The Structure of Transition States: Are They Symmetric?

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The geometries of stable molecules can be accurately measured by spectroscopic and diffraction techniques. The geometries of transition states, on the other hand, cannot be measured by these methods, so that a discussion of their structure must to a certain extent be placed in the same category as a discussion of the mating habits of dinosaurs. But unlike dinosaurs, the transition state has played a dominant role in our interpretation of chemical kinetics for the last 40 years, and it has gradually acquired many of the familiar characteristics of stable molecules.

This elusive transition state, the lowest potential energy barrier between reactants and products, has in fact more properties attributed to it than any other point in configuration space. Its structure and energy determine both the stereochemical outcome of the reaction and the reaction rate. Its location on the potential surface influences the distribution of energy in products,[1] and its force constants account for isotope effects.[2] It can be solvent stabilized or destabilized, it can be aromatic or antiaromatic,[3] it can be acidic or basic.[4]

Indeed, the transition state, as the cornerstone of absolute rate theory (ART), allows us to "understand" kinetic behavior in exactly the same way that we understand thermodynamics: from statistical mechanical principles. By merely attaching asterisks to the appropriate symbols, ART allows us to interpret kinetics and thermodynamics together. In this way entropy, enthalpy, free energy, etc., are added to the list of properties of the transition state. The transition state is also of some formal (perhaps semantic) significance since, without it, it becomes difficult to distinguish between reactants and products (at exactly what bond length does a diatomic molecule become two atoms?).

Yet transition states cannot really be observed: reacting molecules simply do not remain near their transition states long enough to be accurately measured,[5] so that our experimental picture of the transition state is that of a rather broad and fuzzy region of configuration space. The role of ART critic must then largely fall upon the theoretician (someone with access to a computer and a potential energy function) and, indeed, there has been much activity in this research area. Transition states for highly symmetrical reactions such as the internal rotation in ethane,[6] umbrella inversion in ammonia,[6] and some symmetrical S_N2 reactions[7] were first calculated *ab initio* some years ago. More recently, the increased availability of powerful computers has made feasible studies of larger, less symmetrical systems.[8] The increasing number and accuracy of such computations promise to yield an increased understanding of both the degree of validity of ART and how ART should be modified to improve its function as a powerful predictive and interpretive tool of kinetics.

This Account reviews the current status of the transition state, not so much from the point of view of its role in kinetics but rather from the simpler perspective of what its structure, as a saddlepoint on the potential surface, is likely to be or not to be. The particular focus of our attention will be whether or not transition states are highly symmetrical structures of the sort envisioned when constructing orbital correlation diagrams in application of the Woodward–Hoffmann rules.

This question of transition-state symmetry is not only important to those interested in understanding the mechanisms and stereochemical outcomes of reactions, but it is also of immense importance to those interested in computing transition-state geometries by searching potential-energy surfaces. Any prior knowledge of the possible or probable symmetry of a transition state and its mode of decomposition to reactants and products can lead to considerable computational savings.

In this Account, we will examine the problem of transition-state symmetry from three different points of view: rigorous group theoretical and geometric considerations, nonrigorous arguments concerning the force constants of transition states, and the results of numerical computations. From each of these perspectives we will find it difficult to avoid concluding that transition states are very often not the highly symmetrical structures we would like them to be. We begin by reviewing some properties of potential-energy surfaces in order to define terms to be used later in the discussion of symmetry.

James W. McIver, Jr., received his undergraduate training as a biophysics major at Johns Hopkins University. His Ph.D. work in theoretical chemistry, which he undertook with H. F. Hameka at the University of Pennsylvania, was followed by postdoctoral work with J. A. Pople at Carnegie–Mellon University. He joined the chemistry department of the State University of New York at Buffalo in 1969, where he is now Associate Professor. In addition to chemistry, the author's hobbies include vegetable gardening (he and his family live on a small farm), music, and motorcycle racing.

