a \Pi_i X_{av} - \phi_a T \Pi_i X_{av} \quad (15)$$

In eq 15, T is the kinetic energy operator of the clamped nuclei. Functions ϕ_a and X_{av} are to be interpreted in the same way as we did in eq 2 and eq 3. If eq 15 is considered as the perturbation, the ordinary time-dependent perturbation method gives at once the transition probability from the initial state $|bv\rangle$ to the final state $|av'\rangle$ as

$$w(bv \rightarrow av') = (2\pi/\hbar) |\langle av' | H' | bv \rangle|^2 \rho \delta(E_{av'} - E_{bv}) \quad (16)$$

where ρ is the state density. We can then concentrate on the study of the matrix element, $\langle av' | H' | bv \rangle$. If the kinetic energy operator of nuclear motion T is expressed in terms of normal coordinates, eq 15 becomes

$$H' \Psi_{av} = -\hbar^2 \sum_i (\partial \phi_a / \partial Q_i) (\partial / \partial Q_i) (\Pi_i X_{av}) - \frac{1}{2} \hbar^2 \sum_i (\partial^2 \phi_a / \partial Q_i^2) (\Pi_i X_{av}) \quad (17)$$

In view of the Condon approximation, the second summation in eq 17 can be neglected altogether. If we consider, for simplicity, only the effect of the i th vibrational mode, we are concerned with

$$\langle av' | H_i' | bv \rangle = R_i(ab) \langle \Pi_i X_{av'} | \partial / \partial Q_i | \Pi_i X_{bv} \rangle \quad (18)$$

where

$$R_i(ab) = -\hbar^2 \langle \phi_a | \partial / \partial Q_i | \phi_b \rangle \quad (19)$$

Then, by following exactly the way Lin approached dealing with nonradiative processes, the same set of selection rules, eq 6, 8, 9, and 10 is obtained, applicable to chemical reactions in general. However, one remark about the choice of the proper equilibrium configuration at which certain operators are to be evaluated is necessary here. The function Ψ , being the superposition of a set of adiabatic wave functions Ψ_{av} , is of course not stationary. It contains various components, each being a state described by $\Psi_{av} = \phi_a \cdot \Pi_i X_{av}$, where ϕ_a is the wave function for the electrons of the system as though the nuclei were fixed in their instantaneous positions. Each such ϕ_a corresponding to an unknown but definite nuclear configura-

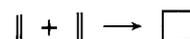
tion can be expanded as the superposition of the set of ϕ_a^0 's, all corresponding to a chosen known nuclear configuration. This is done again by the perturbation method and the Hamiltonian used is given in eq 4. Consider, for example, the expression in our formulation which leads to rule I;

$$\langle \phi_a | \partial / \partial Q_i | \phi_b \rangle = \langle \phi_a^0 | (\partial h_0 / \partial Q_i)_0 | \phi_b^0 \rangle / (E_b^0 - E_a^0) \quad (20)$$

It is important to note that the two functions ϕ_a^0 and ϕ_b^0 generally do not correspond to the same equilibrium nuclear configuration. In dealing with chemical reactions, it is most convenient to expand ϕ_b as the superposition of the set of functions defined at the equilibrium nuclear configuration of the reactant, or of the reacting complex, and to expand ϕ_a as the superposition of those defined at the equilibrium configuration of the product. Since the operator in eq 20 operates on ϕ_b^0 , it must be evaluated at the configuration of ϕ_b^0 . All that is required is that the two configurations belong to the same point group, for otherwise the normal coordinate Q_i could not be properly defined and symmetry arguments could not be introduced at all.

Cases for Rule I. In dealing with chemical reactions, the naive and direct application of the rules of Lin's type not give any useful results, except in very few cases. Two difficulties arise. The first pertains to the more drastic geometrical change forcing the reaction product to go to a point group usually no longer identical with the one the reacting system belonged to. The second difficulty arises because multielectron jumps, instead of single-electron jumps, are commonly observed in chemical reactions. Therefore, the state symmetry consideration may give less information than what can be extracted out by orbital-symmetry considerations.

Fortunately, the removal of the above-mentioned difficulties is possible. In fact, it turns out that the symmetry analyses of certain simple chemical reactions can be carried out smoothly in a systematic manner. We choose to describe and explain the systematic procedure by considering a series of example reactions. The first example to be taken is the dimerization of ethylene. If the reaction proceeds through a mechanism of the



concerted manner, the symmetry changes from the D_{2h} point group to the group D_{4h} . In order to apply our selection rule, we must choose the point group D_{2h} , which is common to both the reacting complex and the product. This is the first step of the systematic analysis. Since we are interested in examining the thermal allowedness of this reaction, we consider first only the ground state configurations. The concerned transition may be designated as $(a_g)^2(b_{1u})^2 \rightarrow (a_g)^2(b_{2u})^2$. In this designation, orbitals are classified according to their symmetries of D_{2h} . Here we observe that one of the physical effects of a vibrational mode to the reacting system is to shift the symmetry of only one of the many molecular orbitals from one representation to another, as far as the second-order perturbation theory is concerned. This implies that the direct product of the type, $(a_g b_{2u}) \Gamma(Q_i) (a_g b_{1u})$, is of the major importance, even though all these orbitals are doubly occupied. By rule I, we easily find $\Gamma(Q_i)$ to be b_{3g} . Now, the construction of the orbital correlation diagram is in order. Consider the diagram depicted in Figure 1a. When we say that two orbitals are correlated, we mean that they either belong to the same representation, or they are coupled by a vibrational mode of the proper representation. The latter type of correlation can only be allowed once in the diagram of a transition, for $\Gamma(Q_i)$ only appears once in the above-mentioned direct product. Obviously, Figure 1a is the only way to correlate the four occupied MO's. We have here a diagrammatic representation of rule I for the transition, i.e.,

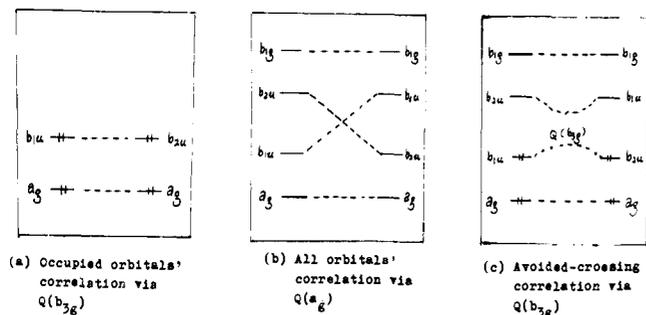


Figure 1. Various orbital correlation diagrams for the reaction (unscaled).

