(25) R. Milstein and R. S. Berry, *J. Chem. Phys.*, **55**, 4146 (1971).
(26) A. D. McLean and M. Yoshimine, *IBM J. Res. Dev., Suppl.*, **11**, 67 (1967); *J. Chem. Phys.*, **47**, 3256 (1967).
(27) P. E. Cade and W. M. Huo, *J. Chem. Phys.*, **47**, 614 (1967).
(28) A. Dedieu and A. Veillard, *J. Am. Chem. Soc.*, **94**, 6730 (1972).
(29) (a) J. Goubeau, R. Baumgartner, and H. Weiss, *Z. Anorg. Allg. Chem.*, **348**, 286 (1966); (b) R. L. Holmes, and R. N. Storey, *Inorg. Chem.*, **5**, 2146 (1966); (c) P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Am.*

Chem. Soc., **89**, 2017 (1967).
(30) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2743 (1955).
(31) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London.
(32) This is actually the difference in energy between the $NH_3F^+-F^-$ ion cluster and separate NH_3F^+ and F^- units.
(33) J. I. Musher, *J. Am. Chem. Soc.*, **94**, 1370 (1972).
(34) R. Ahlrichs, *Theor. Chim. Acta*, **33**, 157 (1974).

Group Theoretical Selection Rules for the Transition States of Chemical Reactions

Richard E. Stanton[1a] and James W. McIver, Jr.*[1b]

Contribution from the Departments of Chemistry, Canisius College, Buffalo, New York 14208, and State University of New York at Buffalo, Buffalo, New York 14214. Received September 20, 1974

Abstract: The transition state of a chemical reaction is the lowest barrier separating reactants and products on a potential energy surface. As such it is a critical point on the surface and its force constant matrix has exactly one negative eigenvalue. The corresponding eigenvector is defined to be the transition vector for the reaction. Schur's lemma implies that the transition vector will belong to one of the symmetry species of the transition state point group provided sufficient care is taken in the choice of the coordinate system. Consideration of the effect of transition state symmetry operations on the reactants and products and on the paths joining them to the transition state leads to a series of theorems governing the transformation properties of the transition vector. In some cases these requirements are incompatible with the known transformation properties of the available symmetry species for the proposed transition state. It is shown that such "transition states" are forbidden; i.e., they cannot be the lowest barriers separating reactants from products. The concept of symmetry forbidden transition states is applied to a series of reactions of gradually increasing complexity. Included (among others) are the classic H + H_2 exchange reaction, the T + CH_4 displacement reaction, the olefin metathesis reaction, the inversion of cyclohexane, and the Cope reaction.

I. Introduction

The concept of the transition state plays a central role both in the formal theory of reaction rates and in the way in which the chemist actually visualizes a reaction. The experimental determination of transition state geometries, however, is a very difficult problem. It is in fact probably fair to say that no currently available experiment or combination of experiments can yield anything better than a fuzzy view of the transition state of any particular reaction. It is natural, therefore, that there has in recent years been a series of attempts to calculate transition state energies and geometries by the various quantum mechanical techniques that were developed for equilibrium states. We shall refer to many of these computations in the body of this paper. The methods employed range from simple Hückel theory to the most expensive ab initio calculations. There have also been papers dealing with the special properties of transition states and with the problems involved in finding these states on a potential surface.

Murrell and Laidler[2a] have emphasized the requirement that the transition state force constant matrix have exactly one negative eigenvalue and have given a formal proof of this condition. Murrell and Laidler also tried to use their theorem to derive selection rules for transition state geometries. In doing so they made no use of group theory and were led into some unwarranted assumptions that destroyed the validity of some of their conclusions. These errors were later pointed out by Murrell and Pratt.[2b]

In this paper we will, like Murrell and Laidler, be looking for selection rules and will make extensive use of the Murrell and Laidler (hereafter M-L) theorem. We avoid the traps associated with faulty geometric intuition by combining the M-L theorem with formal group theory.[3] It might be mentioned that the M-L theorem also has important consequences which go beyond the scope of the present paper. It has been shown elsewhere,[4] for example, that M-L often requires that off-diagonal bond interaction force constants play a dominant role in the transition state, in marked contrast to their ordinarily minor role in equilibrium states.

Salem et al.[5] have defined as "narcissistic reactions" those in which reactants and products are related to one another via some improper rotation. They also discuss conditions which make a symmetric transition state probable or improbable for these reactions and stress the computational advantages associated with knowing the symmetry properties of the transition state prior to carrying out a computer search. These ideas can be generalized. We show that proper as well as improper rotations can convert reactants into products. Moreover, as indicated above, one can in many cases make *rigorous* statements concerning the allowed symmetry of the transition state for such reactions.

To a certain extent the computational advantage of knowing the symmetry of a transition state is the same as in knowing the symmetry of an equilibrium state; it enables one to reduce the number of coordinates that must be varied in the search for the transition state. Since the number of points required to map out a potential surface varies exponentially with the number of internal coordinates and since most reactions of interest involve a large number of coordinates the computational gain in reducing the number of coordinates can be very great. One practical way of achieving this gain is through the introduction of symmetry adapted coordinates. The search for the transition state can then be restricted to the subspace of fully symmetric coordinates.

It has also been shown[6a] that for certain search methods, the time saving advantage of symmetry is retained even when one uses external Cartesian coordinates to describe the system, provided one starts the computer search from a point with the expected symmetry and exploits the fact that the gradient has no nonvanishing asymmetric components.