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(1) For a simple, yet striking, example of this see J. S. Polanyi, *Accounts Chem. Res.*, **5**, 161 (1972).

(2) M. Wolfsberg, *Accounts Chem. Res.*, **5**, 225 (1972).

(3) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 319 ff.

(4) J. L. Kurz, *Accounts Chem. Res.*, **5**, 1 (1972).

(5) O. K. Rice, *J. Phys. Chem.*, **65**, 1588 (1961).

(6) A recent review of *ab initio* calculations of barriers can be found in H. F. Schaefer III, "The Electronic structure of Atoms and Molecules," Addison-Wesley, Reading, Mass., 1972, pp 398–407.

(7) *Cf.* C. D. Ritchie and G. A. Chappell, *J. Amer. Chem. Soc.*, **92**, 1819 (1970); A. Dedieu and A. Veillard, *ibid.*, **94**, 6730 (1972); and references contained therein.

(8) Salem and coworkers have recently reported the structure of the (nonsymmetrical) transition state for the geometrical isomerization of cyclopropane on an *ab initio* potential surface: J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *J. Amer. Chem. Soc.*, **94**, 279 (1972).

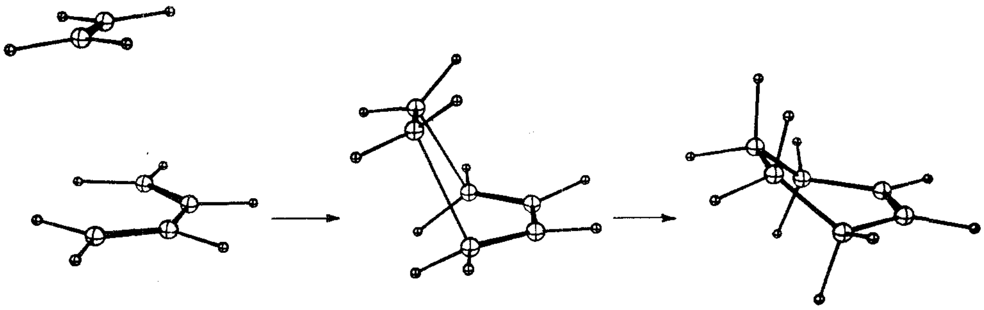

Figure 1. The symmetric, orbital-symmetry-allowed ethylene and butadiene Diels–Alder reaction. The structures shown are those obtained from the MINDO/2 potential surface.

Potential Energy

Classical mechanics provides us with *the* potential energy function as a means of describing the configuration dependence of the forces among interacting bodies. Quantum mechanics is much more generous in that *via* the Born–Oppenheimer approximation there are many potential energy functions for interacting nuclei: one for each electronic state of the system. We are thus faced with many potential energy surfaces which can (and do) intersect one another during the course of a chemical reaction. For thermal reactions involving closed-shell singlet molecules, we generally only look at the lowest potential surface corresponding to a singlet electronic state. In other cases such as photochemical or radical or ionic reactions, surfaces may cross and/or there may not even be a potential-energy barrier. ART, in its present form, cannot generally be applied to such reactions.

In chemistry, the important geometrical structures are stationary points on the potential-energy surface, points of zero potential-energy gradient ($\partial E/\partial X_i = 0$ for all coordinates X_i). Potential-energy minima (equilibrium geometries) are a special kind of stationary point in that the potential energy curvature must be positive along any direction. Mathematically, the curvature of the surface is measured by the force constants F_{ij} $(=\partial^2E/\partial X_i\partial X_j)$. The requirement that the potential energy be a minimum in all directions is equivalent to the requirement that the eigenvalues of the force constant matrix **F** all be positive. The transition state is another special kind of stationary point. Here there must be one and only one independent direction of negative curvature. This means that the force constant matrix of the transition state must have one and only one negative eigenvalue, as was pointed out by Murrell and Laidler.[9] We define the *transition vector* to be the eigenvector of the force constant matrix that corresponds to this negative eigenvalue.