for the rule

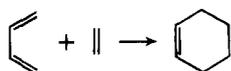
$$(a_g b_{2u}) b_{3g} (a_g b_{1u}) = A_g \quad (21)$$

To go one step further, we also include in the diagram the unoccupied orbitals and draw only correlation lines connecting orbitals of the same species. Figure 1b then results. By observing that there is a crossing between the b_{1u} and b_{2u} shown, we conclude that the coupling between b_{1u} and b_{2u} shown in Figure 1a is but an avoided crossing due to the mode b_{3g} . It has a close resemblance to the state avoided crossing discussed by Salem,¹² at least in origin. We will have more occasions to discuss this point in more detail. It can be seen from Figure 1c that there is a potential barrier of significant height between orbitals b_{1u} and b_{2u} due to symmetry. This enables one to conclude that the reaction under consideration is thermally forbidden. Furthermore, suppose that the initial configuration, $(a_g)^2(b_{1u})(b_{2u})$, is investigated. Rule I for this case takes the form

$$a_g b_{1u} b_{2u} \Gamma(Q_i) a_g b_{2u} b_{1u} = A_g \quad (22)$$

and $\Gamma(Q_i)$ is thus a_g . An adequate diagrammatic representation is Figure 1b and no potential barrier due to symmetry is involved. The dimerization is thus photochemically allowed.

Consider next the Diels–Alder reaction. Here we are con-



cerned with the point group C_2 , and the thermal transition is of the type $(a')^2(a'')^2(a'')^2 \rightarrow (a')(a'')^2(a')^2$. By reasoning given previously, we are concerned with the equation

$$a' a' a'' \Gamma(Q_i) a' a'' a' = A' \quad (23)$$

of which the solution is $\Gamma(Q_i) = a'$. This is an allowed transition, for Figure 2a, the diagrammatic representation of rule I for this case, reveals an absence of a potential barrier from symmetry. Although there is a surface crossing in Figure 2a, the avoided crossing cannot occur. Figure 2b depicts the diagram for such an avoided crossing in which two pairs of orbitals are coupled through the mode a'' . This is a process not within the scope of the second-order perturbation theory.

Although we have analyzed the photochemical dimerization of ethylene, the photochemical behavior of the cyclization between butadiene and ethylene deserves much more discussion. Slight modification of the analysis procedure for open-shell transitions in general must be introduced first. We will discuss it later in this article.

The most informative example is perhaps the famous conrotatory vs. disrotatory problem of the butadiene–cyclobutene intramolecular cyclization. We are now dealing with C_{2v} point group. The ground state to ground state thermal transition of the reaction is $b_1^2 a_2^2 \rightarrow a_1^2 b_1^2$. This is again a closed-shell

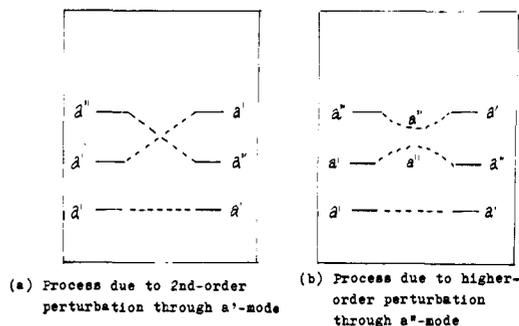
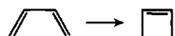


Figure 2. Occupied orbital correlation diagrams for the Diels–Alder reaction.

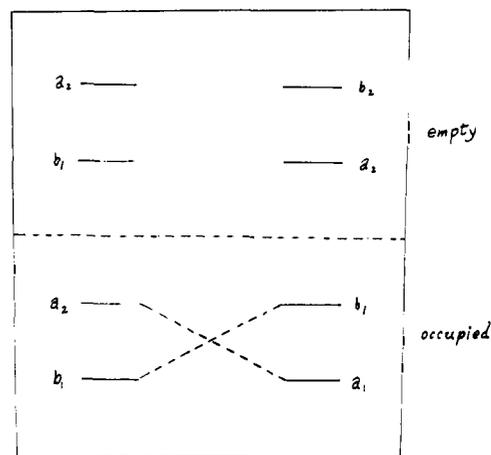


Figure 3. The correlation diagram of the occupied orbitals involved in the butadiene–cyclobutene cyclization (conrotatory mode).

transition and rule I takes the form $b_1 a_2 \Gamma(Q_i) a_1 b_1 = A_1$, which determines $\Gamma(Q_i)$ to be a_2 . The diagrammatic representation is depicted in Figure 3 and it can be shown that the conrotatory mode of the π orbitals in Figure 4 belongs to the a_2 representation. In Figure 3, since the a_2 level correlates with the a_1 level through the perturbation of an a_2 mode, one might argue that there should be a symmetry-imposed barrier between the two levels. However, a closer examination of the topology of any diagram involving an avoided crossing reveals that Figure 3 is not qualified for this to occur. It is observed in Figure 5 that two pairs of levels, each belonging to a common symmetry representation, must be present in order to have an avoided crossing. It is also to be noted that this topology is consistent with the “frontier orbital” concept if all the levels involved are either the highest occupied ones or the lowest empty ones. However, this concept is not essential as far as the avoided crossing problem is concerned. In Figure 3, an unoccupied a_1 level of the reacting complex is lacking, so that the bottom a_1 level of the product can correlate only either with the a_2 level on the left via an a_2 mode, or with the b_1 level on the left via a b_1 mode. The latter choice is obviously a violation of the selection rule for the ground state to ground state transition. Thus, we conclude that the concerned transition is allowed due to the absence of a symmetry-imposed barrier.

We have mentioned that it is possible to correlate the bottom two levels of symmetries b_1 and a_1 through the b_1 mode. Then, in the approximation of the second-order perturbation theory, any other occupied orbital of the reacting complex can correlate only with an orbital of identical symmetry species of the product configuration. Figure 6 is the result of this consideration and the corresponding selection rule is $(b_1 a_2 b_1) b_1 (a_1 b_1 a_2) = A_1$, predicting the allowed transition $b_1^2 a_2 b_1 \rightarrow a_1^2 b_1 a_2$, in agreement with the photochemically allowed conclusion of

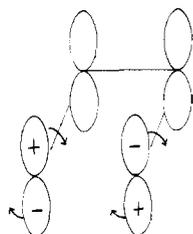


Figure 4. The conrotatory mode belonging to the a_2 species of C_{2v} in the butadiene-cyclobutene cyclization.