The computer search for transition states is influenced by symmetry in another, less obvious way. In trying to locate an equilibrium state one can always take advantage of energy minimization techniques. These are not generally applicable to transition states since the latter correspond to cols on the potential surface. If the energy gradient can be computed cheaply, as in some of the semiempirical methods, one can replace energy minimization techniques by gradient minimization techniques without serious inconvenience.[6b] In an ab initio calculation the gradient is less readily available and the problem of locating a col can be severe. If, however, the symmetry of the transition state is known and if it is also known that the principal direction of negative curvature breaks the symmetry of the transition state one can go back to energy minimization methods to locate the transition state. In this paper we will not be able to guarantee the presence of symmetry elements in the transition state. We will, however, provide rules that eliminate certain symmetries from consideration. For those transition state symmetries that are allowed we also provide criteria for the applicability of energy minimization procedures.

In view of the importance of symmetry, it is somewhat surprising that group theory, the natural tool for its investigation, has received so little attention in the study of transition states. Murrell[7] has noted the usefulness of the Jahn-Teller theorem in eliminating structures with electronic degeneracy from consideration as transition states. We are unaware, however, of any attempt to apply group theory to transition states in the manner that has proved so successful in analyzing the normal vibrations of equilibrium states. It may have been thought that this would lead to little more than a repetition of equilibrium state properties. This turns out not to be the case. The group theoretical theorems derived in this paper are unique to the transition state. This uniqueness can be traced to the fact that in transition state theory there is a vital distinction between displacements toward the reactant or the product side, whereas in equilibrium state theory the question of phase is of relatively little importance.

The theorems themselves are powerful in the sense that they often allow one to rule out certain structures as transition states without the aid of any computation whatsoever. In other cases they allow one to decide whether a col which has actually been located on some computed surface and whose force constants have also been computed can act as a transition state for the reaction of interest, or whether it must be associated with some different reaction. The power implicit in these applications is enhanced by the fact that the theorems are independent of any arguments concerning electronic structure or any particular method, exact or approximate, which may be used in the derivation of a potential surface. In fact the only physical principle we require is the energetic equivalence of structures that can be interconverted by a symmetry operation. Aside from this our results are theorems in geometry. They arise solely from the concept of a transition state on a potential surface.

It must be admitted that the strength of our approach is also its weakness. While we can often rule out certain structures as transition states we cannot say without the aid of detailed computation whether the actual transition state can be reached by a slight distortion of the forbidden structure or whether it lies on a distant part of the potential surface.[8] The abstraction from molecular dynamics which is built into our approach also has its penalties. In some cases, for example, the statically defined transition state is dynamically inaccessible. In such cases the lowest accessible path maximum may seem to violate our theorems. However, this particular difficulty is not peculiar to us. It is characteristic of all transition state theory. Somewhat more peculiar to us is the strictness with which we define transition states. In our terminology only the lowest barrier separating a given set of reactants and products qualifies as a transition state. If two cols are very nearly equal in energy and are both accessible, nature may well utilize each of them. Unless isotopic substitution could distinguish between the product states reached from these cols, however, we would regard the higher energy col as a "forbidden" transition state.

The organization of this paper is largely self-explanatory. The principal theorems and their derivations are presented in section III. In section IV we apply the theorems to a series of increasingly complex reaction systems. These sections form the heart of the paper. The rather long section II sets the stage for these theorems and applications. In this section we discuss the general nature of potential surfaces and transition states. We argue in particular against the possibility of three reaction valleys meeting at a single transition state since this question is closely related to our theorems. We also take up the troublesome issue of the choice of coordinate system and show which aspects of the potential surface are coordinate independent and which are coordinate dependent. Section II also contains (in outline form) the proof of an important lemma concerning paths through the transition state. We use this lemma in section III to derive our symmetry theorems. We conclude section II with a discussion of the nature and effects of transition state symmetry operations and of the applicability of group theory.

II. Preliminary Theory

(a) **The Shape of Potential Surfaces.** Let $\{q_1, q_2, \ldots\}$ be a complete set of nonredundant internal coordinates for a reaction system. The potential energy can be and usually is thought of as a hypersurface lying above the base plane of the q's. Let R and P be two points on this surface corresponding to reactants and products, respectively. If there is any potential energy barrier at all for the reaction then every path from R to P will pass through a point of maximum energy. The transition state T (or a transition state, if the reaction has several equivalent ones) is the lowest energy point in the set of all such path maxima. One can abbreviate this by saying that the transition state is the lowest barrier separating reactants from products.

The definition of a transition state implies that it is a stationary point on the potential surface. (A lowest path maximum cannot lie on the side of a hill, even in many-dimensional space.) This means that the power series expansion of the energy about T will have no linear terms. In setting up this expansion it is convenient to regard the projection of T onto the base plane as the origin of the coordinate system and to regard the q_i as the Cartesian coordinates of the base plane. The energy of a point Q can then be written as

$$E_Q = E_T + \tfrac{1}{2} \mathbf{q}^T \mathbf{F} \mathbf{q} + \tfrac{1}{2} \epsilon_Q s^2 \tag{1}$$

where $\mathbf{F}$ is the transition state force constant matrix

$$F_{ij} = \left(\frac{\partial^2 E}{\partial q_i \partial q_j} \right)_{Q=T} \tag{2}$$

$\mathbf{q}$ is the column matrix of internal coordinates, $\mathbf{q}^T$ is its transpose and s is the (base plane) distance between Q and T.

$$s = \sqrt{\mathbf{q}^T \mathbf{q}} \tag{3}$$

The remainder factor ϵ_Q contains the effects of higher order terms in the expansion. It vanishes as Q approaches T. In the vicinity of T, therefore, the energy will be dominated by the quadratic term

$$E_Q^{(2)} = \tfrac{1}{2} \mathbf{q}^T \mathbf{F} \mathbf{q} \qquad (4)$$

The shape of the surface $E^{(2)}$ is controlled by the eigenvalues of $\mathbf{F}$. We denote these by k_i and write the eigenvectors as $\mathbf{v}_i$.