The transition vector has the important property that the potential energy must decrease as the atoms are displaced along the direction of the transition vector toward reactants or products. The fact that we distinguish between reactants and products allows us to also assign a phase (*i.e.*, a sign) to the transition vector, that is, we can say that the transition vector points from reactants to products (or *vice versa*). The transition vector can be regarded as a small but finite segment of a *reaction path:* a continuous path connecting reactant, transition state, and product with the transition state as the highest energy point on the path.[10] Finally, the transition vector (in an appropriate coordinate system) must belong to one of the irreducible representations of the symmetry point group of the transition state.[11]

The above properties of the transition vector are what allows us to construct rules which govern the symmetry properties of the transition state.[12] These rules can be used to eliminate certain symmetrical structures as possible transition states, to show rigorously that the existence of a transition state for one reaction can imply the existence of a *lower energy* transition state for another, to determine for which reaction, if any, a computed symmetrical structure can serve as transition state, and to aid in computations by determining whether a simple energy minimization search technique can be used to locate a transtion state, or whether a more complicated procedure, such as a gradient minimization technique,[13] is necessary. These symmetry rules represent a novel application of group theory and are the subject of the following section.

Symmetry Rules

Group theory is valuable in the study of transition-state structure for the same reasons that it is useful in the study of molecular vibrations. It provides a means of classifying geometries and normal vibrations, it can greatly reduce the computational labor of obtaining the geometries and force constants of transition states, and for certain reactions it even provides "selection rules" for the allowed structures of the transition states.

In order to characterize the symmetry of a transition state we need to consider both its symmetry point group and the symmetry species of its transition vector. We expect, for example, that the C_s transition state in the orbital-symmetry-allowed[14] 4 + 2 Diels–Alder cycloaddition (Figure 1) will have a totally symmetric transition vector since the plane of symmetry is maintained throughout the orbital correlation diagram. On the other hand, the transition

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[9] J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 371, (1968). If the force constant matrix were to have more than one negative eigenvalue, then the transition state would resemble a hilltop rather than a pass (col). A hilltop cannot be the lowest barrier between any two points, since one could always cross a lower barrier by going around the hill.

[10] We do not attempt to define the reaction path any more precisely than this since any definition in terms of potential energy alone must depend on the arbitrary choice of a coordinate system. A detailed discussion will be given elsewhere.[11]

[11] R. E. Stanton and J. W. McIver, Jr., to be published.

[12] J. W. McIver, Jr., and R. E. Stanton, *J. Amer. Chem. Soc.*, **94**, 8618 (1972).

[13] J. W. McIver, Jr., and A. Komornicki, *J. Amer. Chem. Soc.*, **94**, 2625 (1972).

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

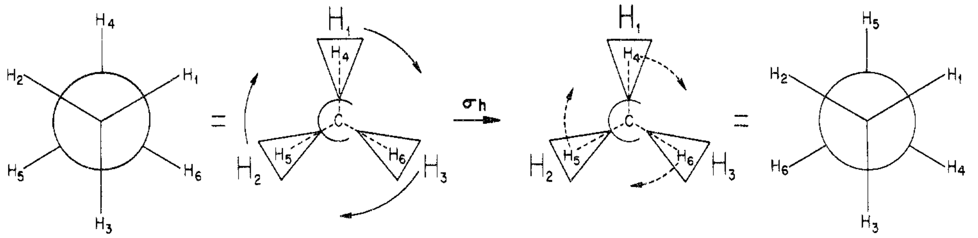
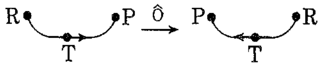


Figure 2. The D_{3h} transition state for the internal rotation in ethane illustrating that the operation σ_h converts reactants into products.