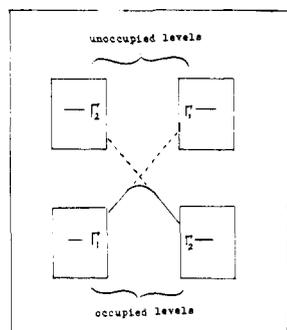


Figure 5. The topological feature of an avoided-crossing diagram.

Woodward and Hoffmann via a disrotatory mode. This is again an open-shell transition and more is to be said later.

As a final example of this section, we consider the cis-trans isomerization of the square-planar MA_2B_2 -type d^8 complexes Eaton once investigated.⁵ In the spirit of the crystal field theory, such a complex can be viewed as a central metal atom situated in the ligand field by which the metal d-orbital degeneracy is lifted up. The isomerization is thus merely the change of d-orbital splitting pattern from one to the other, consistent with the change of the field due to the motion of the ligands. In Eaton's treatment, the fact that the four ligands are not all identical was ignored and a reaction mode of the totally symmetric species of D_2 was proposed. The ground state to ground state transition may then be written as $(d_{xz})^2(d_{yz})^2(d_{z^2})^2(d_{x^2-y^2})^2 \rightarrow (d_{xz})^2(d_{xy})^2(\frac{1}{2}(3^{1/2}d_{z^2} + d_{x^2-y^2}))^2 - (\frac{1}{2}(d_{z^2} - 3^{1/2}d_{x^2-y^2}))^2$. This thermal transition was concluded by Eaton to be disallowed by symmetry, due to the involvement of the "symmetry-uncorrelated" orbital transition, $d_{yz} \leftrightarrow d_{xy}$. This is a result also consistent with rule I, for in this case we can write explicitly $(b_2b_3aa)\Gamma(Q_i)(b_2b_1aa) = A$, by which $\Gamma(Q_i)$ is determined to be b_2 . By looking at the corresponding orbital correlation diagram depicted in Figure 7, we come to the same conclusion of Eaton that the reaction is thermally forbidden because of the presence of a symmetry-imposed barrier between the two levels d_{yz} and d_{xy} . The reaction promoting mode proposed by Eaton which belongs to the symmetry a of D_2 does not have the right symmetry for causing such an orbital avoided crossing process. An obvious guess of the mechanism of such a highly disfavored transformation may involve a joint mode of vibration, i.e., the product of two modes, one belonging to the a representation (the Eaton's mode), and one belonging to the b_2 species depicted in Figure 8b. The b_2 mode proposed here involves the back-and-forth small-angle rotations about the y axis. This is, of course, but a possible candidate for satisfying the selection rule of the reaction. Computational as well as experimental evidence is for the time being unavailable in this laboratory.

Avoided Surface Crossing and Open-Shell Transitions. Salem has once complained about the schematic equation¹² repre-

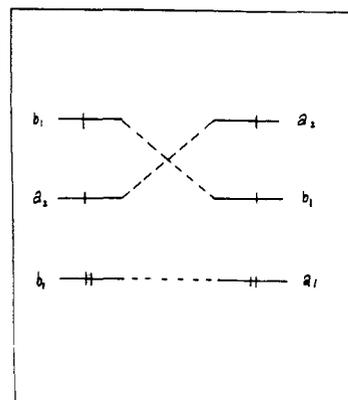
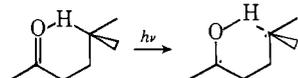


Figure 6. A possible correlation diagram of the butadiene-cyclobutene cyclization through the b_1 mode (disrotatory).

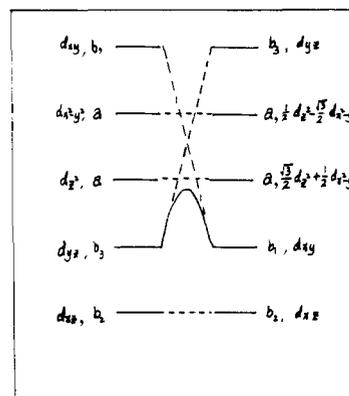
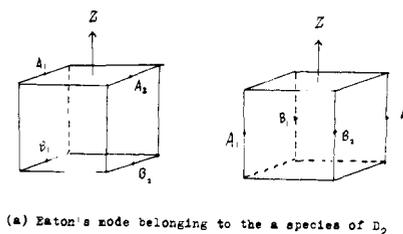
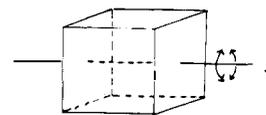


Figure 7. The orbital correlation diagram for the cis-trans isomerization of MA_2B_2 -type square planar molecules.



(a) Eaton's mode belonging to the a species of D_2



(b) The b_2 mode required by symmetry

Figure 8. The two possible modes of motion involved in the cis-trans isomerization of the square-planar d^8 complexes.

sending the photochemical hydrogen abstraction by ketones for the failure of the single sign $h\nu$ to reveal the mechanistic details of the transformation. His search for the mechanism started with the assumption of a conserved plane of symmetry which contains the nuclei directly involved in the electronic excitation. He singled out four states, namely, the reactant ground state ($4\sigma, 2\pi$), the reactant (n, π^*), excited state ($3\sigma, 3\pi$), the primary product ground state ($3\sigma, \pi$), and the primary product excited state ($4\sigma, 2\pi$). The σ, π -electron counting notation¹⁵ for specifying the state symmetry of each state facilitates the construction of the state correlation di-