$$\mathbf{F}\mathbf{v}_i = k_i \mathbf{v}_i \qquad (5)$$

The diagonal elements of $\mathbf{F}$ represent the curvature along the coordinate axes; the geometric vectors $\bar{v}_i$ corresponding to the eigenvectors $\mathbf{v}_i$ can be said to point along the principal axes of curvature; the k_i are then the principal values of curvature. The Murrell and Laidler theorem states that the curvature is negative along one and only one of the principal axes. We assign the subscript zero to this direction and refer to $\bar{v}_0$ as the *transition vector*. Standard variational arguments allow us to characterize $\bar{v}_0$ as the direction of most negative curvature.

The basis for the Murrell and Laidler theorem is simple. The point T would be a minimum, and therefore a stable intermediate rather than a transition state, if all eigenvalues were positive. If two or more eigenvalues were negative the surface above the subspace of these coordinates would resemble a hilltop. One could then find a path from R to P which went around the hill and never passed through energy as high as E_T. Since T is supposed to be the lowest barrier such a path cannot exist and one can rule out the possibility of more than one negative eigenvalue.

The argument above bypasses the question of a zero eigenvalue. If one or more eigenvalues should vanish the shape of the potential surface near T would be influenced by cubic or higher terms in the power series expansion. In a two-dimensional system the existence of one positive and one zero eigenvalue would give the quadratic surface $E^{(2)}$ the shape of a trough with parabolic cross section. The trough could conceivably be bent so as to give a saddle point at T by the fourth-order terms in E. One negative and one zero eigenvalue would give an inverted trough. Again this could be converted to a saddle by quartic terms. A more interesting case is that in which both eigenvalues in a two-dimensional system vanish. If the cubic terms in such a system are nonzero the surface can resemble "three valleys meeting at a point". Surfaces of this nature are also referred to as "monkey saddles". There are many supposed examples in the literature. We discuss one of them (Figure 1) in detail in section IV.

The association of a monkey saddle with cubic force constants can be seen quite easily if one converts the cubic energy expression

$$E^{(3)} = \alpha q_1^3 + \beta q_2^3 + \gamma q_1^2 q_2 + \delta q_1 q_2^2$$

into polar form. With θ measured from q_1 one finds

$$E^{(3)} = (s^3/4)\{(\alpha - \delta)\cos 3\theta + (\gamma - \beta)\sin 3\theta + (3\alpha - \delta)\cos \theta + (3\beta - \gamma)\sin \theta\}$$

This surface has three valleys if the terms in 3θ dominate the terms in θ.

One could have four valleys meet at T if the cubic terms vanished as well as the quadratic terms. We maintain, however, that while many surfaces may have the rough appearance of monkey saddles, a fine mesh inspection will always reveal the transition from a surface dominated by cubic or quartic terms to one dominated by nonzero quadratic terms as one approaches the middle of the saddle. If the quadratic terms lead to a bump (hilltop) or dimple (lake) at the origin

one can expect to find a series of transition states connecting the valleys with one another (Figure 1) or with the lake (Figure 2a). Other than a hilltop or lake the only remaining possibility on a two-dimensional surface is a normal saddle. If this should exist in the middle of a monkey saddle one can expect a path down from T on one side to enter a forking region (Figure 2b) beyond which it can pass into either of two valleys. The existence of such a forking region is implied by the impossibility of terminating the contours $E = E_T$ which separate the high and low regions of the saddle.

The argument for the persistence of quadratic terms at the transition state is essentially an argument against the chance satisfaction of over-determined equations. Its essence has already been stated by Murrell and Laidler. We elaborate as follows. At any point on a surface, whether it be a stationary point or not, one can always construct a force constant (second derivative) matrix and determine its eigenvalues. One can then force a change in these eigenvalues by moving the point at which they are evaluated. It may well be possible by moving the point in an appropriate manner to force one or more eigenvalues to vanish. This freedom of motion does not exist, however, when one is also demanding that the point of evaluation be stationary. Except in the flat asymptotic regions of a reactant or product valley the requirement that all components of the gradient vanish forces the system point to occupy one of a discrete set of sites. It would be an unlikely numerical accident if an eigenvalue should be exactly zero at such a point. One might be able to make the accident take place in a semiempirical method designed specifically for this end. In an unbiased calculation, however, one does not expect the accident to occur any more than one would expect an accidental violation of the Jahn–Teller theorem, of the noncrossing rule for diatomic potential energy curves, or of the Gibbs phase rule in thermodynamics.

(b) Role of the Coordinate System. Although the signs of the principal values of curvature determine the nature of an extremum, neither their numerical values nor the directions of the principal axes have any precise physical significance. Both depend upon the choice of internal coordinates used to describe the system. This is why we call $\bar{v}_0$ the "transition vector" rather than use the more explicitly physical expression "decomposition vector". It seems preferable to reserve the latter name and also expressions like "reaction coordinate", "reaction vector", etc., for analyses which take the dynamics of the system into account. The normal mode of imaginary frequency which arises from a Wilson GF matrix analysis of the dynamics in the vicinity of T, for example, has a unique physical interpretation. It describes the actual (classical mechanical) motion on a minimal energy trajectory through the transition state. It seems fair to call this the reaction (or decomposition) mode. The nature of this motion is, of course, independent of the choice of coordinate system.

