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A Basis for Orbital Symmetry Rules

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The influence of molecular symmetry on reaction rates is examined with an approach in which reactions are viewed as electronic transitions between states of reactants and products (described, in turn, by quasiadiabatic potential surfaces). The molecular Hamiltonian is used to derive selection rules for these transitions. The *complete* Hamiltonian has no useful symmetry. Neglect of non-Born-Oppenheimer and spin-orbit terms (and of other angular momentum coupling terms) leads to an approximate Hamiltonian and to selection rules which form the basis for the Woodward-Hoffmann rules. This approach provides an alternative to the adiabatic potential surfaces, reaction coordinates, and transition state theory used in more familiar discussions of the Woodward-Hoffmann rules. Further, it provides a particularly clear method for discussing violations of these symmetry rules, and for differentiating concerted and nonconcerted reactions.

1. Introduction

The prediction of chemical reaction rates and rate constants is a difficult endeavor. Formal theories of reaction rates[1] are just beginning to be used successfully[2] (at times with great computational expense) for the simplest three-atom exchange reactions and are not presently applicable to more complex problems. The difficulty in analyzing the motion of many-atom systems can, however, be reduced substantially by considerations of symmetry. In molecular quantum mechanics, the classification of electron states of atoms and molecules according to symmetry is fundamental to the construction of correlation diagrams and optical selection rules. By considering symmetry, these rules can be constructed and applied without calculating details of the motion of the electrons and nuclei. Similarly, "symmetry rules" such as those proposed by *Wigner* and *Witmer*[3], *Shuler*[4], and *Woodward* and *Hoffmann*[5], and discussed by many other authors[6], have greatly clarified certain types of problems in kinetics, without requiring elaborate calculation. The Woodward-Hoffmann (W-H) rules for the prediction of relative rates of concerted reactions are based on considerations of the symmetry of the electronic wavefunctions of the chemical reactants and products. These wave functions seldom figure *explicitly* in applications of the W-H rules: because electronic wavefunctions calculated in the Hückel LCAO-MO approximation[7] reflect molecular symmetry in easily predictable ways, a knowledge of the molecular symmetry of the substance(s) of interest, and of the symmetry properties of the Hückel wavefunctions derived previously for these or related materials, normally is sufficient for an application of the W-H rules.

The Hückel wavefunctions, on which the application of the W-H rules usually depends, are calculated with an approximate Hamiltonian: any influence of nuclear motion on the electronic wavefunction is neglected (the Born-Oppenheimer approximation); angular momentum terms (molecular, electronic spin-orbit, and nuclear and electronic spin) are ignored; and electron-electron interactions are incorporated semi-empirically. The enormous predictive success of the W-H rules indicates that the neglected terms are normally unimportant for the success of *qualitative* arguments based on orbital symmetry. *Nonetheless, the complete molecular Hamiltonian does not have the symmetry required to provide a rigorous basis for the W-H rules*, and a more complete calculation, including Born-Oppenheimer terms and consideration of angular momentum may, in principle, lead to predictions different from those of the W-H rules.

The purpose of this article is to discuss a number of aspects of symmetry rules in chemical kinetics, particularly the W-H rules. We present a theoretical framework with which we:
- derive symmetry rules and their limits of applicability
- provide operational definitions of the concepts of concerted and nonconcerted reactions
- derive extensions of present symmetry rules.

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The utility of our analysis is tested for various applications. Further, we show that symmetry rules for reactions can be obtained as *selection rules* analogous to those used in optical spectroscopy.

Our interest is in the influence of symmetry on reaction rates and in the assumptions underlying the symmetry rules, not in the detailed calculation of rates for specific reactions. Recent work on photodissociation of polyatomic molecules[8] and dynamics of simple rearrangement reactions[2b] indicates, however, that the types of methods discussed here can be used to provide quantitative estimates of rates.

Our treatment of reaction rates clarifies the relationship between the relatively high symmetries assumed in applying these rules and the much lower symmetry actually characteristic of the complete molecular Hamiltonian. Two other worthwhile features emerge from this development. First, it is possible to derive relatively compact expressions which give the reaction rates in terms of the complete Hamiltonian (including nuclear and non-Born-Oppenheimer terms) and appropriate wave functions of reactants and products. This expression can be separated into a part having the symmetry assumed in the W-H rules (that is, the symmetry of the nuclear framework), and other parts that do not have this symmetry. The experimental observation that many reactions obey the W-H rules then makes it possible to identify terms in this rate expression that are normally *not* important in determining reaction rates. Thus, the observation that certain features of reaction rates are adequately described by terms having symmetries characteristic of only a part of the complete molecular Hamiltonian permits an estimation of the relative importance of the remaining parts in determining reaction rates. Second, by identifying explicitly the terms in the Hamiltonian that do not have the symmetry of the molecular framework, it is possible to suggest areas and circumstances in which the W-H rules might be expected to fail. Our discussion proceeds in four stages:

First, we describe the distinction between "adiabatic" and "quasiadiabatic" potential surfaces[*], and indicate the advantages of the latter in discussing the role of symmetry in the reaction rates. Briefly, *adiabatic* potential surfaces are those which organic chemists commonly use in discussing kinetics (Fig. 1). A continuous surface connects reactants and products, and the lowest energy path between the two is called the "reaction coordinate". The "activated complex" or "transition state" is considered as a discrete species at the position of highest energy along that path. A complete adiabatic surface is generated with a single electronic Hamiltonian: reactants, products, and intermediates are represented by eigenfunctions of this Hamiltonian calculated for different sets of nuclear coordinates. A reaction is the result of the motion of nuclei; since the adiabatic surface is continuous, reactants and products belong to the same electronic state. In the present work, a distinct *quasiadiabatic* potential surface is required for reactants and products; each is calculated using a procedure specifically designed to *eliminate* all of the interactions which provide the driving force for reaction. The wave functions used to represent these artificially non-reacting species are *not* eigenfunctions of the Hamiltonian for the complete system. A reaction is considered as an electronic transition between the quasiadiabatic surface (state) of the reactants and the quasiadiabatic surface of the product. The transition state may be viewed as the nuclear configuration at or near the crossing of these two surfaces. Although the quasiadiabatic picture of a reaction is not the one customarily used in physical organic chemistry, *Evans*[9] proposed and made innovative use of quasiadiabatic energy surfaces, as early as 1938, for a discussion of the electronic theory of reactions.

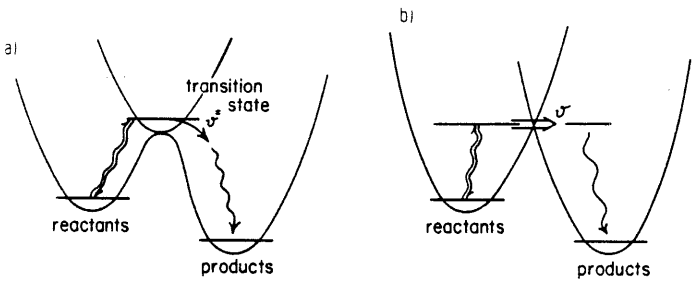


Fig. 1. A reaction in an adiabatic model (a) is represented by a smooth progression of nuclear positions within a *single* electronic state. All interactions present in the real physical system are, in principle, included in this representation. The highest energy species in this progression is called the transition state or activated complex, and, within the usual activated complex theory, is assumed to be in thermodynamic equilibrium with the ground state of the reactants. Its decomposition to products is the result of molecular motion along a vibrational coordinate having a negative force constant. A reaction in a quasiadiabatic model (b) is treated as a transition between electronic states of distinct species—"reactants" and "products".

[*] In this context, adiabatic and quasiadiabatic should be considered as arbitrary labels, with no obvious connection to the word adiabatic as used in classical thermodynamics.

Second, we state and develop an equation that describes the rate of a concerted reaction in terms of the quasiadiabatic wave functions for reactants and products, and the Hamiltonian of the reacting system. This equation permits the rate to be expressed in terms of contributions from several well-defined, although not necessarily easily calculated, quantities: overlap integrals of electronic wave functions; overlap integrals of nuclear wave functions; nuclear geometry at the intersection of the two quasiadiabatic potential surfaces; non-Born-Oppenheimer terms; and spin-orbit terms. Those terms which must be negligible for the reaction to follow orbital symmetry rules of the W-H type are easily identified.

Third, we study various contributions to the rate expression for reactions which are forbidden according to electronic symmetry rules of the W-H type. Examination of the vibronic and spin-orbit contributions to the rate shows that these also follow symmetry rules. These rules differ significantly from the W-H rules, however, and are neither generally nor easily applicable. These discussions are illustrated with the example of the closure of butadiene to cyclobutene.

Fourth, we discuss the concepts of concerted and nonconcerted reactions, and present useful (operational) definitions.

Our analysis emphasizes that many organic reactions classified according to the simplest electronic symmetry rules (W-H) as allowed or forbidden can in fact be categorized according to varying degrees of reactivity, and that reactions forbidden by these simplest rules may at times proceed at significant rates. Several representative reactions are classified in terms of "orders of forbiddenness". Identification of those terms in the complete rate equation that are not taken into account in the W-H treatment makes it possible to suggest reaction types in which violations of orbital symmetry rules might be expected.

2. Adiabatic and Quasiadiabatic Potential Surfaces

Most discussions of reaction kinetics based on transition state theory presuppose a single, continuous, potential surface connecting reactants and products. The points on this surface are calculated by assuming the nuclei to be stationary (the Born-Oppenheimer approximation) and solving the Schrödinger equation (1) to obtain electronic energies and wavefunctions for selected nuclear positions,

$$H_e(r, R_0)\Phi_i(r, R_0) = E_i(R_0)\Phi_i(r, R_0) \quad (1)$$

Here, H_e is the electronic Hamiltonian, r are the electronic coordinates, R_0 are the (fixed) nuclear coordinates, $\Phi_i(r, R_0)$ is the eigenfunction which describes a particular (i-th) electronic state (say the ground state, for thermal reactions) at the chosen values of R_0, and $E_i(R_0)$ is the associated electronic energy[*]. By varying the coordinates R_0 to correspond to the forming and breaking of bonds hypothesized for the reaction, we trace out a reaction coordinate. Many approximations have been introduced to make this procedure practical in the Hückel approximation; in particular, a limited number of atomic orbitals are used as the basis set, and two-electron terms and certain integrals are neglected.

For example, for the exchange of a hydrogen atom between dihydrogen and a hydrogen atom

$$H_A - H_B + H_C \rightarrow H_A + H_B - H_C$$

one can calculate the changes in energy accompanying the transfer of H_B from H_A to H_C by assuming a linear arrangement of three nuclei, choosing one distance, and minimizing the total energy of the system by varying the second distance. The results of such a calculation are summarized in Figure 2a. It is, of course, not generally useful to consider potential energies varying with a single distance for any purpose but schematic illustration; we shall do so here since a qualitative representation is all that is required. Surfaces generated in this way by the solution of Eq. (1) for the particular chosen system are called *adiabatic*. We emphasize that since a single Hamiltonian is used to calculate the energies and wavefunctions of nuclear configurations corresponding to what we call the reactants, products, and intermediates between the two, and since the resulting surface is continuous, all of these species are normally in the same electronic state: that is, they have the same electronic wave function.