vector must be antisymmetric under a reflection for symmetric transition states in Narcissistic reactions[15] (reactions in which the reactant is the mirror image of the product). These ideas can be formally generalized into the following rules governing the symmetry species of the transition vector.[11,12] (1) *The irreducible representation of the transition vector must be symmetric under symmetry operations of the transition state which leave reactant or product unchanged.* (2) *The irreducible representation of the transition vector must be antisymmetric under symmetry operations of the transition state which convert reactants into products.* Finally, because of the requirement that there be only one (*e.g.*, nondegenerate) negative eigenvalue of the transition-state force constant matrix we know that (3) *the transition vector cannot belong to a degenerate representation of the transition state's point group.*

The proofs of theorems 1 and 2 are based on formal group theoretical and geometrical arguments.[11] They can be visualized, however, with the aid of diagrams similar to **1**. Here, the solid line represents a reaction path connecting a reactant, R, a transition state, T, and a product, P. The transition vector is represented by the arrow at T. A symmetry operation (Ô) of T which converts R into P must also convert every point on the path connecting R and T to a corresponding point on the product side, and must therefore reverse the direction of the transition vector and hence change its sign (theorem 2). The nondegenerate (by theorem 3) irreducible representation of the transition vector will thus have a character of −1 for this symmetry operation. Similarly, the representation of the transition vector must have a character of +1 for operations which leave reactant or product unchanged. By considering the effect of each symmetry operation of the point group of T one can determine, with the aid of a character table, the required symmetry species of the transition vector. A computed structure which does not have a transition vector corresponding to this symmetry species can be ruled out as a transition state for the reactants and products considered, although it may be a transition state for some other reaction.



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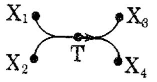
In order to understand more clearly the nature and applications of these rules, let us consider the special case of a degenerate system of reactants and products in which different symmetry operations of T convert a reactant into more than one distinct product. In cases such as this the symmetry rules rigorously exclude T as the *lowest* transition state in the degenerate system. In a fourfold degenerate system, for example, let us assume that we have found a symmetric stationary point T which we suspect of being a transition state and let us suppose that its force constant matrix has a single negative eigenvalue with a corresponding eigenvector that is symmetric under operations which convert species X_1 into X_2 and antisymmetric under operations which convert X_1 into X_3 and X_4. According to theorem 2, T can be a transition state for the reactions $X_1 \rightarrow X_3$ and $X_1 \rightarrow X_4$ but not the reaction $X_1 \rightarrow X_2$. This situation is illustrated in the reaction path diagram **2**. Since the transition vector can be regarded as finite in length,[11] and since it is symmetric under operations which convert X_1 into X_2, the paths connecting X_1 and T and X_2 and T must meet at a point of lower energy (and different symmetry) than T, implying the existence of a lower barrier separation X_1 and X_2.[16] We conclude that nature is not disposed toward having such symmetrical structures as the lowest transition states in degenerate reactions.



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In order to develop a simple scheme for applying these rules to actual examples, we recall the meaning of a symmetry operation as it is defined in the theory of molecular vibrations. Here a symmetry operation is neither a pure rotation (proper or improper) in space nor a permutation of the nuclei since neither definition leads to any useful information. It is rather the combination of a pure rotation of a molecule in space and a permutation of the nuclei back to the vicinity of their original positions. When applied to a symmetric molecule, it leaves the structure unchanged. When applied to a distorted molecule, it gives another distorted molecule. This is more easily visualized if we attach arrows to the nuclei of the symmetric structure and imagine sliding the nuclei to the heads of the arrows to get the distorted molecule. The effect of the symmetry operation is then to rotate the arrows while leaving the nuclei unchanged. This is illustrated in Figure 2 for the internal rotation in ethane. Here, the "distorted" structure, the ends of the arrows, represents staggered ethane, and the arrows themselves indicate a reac-

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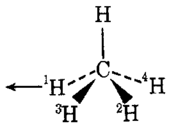
(15) L. Salem, *Accounts Chem. Res.* **4**, 322 (1971).