The dependence of the k_i and $\bar{v}_i$ on the choice of coordinate system can be attributed to the freedom one has in assigning potential energy base plane locations to molecular configurations. One exercises this freedom each time one treats a particular set of internal coordinates as the Cartesian coordinates of the base plane. Since most internal coordinate transformations are nonorthogonal they have the effect of changing the base plane distances between points corresponding to different molecular configurations. This means that the potential energy contours will ordinarily change shape under an internal coordinate transformation. This in turn implies not only that the principal axes of curvature will change their direction, but also that the new directions will usually be *physically* distinct from the old directions. One can understand this as follows. In any coordi-
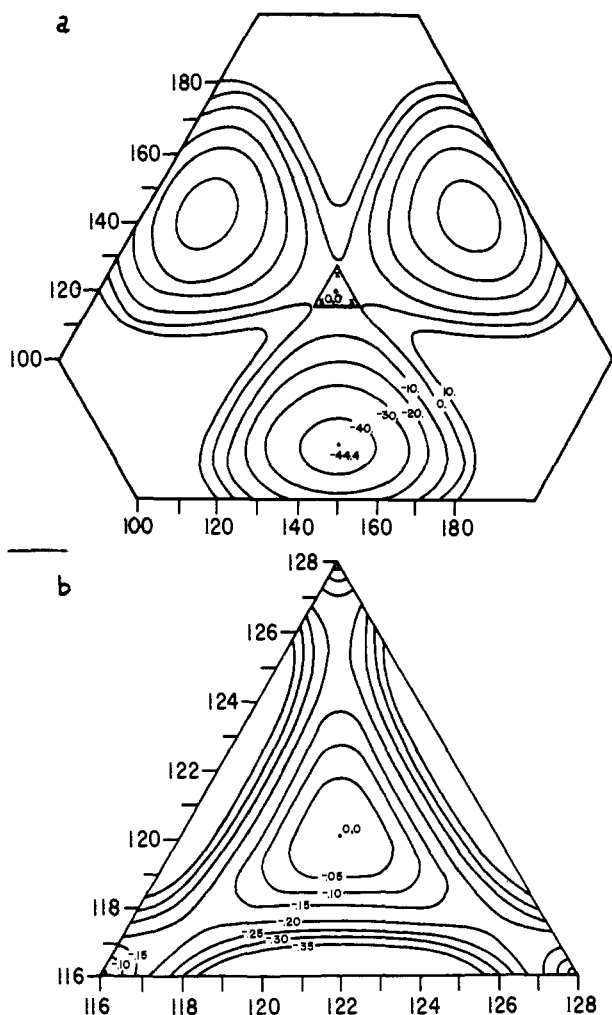
Figure 1. (a) Apparent "monkey saddle" on the potential energy surface for $C_5H_5^-$. The coordinates are the dihedral angles between the three-membered rings. Intraring coordinates have been held constant in the calculation. Energies are in kcal/mol. (b) Close-up view of the central region of (a) showing a potential energy maximum and three equivalent, normal transition states connecting the equilibrium states.
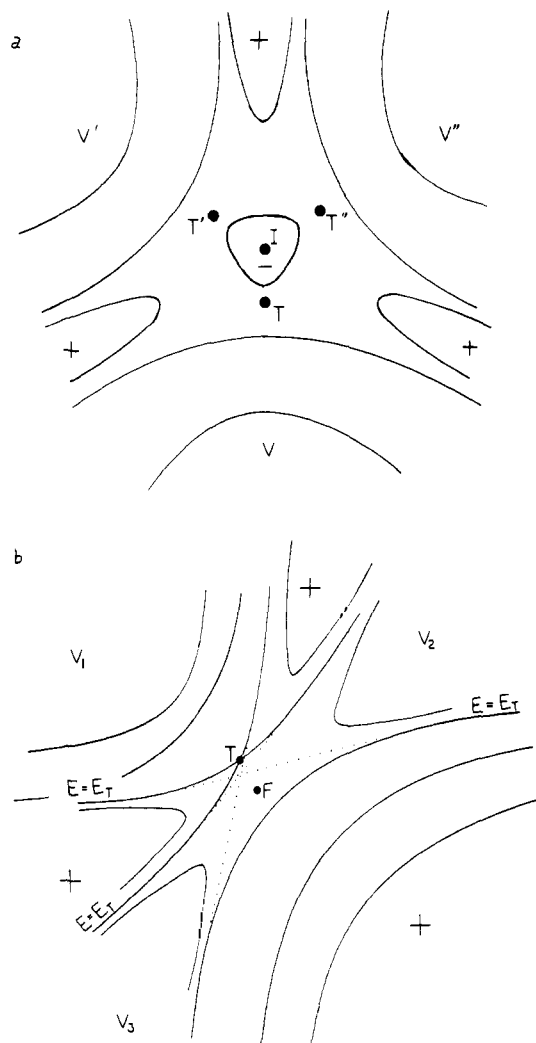

Figure 2. (a) Potential energy minimum corresponding to a stable intermediate I at the confluence of three equivalent reactant valleys. The valleys are connected with I via three normal saddle points. The + and − signs indicate regions of high and low potential energy. (b) Possible shape of a potential surface at the confluence of three inequivalent reactant valleys. T is the transition state joining V_1 with V_2 and V_3. The forking point F, which lies lower in energy than T, has been (somewhat arbitrarily) identified with the transition state joining V_2 and V_3. The dotted lines, which are only approximately tangent to the contours $E = E_T$, intersect at a point which could be interpreted as the center of an asymmetric monkey saddle in a far-off view of the surface.

nate system the contours of the quadratic surface $E^{(2)}$ will cross the principal axes at right angles. Suppose the contour c and the principal axis x associated with the coordinates $\{q_1, q_2, \ldots\}$ transform into the contour c' and the *line x'* under a nonorthogonal transformation to the coordinates $\{q_1', q_2', \ldots\}$. Since angles are not conserved under a nonorthogonal transformation there is no reason to expect c' and x' to be orthogonal to one another. If they are not, then x' cannot lie along a principal axis in the primed coordinate system.