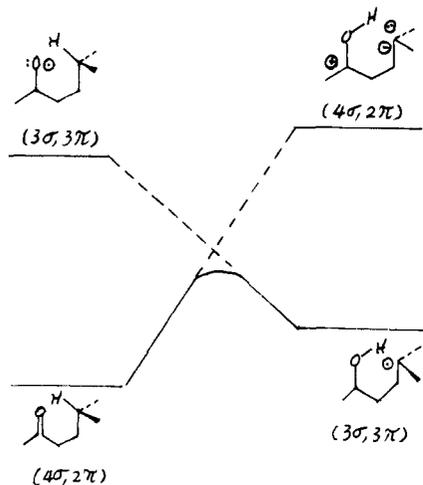
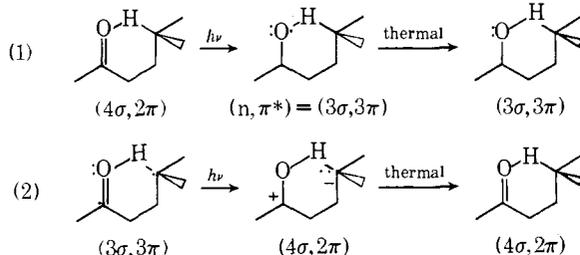


Figure 9. The state correlation diagram of the photochemical hydrogen abstraction by ketones.

agram shown in Figure 9. The mechanistic schemes proposed by Salem for the forward and backward reactions are shown in Scheme I. By looking at the state correlation diagram, it can

Scheme I



be seen that a surface crossing is involved. The group-theoretic analysis of the scheme shown above is almost trivial. We are again considering the C_s point group. The promoting modes for both of the two indicated thermal reactions proposed by Salem belong to the totally symmetric species. Thus, the allowed orbital-symmetry changes can only be $a' \leftrightarrow a'$ and $a'' \leftrightarrow a''$, or $\sigma \leftrightarrow \sigma$ and $\pi \leftrightarrow \pi$. This gives rise to the surface crossing.

However, Salem also observed that if during the reaction, some of the nuclei moved slightly out of the symmetry plane, an avoided surface crossing would result. He even calculated the interaction matrix element $H'_{A'A''} = z \langle {}^1A' | \partial V / \partial z | {}^2A'' \rangle$ in order to estimate the effect of the out-of-plane motion to the energy barrier.¹² In the matrix, z is the variable which measures the extent of the out-of-plane motion. The wave functions for the $(4\sigma, 2\pi)$ and the $(3\sigma, 3\pi)$ states, although designated by A' and A'' , respectively, were assumed by Salem to belong to the pseudo A' and the pseudo A'' symmetries. In other words, the reacting system was assumed to deviate slightly from the C_s symmetry so that the surface-crossing prediction was no longer valid under such an assumption.

In view of the symmetry considerations presented in this paper, we choose to say that the transition between the reactant $(4\sigma, 2\pi)$ state and the product $(3\sigma, 3\pi)$ state is carried through by the out-of-plane promoting mode of a'' type. We confine ourselves in the analysis of the C_s group and rule I now reads as $a'a''a'' = A'$. Figure 10 shows that the a'' -type motion facilitates the rehybridization of the oxygen atomic orbitals from the sp^2 hybrid to the sp^3 one. Room is made for electrons on the alkyl hydrogen to be seated on the carbonyl oxygen. The "memory" for the intended crossing can be easily understood by considering the wave function

$$\Psi = \Psi_0 + \sum_k (z \langle \Psi_0 | \partial V / \partial z | \Psi_k \rangle / (E_0 - E_k)) \Psi_k \quad (24)$$

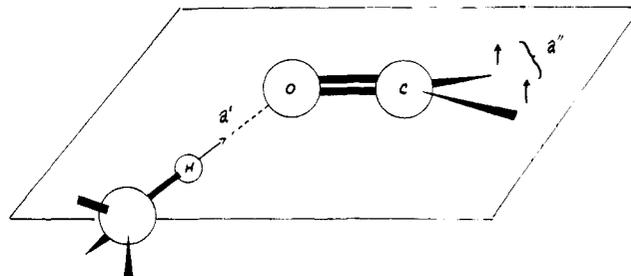


Figure 10. Promoting modes for the reaction of hydrogen abstraction by ketones. The a' -type mode which facilitates the shortening of the distance between the alkyl H and the carbonyl O atoms.

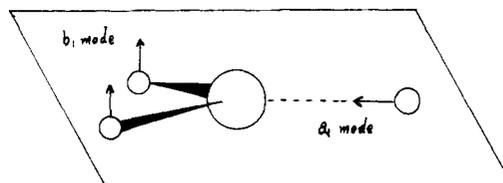
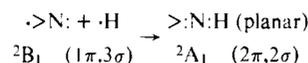


Figure 11. The promoting modes for the conceptual reaction: $>N: + \cdot H$ (${}^2B_1 (1\pi, 3\sigma) \rightarrow >N:H$ (${}^2A_1 (2\pi, 2\sigma)$) (planar).

The contribution of Ψ_k may be significant only if $E_0 - E_k \approx 0$. It is seen in Figure 10 that $E_{A'} - E_{A''} \approx 0$ occurs only at the crossing region, implying that the distance between the carbonyl oxygen and the alkyl hydrogen atoms must be close enough. In other words, the a'' -type motion may be important only with the aid of the a' -type motion, which brings the O and the H atoms together. This gives rise to the symmetry-imposed barrier appearing in Figure 9 and the reaction is thermally disallowed.

The situation is similar for the conceptual reaction



discussed by Evleth, Horowitz, and the author.¹⁶ The reacting system belongs to the point group C_{2v} and the transition of interest is of the type $B_1 \leftrightarrow A_1$. The out-of-plane bending motion depicted in Figure 11, which has the b_1 symmetry, is thus required. Again, it is this bending motion that facilitates the rehybridization of the nitrogen atomic orbitals, allowing the electron of the H atom to move closer to the nitrogen. Another pictorial way of looking at this problem is simply the following. In the $(1\pi, 3\sigma)$ state, there are two σ electrons around the N atom and one around the H atom. The two σ orbitals involved are to interact with each other when the N and the H atoms move closer. By Pauli's exclusion principle,¹⁷ only two of the three σ electrons between atoms N and H can be seated in the resulting σ MO of lower energy and the remaining σ electron must go either to the other σ MO of an antibonding nature, or to the π orbital which was initially only half full. This latter choice is energetically favored and is accomplished through the vibronic coupling of the b_1 vibrational mode.