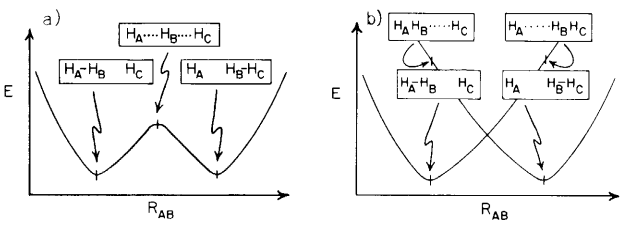


Fig. 2. Schematic adiabatic (a) and quasiadiabatic (b) potential surfaces for $H_A - H_B + H_C \rightarrow H_A + H_B - H_C$. For all curves, the distance between H_A and H_C, R_{AC}, is fixed, and R_{AB} is varied. In the left-hand curve for the quasiadiabatic surfaces, no interaction is allowed between H_B and H_C at any value of R_{AB}; for the right-hand curve, no interaction between H_A and H_B is allowed.

[*] Of course, this term also contains the Coulomb energy of the nuclear skeleton at rest.

Alternative theoretical methods for studying reaction rates are available, although they are not commonly used in physical-organic chemistry. The one employed throughout this paper involves calculations of two distinct potential surfaces, one for reactants and one for products. Reaction is considered to result from a transition between them. The procedure used to construct these so-called *quasiadiabatic* potential surfaces (and the corresponding electronic states) is based on calculating energies and wavefunctions for systems in which certain interactions actually present and crucial for the reaction to occur are intentionally omitted. This procedure is thus not based on finding electronic eigenfunctions for the chosen reacting system, and is thus very different in spirit from that used for adiabatic surfaces[10]. Typically, for the reaction of $H_A - H_B$ with H_C, the calculation of a quasiadiabatic surface for the three-atom system that forms the reactants determines the energy of that configuration with explicit *exclusion* of bonding between H_C and $H_A - H_B$. The calculation of the quasiadiabatic surface of the products, that is the calculation for $H_A + H_B - H_C$, is done with explicit *exclusion* of bonding between H_A and $H_B - H_C$. The results of these calculations can be represented schematically by two intersecting potential energy curves (Fig. 2). The electronic quasiadiabatic wave functions are not eigenfunctions of the Hamiltonian of the complete system, because this Hamiltonian includes *all* the interactions present in the system. The quasiadiabatic wave functions explicitly exclude all *bonding* interactions between products and reactants.

Both adiabatic and quasiadiabatic representations have attractive features for describing chemical reactions. The former is more readily appreciated physically, and seems conceptually simple. Construction of an adiabatic energy surface involves assuming a position for the nuclei and then calculating the total electronic energy of the system at this position. This calculation is repeated for any nuclear positions that are considered relevant to the problem being considered. The resulting adiabatic energy surface thus (in principle) provides the correct energy of the system as a function of the nuclear positions. The continuous rearrangement of the nuclei from reactant to product configurations traces a path on this surface. The lowest energy path from reactants to products is frequently called the "reaction coordinate". The transition state is just the point of highest energy along this coordinate. In the activated complex theory, which is formulated with the adiabatic energy surface, the rate is determined by the curvature of the surface (that is, by the force constants) at the saddle point corresponding to the transition state. Adiabatic potential surfaces have the appeal of being "physically measurable", in the sense that they give the correct energy for the best approximation to this energy that can be calculated (with the particular procedure used) for any assumed set of nuclear positions. They have, however, a deficiency as the basis for discussing the influence of symmetry.

The reason for this will become clear as we proceed. At this point we only note that once the adiabatic energy surface is calculated the electronic wave function is eliminated from the problem. If we want to compute the rate of reaction numerically we have to solve the mechanical equations of motion (classical or quantum) with the adiabatic energy surface serving as potential energy. For instance, in Figure 3 we give a simple one-dimensional representation of this point,

where we show the adiabatic energy surface along the lowest path from reactants to products (usually called reaction coordinate). The total energy of the system is a constant and hence a straight line. The difference between the two lines is the kinetic energy of the nuclei, which changes as the reaction proceeds. The potential energy allows us to compute the forces exerted on the moving (reacting) nuclei, at any given nuclear configuration. Nowhere is the electronic symmetry of reactants and products obviously present in this type of treatment.

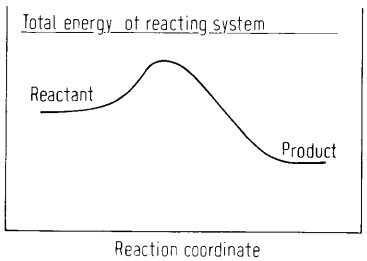


Fig. 3. Typical reaction coordinate. The level of the total energy of the reacting system, which is constant, is indicated by the horizontal line.

In the quasiadiabatic scheme the situation is conspicuously different. The reaction is considered to be a transition from the potential surface (*i. e.* the electronic state) of the reactants to the potential surface (*i. e.* the electronic state) of the products. We emphasize that the adiabatic and quasiadiabatic ways of describing reactions are equivalent and the choice of one of them depends on the problem to be solved. For a discussion of electronic symmetry it is more convenient to use a representation that displays the electronic degrees of freedom. The reader will discover, as he proceeds, that the language of the symmetry rules is that of the quasiadiabatic representation.

The quasiadiabatic potential surfaces do not necessarily give the correct energies, because the bonding interactions that are responsible for conversion of reactants to products are explicitly omitted in their calculation. For nuclear configurations which can be identified clearly as "products" or "reactants", quasiadiabatic potential surfaces give energies very close to those of adiabatic surfaces; for intermediate configurations, however, the two types or surfaces are very different. Although the idea of a reaction as a transition between two electronic states seems qualitatively more complex than that of a smooth progression along a reaction coordinate, the quasiadiabatic approach offers a great advantage for discussions of the influence of symmetry on rate. The reaction is considered as an electronic transition from a state of the reactant to a state of the product, and it is possible to calculate the rate using an expression of the form of Eq. (2)[16g].

$$k_{\text{reactant}\rightarrow\text{product}} \sim \langle\psi^{\text{product}}|\text{Operator}|\psi^{\text{reactant}}\rangle^2 \quad (2)$$

$$\text{Intensity} = k_{\text{ground}\rightarrow\text{excited}} \sim \langle\psi^{\text{excited}}|O_{\text{dipole}}|\psi^{\text{ground}}\rangle^2 \quad (3)$$

Once the symmetry of the appropriate operator and that of the wave functions ψ^{product} and ψ^{reactant} have been identified, then it is easily possible to establish whether the rate must be small *on the basis of symmetry* (it may, of course, be small, for reasons unrelated to symmetry). This type of procedure has abundant precedent in the development of optical selection rules (that is, in procedures for estimating the rules of spectroscopic transitions), where expressions of the same form are used [Eq. (3)]. The ability to classify reaction rates in terms of symmetries is of obvious pertinence to the W-H rules. This approach is also very convenient in dealing with "unusual" contributions to the kinetics, such as the dynamic effects arising from non-Born-Oppenheimer terms or spin-orbit coupling, which may cause violations of the W-H symmetry rules, much in the way in which they cause violations of the selection rules in spectroscopy. Such terms are not presently included in transition state theory.

To illustrate the construction of adiabatic and quasiadiabatic surfaces in an example directly relevant to pericyclic reactions, we consider the closure of butadiene to cyclobutene. For a qualitative discussion of an adiabatic potential energy surface for this transformation we consider only the interconversions of molecular orbitals formed from four atomic orbitals. Hückel-level calculation of the adiabatic potential surface would proceed with the solution of the secular determinant in the usual way for various nuclear coordinates corresponding to butadiene, cyclobutene, and plausible geometries intermediate between these extremes

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} & 0 & \beta_{14} \\ & \alpha_2 - E & \beta_{23} & 0 \\ & & \alpha_3 - E & \beta_{34} \\ & & & \alpha_4 - E \end{vmatrix} = 0 \quad \text{adiabatic}$$

Changes in the magnitudes of the resonance ($\beta_{ij} = \langle i|H|j\rangle$) and Coulomb ($\alpha_i = \langle i|H|i\rangle$) integrals with geometry lead to changes in the energies of the molecular orbitals, and generate the associated adiabatic potential surfaces (Fig. 4a).

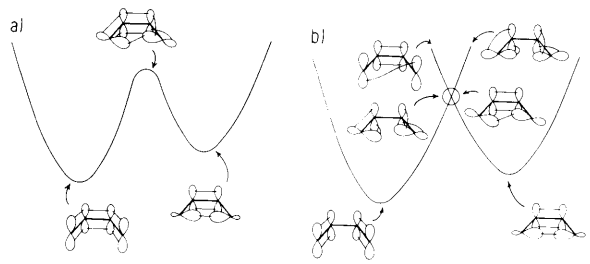


Fig. 4. Schematic adiabatic (a) and quasiadiabatic (b) potential surfaces describing the conrotatory interconversion of cyclobutene and butadiene. The lines connecting orbitals indicate those interactions included in the calculation. These interactions may, of course, range from large to zero (as shown by the magnitude of β_{12} in the adiabatic calculation).

Two different Hamiltonians are used for computing the quasiadiabatic states for butadiene and cyclobutene: neither is that used for the adiabatic calculation. For butadiene we take β_{23} and β_{14} to be zero, regardless of the nuclear configurations, to exclude from the quasiadiabatic electronic state of butadiene the bonding interactions characteristic of cyclobutene (Fig. 4). Similarly, the quasiadiabatic Hamiltonian for cyclobutene has β_{34} and β_{12} equal to zero to exclude the bonding interactions characteristic of butadiene.

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} & 0 & 0 \\ & \alpha_2 - E & 0 & 0 \\ & & \alpha_3 - E & \beta_{34} \\ & & & \alpha_4 - E \end{vmatrix} = 0 \quad \text{quasiadiabatic "butadiene"}$$

$$\begin{vmatrix} \alpha_1 - E & 0 & 0 & \beta_{14} \\ & \alpha_2 - E & \beta_{23} & 0 \\ & & \alpha_3 - E & 0 \\ & & & \alpha_4 - E \end{vmatrix} = 0 \quad \text{quasiadiabatic "cyclobutene"}$$

This way of constructing the quasiadiabatic states gives the correct electronic symmetry of both butadiene and cyclobutene. Having imposed the conditions which characterize this pair of quasiadiabatic calculations, we can calculate potential surfaces relevant to the interconversion of butadiene and cyclobutene by varying appropriate parameters but the shape of these surfaces will depend on the parameters varied. Thus, calculations in which only the distance between C^1 and C^4 is allowed to vary will produce excited states of butadiene and cyclobutene which differ significantly in shape; calculations in which the torsional angles Φ around the C^1—C^2 and C^3—C^4 bonds are also allowed to vary produce structures that are more closely related geometrically. We shall discuss later, in more detail, the importance of this difference for the rate of the reaction[*].