Let us consider the algebra of an internal coordinate transformation. Although this is usually nonlinear as well as nonorthogonal, we can always regard it as linear provided we restrict our attention to regions near T where the quadratic energy $E^{(2)}$ is dominant. Thus, we can write

$$q' = aq \qquad (6)$$

where a is a constant matrix. If the new coordinates are nonredundant the matrix a will also be nonsingular and we can make use of its inverse.

$$b = a^{-1} \qquad (7)$$

$$q = bq' \qquad (8)$$

The transformation of the force constant matrix follows

from a comparison of the expressions for $E^{(2)}$ in the two-coordinate systems.

$$E^{(2)} = \frac{1}{2} q'^T F' q' \qquad (9)$$

$$F' = b^T F b \qquad (10)$$

Note that (10) is not a similarity transformation.

The kinetic energy of the system is

$$T = \frac{1}{2} \dot{q}^T G^{-1} \dot{q} \qquad (11)$$

The matrix G^{-1} undergoes the same transformation as F Its inverse, however, undergoes the transformation

$$G' = aGa^T \qquad (12)$$

The product matrix GF, therefore, undergoes the similarity transformation

$$(GF)' = a(GF)a^{-1} \qquad (13)$$

The difference between (10) and (13) provides an algebraic explanation for the difference in the transformation proper-
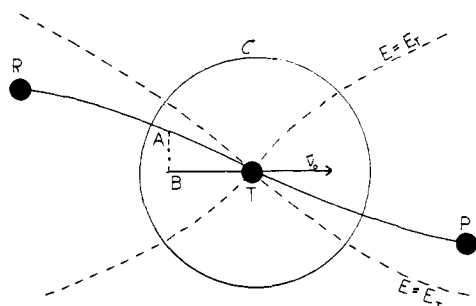
Figure 3. Schematic representation of the possibility of reaching the tail of the transition vector by a path which lies below E_T.
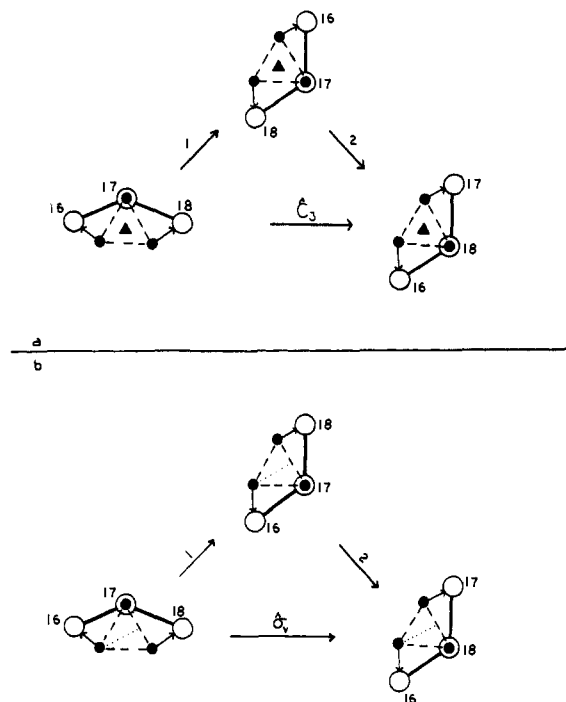

Figure 4. (a) Conversion of one ozone isomer to another by rotation of the atomic displacement vectors. The standard point group symbol ▲ shows the location of the symmetry axis of the D_{3h} reference structure. (b) The same isomerization, produced this time by reflection of the displacement vectors in a symmetry plane (dotted line) of the reference structure.

ties of the normal modes of vibration and the principal axes of curvature.

The eigenvalues of $\mathbf{F}'$ satisfy the relation

$$\prod_i k_i' = \det \{\mathbf{F}'\} = (\det \mathbf{b})^2 \prod_i k_i \qquad (14)$$

Since $\det \{\mathbf{b}\}$ can differ from unity when $\mathbf{b}$ is nonorthogonal, eq 14 implies that the principal values of curvature can change with a change of internal coordinates. On the other hand, since $\det \{\mathbf{b}\} \neq 0$ as long as both sets of coordinates are nonredundant, eq 14 also implies that the argument concerning the nonexistence of zero eigenvalues is independent of the choice of coordinate system. One can go further. One can always regard the q_i' as having evolved continuously from the q_i except perhaps for a permutation of subscripts. If we apply (14) to each stage of this evolution we can conclude that the sign of the product of the eigenvalues remains constant and the product does not go through zero. This implies that the number of negative eigenvalues is constant, a comforting conclusion in light of the coordinate dependence of the detailed features of the surface.

(c) Reaching the Tail of $\bar{v}_0$. The following lemma will be useful in proving the theorems of section III. Given that T is a transition state for some reaction and that $\bar{v}_0$ is the transition vector (in whatever coordinate system we happen to choose), we claim that it is always possible to move from reactants R to some point B lying along $\bar{v}_0$ at a finite distance from T on the reactant side, without ever going as high in energy as E_T. The concept and the method of proof are both illustrated in Figure 3.