(16) The only way in which T could be the lowest transition state in the system is if it were to be the transition state for all of the degenerate reactions in **2**, *i.e.*, if the four paths were required to meet at T itself rather than at the ends of the transition vector. It can be shown[11] that this can occur only if the "negative" eigenvalue of the force constant matrix is *exactly* zero and that there is no compelling reason why this should be true at points at which the first derivatives are also zero (stationary points).

tion path. As shown, the operation σ_h of the D_{3h} transition state converts reactant into product.

From similar diagrams it can be seen that the operations σ_v and $\mathbf{S}_3$ also convert reactant into product, whereas $\mathbf{E}$, $\mathbf{C}_2$, $\mathbf{C}_3$, and $\mathbf{C}_3{}^2$ leave reactant unchanged. An examination of the D_{3h} character table shows that, among the nondegenerate representations, only the A_1'' species is symmetric under $\mathbf{E}$, $\mathbf{C}_2$, $\mathbf{C}_3$, and $\mathbf{C}_3{}^2$ and antisymmetric under σ_v, σ_h, and $\mathbf{S}_3$. Accordingly, the transition vector must belong to the A_1'' representation, just as we would expect since this is the symmetry species of the torsional mode. If we should find, upon calculation, that the transition vector belongs to some other irreducible representation, then we would know that the D_{3h} eclipsed structure is not the transition state in the internal rotation. In the Diels-Alder example (Figure 1), the transition vector must be totally symmetric, since all of the elements of the C_s transition state are shared with the boat cyclohexene (theorem 1).

As an example of a transition state in a degenerate system, let us consider the C_{4v} symmetry structure **3**



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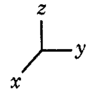


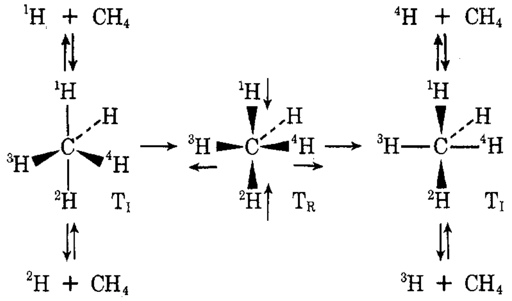
which has been suggested as the transition state for the configuration retaining reaction and which has

$${}^{1}\mathrm{H} + \mathrm{CH}_4 \longrightarrow \left\{ \begin{array}{l} {}^{3}\mathrm{H} + \mathrm{CH}_4 \\ \text{or} \\ {}^{4}\mathrm{H} + \mathrm{CH}_4 \end{array}\right.$$

been the subject of several computational studies.[17] The displacement arrow in **3** represents the reactant ${}^{1}H + CH_4$. The results of applying the C_{4v} symmetry operations to this arrow are as follows: C_4 and $\sigma_d(xz)$ convert ${}^{1}H + CH_4$ into ${}^{4}H + CH_4$; $C_4{}^{-1}$ and $\sigma_d(yz)$ convert it into ${}^{3}H + CH_4$; $C_4{}^2$ and σ_v (${}^{3}HC^{4}H$) convert it into the configuration-inverted product ${}^{2}H + CH_4$; and E and σ_v (${}^{1}HC^{2}H$) leave it unchanged. An application of the symmetry rules to these results leads us to conclude that if the C_{4v} structure is the transition state for the configuration-retention reaction, then its transition vector must belong to the B_1 representation since this is the only nondegenerate representation that is antisymmetric under C_4, $C_4{}^{-1}$, and the two σ_d's and symmetric under E and σ_v. Moreover, we conclude that the C_{4v} structure cannot be the transition state for the configuration-inversion reaction since there is no irreducible representation of C_{4v} which is nondegnerate and antisymmetric under $C_4{}^2$.