3. The Transition Probability for Chemical Reactions

3.1. General Theory

A reaction can be treated as an electronic transition between two different electronic states corresponding to two different quasiadiabatic potential surfaces, one for reactants and one for products. The reactant system is taken to be in a given quasiadiabatic electronic state and in a given nuclear state (specified in terms of the rotation, vibration, and relative motion of reactants) corresponding to the given total energy of the reacting system. This energy may be determined by an equilibrium thermal distribution or by a non-equilibrium photoexcitation. *The state of the reactants, constructed as described to exclude the bonding interactions that characterize reaction, is not a stationary (time-independent) state of the complete Hamiltonian.* A stationary state description, based on the available quasiadiabatic wave functions, would require mixing of reactant and product states. Since the reactants are not in a stationary state, there is a time-dependent probability that they will undergo a transition to a state of the product. The rate of the transition between reactant and product states (as between all non-stationary states in quantum mechanics) is calculated in terms of an integral of the form $\langle\psi^{\text{product}}|\text{Operator}|\psi^{\text{reactant}}\rangle$ [Eq. (2)]; the practical problem is to define the appropriate operator for the reaction and to try to develop methods of estimating the magnitude of this integral without resorting to detailed computation.

It is helpful in describing the techniques used to calculate these transition probabilities from reactants to products (*i.e.* rates of reaction) to begin by describing an analogous and more familiar problem: *viz.* that of the electronic excitation of a molecule by the absorption of a photon[12]. The excitation is a transition between different electronic states (that is, between different adiabatic potential energy surfaces). The interaction of the dipole moment of the molecule and the electromagnetic field of the light provides the driving force for the transition: the dipole moment operator is the required operator. Two familiar assumptions are usually used in obtaining an expression for the transition probability: first, that the motion of the electrons is so much faster than that of the nuclei that only the nuclear positions influence the electronic wave functions and that the nuclear movements are not important (the Born-Oppenheimer approximation); second, that the electronic transition is sufficiently rapid that the nuclei are effectively motionless during the transition (the Franck-Condon approximation). The selection rules of optical spectroscopy follow from consideration of the symmetry properties of the initial state, the final state, and the dipole moment operator. We emphasize that these selection rules reflect approximations made concerning wave functions (Born Oppenheimer and Franck-Condon approximations, neglect of spin-orbit coupling, *etc.*) and the mechanism of interaction of light with the molecule (dipole moment approximation). If different assumptions are made, different selection rules may result. In general, the less drastic the assumptions, the weaker are the resulting selection rules.

Any given set of approximations yields a set of selection rules. If the system is not adequately described by these approximations, however, lines appear in experimental spectra which are not predicted on the basis of these selection rules. Such lines are sometimes called "forbidden". This adjective essentially implies that an improved analysis containing less drastic approximations is required to reconcile experiment and theory; that is, that the analysis should take into account more interactions in the initial and final state and more complicated (and usually smaller) interactions between light and the molecule. Thus in optical spectroscopy there exists a hierarchy of selection rules depending on the level of analysis.

We find a similar situation for chemical reactions. Symmetry rules such as the W-H rules can be derived as selection rules for the electronic transition from the quasiadiabatic electronic state of the reactants to that of the products. The essential difference between the W-H rules and the spectroscopic selection rules is the difference between the operator which causes the transition of interest: for spectroscopy it is, in the simplest case, the dipole moment operator, while for chemical reaction it is, again in the simplest case, an operator whose properties are outlined below. Since we are concerned here only with the development of symmetry rules for chemical reactions, it will be necessary to describe this operator only in sufficient detail to establish its symmetry properties and the symmetry properties of its constituent parts. Much of what follows will involve qualitative arguments, and mathematical development will be held to the minimum required to sketch the form of the important integrals. Detailed discussions of the basis for these arguments can be found elsewhere[6g, 13].

As the basis for our discussion of the influence of symmetry on reaction rates, we assume that for a reaction of interest, the appropriate quasiadiabatic potential surfaces and wavefunctions are available for reactants and products. We further assume the reaction to be concerted and mean thereby that only two quasiadiabatic surfaces are important for the transition from reactants to products (Fig. 1b). Although in most cases this definition corresponds closely to the one commonly used (a concerted reaction is one taking place in one step,

[*] Quasiadiabatic descriptions make it possible to consider most reactions as electronic transitions; this feature is convenient in the study of the role of the electronic symmetry on rates. There are, however, reactions ($CO_2 \rightarrow CO + O$ is one example) which actually include a transition from one electronic *adiabatic* surface to another (here spin angular momentum is not conserved) [11]. In such unusual cases the situation is reversed: the adiabatic states make it possible to consider the reaction as an electronic transition while the quasiadiabatic ones for this example would describe the reaction as a continuous evolution over a potential barrier located between reactants and products.

without intermediates) a detailed discussion of the relation between the two definitions will be deferred to a later section of this paper. The rate of the reaction—that is, the rate at which reactants are converted into products—is calculated from the probability of a transition from each state of the reactants (electronic and nuclear) to each state of the products. The probability of that transition is proportional to the square of a quantity T, called the transition matrix. The reaction rate constant is obtained by taking the average of $|T|^2$ over the thermal (Boltzmann) population of all states of the reactants. The transition matrix T can be written as the sum of three terms [Eq. (4)][1,3]:

$$T = T_1 + T_2 + T_3 \tag{4}$$

In this expression, T_1 is the term that gives rise to electronic orbital symmetry rules; T_2 contains contributions to the rate from non-Born-Oppenheimer terms; T_3 describes spin-orbit contributions.

The term T_1 is given by Eq. (5),

$$T_1 = \langle\langle \Phi_N^p(R) | \langle \psi_e^p(r,R) | O | \psi_e^r(r,R) \rangle | \Phi_N^r(R) \rangle\rangle \tag{5}$$

where the superscripts r, p refer to reactants and products respectively. This expression differs from those normally encountered in electronic theory of molecules in that it depends on both electronic ($\psi_e(r,R)$) and nuclear ($\Phi_N(R)$) wave functions. The integration over the electronic coordinates r is indicated by single brackets

$$\langle \psi_e^p(r,R) | O(r,R) | \psi_e^r(r,R) \rangle \equiv \int \psi_e^{p*}(r,R) | O(r,R) | \psi_e^r(r,R) \, dr \tag{6}$$

and the integration over the nuclear coordinates R by double brackets[14]:

$$\langle\langle \Phi_N^p(R) | O'(R) | \Phi_N^r(R) \rangle\rangle \equiv \int \phi_N^*(R) | O'(R) | \Phi_N^r(R) \, dR \tag{7}$$

A detailed definition of the operator O requires complicated arguments, and is neither within the scope of this article nor required for an understanding of the influence of molecular symmetry on reaction rate. In what follows, we will simply assert without proof the results of development and simplification of the expression for T_1 given by Eq. (5), and for corresponding expressions for T_2 and T_3. The mechanics of this development is described elsewhere[6g, 13, 28]. Thus, the electronic part of Eq. (5) is given by

$$\langle \psi_e^p(r,R) | O(r,R) | \psi_e^r(r,R) \rangle = \langle \psi_e^p(r,R) | H_e(r,R) | \psi_e^r(r,R) \rangle \tag{8}$$

+ other (neglected) terms[*].

[*] The terms left unspecified originate from the fact that we have confined the model to only two electronic states, one for products and one for reactants, and disregarded the possible (but usually unlikely) contributions of electronically excited states; and from the fact that the electronic quasiadiabatic states of the reactants are not necessarily orthogonal to those of the products [13]. Terms due to lack of orthogonality have the same symmetry properties as the term written in Eq. (8) and hence may for simplicity be omitted. The operator $H_e(r,R)$ is the electronic Hamiltonian of the complete reacting system (including all interactions between all nuclei and electrons).

The second term in the transition matrix T is given by

$$T_2 = -\frac{\hbar^2}{2} \sum_i \frac{1}{M_i} \left\{ \left\langle\left\langle \Phi_N^p(R) \left| \left\langle \psi_e^p(r,R) \left| \frac{\partial}{\partial R_i} \right| \psi_e^r(r,R) \right\rangle \frac{\partial}{\partial R_i} \right| \Phi_N^r(R) \right\rangle\right\rangle \right.$$
$$\left. + \left\langle\left\langle \Phi_N^p(R) \left| \left\langle \psi_e^p(r,R) \left| \frac{\partial^2}{\partial R_i^2} \right| \psi_e^r(r,R) \right\rangle \right| \Phi_N^r(r,R) \right\rangle\right\rangle \right\} \tag{9}$$

Here M_i is the mass of the i-th nucleus and the summation extends over all the nuclei. Notice that both the operator $\partial^2/\partial R_i^2$ in Eq. (9) and the electronic Hamiltonian $H_e(r,T)$ in Eq. (8) are totally symmetric, which means that the terms $\partial^2\psi(r,R)/\partial R_i^2$ and $H_e(r,R)\psi(r,R)$ have the same symmetry as $\psi(r,R)$. The second term in Eq. (9), therefore, has the same symmetry properties as T_1. Due to this symmetry equivalence and to the fact that this term is generally much smaller than the first one in Eq. (9), we shall neglect it. The remaining first term in Eq. (9) represents the contribution to the transition probability (and hence to the rate) from any coupling of the motion of the nuclei to that of the electrons. Such terms, called non-Born-Oppenheimer terms, appear in an analogous way in spectroscopy[12].

There is a simple way of seeing the origin of the coupling term involving the operator $\partial/\partial R_i$ in the non-Born-Oppenheimer contribution T_2. In quantum chemistry the electronic wave functions and energies are calculated with an electronic Hamiltonian in which the nuclei are usually held fixed. In most cases, the electronic states thus calculated (Born-Oppenheimer states) are an excellent approximation. Within that approximation, the system is confined to a single electronic state and transitions between electronic states are not possible. The removal of the approximation of fixed nuclei must take into account the velocity (hence, kinetic energy) of the nuclear motion. The velocity of the nuclei is represented by an operator proportional to $\partial/\partial R_i$ which appears in T_2 and induces transitions between the Born-Oppenheimer states.

The third term in the transition matrix, T_3, describes contributions to the rate from spin-orbit interactions and is given by

$$T_3 = \langle\langle \Phi_N^p(R) | \langle \psi_e^p(r,R) | H_{SO} | \psi_e^r(r,R) \rangle | \Phi_N^r(R) \rangle\rangle \tag{10}$$

where H_{SO} is the spin-orbit Hamiltonian. This term could, in principle, be expanded to include contributions to the rate from other couplings of angular momentum terms. For instance, the various interactions between electronic spin, nuclear spin, and molecular motion that determine the rates of processes important in CIDNP experiments could be included here. Spin-orbit interactions may become important whenever electron spin and orbital angular momentum are coupled, characteristically in radicals having heavy atoms.

We shall show that electronic symmetry rules for reaction rates of the W-H type originate in the T_1 term and that for reactions classified as "symmetry forbidden" by the W-H rules T_1 is small. T_2 and T_3 may, however, be sufficiently large, compared to T_1, to make a symmetry forbidden reaction proceed rapidly. The success of W-H rules depends in part on the fact that contributions to the rate from T_2 and T_3 are normally negligibly small. Even if T_2 and T_3 are small, however, it is not necessarily the case that the relative magnitude of T_1 (and

hence of T) for two competitive processes can always be deduced solely from symmetry considerations.

3.2. Electronic Symmetry Rules of the Woodward-Hoffmann Type

In the remainder of this section we derive the conditions which lead to symmetry rules, and discuss certain conditions under which these rules fail.

We emphasize that the form of these rules depends on the level of approximation with which the system is described. In particular, the W-H rules emerge from the most simplified treatment, in which virtual transitions among excited electronic states of reactant and products, the non-Born-Oppenheimer terms, and spin-orbit coupling are ignored; the Franck-Condon approximation is used; and the electronic wave functions are generated by the Hückel method. Various other possible approximations are discussed in Section 4.