The smooth curve from R through T to the product region represents a many-dimensional reaction path having T as a proper maximum. Point A lies on this path and inside the base plane hypercircle C. The role of this hypercircle is to mark off a boundary inside which the surface is essentially quadratic. Point B is the projection of A onto the direction of the transition vector. If one follows the straight (dashed) line from A to B the quadratic energy $E^{(2)}$ will decrease monotonically since all of the contributions from the principal coordinates of positive curvature will go steadily to zero while the negative contribution from the transition coordinate remains constant. This suggests that the modified path R to A to B meets the demands of our lemma. A rigorous proof that the total energy E on this path never goes as high in energy as E_T requires careful "epsilonic" consideration. Basically, what one must show is that nonquadratic terms do not upset the argument outlined above. One can do this by giving some attention to the radius of the hypercircle C. The relevant details are included in the Appendix.

In applying the above lemma we shall find it convenient to shorten $\bar{v}_0$ in such a way that B lies at the tail while the center of $\bar{v}_0$ lies at T.

(d) Symmetry Operations. In ordinary vibration theory the equilibrium configuration not only determines the point

group of the molecule, it also provides a set of labeled reference positions to which one can attach unlabeled displacement arrows showing the atomic positions in any nonequilibrium configuration. As Schonland,[9] McWeeney,[10] and other authors of group theoretical texts point out, the unlabeled arrows can be regarded as the objects of the symmetry operations. The effect of a rotation or reflection of these arrows is to convert one distorted molecular configuration into another of the same energy.

Our definition of a symmetry operation is essentially the same as that in vibration theory. The only real difference is in the choice of reference state. Rather than the equilibrium configuration we will be using whatever symmetric structure is under consideration as a possible transition state. The displacement arrows can then point to the equilibrium locations of the atoms in the reactant or product stages of the reaction. Alternatively, they could represent the short displacements from the transition state characteristic of the quadratic portion of the potential surface near T, or they could indicate any arbitrary point on a reaction path from R to P. In addition one could use a particular set of displacement vectors to represent the many-dimensional transition vector, just as in the analogous normal mode problem.

Figure 4 illustrates our meaning. The solid circles represent atomic locations in a symmetric, isotopically substituted ozone structure. The displacement arrows point to the equilibrium locations of the atoms in two different equilibrium states (open circles) which serve as reactants and products for the pseudorotation.[11] Step 1 in Figure 4a is a rotation of the entire structure about the threefold symmetry axis. The mathematical effect of this rotation on the Cartesian displacement coordinates can be expressed as

$$\text{rot} \begin{pmatrix} \mathbf{X}^{16} \\ \mathbf{X}^{17} \\ \mathbf{X}^{18} \end{pmatrix} = \begin{pmatrix} \mathbf{RX}^{16} \\ \mathbf{RX}^{17} \\ \mathbf{RX}^{18} \end{pmatrix} = (\mathbf{I} \otimes \mathbf{R}) \begin{pmatrix} \mathbf{X}^{16} \\ \mathbf{X}^{17} \\ \mathbf{X}^{18} \end{pmatrix} \quad \begin{matrix} (15) \\ (16) \end{matrix}$$

where $\mathbf{R}$ is the 3×3 orthogonal matrix representing the rotation of an arbitrary vector, $\mathbf{I}$ is a 3×3 identity matrix, and the cross $\otimes$ implies direct product multiplication. Since step 1, like every rotation or reflection, leaves all interatomic distances unchanged, it can have no effect on the potential energy. Step 2 can be thought of as a back rotation of the reference framework. However one pictures this step, its effect is to permute nuclei of like charge among themselves. This step changes individual (labeled) interatomic distances, but again leaves the energy unchanged. The net result of steps 1 and 2 is a rotation ($\hat{C}_3$) of the displacement vectors which leaves the labels behind. The mathematical representation of this operation is

$$\hat{C}_3 \begin{pmatrix} \mathbf{X}^{16} \\ \mathbf{X}^{17} \\ \mathbf{X}^{18} \end{pmatrix} = \left\{ \begin{pmatrix} 001 \\ 100 \\ 010 \end{pmatrix} \otimes \mathbf{R} \right\} \begin{pmatrix} \mathbf{X}^{16} \\ \mathbf{X}^{17} \\ \mathbf{X}^{18} \end{pmatrix} \quad (17)$$

$$= \Gamma(\hat{C}_3) \begin{pmatrix} \mathbf{X}^{16} \\ \mathbf{X}^{17} \\ \mathbf{X}^{18} \end{pmatrix} \quad (18)$$

A general symmetry operation $\hat{O}$ would be represented by

$$\Gamma(\hat{O}) = \mathbf{P}(\hat{O}) \otimes \mathbf{R}(\hat{O}) \quad (19)$$

This detailed mathematical representation helps to clarify a surprising feature of the diagrams. In Salem's work it seems to have been assumed that only a reflection or other improper rotation could convert chemical reactants into products. An example of such a conversion is shown in Figure 4b. Figure 4a shows, however, that the same conversion of one ozone molecule into another can be achieved by a proper rotation of the displacement vectors. This result is not exceptional. The majority of the examples discussed in this paper involve the conversion of reactants into products by a proper rotation. The reason this is possible is that in each case the "rotation" actually includes a permutation that changes interatomic distances between labeled atoms.

In practice we have found intuition to be treacherous when we are trying to determine the effect of a transition state symmetry operation on a reactant molecule. We have usually resorted to models and drawings of the type described above. One rule which allows us to bypass these drawings is the following: the operation $\hat{O}$ will leave reactants unchanged if the transition state T and reactant state R "share" $\hat{O}$ as a covering operation. In saying that $\hat{O}$ (e.g., $\hat{C}_3$, $\hat{\sigma}$, . . .) is "shared" we mean not only that a covering operation of the type indicated is present in both R and T but also that it produces the *same* atomic permutations in each state. The validity of this rule is easily proved by reflection on the formal definition of a transition state symmetry operation given above.