Thus, the type A avoided surface crossing¹² studied by Salem may be rationalized in the following way. Each sheet of the potential energy surface may be specified by its symmetry. Two sheets of identical symmetry never cross due to the operation of the configurational type interaction. When two sheets of different symmetries meet at some point along the reaction coordinate, the topology of the orbital correlation diagram (Figure 5) can be used as the criterion for detecting an avoided surface crossing. We also believe that any avoided surface crossing appearing in the orbital correlation diagram results in an avoided crossing also in the state correlation diagram. The opposite statement is also believed to be true, al-

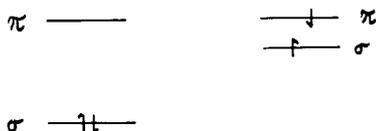


Figure 12. Salem's avoided crossing without orbital crossing.

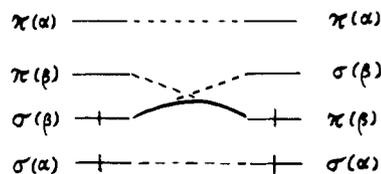


Figure 13. The modified diagram of Figure 12 based on a different MO approximation.

though Salem has concluded oppositely by considering the conceptual transition $(0\pi, 2\sigma) \leftrightarrow (1\pi, 1\sigma)$. We argue that Figure 12, which is the basis of Salem's arguments, is merely the result of the mathematical approximation of orbital energies. A different approximation may give different results. Suppose that the approximation known as "different-orbitals-for-different-spins" method is used for describing any open-shell system. Figure 12 is then to be replaced by Figure 13 and the presence of an orbital avoided crossing is obvious. If the reaction leading to the formation of the planar NH_3 molecule is studied this way, the orbital correlation diagram becomes the one shown in Figure 14, indicating a thermally forbidden transition. The hydrogen abstraction reaction can be similarly analyzed.

Some digression about the use of the chosen MO approximation may seem not unnecessary here. The set of MO's obtained by this method is generally called the unrestricted Hartree-Fock type, and authors like Pople and Nesbet,¹⁸ Lowdin,¹⁹ Pratt,²⁰ Hurst, Gray, Brigman, and Matsen,²¹ and Amos and Snyder²² are the pioneer workers in the development of this field. For our purpose, the obvious advantage of using this approach is that an open-shell state may now be described by a single determinantal wave function. The state symmetry of such a state is, of course, the direct product of all the individual orbital symmetries. Furthermore, since a chemical reaction can actually be viewed as a process involving the destruction, the construction, and the reordering of all the orbitals of a super molecule under the influence of the set of molecular vibrations, or other operators, the set of MO's which takes into better account the correlation among the orbitals is deemed to give a better description of the reacting system. A brief consideration of the lithium atom, which is the simplest multielectron open-shell system, may reveal the superiority of the unrestricted Hartree-Fock description with regard to the orbital correlation problem. The Hartree type wave function of the Li atom is of the form

$$\Psi(\text{Li}) = \phi_1 \phi_2 \phi_3 \quad (25)$$

where the ϕ_i 's are the individual orbitals for the individual electrons. In this independent electronic motion approach, the ϕ_i 's are to be so chosen that there is no orbital correlation whatsoever. Such a choice is impractical and the best one can do is to choose the ϕ_i 's from an orthogonal set. It is to be recognized that there are two kinds of orthogonality, called the positionwise and the spinwise. This can be expressed by writing

$$\int \phi_i(s) \phi_j(s') d\tau = \delta_{ij} \delta_{s's'} \quad (26)$$

where $d\tau$ is the volume element in the position-spin direct product space and the $\delta_{mm'}$'s are the Dirac delta functions. Suppose now we choose to describe the Li atom by the wave

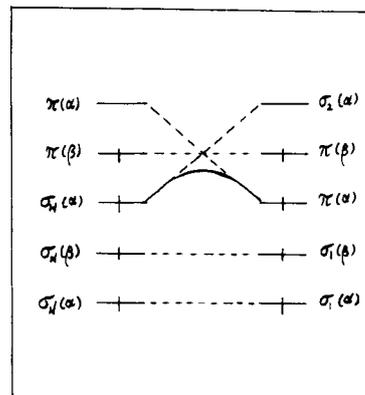


Figure 14. Orbital correlation diagram for the conceptual reaction: $>\text{N}: + \cdot\text{H} \rightarrow >:\text{N}:\text{H}$ (planar)

Table I. Spin-Orbit Coupling for D_2 Point Group

| | σ_x | σ_y | σ_z |
|----------------|----------------|----------------|----------------|
| ^3A | $^1\text{B}_3$ | $^1\text{B}_2$ | $^1\text{B}_1$ |
| $^3\text{B}_1$ | $^1\text{B}_2$ | $^1\text{B}_3$ | ^1A |
| $^3\text{B}_2$ | $^1\text{B}_1$ | ^1A | $^1\text{B}_3$ |
| $^3\text{B}_3$ | ^1A | $^1\text{B}_1$ | $^1\text{B}_2$ |

function

$$(\text{Li ground}) = 1s(\alpha)1s(\beta)2s(\alpha) \quad (27)$$

where hydrogen orbitals are used and the arguments α and β refer to spins. The first two orbitals $1s(\alpha)$ and $1s(\beta)$ are orthogonal only in the spin-wise sense. The first $1s(\alpha)$ orbital is orthogonal to the third $2s(\alpha)$ only spatially. The orthogonality between $1s(\beta)$ and $2s(\alpha)$ is in both the two senses, implying a different pairwise orbital correlation. One way to equalize the pairwise correlations is simply to replace $1s(\beta)$ by an orbital spatially different from $1s(\alpha)$. The use of the unrestricted Hartree-Fock wave functions is thus intuitively justified, especially when dealing with problems in which the orbital correlation plays an essential role. It is, of course, understood that the wave functions have been antisymmetrized and properly spin projected.