3.2.1. The Role of Nuclear Overlap

Using Eqs. (5) and (8) we can write T_1 as:

$$T_1 = \int \Phi_v^p(R)\Phi_v^r(R)\,dR\,\langle\psi_e^p|H_e|\psi_e^r\rangle \tag{11}$$

The term $\langle\psi_e^p|H_e|\psi_e^r\rangle$ depends on the electronic wavefunctions and the electronic Hamiltonian and will be referred to as the electronic part of T_1; the product $\Phi_v^p(R)\Phi_v^r(R)$ depends on nuclear wave functions only and will be called the nuclear part of T_1. A similar classification can be made for T_2 and T_3, given by Eqs. (9) and (10). The W-H and other electronic symmetry rules originate from the electronic part of the transition matrix. The existence of such rules presupposes, however, certain properties for the nuclear part. These properties are discussed in this subsection.

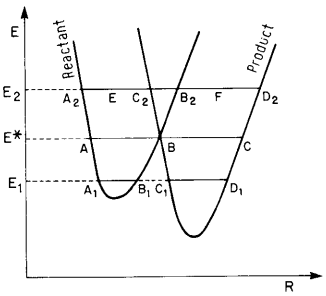


Fig. 5. Illustration of regions of substantial nuclear overlap for reactants and products. The heavy lines represent the quasiadiabatic energy surfaces of reactants and products. The light lines represent the nuclear configurations at which, for a given total energy of the reacting system, the nuclear wave functions (either one or both) are different from zero. For this qualitative discussion we neglect the small classically forbidden regions outside the wells of the heavy lines. At energy E_1, Φ_v^r is non-zero between A_1 and B_1 and Φ_v^p is non-zero between C_1 and D_1. The product $\Phi_v^r\Phi_v^p$ is therefore zero for all nuclear coordinates. At energy E_2, Φ_v^r is non-zero for nuclear configurations between A_2 and B_2, and Φ_v^p is non-zero for nuclear configurations between C_2 and D_2. Hence $\Phi_v^r\Phi_v^p$ is non-zero only between C_2 and B_2.

The functions $\Phi_v^p(R)$ and $\Phi_v^r(R)$ describe the nuclear positions and momenta[13]. The integral (11) for T_1 is non-zero only for those energies for which the two nuclear wavefunctions have an appreciable overlap (Fig. 5): that is, when the positions and momenta of the nuclei in the reactant and product configurations described by the chosen quasiadiabatic wavefunctions are similar. The nuclear overlap is zero at low energies, first becomes non-zero near the energy E^* at the crossing of the two quasiadiabatic surfaces, and then generally grows with the energy. We denote by $\Delta(E)$ the set of all nuclear configurations R for which, at a given total energy E, the product $\Phi_v^r(R)\Phi_v^p(R)$ is not zero. In the illustrative example presented in Figure 5, $\Delta(E_2)$ is the set of all nuclear configurations between C_2 and B_2. The integral (11) can be taken over $\Delta(E)$ only; no other nuclear configurations contribute to the integral T_1 since $\Phi_v^r(R)\Phi_v^p(R)$ is zero for R outside $\Delta(E)$.

$$T_1 = \int_{\Delta(E)} \Phi_v^p(R)\Phi_v^r(R)\,dR\,\langle\psi_e^p|H_e|\psi_e^r\rangle \tag{12}$$

The immediate conclusion from this analysis is that the rate of reaction is zero if $\Delta(E)$ is zero, and that the energy of crossing, E^*, corresponds to the activation energy of transition state theory, since $\Delta(E) \neq 0$ for $E \geq E^*$ (Fig. 5). The physical picture which emerges from Eq. (12) is the following. If the energy is less than E^*, the nuclear overlap and the contribution to the rate from T_1 are zero. If the energy is greater than E^* the nuclear overlap is not zero and the reaction rate is therefore not restricted to zero by the nuclear wavefunctions. (We neglect discussions of tunneling, which do not alter the argument substantially.) If thermal or optical excitation increases the energy of reactants to E_2 (Fig. 5), the state of reactants will be $\psi_e^r(r,R)\Phi_v^r(R)$ and the nuclei will oscillate between A_2 and B_2 on the quasiadiabatic energy surface of reactants (corresponding to ψ_e^r). Since this state is not a stationary state of the total Hamiltonian, a transition may occur to the state of the products, described by the wavefunction $\psi_e^p(r,R)\Phi_v^p(R)$ (Fig. 5). In this state the nuclei will oscillate between C_2 and D_2 on the quasiadiabatic energy surface of the products. The probability of this transition is proportional to $|T_1|^2$. Loss of energy from the product at energy E_2 will produce a stable species with energy less than E^*, and complete the conversion of reactant to product.

This analysis of T_1 can be easily extended to T_2 and T_3 and indicates that regardless of the corresponding electronic parts of these terms, reaction occurs only if $\Delta(E) > 0$, and only at nuclear configurations contained in $\Delta(E)$. Since $\Delta(E)$ represents those nuclear configurations which are accessible from both reactant and product state we reach the following conclusions: regardless of how favorable the electronic conditions may happen to be, a reaction occurs only through conformations in which reactants and products have similar shapes. If the reacting molecules are excited specifically, so that the region of nuclear configurations $\Delta(E)$ available to both reactants and products is increased, the reaction will be faster. If the attainment of a common nuclear configuration for reactants and products is prevented by, say, a bulky group, then the reaction rate will be decreased.

These conclusions can be illustrated by a pertinent example provided by the reaction[15a]

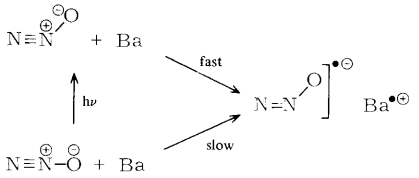
$$N_2O + Ba \rightarrow N_2 + BaO^*$$

BaO is produced in an electronically excited state and the rate of the reaction can be monitored, in a molecular beam

experiment, by measuring the light emission from BaO*. The mechanism is assumed to be

$$N_2O + Ba \rightarrow N_2O^{\bullet\ominus} + Ba^{\bullet\oplus} \rightarrow N_2 + BaO^*$$

where both the charge transfer and the molecular rearrangement occur in a single collision. Since N_2O is linear and $N_2O^{\bullet\ominus}$ is bent, then according to the above discussion the reaction rate should increase if the N_2O bending vibration ν_2 is excited. Experiments show indeed a substantial increase of the rate with excitation of this vibration. Similar arguments



underlie the theory of electron-transfer reactions developed by *Marcus*[15b].

3.2.2. The Role of Electronic Symmetry; Franck-Condon Approximation

After clarifying qualitatively the role of the nuclear part in the transition matrix, let us analyze the role of the electronic term in T_1

$$F_1(R) \equiv \langle \psi_e^p | H_e | \psi_e^r \rangle = \int \psi_e^p(r,R) H_e(r,R) \psi_e^r(r,R)\, dr$$

Through Eq. (11), the values of $F_1(R)$ for all nuclear coordinates in $\Delta(E)$ influence the rate. Suppose, however, that the major contribution to T_1 comes from nuclear configurations in a small range of nuclear coordinates around R_0 so that we can reasonably assume that the electronic term $F_1(R)$ may be evaluated with sufficient accuracy by taking into consideration only the region around R_0. (This assumption is equivalent to the Franck-Condon approximation.) We further assume that the nuclear configuration R_0 has some useful symmetry. Since the electronic Hamiltonian is totally symmetric, the electronic wave functions of reactants and products have the same symmetry properties as the nuclei (that is they belong to the irreducible representations of the group generated by R_0). If the electronic wave function of reactants has a different symmetry than that of the products (that is, if reactants and products belong to different representations) we call the reaction symmetry forbidden. All other reactions are symmetry allowed. To avoid confusion, we should emphasize that the precise meaning of such a statement depends upon the electronic functions ψ_e^r and ψ_e^p chosen to describe the system; Hückel wave functions would lead to slightly different conclusions than SCF ones. We discuss this issue in detail later.

Let us now return to Eq. (11) for T_1 and see under what conditions symmetry forbidden reactions are slow. For some symmetrical nuclear configuration R_0 for which reactants and products have different electronic symmetry we have for the electronic integral

$$F_1(R_0) \equiv \langle \psi_e^p(r,R_0) | H_e(r,R_0) | \psi_e^r(r,R_0) \rangle = 0 \qquad (13)$$

The expression $F_1(R)$ contributes to the rate T_1 [Eq. (11)] not only through its value at R_0, however, but also through its value at all nuclear configurations R contained in $\Delta(E)$. By continuity, if $\langle \psi_e^p | H_e | \psi_e^r \rangle$ is zero at R_0 it will be very small close to R_0. If $\Delta(E)$ is just such a small neighborhood of R_0 (that is, if the Franck-Condon approximation holds), then we can predict from the fact that ψ_e^r and ψ_e^p have different symmetries that T_1 is very small. If $\Delta(E)$ is large, however, we cannot make such a statement since nuclear configurations R which are inside $\Delta(E)$ but far from R_0 may result in a substantial value for T_1.

We can summarize this discussion with the following symmetry rule: a symmetry forbidden reaction will have a very small rate if T_2 and T_3 are negligible, and $\Delta(E)$ is small (corresponding closely to the Franck-Condon approximation made in spectroscopy). Of course, in order to be able to speak of a symmetry forbidden reaction in the first place, $\Delta(E)$ must contain a symmetrical nuclear configuration. For reactions which occur through nonsymmetric nuclear configurations there are no symmetry restrictions. We note also that the various approximations needed to derive the symmetry rules break the coupling of the total angular momentum[6g]. Hence symmetry rules are obtained if the components of the total angular momentum (electron spin, electronic orbital, nuclear, *etc.*) are conserved separately.

The general electronic symmetry rules derived contain as a particular case the Woodward-Hoffmann rules. The success of the latter, in dealing with many examples, indicates that the conditions of validity established are satisfied in most cases. There are, however, situations when these conditions are not satisfied. One example has been already presented: excitation of the bending mode of N_2O increases both $\Delta(E)$ and $\Phi_N^p \Phi_N^r$ and leads to an increase in the rate of the reaction

$$Ba + N_2O \rightarrow BaO^* + N_2$$

although the *electronic part* of T *has remained unchanged.*

We must emphasize that the symmetry of the electronic wave functions can tell us, under the circumstances specified above, whether a symmetry forbidden reaction is very slow. If, however, the reaction is allowed by symmetry (*i.e.*, if ψ_e^r and ψ_e^p have the same symmetry), it is not necessarily true that $\langle \psi_e^r | H_e | \psi_e^p \rangle$, and the rate, are large. Poor overlap may cause $\langle \psi_e^r | H_e | \psi_e^p \rangle$ to be small.

3.3. Violations of Electronic Symmetry Rules

We have seen that electronic symmetry rules are valid if we neglect coupling of electronic spin (T_3 small), make the Born-Oppenheimer approximation (T_2 small), and a Franck-Condon approximation [see Eqs. (11), (12) and accompanying discussion]. When any one of these conditions is not satisfied, then the electronic symmetry rules are violated and "forbidden reactions" may have large rates. Here we analyze these violations for the purpose of clarifying their origin and finding ways of increasing the rate of symmetry forbidden reactions.