(e) Symmetries of the Principal Axes. The symmetry properties of the principal axes of curvature are (like their directions) coordinate dependent. If one chooses symmetry adapted internal coordinates, by which we mean coordinates which generate a fully reduced unitary representation of the reference state point group, then the force constant matrix will be block diagonal and each eigenvector will belong to one of the irreducible representations of the point group. The proof, which depends upon Schur's lemma and the invariance of the electronic energy under a symmetry operation, is given in detail by McWeeny.[12] Since the principal axes retain their geometric significance under a unitary transformation the symmetry properties of the eigenvectors will be preserved if one changes from symmetry adapted internal coordinates to any other set connected with the symmetry adapted set by a unitary transformation. The following simple criterion determines the existence of

such a transformation; there exists a unitary transformation from a set $(q_1, q_2, \ldots)$ to a symmetry adapted set of coordinates if and only if the group representation generated by the q_i is itself unitary.[13] This condition will not always be satisfied in practice. When it breaks down one has no guarantee that the eigenvectors of $\mathbf{F}$ will belong to definite symmetry species. This means that if one constructs a potential energy surface for a system without special regard for the choice of coordinate system one may well find that the transition vector fails to satisfy the symmetry conditions derived in section III. This failure, however, will be only formal. The selection rules based on the theorems depend only on the underlying symmetry of the physical system and are independent of the coordinate system.[14]

III. Theorems

We now prove a series of theorems concerning the symmetry species of the transition vector. In each case we assume that the coordinate system has been chosen so that the eigenvectors of the force constant matrix belong to symmetry species of the full transition state point group. Other limitations on the applicability of the theorems and interpretations of their exact meaning are given with the proofs.

I. The transition vector cannot belong to a degenerate representation of the transition state point group.

II. The transition vector must be antisymmetric under a transition state symmetry operation which converts reactants into products.

Corollary A. No structure can serve as a transition state for a given reaction if a $\hat{C}_3$ rotation or other odd degree symmetry operation associated with the structure converts reactants into products.

Corollary B. If the transition state point group includes a symmetry operation which converts reactants into products then the energy of the transition state will be a local minimum in the subspace of coordinates belonging to the wholly symmetric representation of the group.

III. The transition vector must be symmetric with respect to a symmetry operation which leaves either reactants or products unchanged.

Corollary. If each symmetry operation in the transition state point group leaves either reactants or products unchanged, then the transition state will be a saddle point with one negative principal value of curvature in the subspace of the fully symmetric coordinates as well as in the space of all coordinates.

IV. If the transition vector for the reaction $R_1 \rightarrow P_1$ is symmetric under a symmetry operation $\hat{O}$ which converts reactants R_1 into the equivalent reactants R_2 and P_1 into P_2, then there exist lower energy transition states for the reactions $R_1 \rightarrow R_2$ and $P_1 \rightarrow P_2$; if the transition vector is antisymmetric under $\hat{O}$ then there exists a lower energy transition state for the reaction $R_1 \rightarrow P_2$.

Theorem I (hereafter simply I) is an immediate consequence of the requirement that a transition state have only one principal axis of negative curvature. While this is fairly obvious the scope of the theorem may not be. Under the heading of "degenerate" representations we include not only the twofold or higher dimensional irreducible representations of the point group but also any complex one dimensional representations the group may happen to possess. The reason is that in the diagonalization of $E^{(2)}$ a complex representation can only appear in conjunction with its complex conjugate and the two then have equal eigenvalues.[15] Examples of such symmetry species are the so called E representations of the point groups C_3 and C_4 and the E_1 and E_2 representations of C_6.

Our proof of II is best explained through the use of Figure 5a. The solid line represents a (multidimensional) path
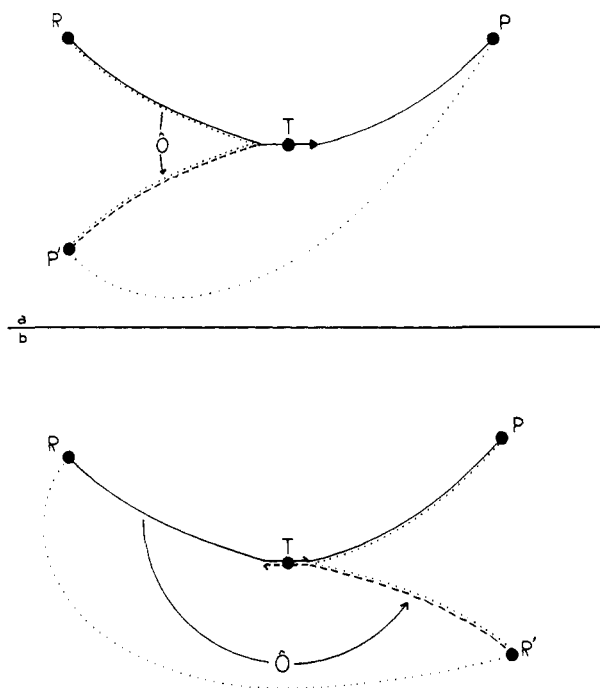
Figure 5. Diagrammatic basis for the proofs of theorems II and III.

leading from R through the transition state T to the products P. The path is chosen so that every point on the way to T lies lower in energy that E_T. The lemma established in section II allows us to demand that this path also follow the transition vector for some short but finite distance on each side of T. Let $\hat{O}$ be some transition state symmetry operator which transforms R either into P or into products P′ that can be converted into P by following some path (dotted) that requires either no expenditure of energy or at most an amount known to be less than the barrier height for the reaction. (In a decomposition reaction, for example, P′ might differ from P in the relative orientation of separated molecules. Alternatively, the dotted path might involve low energy conformational changes.) The application of $\hat{O}$ to the solid curve will convert each point into an energetically equivalent point on the path (dashed line) joining P′ and T. Let us suppose that contrary to II the transition vector were symmetric under $\hat{O}$. The paths R → T and P′ → T would then merge at the tail of the transition vector where the energy is definitely less than E_T. If this were the case, however, we could follow a path R → P′ → P (dotted line) from reactants to products which at no point went as high in energy as E_T. Since this contradicts the supposition that T is the lowest barrier the transition vector cannot be symmetric. Since I rules out all degenerate representations the transition vector must be antisymmetric under $\hat{O}$, as was to be proved.