A Case of Intersystem Crossing Type. The tetrahedral to square planar isomerization of a d^8 transition metal complex may not be as trivial as Eaton⁵ once expected. The process involves a transition between two states of different spin multiplicities, making the internal conversion type selection rule not applicable at all. The ground state configuration of the T_d structure is $e^4t_2^4$ of triplet multiplicity. If the nuclear motion responsible for the isomerization $T_d \leftrightarrow D_{4h}$ is the one proposed by Eaton, the point group to be considered is D_2 and the ground state symmetry of the T_d structure may be written as $^3\text{B}_1 + ^3\text{B}_2 + ^3\text{B}_3$. The ground state symmetry of the D_{4h} structure is simply ^1A because of its closed configuration. The transitions of interest are then $^3\text{B}_1 \rightarrow ^1\text{A}$, $^3\text{B}_2 \rightarrow ^1\text{A}$, and $^3\text{B}_3 \rightarrow ^1\text{A}$. By consulting with Table I, it is an easy matter to predict the following:

- | | |
|---|-------------|
| (i) $^3\text{B}_1 - (\text{spin-vibronic } (b_1)) \rightarrow ^1\text{A}$ | by rule 11 |
| (ii) $^3\text{B}_2 - (\text{spin-vibronic } (b_2)) \rightarrow ^1\text{A}$ | |
| (iii) $^3\text{B}_3 - (\text{spin-vibronic } (b_3)) \rightarrow ^1\text{A}$ | |
| (iv) $^3\text{B}_1 - (Q(a)) \rightarrow ^3\text{B}_1 - (\sigma_z) \rightarrow ^1\text{A}$ | by rule 111 |
| (v) $^3\text{B}_2 - (Q(a)) \rightarrow ^3\text{B}_2 - (\sigma_y) \rightarrow ^1\text{A}$ | |
| (vi) $^3\text{B}_3 - (Q(a)) \rightarrow ^3\text{B}_3 - (\sigma_x) \rightarrow ^1\text{A}$ | |
| (vii) $^3\text{B}_1 - (\sigma_z) \rightarrow ^1\text{A} - (Q(a)) \rightarrow ^1\text{A}$ | by rule 1V |
| (viii) $^3\text{B}_2 - (\sigma_y) \rightarrow ^1\text{A} - (Q(a)) \rightarrow ^1\text{A}$ | |
| (ix) $^3\text{B}_3 - (\sigma_x) \rightarrow ^1\text{A} - (Q(a)) \rightarrow ^1\text{A}$ | |

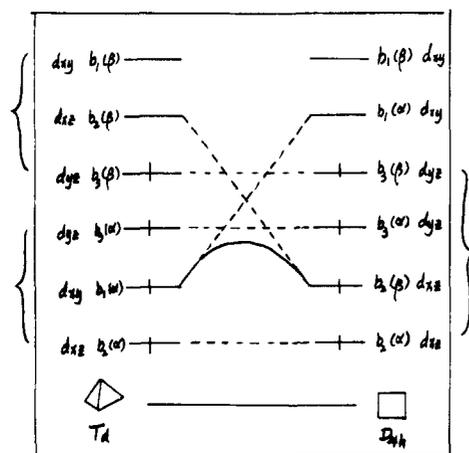


Figure 15. Partial orbital correlation diagram for the indicated transition through path (iii) of the four-coordinated d^8 metal complex.

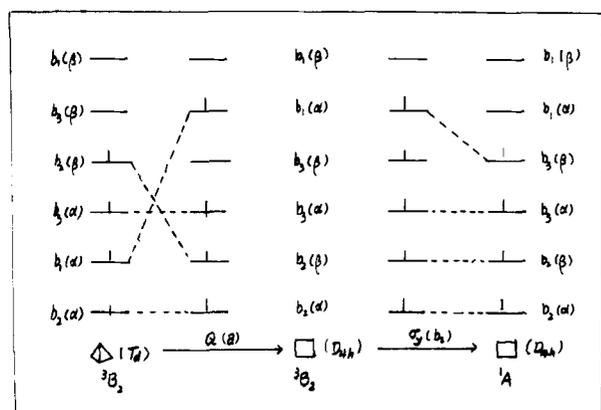


Figure 16. The partial orbital correlation diagram for the indicated transition through path V of the four-coordinated d^8 metal complex.

In order to examine the allowedness of all these pathways, it is necessary to construct all the orbital correlation diagrams. As far as the symmetries are concerned, the nine pathways may be grouped into three sets according to the selection rules they obey. Figure 15 depicts the partial orbital correlation diagram for the pathway (iii). Again, a symmetry-imposed barrier appears. However, this barrier is expected to be small due to the small energy spacing of the various d levels. This may open up the possibility of accumulating enough energy in the particular spin-vibronic mode of b_3 , allowing the reacting system to go over the top of the barrier. In other words, no definite conclusion pertaining to the allowedness can be drawn from symmetry considerations alone. The most interesting feature of this diagram is that it adds a new case of surface avoided crossing to those Salem has investigated. The occurrence of this noncrossing is not due to the effect of vibronic coupling, or, in Salem's language, the effect of slight symmetry deviation, but to the effect of the spin-vibronic coupling.

The analyses of transitions through paths (i) and (ii) are similar and we shall say no more. Next, consider the pathway (v). The partial orbital correlation diagram is shown in Figure 16, in which no symmetry-imposed barrier is present. However, the 3B_2 state of the D_{4h} structure is in fact an electronically excited state of the same structure. The reaction profile may look like the curve shown in Figure 17. Again, computational effort is required for determining its allowedness. Similar analyses leading to similar results may be expected for paths (iv) and (vi). There is no need to consider the last three paths, for the symmetry features are exactly the same as those involved in the first three pathways. One difference to be men-

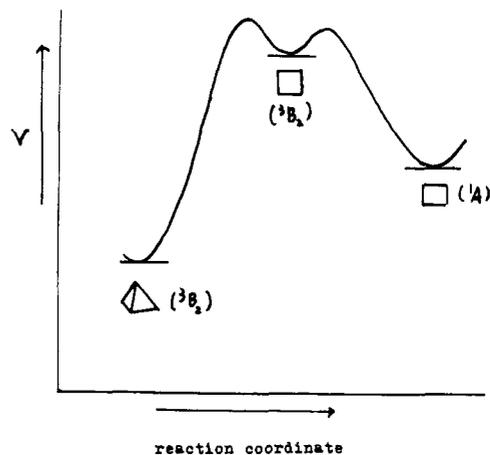


Figure 17. The reaction profile of the transition shown in Figure 16 (unscaled).