3.3.1. Violations Caused by the Interaction of Electronic and Nuclear Motion (Vibronic Violations)

Let us analyze a symmetry-forbidden reaction for which the spin-orbit coupling contribution to the rate is unimportant ($T_3 \approx 0$). If we assume that $\Delta(E)$ is small, then the term T_1

will be practically zero. Under these conditions the rate is given by $T \approx T_2$; if T_2 is very small the forbidden reaction is slow. If T_2 is large the "forbidden" reaction is fast, in violation of the predictions of electronic symmetry rules.

The term T_2, given by Eq. (9) has a structure which is very similar to that of T_1, and it is useful again to speak of a nuclear contribution $\langle\langle \Phi_N^p | \partial \Phi_N^r / \partial R_i \rangle\rangle$ and an electronic contribution $\langle \psi_e^p | \partial \psi_e^r / \partial R_i \rangle$. As in the case of T_1, it is possible to make some qualitative predictions about the behavior of these terms. The contribution from the nuclear part can be increased by exciting those nuclear motions that make more nuclear configurations accessible to both reactants and products. The magnitude of the electronic term has not been calculated for quasiadiabatic states. It is, however, generally considered to be small for adiabatic states and is probably also small for quasiadiabatic ones. Its small magnitude does not preclude it from playing an important role in *large molecules* where the number of nuclear states is enormous and the contribution of a small electronic term is summed over all the nuclear states involved; the compounded effect may be significant. In fact, this term is known to cause fast radiationless transitions in large molecules[16]. In solids, which we may consider to be large molecules with periodic symmetry, these electronic integrals are responsible for important effects like superconductivity[17], exciton migration[18], electrical resistance[19], *etc.*

In the case of T_1 the magnitude of the electronic contribution depends on the symmetry of the electronic functions. The magnitude of the electronic part of T_2 is not determined by symmetry except for special situations. To justify this assertion, we use the fact that for small displacements around some symmetrical configuration, R_0, the symmetry coordinates Q_i and the nuclear positions R_i are linear combinations of each other[20]:

$$Q_j = \sum_i A_{ji} R_i$$

Here A_{ji} are numerical coefficients. Hence

$$\left\langle \psi_e^p \left| \frac{\partial}{\partial R_i} \right| \psi_e^r \right\rangle = \sum_j \left\langle \psi_e^p \left| \frac{\partial}{\partial Q_j} \right| \psi_e^r \right\rangle \frac{\partial Q_j}{\partial R_i} = \sum_j A_{ji} \left\langle \psi_e^p \left| \frac{\partial \psi_e^r}{\partial Q_j} \right. \right\rangle$$

At a symmetric nuclear configuration R_0, the terms $\psi_e^p(r, R_0)$, $\psi_e^r(r, R_0)$, and Q_i have a definite symmetry[20, 21], and some, *but not all*, of the integrals $\langle \psi_e^p | \partial \psi_e^r / \partial Q_j \rangle$ are zero (by symmetry). Hence

$$\left\langle \psi_e^p \left| \frac{\partial}{\partial R_i} \right| \psi_e^r \right\rangle = \sum_j A_{ji} \left\langle \psi_e^p \left| \frac{\partial \psi_e^r}{\partial Q_j} \right. \right\rangle$$

where now the summation eliminates those Q_i for which symmetry annihilates the corresponding integral. Since the summation on the right of this equation is not constrained to be zero by symmetry, we cannot predict the magnitude of T_2 from consideration of symmetry. *Only in the special case in which one symmetry coordinate is adequate to describe the reaction can T_2 be estimated from symmetry.* For example, in a reaction of the type $A + BA \rightarrow AB + A$ this reaction coordinate may be $A \rightarrow \leftarrow B \cdots A \rightarrow$, which indeed tends to break the molecule in the desired way. Let us assume that the displacements $A \leftarrow B \rightarrow A$ and $\begin{array}{ccc} & \uparrow & \\ A \cdots & B & - A \\ \downarrow & & \downarrow \end{array}$ are not capable of promoting the reaction, since they are not likely to create nuclear configurations that are accessible to the product. Hence we should consider that only $\langle \psi_e^r | \partial \psi_e^p / \partial Q_1 \rangle$, in which Q_1 denotes the symmetry coordinate $A \rightarrow \leftarrow B \rightarrow A$, contributes to T_2 in Eq. (9). If the reaction is symmetry forbidden and ψ_e^r and ψ_e^p have different symmetry, $\langle \psi_e^r | \partial \psi_e^p / \partial Q_1 \rangle$ need not be zero. In fact, Q_1 and therefore $\partial / \partial Q_1$ are of symmetry Σ_u^+. Assume, for example, that the electronic states are of symmetry Σ_g^+ and Σ_u^+. The integral $\langle \Sigma_g^+ | \partial / \partial Q_1 | \Sigma_u^+ \rangle$, which appears in T_2, need not be zero since Q_1 is of symmetry Σ_u^+, and the derivative $\partial / \partial Q_1 \, \Sigma_u^+$ is totally symmetric. In this illustrative example the electronic symmetry, through $\langle \psi_e^p | H_e | \psi_e^r \rangle$, causes T_1 to be very small while there is no indication that the term T_2, with electronic part $\langle \psi_e^p | \partial \psi_e^r / \partial Q_1 \rangle$, has to be small. If in this example the reaction is symmetry allowed, and the electronic states have the same symmetry, say Σ_g^+, the electronic contribution to T_2 is $\langle \Sigma_g^+ | \Sigma_u^+ | \Sigma_g^+ \rangle$ and it is zero. In this case T_2 must be negligible, for symmetry reasons, while T_1 is not. The argument is qualitative: it clearly is not possible to estimate the magnitude of T_2 relative to T_1 using these considerations. Nonetheless, the argument establishes a link between molecular symmetry and T_2 that corresponds to different "rules" than those of T_1 (which are essentially of Woodward-Hoffmann type) and is potentially useful in simple reactions in suggesting types of vibrational motions that might contribute to increasing the rate of those reactions which are forbidden according to electronic symmetry rules.

3.3.2. Interaction between Electron Spin and Electron Orbital Motion

Let us now analyze a symmetry forbidden reaction for which T_1 and T_2 are both zero, so that the rate depends on T_3 only. If T_3 is large the symmetry forbidden reaction is fast and we have what is called a spin-orbit violation of symmetry rules. It is usually assumed that the spin-orbit coupling is small and a negligible part of the Hamiltonian, as far as the rate of chemical reactions is concerned. This assumption is not necessarily correct. Assume that the reactant electronic wavefunction ψ_e^r is a singlet and the product ψ_e^p is a triplet. In this situation the electronic parts of T_2 and T_3, *i.e.*, $\langle \psi_e^p | H_e | \psi_e^r \rangle$ and $\langle \psi_e^p | \partial \psi_e^r / \partial R_i \rangle$, are zero, due to the orthogonality of the spin part of the wavefunction. The only surviving term in T is T_3. Hence

$$T = T_3 = \int_{\Delta(E)} \Phi_N^p(R) \Phi_N^r(R) \, dR \, \langle \psi_e^p | H_{SO} | \psi_e^r \rangle \tag{13a}$$

The rate of the reactions between singlet and triplet states is determined by T_3 (spin-orbit coupling) only. Since the spin-orbit coupling Hamiltonian H_{SO} is *not* totally symmetric[22], T_3 does not have to be small when the reaction is forbidden according to electronic symmetry rules (ψ_e^r and ψ_e^p have different symmetries). As an example consider the reaction[11]

$$CO_2(^1\Sigma_g^+) \rightarrow CO(^1\Sigma^+) + O(^3P)$$

Schematic energy surfaces are presented in Figure 6. The reactant state is singlet and the product state is triplet. Therefore T ($=T_3$) is given by Eq. (13a). The spin-orbit coupling term can be estimated from spectroscopic measurements to be about $50\,cm^{-1}$. The nuclear wavefunction can be computed for a simple model. The resulting rate coefficient agrees well with the measured one[11], indicating that the spin-orbit coupling is indeed the necessary interaction for this reaction.

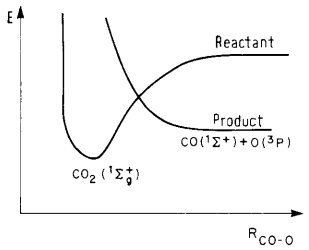


Fig. 6. Schematic energy surfaces for the reaction $CO_2(^1\Sigma_g^+) \rightarrow CO(^1\Sigma^+) + O(^3P)$.

The spin-orbit coupling may be enhanced in the presence of heavy atoms and inclusion of heavy atoms in reactants should increase the probability that they will take part in symmetry forbidden reactions.

3.3.3. The Role of Nuclear Motion. Violation of Electronic Symmetry Rules Due to Dynamics

We have already stressed the importance of the properties of the nuclear wave functions. If $\Delta(E)$ [see Eq. (12)] is very large and the nuclear overlap is very large, predictions of the magnitude of T_1, based on electronic symmetry alone, become doubtful. The difficulties in computing the nuclear wave functions make it impractical to propose any general calculational approaches to predicting violations of symmetry rules due to dynamics. Qualitatively, however, such violations occur when it is possible for the reactants to "look" like the product or *vice versa*: that is, for instance, when readily accessible vibrational states of the reactant(s) produce nuclear positions that closely resemble those of accessible vibrational states of the product(s). This results in an increase of the nuclear overlap, and in an increase in T_1 [Eq. (11)]. This qualitative consideration suggests that a plausible approach to increasing the rate of a symmetry forbidden reaction is to increase the vibrational energy of the reactant, most simply (but inefficiently) by heating, but also possibly by selective laser excitation of particular vibrational modes. A particularly pertinent example is provided by the reaction of H_2 and I_2. This reaction proceeding through a C_{2v} trapezoidal configuration is symmetry forbidden[123] (Fig. 7). Classical mechanical calculations[24] of reactive collisions indicate that as long as I_2 is in the vibrational ground state the reaction does not occur through a trapezoidal nuclear configuration, in agreement with the prediction of the W-H symmetry rules. If I_2 is, however, vibrationally excited, half of the reactive trajectories go through the trapezoidal configurations, contrary to the predictions of W-H rules.

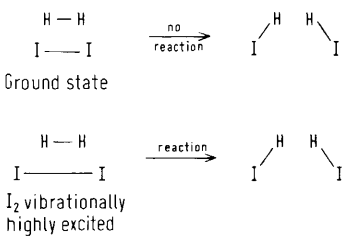


Fig. 7. Possible violation of the symmetry rules: a forbidden reaction is made possible by vibrational excitation.

4. Hierarchy of Symmetry Rules: *cis*-Butadiene—Cyclobutene Conversion

4.1. Molecular Orbital Description of Electronic Wave Functions

In the discussion of the previous Section we derived electronic symmetry rules without specifying any particular procedure for generating electronic wave functions. We shall now schematically illustrate the computation of the electronic part of T_1 for a specific example (butadiene → cyclobutene) and state the electronic symmetry rules in terms of the symmetry properties of Hückel *molecular orbitals* (as opposed to the symmetries of the *total electronic wave functions* used in the discussions of the previous section). We neglect here any contributions to the rate from T_2 and T_3. The reliability of the predictions resulting from these procedures depends on the quality of the electronic wave functions: different predictions might emerge, for example, from consideration of Hückel and SCF wave functions[13]. In such instances, it is worthwhile to understand the origin of the discrepancy and the ways of determining the correct prediction.