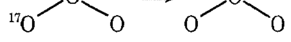
Finally, if the C_{4v} structure is the transition state for the configuration-retention reaction, then there must exist a *lower energy* transition state of *different symmetry* for the inversion reaction. The reaction path diagram for this situation is then **2**, with X_1 representing ${}^{1}H + CH_4$; X_2, ${}^{2}H + CH_4$, etc.; and with T representing the C_{4v} structure. Reaction Scheme I illustrates this diagram. Here T_R represents the C_{4v} transition state for the retention reaction and the arrows in T_R indicate displacements of the hydrogens along the B_1 transition vector. The structures T_I represent the lower energy D_{3h} transition states in the inversion reactions. We can regard T_R as being the transition state in the Berry pseudorotation of T_I, in analogy to PF_5 and related systems.[18]

Scheme I



It is perhaps worth noting that diagram **2** can also apply to transition states with less than C_{4v} symmetry such as the C_{2v} (which has no degenerate representations) structure **3** where the labeled hydrogens lie at the corners of a rectangle rather than a square. Like the C_{4v} structure, C_{2v} can be a transition state in the $H + CH_4$ system, but not the lowest energy one.

The example above involved transition states with two- and fourfold axes. From some detailed considerations (*e.g.*, by examining all of the point group character tables) it can be shown that any structure in which rotation about an oddfold axis converts reactants into products cannot be a transition state for any of the degenerate reactions. Thus, for example, the equilateral triangle cannot be the transition state in the ozone pseudorotation **4**.



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Force Constants

The symmetry rules discussed above are rigorous and are valid for both exact and approximate potential surfaces. With the aid of some simplifying (and perhaps drastic) assumptions, we can use symmetry in quite a different manner to characterize some transition-state geometries. Let us again consider the Diels-Alder reaction (Figure 1) and let us *assume* that the only important degrees of freedom are the two bond lengths R_1 and R_2, which correspond to the two new C-C bonds being formed. Specifically, we assume that the only significant contributions to the transition vector are changes in R_1 and R_2. If there is a barrier at all to the reaction, there must be one within the C_s symmetry.

Suppose we have somehow found this symmetric barrier, that is, we have calculated a geometry that is stationary and its energy is a maximum with respect to the symmetric stretching of the two bonds being formed in accordance with theorems 1-3. The relevant force constants are $K = \partial^2E/\partial R_1{}^2 = \partial^2E/\partial R_2{}^2$ and $K' = \partial^2E/\partial R_1\partial R_2$. The eigenvalues of this 2 × 2 force constant matrix are $K + K'$ for the sym-

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(17) S. Ehrenson and M. Newton, *Chem. Phys. Lett.*, **13**, 24 (1972; K. Morokuma and L. Davis, *J. Amer. Chem. Soc.*, **94**, 1661 (1972), and references contained therein.

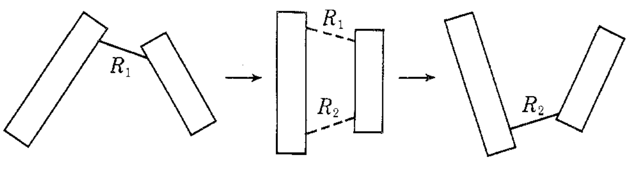
(18) See K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970), and references contained therein.

metric stretch and $K - K'$ for the antisymmetric stretch of R_1 and R_2. By hypothesis $K + K'$ must be negative. If we now look at a 1000 + 1000 cycloaddition rather than the 4 + 2 Diels–Alder, then we can safely regard K' as being zero at the symmetric barrier. In this case K must then be negative so that both eigenvalues will be negative. The structure will then be a maximum in two dimensions, and therefore not a transition state. The true transition state will not be symmetric and will have a lower energy than the symmetric structure. If we assume that K is roughly independent of the distance between the two bonds,[19] then K should also be negative for the 4 + 2 cycloaddition. The interaction constant K' must then be positive and larger in magnitude than K if $K + K'$ is to be negative and $K - K'$ positive, as is required for the symmetric structure to be the transition state.