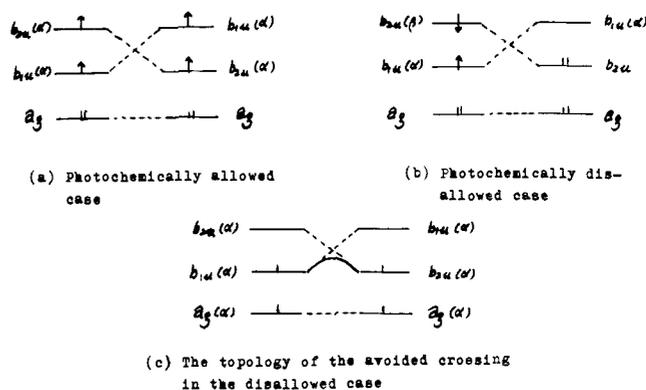
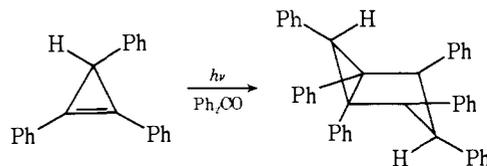


Figure 18. The different photochemical behavior of triphenylcyclopropene at excited states of different multiplicities.

tioned here is that in the last three pathways, spin operators are responsible for the avoided surface crossing.

Other Photochemical Reactions. It is well known that in photochemistry, molecules from the excited singlet and triplet states may undergo entirely different photochemical reactions. For example, triphenylcyclopropene is stable to direct photolysis involving the singlet excited state, but in the presence of benzophenone, it undergoes dimerization from the triplet excited state.²³ This is but one variation of the ethylene dimerization which has already been shown to be photochemi-



cally allowed. However, this surely does not explain the stability of the excited singlet state against direct photolysis. To bypass this difficulty, we again consider the unrestricted Hartree-Fock orbital correlation diagram. Consider first the allowed case of the problem. The orbital correlation diagram is shown in Figure 18a. There is an orbital crossing between the orbitals $b_{1u}(\alpha)$ and $b_{2u}(\alpha)$, where the argument α refers to the spin. Since the concerned two crossing electrons are of the same spin, they can only stay in two orbitals spatially orthogonal. In other words, the indicated orbital crossing is guaranteed by the Pauli exclusion principle and the arguments given previously to the Li atom. On the other hand, the two electrons involved in Figure 18b are of opposite spins, so that when the two surfaces $b_{1u}(\alpha)$ and $b_{2u}(\beta)$ meet at the crossing

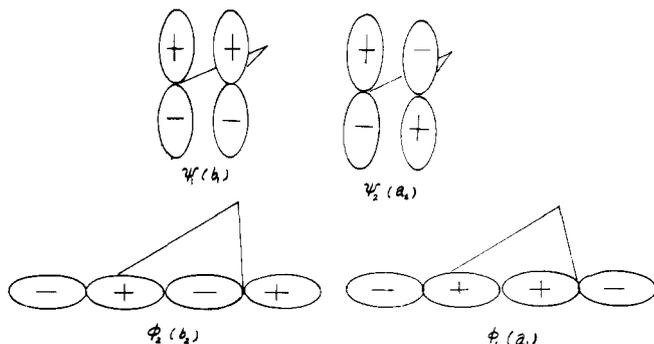
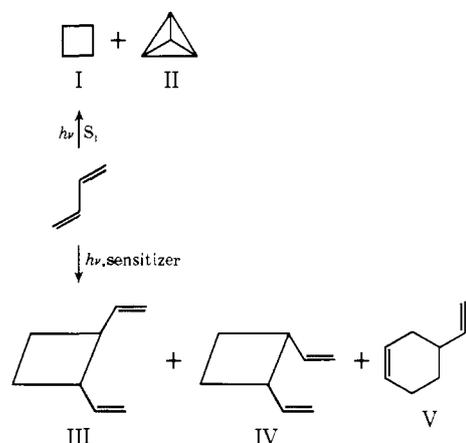


Figure 19. MO's involved in the transformation VIII.

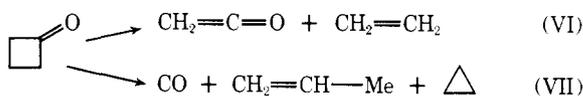
region, spatial orbital interaction is expected in view of the equalization of the pairwise orbital correlations discussed earlier. This gives rise to an avoided crossing, resulting in a forbidden transition, $a_g^2 b_{1u}(\alpha) b_{2u}(\beta) \rightarrow a_g^2 b_{2u}^2$ through the b_{3g} mode. The topology of this noncrossing diagram depicted in Figure 18c is consistent with the general diagram, Figure 5.

Arguments of this kind can apply equally well to the photochemistry of butadiene. When sensitizer is used, for reasons resulting in the diagram of Figure 18a, the only important reaction pathway is of the photochemically allowed ethylene dimerization type.²⁴ It becomes disallowed in the unsensitized case due to the presence of a symmetry-imposed barrier in Figure 18c. The formation of compounds I, II, and V is be-



lieved to be the contribution of higher order perturbation processes based on similar symmetry analyses. This is particularly obvious for the formation of compound II, since two σ orbitals must be formed by changing the symmetries of two π orbitals. Although, like the unsensitized ethylene dimerization, reactions leading to products I and II are also disallowed if considered as second-order perturbation processes, the absence of compounds III and IV in the unsensitized case may be attributed to the unfavorable entropy factor.

The Norrish type I processes in photochemistry also exhibit certain interesting symmetry features. Consider a saturated cyclic carbonyl compound undergoing the direct photolysis.



The known fact of reactions of this type is the cleavage of a carbon-carbonyl bond.²⁵ Nothing much can be said about the reaction VI, for the definite geometry of the reacting complex is unknown to the author.²⁶ However, it has been established that the reaction occurs via the excited singlet state²⁷ and hence rule I is applicable. For reaction VII, the cyclopropane is

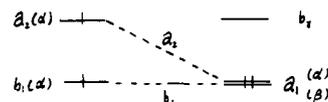
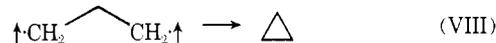


Figure 20. The orbital-correlation diagram of the transformation VIII due to the spin-vibronic coupling.

thought to arise from the triplet cyclobutanone decomposition.²⁷ We are thus concerned with the symmetry behavior of the transformation shown below (VIII). The orbitals involved



are shown in Figure 19. By rule II, if the point group C_{2v} is considered, we have

$$(b_1(\alpha)\partial_2(\alpha))b_2(\text{spin-vibronic})(a_1^2) = {}^1A_1$$

The construction of the orbital correlation diagram differs slightly from the other cases already considered. In Figure 20, the representation of the spin-vibronic coupling operator, b_2 , must be factored as $a_2 b_1$, indicating that we are in fact dealing with a composite operator having a spin fraction and a spatial fraction. This factorization is indeed implied by the form of the operator $(\partial h_{so}^0 / \partial Q)_0$. The diagram in Figure 20 thus corresponds to a process involving a simultaneous change in spin as well as in spatial distribution. Although the diagram shows an absence of the topological feature of a forbidden transition, one should recall that a transition involving spin inversion is commonly called spin forbidden due to the much smaller probability.