We begin our analysis by evaluating the relative magnitudes of the electronic part of T_1 [Eq. (13)] for four cases—thermal and photochemical conrotatory and disrotatory ring closures and compare the procedure with that used in a W-H analysis. The W-H rules predict that the conrotatory pathway is thermally allowed and photochemically forbidden, and that the disrotatory pathway is thermally forbidden and photochemically allowed.

4.1.1. Thermal Reactions

The classification of the Hückel molecular orbitals for butadiene and cyclobutene orbitals by symmetry is too familiar to require discussion, but is summarized in Figure 8 for reference. One typical wavefunction for ground-state butadiene

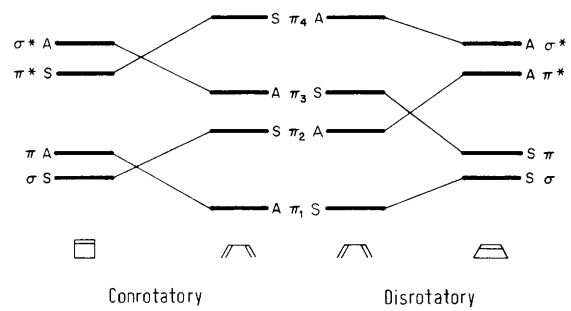


Fig. 8. Correlation diagram for Hückel molecular orbitals used for quasi-adiabatic description of conrotatory and disrotatory ring closure of butadiene.

is Eq. (14): In this expression, $\pi_1(1)$ indicates that the π_1 orbital contains an electron arbitrarily labeled 1. Eq. (14)

neglects the fact that it is not permissible to label electrons: equally valid distributions of electrons would be those given by Eqs. (15a) and (15b). The correctly antisymmetrized wave function for butadiene is therefore given by the appropriate Slater determinant [Eq. (16)].

$$\psi_r' = \pi_1(1)\pi_1(2)\pi_2(3)\pi_2(4)\Phi\xi(R) \tag{14}$$

$$\psi_r'' = \pi_1(3)\pi_1(4)\pi_2(1)\pi_2(2)\Phi\xi(R) \tag{15a}$$

$$\psi_r''' = \pi_1(3)\pi_1(1)\pi_2(4)\pi_2(2)\Phi\xi(R) \tag{15b}$$

$$\psi^r = \frac{1}{\sqrt{4!}} \begin{vmatrix} \pi_1(1) & \pi_1(2) & \pi_1(3) & \pi_1(4) \\ \pi_1(1) & \pi_1(2) & \pi_1(3) & \pi_1(4) \\ \pi_2(1) & \pi_2(2) & \pi_2(3) & \pi_2(4) \\ \pi_2(1) & \pi_2(2) & \pi_2(3) & \pi_2(4) \end{vmatrix} \Phi\xi(R)$$

$$\equiv \det\{\pi_1(1)\pi_1(2)\pi_2(3)\pi_2(4)\}\,\Phi\xi(R) \tag{16}$$

Similar equations can be written for cyclobutene. Thus, using a one-electron Hamiltonian, Eq. (17), we can express Eq. (12) explicitly, for the reaction of interest, as Eq. (18):

$$H_e(r,R) = \sum_{i=1,4} H_i(r,R) \tag{17}$$

$$T_1 = \int_{\Delta(E)} \Phi\mathfrak{R}(R)\Phi\xi(R)\,dR\,\langle \det\{\sigma(1)\sigma(2)\pi(3)\pi(4)\} \left| \sum_{i=1,4} H_i(r,R) \right| \det\{\pi_1(1)\pi_1(2)\pi_2(3)\pi_2(4)\}\rangle \tag{18}$$

This expression for T_1, fully expanded, contains an inconveniently large number of terms. Fortunately it is unnecessary to evaluate all of these terms explicitly. Since we are interested initially only in the influence of molecular symmetry on T_1, we need only estimate the largest terms in this expression. To find these largest terms, consider two typical terms, for a thermal, conrotatory process as given in Eqs. (19) and (20); for convenience, these terms are also presented in a simplified form in which only the symmetry[*] of the appropriate molecular orbital is indicated.

$$\langle\sigma(1)|H_1|\pi_1(1)\rangle\langle\sigma(2)|\pi_1(2)\rangle\langle\pi(3)|\pi_2(3)\rangle\langle\pi(4)|\pi_2(4)\rangle = \\ = \langle S|H|A\rangle\langle S|A\rangle\langle A|S\rangle\langle A|S\rangle \tag{19}$$

$$\langle\sigma(1)|\pi_2(1)\rangle\langle\sigma(2)|H_2|\pi_2(2)\rangle\langle\pi(3)|\pi_1(3)\rangle\langle\pi(4)|\pi_1(4)\rangle = \\ = \langle S|S\rangle\langle S|H|S\rangle\langle A|A\rangle\langle A|A\rangle \tag{20}$$

Evaluation of these products of integrals requires remembering that $\langle S|H|A\rangle = \langle A|H|S\rangle = \langle A|S\rangle = \langle S|A\rangle = 0$: thus, on the basis of symmetry considerations above, all four terms in Eq. (19) are zero (at the chosen fixed, symmetrical nuclear configuration which serves to classify the MOs according to symmetry) and none of the four in Eq. (20) need be zero.

In general, for a system with n electrons: Expansion of the expression analogous to (18) affords a large number of terms [analogous to (19) and (20)], each being the product of n integrals of type $\langle\phi^p(i)|\phi^r(i)\rangle$ and (once per term) of type $\langle\phi^p(i)|H_i|\phi^r(i)\rangle$. *One* such integral is to be assigned to *each* of the n electrons in *each* term. ϕ^r is a singly or doubly occupied reactant orbital in the given reactant configuration, ϕ^p is a singly or doubly occupied product orbital in the given product configuration; all possible permutations of the orbitals occur in the various terms on assignment of these reactant and product orbitals to the electron i. However, each individual term reflects the given reactant and product configuration: a reactant orbital which is doubly occupied in the reactant will appear *twice* in the n integrals of each term, a singly occupied one *once*, and an unoccupied one *not at all*; the same applies to the product orbitals. The largest, *i.e.* dominant, terms obtained on expansion are those in which most of the n integrals $\langle\phi^r(i)|\phi^p(i)\rangle$ and $\langle\phi^r(i)|H_i|\phi^p(i)\rangle$ are characterized by the orbital ϕ^r and the orbital ϕ^p having the same symmetry; hence, it immediately follows that one of the dominant terms is obtained by making maximum possible use in its integrals $\langle\phi^p(i)|\phi^r(i)\rangle$ and $\langle\phi^p(i)|H_i|\phi^r(i)\rangle$ of those reactant orbitals ϕ^r and product orbitals ϕ^p which correlate with one another in the W-H orbital correlation diagram for the two reactant and product configurations under discussion! In what follows, we discuss only these largest terms which are easily determined by inspection of a W-H orbital correlation diagram. The number of integrals in a possible dominant term which are equal to zero for symmetry reasons is, of course, equal to the number of electrons which have to change orbitals in an orbital correlation diagram (formally, say at an orbital crossover point) in order that a given reactant configuration be transformed into a given product configuration along the correlation diagram.

For a thermal disrotatory ring closure, inspection of the correlation diagram (Fig. 8) immediately yields the following representative dominant term:

$$\langle\pi_1(1)|H_1|\sigma(1)\rangle\langle\pi_1(2)|\sigma(2)\rangle\langle\pi_2(3)|\pi(3)\rangle\langle\pi_2(4)|\pi(4)\rangle = \\ = \langle S|H|S\rangle\langle S|S\rangle\langle A|S\rangle\langle A|S\rangle \tag{21}$$

Since this ring closure (*i.e.* transition from the reactant configuration $\pi_1^2\pi_2^2$ to the product configuration $\sigma^2\pi^2$) involves changeover of two electrons from the π_2 orbital into the π orbital, two integrals in term (21) must be equal to zero for symmetry reasons, as is confirmed by inspection of this term.

The expressions in Eqs. (20) and (21), which represent the electronic part of T_1 for thermal conrotatory and disrotatory ring closure respectively, are qualitatively different: two of the terms in Eq. (21) are zero by symmetry; none is zero in Eq. (20). Since the magnitude of T_1 is related to the rate, the relative magnitudes of these expressions estimate the relative contributions to the rate attributable to molecular symmetry. Since Eqs. (20)–(21) represent the electronic part of T_1, they determine the rate through integrals over the nuclear coordinates [see Eq. (11)]; for the thermal disrotatory ring closure, for example, the appropriate integral is:

$$T_1(E) = \int_{\Delta(E)} \Phi\xi\,\Phi\mathfrak{R}\,\{\langle S|H|S\rangle\langle S|S\rangle\langle A|S\rangle\langle A|S\rangle\}\,dR$$

The terms $\langle A|S\rangle$ are zero for a symmetric nuclear configuration inside $\Delta(E)$. Since $\Delta(E)$ is assumed small, the values of $\langle A|S\rangle$ for all nuclear coordinates inside $\Delta(E)$ are very small: we designate the contribution of each of those small terms to T_1 by ε, and classify the size of T_1 by the number of the terms of magnitude ε which appear in the integral. Thus, T_1 for the thermal disrotatory reaction is of order ε^2, since two small terms appear in T_1. The same argument indicates that the magnitude of T_1 for the thermal conrotatory

[*] S stands for symmetric and A for antisymmetric.

ring closures, whose electronic part is given by Eq. (18), is of order $\varepsilon^0 = 1$. (In Section 4.1.2, which is concerned with the photochemical reaction, we show that T_1 for conrotatory and disrotatory photochemical ring closure is of order ε.) Then, since $|T_1|^2$ is the quantity related to rate, it is possible to classify the different types of conversions of butadiene to cyclobutene in terms of their "degree of forbiddenness", which is the exponent of ε in T_1. On grounds of symmetry alone, the quantity ε is a small number compared to integrals like $\langle S|S\rangle$ or $\langle A|A\rangle$; the greater the exponent of ε the smaller will be the value of $|T_1|^2$ due to the electronic integral. Qualitatively, there will be as many terms of magnitude ε in $T_1(E)$ as there are electrons that cross, in going from reactants to products, between orbitals of different symmetry.

This treatment thus differs from the standard W-H treatment in permitting "degrees of forbiddenness" rather than restricting reactions to the two categories of "symmetry allowed" and "symmetry forbidden". One should however be aware of the qualitative nature of this argument. Though each "symmetry forbidden" matrix element $\langle S|A\rangle$ or $\langle S|H|A\rangle$, contributes with a very small term ε, it is possible that different reaction pathways give ε's of different magnitude. If this difference of magnitude is large, though both ε are very small, our classification according to the powers of ε is not useful. Also, terms like $\langle S|S\rangle$ or $\langle A|A\rangle$ which need not be small by symmetry may be small for other reasons. Our classification based on powers of ε implicitly assumes that $\langle A|S\rangle \ll \langle S|S\rangle$ or $\langle A|A\rangle$. A test of these conditions for the case at hand is necessary before accepting this classification.