In summary, this simple two-dimensional model of cycloadditions leads us to conclude that if the transition state is symmetric, then the force constant K is negative, the interaction constant K' is positive and greater in magnitude than K, and finally the probability of the transition state being symmetric diminishes as the distance between R_1 and R_2 increases.

A related analysis can be applied to sigmatropic shifts in which one bond is forming while the other is breaking, as in Scheme II. Again, we must assume that changes in R_1 and R_2 dominate the transition vector. Here, we require the symmetrical intermediate structure to be such that energy is minimized with respect to symmetric degrees of freedom so that $K + K'$ is positive. There may, of course, be more than one such intermediate, and the arguments apply to all of them. (Alternatively, the only energy-minimized symmetric structure may correspond to two isolated fragments, in which case the transition state will be unsymmetrical.) The biallyl Cope rearrangement is an example of a [3,3] sigmatropic shift and the ozone pseudorotation 5 is a [1,2] process.

Scheme II



If we again assume that K is independent of the distance between R_1 and R_2, then K must be positive, since K' is zero for the [1000,1000] sigmatropic shift. The symmetric intermediate will thus be a minimum (a stable intermediate) unless K' is positive and greater in magnitude than K, in which case the symmetric structure becomes the transition state. Also, as we predicted for cycloadditions, the probability of the transition state being symmetric diminishes with increasing distance between R_1 and R_2. In both types of reactions, the "threshold" distance between R_1 and R_2 at which a symmetric intermediate ceases to be a transition state must be determined from more detailed considerations, such as by numerical computation of these geometries and force constants. It should be noted that this type of analysis can be extended to any symmetrically equivalent coordinates involved in the transition vector, not just bond lengths.

Computational Results

At present, it appears that the detailed geometries of transition states can best be examined by computing these structures on approximate potential energy surfaces. Some results of relatively accurate *ab initio* calculations were mentioned in the introduction. Because of their computational expense, however, such calculations are generally limited to rather small systems. For this reason there has been a great deal of activity in the area of developing and applying semiempirical molecular orbital methods.[20] In the study of potential surfaces, where it is desirable to have both the energy and its gradient, the semiempirical methods are an order of magnitude less expensive than even a modest *ab initio* calculation. Interpreted cautiously, the results of semiempirical calculations can provide us with valuable information concerning the nature of chemical reactivity. Below we list some of the more interesting results obtained by semiempirical molecular orbital calculations for cycloaddition reactions and the Cope rearrangement.

Cycloadditions. MINDO/2[21] calculations of the symmetric barriers for the addition of methylene to ethylene (to form cyclopropane), the dimerization of ethylene (both the forbidden and allowed processes), and the ethylene plus butadiene Diels–Alder reaction give, in each case, a force constant matrix with more than one negative eigenvalue and therefore suggest that the transition state for each reaction is unsymmetrical.[22] Commensurate with this result, Hoffmann and coworkers, using the extended Huckel method,[23] and Dewar and coworkers[24] using MINDO/2 (which was developed in Dewar's laboratory), report that there is no potential barrier for the unsymmetrical addition of methylene to ethylene.

An interesting feature of the MINDO/2 results for the dimerization of ethylene is that, although neither symmetric structure is a transition state, the $2_s + 2_s$ orbital-symmetry-forbidden structure is slightly lower in energy than the allowed $2_s + 2_a$ structure, suggesting that steric or other effects overshadow the effects of orbital-symmetry conservation. Although the correct transition state on the MINDO/2 surface has not yet been located, Hoffmann and coworkers, in an extended Hückel study of the tetramethylene diradical, suggest that the diradical "intermediate" in the dimerization of ethylene is in fact a transition state (a barrier) located on a very flat part of the potential surface (a "twixtl") the flatness of the surface accounting for the loss of stereospecificity.[25]

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(19) This is certainly true for stable molecules where bond stretching force constants are remarkably transferable. Although it also seems reasonable for transition states, the validity of this assumption is by no means proven.