If the pathways obeying the selection rule III are studied, we have then,

$$b_1(\alpha)a_2(\alpha) \xrightarrow{\sigma_x} a_2^2 \xrightarrow{a_2} a_1^2 \quad (\text{IX})$$

$$b_1(\alpha)a_2(\alpha) \xrightarrow{\sigma_x} b_1^2 \xrightarrow{b_1} a_1^2 \quad (\text{X})$$

$$b_1(\alpha)a_2(\alpha) \xrightarrow{\sigma_y} a_1(\beta)a_2(\alpha) \xrightarrow{a_2} a_1^2 \quad (\text{XI})$$

$$b_1(\alpha)a_2(\alpha) \xrightarrow{\sigma_z} b_1(\alpha)a_1(\beta) \xrightarrow{b_1} a_1^2 \quad (\text{XII})$$

Since the a_2 level is of higher energy than the b_1 level, the pathway X is expected to be more favorable than the pathway IX. In other words, other things being equal, the disrotatory promoting mode is more important here. In pathways XI and XII, much more ought to be studied, for they all involve the intermediate states not belonging to the point group C_{2v} . Note that the a_1 level of the system belongs to the nuclear configuration of the product, which is a closed triangle, while the b_1 and a_2 levels belong to that of the reacting complex with the ends open. Thus, the intermediate states of pathways XI and XII are neither closed nor open, but halfway in between. The consideration of the point group C_s is therefore more adequate. The selection rule now becomes

$$\pi_1\alpha(a'')\pi_2\alpha(a'') \xrightarrow{\sigma_1, \sigma_2} \pi_1\alpha(a'')\sigma\beta(a') \xrightarrow{a''} \sigma^2$$

where π_1, π_2 designate the two p orbitals of carbons 1 and 2, and σ designates the in-phase σ orbital of the product. The orbital motion can then be represented by graphs shown in Figure 21. Here, only a negligible overlap between the two π -type p orbitals has been assumed. The activation energy due to the nuclear geometrical rearrangement is expected to be low; however, it is again spin forbidden. Pathways obeying rule IV can be studied similarly.

To explain the formation of propylene in reaction VII, it is observed that the C_{2v} point group is in this case completely

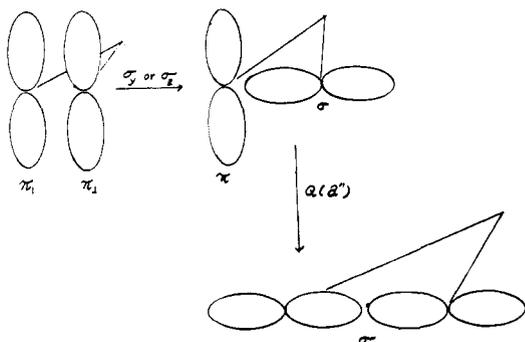


Figure 21. An alternate view of the pathways XI and XII.

destroyed. This implies that the promoting mode cannot belong to any single symmetry species of C_{2v} . Two assumptions need be examined. If the reaction is assumed to proceed to completion in one step, the violation of the C_{2v} selection rule forces us to consider the smaller C_1 trivial group. No useful information can be derived. If more steps are involved, it is conceivable that there might be involved a b_2 -type motion corresponding to the hydrogen migration from the central carbon to one of the two terminal carbons, and a b_1 -type motion of the other hydrogen atom attached to the central carbon, bringing itself into the C-C-C plane. The required spin inversion may take place simultaneously or separately because of the selection rules II, III, and IV. At any rate, as far as the second-order perturbation theory is concerned, the second assumption is disfavored.

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- (27) The same as ref 25.

The Electronic Structure of Methylene Radical Anion and Its Dimer

Robert B. Davidson* and Mark L. Hudak

Contribution from the Chemistry Department, Amherst College, Amherst, Massachusetts 01002. Received September 17, 1976

Abstract: Nonempirical molecular orbital calculations are used to construct a Walsh diagram for methylene radical anion, CH_2^- ; the best 4-31G calculation done gives $E_T = -38.7814$ hartrees at $r_{\text{CH}} = 1.145 \text{ \AA}$ and $\theta_{\text{HCH}} = 99^\circ$. The effects of various model substituents on the carbanion-like σ lone pair and on the free radical-like odd p electron of the central carbon atom are explored in a series of CNDO/2 semiempirical molecular orbital calculations. These suggest that good π acceptor substituents will narrow or even reverse the gap between the two valence orbitals, providing an opportunity to manipulate reactivity. The dimer of CH_2^- , which has been suggested as an intermediate in the production of ethylene from the monomer, is examined in another series of nonempirical SCF calculations. They indicate that the dimer lies in a metastable local minimum of the potential energy hypersurface for the dimerization reaction; the lowest calculated 4-31G energy is -77.4203 hartrees. The calculations are used to discuss related experimental data.

The intriguing, highly reactive species CH_2^- , the radical anion of methylene, seems to be produced in surprising abundance when methylene halides are treated with strong reducing agents in solution;¹ the same ion has been prepared in the gas phase by electric discharges in CH_4 or CH_2N_2 .² The novelty of this molecule, its potential for reactivity characteristic of either free radical or carbanionic functionality, and the possibility of its dimerization in solution to form the dianion of ethylene¹ led us to study its electronic structure (and that of its dimer) in a series of molecular orbital calculations.

The corresponding neutral species, CH_2 , has been exhaustively examined, both theoretically³ and experimentally.⁴ It is especially interesting to the theorist because it is the archetypal diradical:⁵ a molecule in which the presence of two electrons to be distributed among two nearly degenerate orbitals produces an exquisite sensitivity to geometric change and substitution.⁶ The extra electron in CH_2^- removes some of the interesting ambiguity in the assignment of ground state configuration but simultaneously alters the delicate balance of orbital energies which determines structure and reactivity in