4.1.2. Photochemical Reactions

Since photochemical disrotatory and conrotatory ring closure have been the subject of numerous discussions and calculations[25], which sometimes seem to indicate the inadequacy of W-H rules in describing these reactions, we shall analyze such reactions in detail from the point of view of the present paper. Past discussions of these matters involved the details of the adiabatic energy surfaces and we find it useful to explore, for this particular example, the connection to our quasiadiabatic description. We shall use here quasiadiabatic wavefunctions which give a reasonable description of the two electronic states in the region of nuclear configuration in which the reactant resembles the product. For this purpose we modify the method described in Section 2 and choose the wavefunctions for the disrotatory, photochemical reaction to be:

$$S_1 = a_1 \det\{\pi_1 \pi_1 \pi_2 \pi_2\} + b_1 \det\{\sigma \sigma \pi^* \pi^*\} \tag{22}$$

$$A_1 = a_2 \det\{\pi_1 \pi_1 \pi_2 \pi_3\} + b_2 \det\{\sigma \sigma \pi^* \pi\} \tag{23}$$

$$S_2 = a_3 \det\{\pi_1 \pi_1 \pi_3 \pi_3\} + b_3 \det\{\sigma \sigma \pi \pi\} \tag{24}$$

Here, for example, S_1 corresponds to the ground state of butadiene when $a_1 = 1$ and $b_1 = 0$. The molecular orbitals used to form the determinants are those summarized in Figure 8. The second determinant in this expression serves to characterize the system in a state (for example, at high energy) which resembles cyclobutene sufficiently that MOs derived from butadiene no longer provide an adequate description: in these intermediate states, both a_1 and b_1 are non-zero. Variations in a_1 and b_1 provide a method of describing the system at any point in-between ground-state butadiene and cyclobutene in the corresponding doubly excited configuration. Equations (23) and (24) provide analogous descriptions of states which correspond at one extreme ($a = 1$, $b = 0$) to singly-excited and doubly-excited configurations of butadiene.

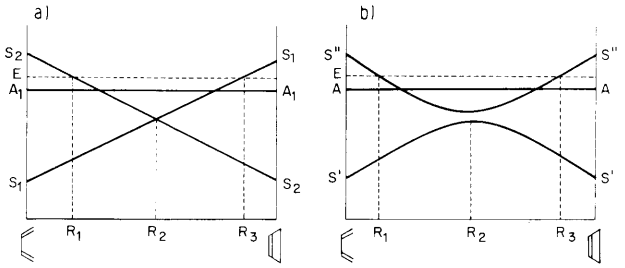


Fig. 9. Schematic quasiadiabatic (a) energy surfaces for the photochemical disrotatory electrocyclic reaction of butadiene to cyclobutane and corresponding adiabatic surfaces (b).

In Figures 9a and 9b we represent schematically the corresponding quasiadiabatic and adiabatic surfaces. The adiabatic surfaces resemble the results of van der Lugt and Oosterhoff[25].

The mechanism of reaction in the quasiadiabatic representation is as follows. Since only A_1 carries oscillator strength, the reaction starts with the molecule excited to A_1, at some energy E (see Fig. 9a). Because the energy surface of A_1 is fairly flat, as can be seen from the schematic correlation diagram Figure 9a or from the Lugt and Oosterhoff calculation, the molecule undergoes large amplitude oscillations along the reaction coordinate. For nuclear positions located at the right of R_1 (Fig. 9a) the electronic transition $A_1 \rightarrow S_2$ which generates vibrationally excited products becomes possible. In direct competition with this process, for nuclear configurations to the left of R_3, the transition $A_1 \rightarrow S_1$ is possible: this transition generates vibrationally excited reactants. If we assume that vibronic and spin-orbit contributions are small, then the rates of these transitions are determined by T_1. For the case $A_1 \rightarrow S_2$

$$T_1 = \int_{V(E)} \Phi_{\mathcal{R}} \Phi_{\mathcal{R}} \langle A_1|H_e|S_2\rangle \, dR$$

Let us analyze the electronic part $\langle A_1|H_e|S_2\rangle$ from the point of view of the symmetry of the molecular orbitals. We see that A_1 is composed of two determinants [Eq. (23)] and inspection of Figure 8 indicates that both determinants have the same symmetry. The same is true for the determinants used in S_2. Hence all the terms in $\langle A_1|H_e|S_2\rangle$ have the same symmetry properties as:

$$\alpha \equiv \langle \det\{\pi_1 \pi_1 \pi_2 \pi_3\}|H_e|\det\{\sigma \sigma \pi \pi\}\rangle$$

If we repeat the analysis of Section 4.1.1, we find that the largest terms in α are represented by

$$\langle \pi_1|H_e|\sigma\rangle\langle \pi_1|\sigma\rangle\langle \pi_2|\pi\rangle\langle \pi_3|\pi\rangle = \langle S|S|S\rangle\langle S|S\rangle\langle A|S\rangle\langle S|S\rangle \sim \varepsilon^1$$

Thus the photochemical disrotatory ring closure is of order of forbiddenness one. By contrast, our previous analysis indicated that T_1 for the thermal disrotatory ring closure is of order ε^2 and this reaction is of order of forbiddenness two.

Hence, a disrotatory ring closure is predicted to take place more readily by a photochemical than by a thermal path.

There is no contradiction between this description of the reaction and that resulting from the adiabatic representation[25]: the latter however hides the role of symmetry. The quasiadiabatic process $A_1 \rightarrow S_2$ (see Fig. 9a) becomes in the adiabatic picture (Fig. 9b) $A \rightarrow S''$ (at configurations to the right of R_1) followed by $S'' \rightarrow S'$, at configurations around R_2. These transitions are due to non-Born-Oppenheimer coupling (between the *adiabatic states*) which may be quite important at R_2 since the electronic gap between S′ and A is small. This adiabatic description of the reaction may seem different from that provided by the correlation diagrams and this apparent discrepancy has created some confusion. The adiabatic description is however equivalent to the quasiadiabatic one, which in turn is equivalent to the one provided by the correlation diagrams.

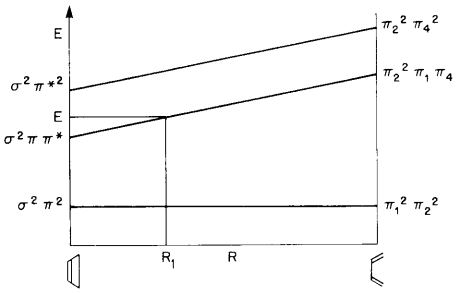


Fig. 10. Quasiadiabatic states for the conrotatory photochemical opening of cyclobutene to give butadiene.

The quasiadiabatic states for the conrotatory ring opening are presented in Figure 10. Since reactant and product states do not cross there is no possibility of an electronic transition which will lead to excited products.

We have ignored in the analysis kinetic factors that may become important in photochemical reactions, like radiative or radiationless de-excitation of the reactant state.

The discussion in this section serves to illustrate the electronic symmetry rules at the simplest level possible, when a Hückel description is used for the electronic wave function. Such rules are valid when $\Delta(E)$ is very small and the non-Born-Oppenheimer and spin orbit coupling are negligible. Under these circumstances we derive all the conclusions obtained from the original W-H rules. The rules derived here give more details about the reaction, indicating the possible existence of degrees of forbiddenness, and point out the important role that the overlap of the molecular orbitals plays in the electronic part of T_1, and hence in the rate.

4.2. Hierarchy of Symmetry Rules

We have emphasized at various places in this paper the fact that the predictions made by using the electronic symmetry rules depend on the degree of information that we have about the quasiadiabatic electronic wave functions. We illustrate this point now with the example of the ring closure reaction of butadiene. We represent the wave functions of both reactant and product, schematically, by indicating the symmetry of the molecular orbitals used to construct them. For the thermal disrotatory ring closure the reactant wave function is represented (Section 4.1.1) by SSAA, and that of the product by SSSS. As we have already discussed, when we know the symmetry of *each molecular orbital*, we can predict for this reaction an order of forbiddenness of two. Now let us assume that we want to use the electronic symmetry rules to predict the rate, but we know only the symmetry of *the wave functions* of the reactants and products (from spectroscopic measurements, for example) and know nothing about the symmetry of the molecular orbitals from which the wave function is built. For the disrotatory thermal ring closure the wave functions of reactants and products are both symmetric (the SSAA behaves upon reflection in the symmetry plane like SSSS since AA does not change sign). Therefore based on this information alone, using electronic symmetry rules, we see that the reaction is allowed; to be precise, this means that we cannot use electronic symmetry to state that the reaction is slow. Obviously the two predictions are different and the one based on the knowledge of the symmetry of the MOs is more useful. Different degrees of information need not lead to different conclusions. For example, in the case of reactions which can be represented as transitions from SSSA to SSSS or SAAA to SSSS, the symmetry of the electronic wave function of the reactants is different from that of the products and if we do not know the symmetry of the MOs we predict that both reactions are forbidden. The same prediction is made if the symmetry of the MOs is known and used, but in this case we gain the additional information that the first reaction (SSSA→SSSS) has an order of forbiddenness one while the second (SAAA→SSSS) has an order of forbiddenness three.

These examples illustrate how additional knowledge of the symmetry of MOs provides us with additional information which can change our ability to predict the outcome of the reaction. Thus a hierarchy of rules is possible, according to the details of knowledge of the symmetry of the wave function. This point has been made by *Silver*[6h] in a discussion based on a different approach.

4.3. The Role of the Electronic Interactions

In the previous subsection we have seen how the use of Hückel MO theory, which gives information about the symmetry of MOs, aids in learning more details about the rate of reaction. Hückel theory has, however, the disadvantage that it ignores to a large extent the interaction between electrons. In this section we discuss the effect that inclusion of electronic interactions, at the level of Hartree-Fock theory, has upon the predictions of reaction rates based on electronic symmetry.

It is very simple to take account of this interaction in the present approach in the electronic Hamiltonian H_e, which appears in the electronic part of T_1. If we write $H_e = H_e^{(1)} + H_e^{(12)}$, for the one- and two-electron parts ($H_e^{(12)}$ are the coulomb interactions between electrons), the two-electron operator contributes to T_1 terms of the form $\langle \psi_e^p | H_e^{(12)} | \psi_e^r \rangle$. For the thermal disrotatory reaction, for example, $\psi_e^r = \det\{SSAA\}$ and $\psi_e^p = \det\{SSSS\}$ and a representative two-electron term in $\langle \det\{SSSS\} | H_e^{(12)} | \det\{SSAA\} \rangle$ is $\langle SS | H_e^{(12)} | AA \rangle \langle S|S \rangle \langle S|S \rangle$. The one-electron contribution is, as already discussed, $\langle A|S \rangle \langle A|S \rangle \langle S | H_e^{(1)} | S \rangle \langle S|S \rangle$. The two-electron term has an order of forbiddenness zero, since SS

has the same symmetry as AA; the one-electron term has an order of forbiddenness two. In this particular case, the symmetry thus does not require that T_1 be small, although the one-electron contribution to T_1 is, in fact, very small. If the two-electron term is important (in other words, if the Hückel approximation is very poor) we will observe violations of the W-H rules. The success of W-H rules indicates that the joint contribution of all two-electron terms to T_1 is generally small. One should, however, keep them in mind as potential sources of violation of the rules. Notice also that for a reaction which can be described as SSSA→SSSS, and which has an order of forbiddenness one, the two-electron terms behave like the one-electron ones. Indeed both $\langle SA|H_e^{(12)}|SS\rangle$ and $\langle S|H_e^{(1)}|A\rangle$ are of order ε. Therefore the electronic interactions may change the predictions of the symmetry rules, based on one-electron terms, only in the case or reactions with order of forbiddenness two.