(20) For a review of some of these methods, see H. H. Jaffé, *Accounts Chem. Res.*, **2**, 136 (1969), and J. A. Pople, *ibid.*, **3**, 217 (1970).

(21) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

(22) J. W. McIver, Jr., *J. Amer. Chem. Soc.*, **94**, 4782 (1972).

(23) R. C. Dobson, D. M. Hayes, and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6188 (1971).

(24) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Amer. Chem. Soc.*, **94**, 9095 (1972).

(25) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970). This may be an even more general property of diradicals. See L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

Cope Rearrangement. Dewar and coworkers have calculated the structure of the symmetric intermediates in the biallyl Cope rearrangement[26] and also in some semibulvalene Cope rearrangements,[27] the calculated energies of the latter agreeing remarkably well with experimental activation energies. In the biallyl rearrangement, it was found that the "chair" form of the intermediate was more stable than the "boat" form, in agreement with the classic Doering and Roth experiment.[28] Additional MINDO/2 calculations of the biallyl rearrangement reveal that both the chair and boat symmetric structures actually are shallow minima and the two transition states are nonsymmetrical structures lying between the intermediates and biallyl.[29] All of these results are in complete accord with the symmetry arguments of the preceding section since we would expect a small interaction force constant between the two partially broken bonds in these systems.

Conclusions

On the basis of these calculations (and the preceding symmetry arguments), it would appear that Nature is not being cooperative in giving us nicely symmetrical transition states. Perhaps we should not be too surprised, though, since there is no *a priori* reason why they should be symmetric. We impose symmetry on a transition state for reasons of simplicity. Thus, the symmetric intermediate structure in a Woodward–Hoffmann correlation diagram need not be the actual transition state, just as the "reactant" and "product" symmetric structures need not be the actual equilibrium geometries of these species. In the Woodward–Hoffmann "allowed" Diels–Alder reaction, for example (Figure 1), the correlation diagram requires that a plane of symmetry be maintained throughout the reaction. Yet, this is an example in which neither the reactant nor the product possesses this symmetry plane,[30] so why should the transition state? If it should turn out that the correct transition states are nearly symmetrical, then of course there would be little effect on predicted rates or stereochemistry. This can be settled however, only by more extensive calculations, calculations that are currently under way in several research groups.

Many of the ideas reported here are the result of a collaborative effort. In particular, the symmetry rules were worked out jointly with Professor R. E. Stanton and much of the remaining discussion resulted from conversations with and encouragement by Professor Harry F. King. The MINDO calculations were done with an able graduate student, Andrew Komornicki, and Professor C. D. Ritchie critically read the manuscript and made many helpful suggestions. I am grateful to them all. I also wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support and the Computing Center of the State University of New York at Buffalo for generous allotments of computer time.

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Some Molecular Rearrangements of Organosilicon Compounds

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The growing interest in recent years in organosilicon chemistry, made despite the gloomy predictions of F. S. Kipping in 1936 that "the prospects of any immediate and important advance in this section of organic chemistry do not seem to be very hopeful,"[1] has been catalyzed both by the commercial development of the silicones and, more recently, by the interest of chemists in introducing new and exotic hetero atoms into molecules for a wide variety of reasons.

The interests in our laboratory have focused on organosilicon compounds which have functional groups (OH, $\mathrm{C{=}O}$, $\mathrm{S{\rightarrow}O}$, $\mathrm{C{=}N}$ etc.) attached to carbon adjacent to silicon, where the interactions of these groups with the silicon atom may lead to, or facilitate, a variety of molecular rearrangements. Most of the rearrangements described below are restricted to cases studied in the author's laboratory which involve interactions between silicon and oxygen: these constitute only a small part of a growing literature on molecular rearrangements of organosilicon compounds.

In the 1950's Gilman and coworkers[2-4] found that

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