4.4. Role of Orbital Overlap

The principle of maximum bonding, which states that the reaction pathway is likely to be along the pathway of maximum MO overlap, is intimately connected to the symmetry rules by the present approach. In fact, in our approach the symmetry of molecular orbitals is used to determine whether the overlap between the MOs of the quasiadiabatic wave function of reactant and products is small. Poor overlap makes T_1 very small and leads to the same effect as selection rules based on the symmetry of the electronic wave function. Since the overlap between two MOs may be zero even if the symmetry does not require it to be so, it is useful to analyze the overlap whenever possible. For example let us compare again the disrotatory photochemical reaction with the disrotatory thermal reaction.

Figure 8 shows that the leading term in the electronic part of T_1 for the disrotatory photochemical reaction is

$$\langle\pi_1|H_e|\sigma\rangle\langle\pi_1|\sigma\rangle\langle\pi_2|\pi\rangle\langle\pi_3|\pi\rangle=\langle S|S|S\rangle\langle S|S\rangle\langle A|S\rangle\langle S|S\rangle$$

while that for the disrotatory thermal reaction is

$$\langle\pi_1|H_e|\sigma\rangle\langle\pi_1|\sigma\rangle\langle\pi_2|\pi\rangle\langle\pi_2|\pi\rangle=\langle S|S|S\rangle\langle S|S\rangle\langle A|S\rangle\langle A|S\rangle$$

The only difference is the replacement of $\langle\pi_3|\pi\rangle=\langle S|S\rangle$ in the expression for the photochemical reaction by $\langle\pi_2|\pi\rangle=\langle A|S\rangle$ to obtain the thermal one. Since $\langle A|S\rangle$ must be very small by symmetry and $\langle S|S\rangle=\langle\pi_3|\pi\rangle$ does not have to be, the symmetry rules predict that the thermal reaction is the slower of the two. This prediction will be inaccurate if the overlap of $\langle S|S\rangle=\langle\pi_3|\pi\rangle$ is very poor so that this term is in fact as small as $\langle\pi_2|\pi\rangle$. In this simple case, however, the overlap is large and the conclusion derived by using symmetry alone correct. In general, in comparing the photochemical (one electron excitation) with the thermal reaction, on pathways of the same symmetry (*e.g.*, both disrotatory), one has to compare the overlaps ⟨HOMO reactant|HOMO product⟩ and ⟨LUMO reactant|HOMO product⟩. If the latter is larger, then the photochemical reaction is faster.

The principle of maximum overlap has a broader validity than the electronic symmetry rules. The latter may be viewed as a particular case of the former in which the symmetry of the MOs is used to establish the existence of a very poor overlap. The principle of maximum overlap has the same limitations as the electronic symmetry rules in that both neglect possible coupling of electron spin, and both require the Born-Oppenheimer and Franck-Condon approximation. Thus both are restricted to consideration of electronic motion only; the neglect of nuclear motion limits the predictive value of these analyses of chemical kinetics.

5. Concerted and Nonconcerted Reactions

A definition of "concerted" and "nonconcerted" reactions is an integral part of any examination of symmetry rules for reaction rates, because these rules are usually applied to concerted reactions[126]. The traditional view is that a concerted reaction is one in which there is no intermediate. All bonds that break or form during the reaction do so simultaneously. A nonconcerted reaction is one in which there is an intermediate. These are useful qualitative notions. The discussions of the preceeding sections provide a framework with which to give operational definitions of both concerted and nonconcerted reactions.

We define a concerted reaction as one which consists of a *single* electronic transition from the quasiadiabatic state of reactants to that of the products. A nonconcerted reaction is one in which at least *two uncorrelated electronic transitions* are needed to complete the reaction. The most common situation which may give rise to a nonconcerted process is one in which three quasiadiabatic electronic states are required to describe the conversion of reactants to products (Fig. 11b). One describes the reactants, one the products and the third one (denoted I in Fig. 11b) is called the intermediate. The two electronic transitions required to make the reaction nonconcerted are, in this case, the transition from the state of reactants to that of the intermediate and a second transition from the intermediate state to that of the products. In this section we discuss nonconcertedness as it appears in reactive processes that may be characterized by three electronic states only. The need to consider more electronic states may arise but the discussion of such a situation is a straightforward generalization of the three-state case.

The points to be discussed here qualitatively are: 1) Since we define a nonconcerted reaction as one which requires two electronic transitions to complete the reaction, we must explain why the electronic symmetry rules break down for nonconcerted reactions and what the new symmetry rules are, if any. 2) How can one establish by a simple calculation whether a reaction is nonconcerted? 3) What is the connection between the present definition of nonconcertedness and the ones existing in the literature?

To answer the first question, let us consider the case presented in Fig. 11b. For energy E_1 (the energy at R_1) the direct transition reactant→product by a single electronic transition is not possible since the overlap of the nuclear wave functions is extremely small. It is, however, possible to have a transition reactant→intermediate since the nuclear overlap is fairly substantial around the nuclear configuration R_1, cor-

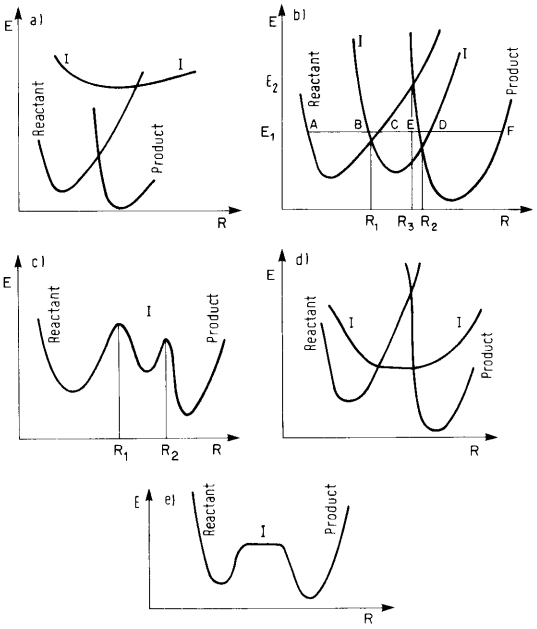


Fig. 11. a) A reaction for which the third electronic state (intermediate) (I) is too high to be accessible. The state I is not populated and the reaction is concerted. b) The third quasiadiabatic electronic state is low enough and the transitions R→I and I→P are energetically possible. At energy E_1 the reaction is nonconcerted. At energies around E_2 the reaction is both concerted and nonconcerted (see text for details). c) Adiabatic energy surface corresponding to the case of Fig. 11b. d) A flat intermediate quasiadiabatic energy surface which may be expected in the case of a diradical. e) The flat barrier on the adiabatic energy surface corresponding to Fig. 11d.

responding to the crossing of the energy surfaces of reactant and intermediate (Fig. 11b). Once the system is in the electronic state I the nuclei undergo oscillatory motion with the amplitude BD. Within a period of oscillation (10^{-13} s) the nuclei visit the region ED, in which the nuclear wave function in the state I overlaps well with that in the state P. A transition from I to P becomes possible and when this happens the reaction is completed. One can show that the electronic part of the transition probability for two uncorrelated transitions, corresponding to the part T_1 for concerted reactions, is of the type[13, 28]:

$$\langle\psi_e^P|H_e|\psi_e^I\rangle_{R_2}\langle\psi_e^I|H_e|\psi_e^R\rangle_{R_1} \tag{25}$$

where the subscripts R_1 and R_2 indicate that only the nuclear configurations located around R_1 and R_2 need to be considered. The derivation of the electronic symmetry rules for concerted reactions has been based on the fact that the electronic part of the transition matrix has the form $\langle\psi_e^P|H_e|\psi_e^R\rangle_{R_1}$ and the electronic states of *reactants and products* appear in the same matrix element. Integrals of this form do not occur in descriptions of the electronic part of a nonconcerted reaction, given by Eq. (25), and therefore the simple electronic symmetry rules which apply to concerted reactions do not apply. Other rules are, however, possible[28]. We can regard the two terms of Eq. (25) as electronic parts of two independent concerted reactions, one represented by R→I and the other by I→P. Hence symmetry rules apply for each of these terms separately. If, for example, R_1 is very close to a symmetric nuclear configuration R_1^0, and the wave functions ψ_e^R and ψ_e^I have different symmetry (they belong to different irreducible representations of the group generated by R_1^0), the reaction R→I is forbidden. Its rate, and correspondingly the rate of the nonconcerted reaction will be slow. The same argument applies separately to the "step" I→P, at nuclear configurations R_2. More details may be found in Ref.[28].

Concerning the second question: After clarifying how the involvement of a third state can make the reaction nonconcerted, let us indicate very briefly how one can test whether a given process is concerted or not. One should start by listing the chemical structures that are likely candidates for an intermediate. Then quasiadiabatic states should be constructed for each intermediate, at the level of simple Hückel theory. For example, in the case of butadiene ring closure one may think of a diradical with unpaired electrons at C^1 and C^4. A quasiadiabatic state for the diradical can be constructed by using a $2p_z$ orbital on each of the carbons labeled 2 and 3 and two localized orbitals for the single electrons on C^1 and C^4[29]. The electronic energy surface may be located with respect to the reactants and products as shown in Figure 11a. In this case the reaction is concerted. If the results are as shown in Figure 11b then at energies $E \approx E_1$ the reaction is nonconcerted. If the energy is raised (thermally or through laser induced vibrational excitation) close to E_2 the concerted reaction R→P starts competing with the nonconcerted one. This possibility of simultaneous coexistence of concerted and nonconcerted pathways has been inferred from experimental data[30].

Regarding the third question: Previous definitions of nonconcertedness[26a–d, 27] can be all derived from the present one. The adiabatic surface corresponding to the nonconcerted reaction (Fig. 11b) is shown in Figure 11c. We see that the presence of the intermediate state in Figure 11b creates a well in the adiabatic state of Figure 11c located between reactants and products. One of the early definitions of nonconcertedness required such a well (for a discussion of this see Ref. [27b]). There is, however, a possibility that the intermediate state may have a flat or a sloped shape between the points of intersection with the reactant and product surfaces. Computations show that a flat surface is very likely, for example, in the case of diradical intermediates[27a, 29]. Such a situation can be seen in Figure 11d which represents a nonconcerted reaction. The corresponding adiabatic surface is flat (Fig. 11e) and does not have a well. The possibility that a flat barrier, or an adiabatic surface, can be associated with nonconcertedness has been proposed in the literature[27a]. Finally, our description of a nonconcerted process fully agrees with and substantiates, in an obvious way, the one proposed by *Doering* and *Sachdev*[27c] which involves in the intermediate a set of vibrational states.

Thus, this formalism for reaction rates incorporates naturally inferences drawn from experimental studies concerning the characteristics required for a reaction to be nonconcerted. It does not answer explicitly[28] the question of the minimum lifetime required for the definable existence of an intermediate, but instead indicates that this question is not a useful one, since there is a smooth continuum of possible processes ranging from concerted to nonconcerted.

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