IIA can be proved as follows. Let T be some state under consideration as a transition state for the reaction of interest and let $\hat{O}$ be some odd degree symmetry operator associated with T that converts reactants into products in the generalized sense described above. If T is actually a transition state then (from II)

$$\hat{O}\vec{v}_0 = -\vec{v}_0 \tag{20}$$

and, further

$$\hat{O}^{2n+1}\vec{v}_0 = -\vec{v}_0 \tag{21}$$

for every integer n. On the other hand, if $\hat{O}$ is odd then there exists some n such that

$$\hat{O}^{2n+1} = \hat{I} \tag{22}$$

where I is the identity operator, and this implies

$$\hat{O}^{2n+1}\vec{v}_0 = +\vec{v}_0 \tag{23}$$

which contradicts (21). One can avoid this contradiction only by rejecting T as a transition state.

The significance of IIB is primarily computational. It provides one with a sufficient criterion for the use of energy minimization techniques in the search for a transition state. The proof of the corollary is almost immediate. If T is allowed only a single principal axis of negative curvature, and if II requires that this lie in a direction which destroys the symmetry of the point group (as implied by the antisymmetry of the transition vector), then the curvature must be positive in all directions which retain the full symmetry of the structure and the energy must be a minimum in the subspace of these directions.

There is one restriction on the applicability of II and its corollaries. In developing the argument we implicitly assumed that a minimal energy path need pass through only one point with energy as high as E_T. If each minimal path is in fact forced to to go through a series of equivalent transition states T_1, T_2, ..., as in some symmetric multi-step reactions, then the lemma of section II and the analysis above can be applied directly only to T_1, the first transition state encountered along the path from R to P. (The requirement $E < E_T$ would not be satisfied in a path joining R to T_2.) Even in this case, however, the equivalence of T_1 and T_2 would ordinarily allow one to transfer information about one state into information about the other.

Figure 5b is a theorem III analog of Figure 5a. We suppose that some transition state symmetry operator $\hat{O}$ converts R either into itself or some state R′ that can be reached from R by a low energy path. Since $\vec{v}_0$ cannot belong to a degenerate representation (theorem I) it must be either symmetric or antisymmetric under $\hat{O}$. The diagram shows what happens if contrary to III the transition vector is assumed to be antisymmetric. The vector $\vec{v}_0$ (solid arrow) is converted into $-\vec{v}_0$ (dashed arrow) by $\hat{O}$ and the path joining R with the tail of $\vec{v}_0$ is converted into the energetically equivalent dashed path joining R′ with the tail of $-\vec{v}_0$. If this should occur the system could move from R to P via the dotted path which is lower at all points than E_T. Since T is the lowest barrier between reactants and products such a path cannot exist and the supposed violation of III cannot occur.

The above argument takes care of the case $\hat{O}R = R′$. A completely similar argument shows that $\vec{v}_0$ must also be symmetric under any operation that either leaves P unchanged or converts P into a product state P′ that can be reached from P by a low energy path. We omit the details.

Theorem III (like theorem II) requires modification if every minimal energy path joining R and P passes through two or more equivalent transition states. If this should be the case then the reactant form ($\hat{O}R = R′$) of the theorem is applicable only to the last transition state encountered on the path from R to P, while the product form ($\hat{O}P = P′$) is applicable only to the first state on this path.

The corollary to III can be proved in much the same way as IIB. The information it gives, however, is somewhat negative and somewhat indefinite. On the one hand it provides the discouraging information that energy minimization techniques cannot be used in the search for the transition state. On the other hand, in stating that the transition state, if it exists at all in the space of the totally symmetric coordinates, must be a col in that space, it does not provide a criterion for telling which col of the many that might be encountered is the transition state. A high energy col which

separates reactants and products in the symmetric subspace may be avoidable when one moves out of the subspace whereas another, lower energy col may not be.

The subject matter of theorem IV differs from that of theorem III in that we make no assumption about the paths joining the reactant states R_1 and R_2 or the product states P_1 and P_2. In fact the theorem is interesting only when one of the processes $R_1 \rightarrow R_2$ or $P_1 \rightarrow P_2$ is thought to involve a significant activation energy. If it is known in advance that neither of these processes involves any serious energy expenditure then IV provides no information beyond that already implied by II or III. With this understood, we can still derive IV using the same arguments that led to the earlier theorems. By II we know that if T, the transition state for $R_1 \rightarrow P_1$, were also to be the transition state for $R_1 \rightarrow R_2$ then the transition vector would have to be antisymmetric under $\hat{O}$. If the transition vector is actually symmetric we can conclude, just as in the argument leading to II, that there is a path joining R_1 to R_2 that lies lower in energy than E_T. The remaining parts of the theorem can be proved in a similar manner. As usual, however, one must be cautious in applying the theorems to reactions in which every minimal energy path from R_1 to P_1 is forced to go through two or more equivalent transition states. When this occurs the conclusions dealing with $R_1 \rightarrow R_2$ and $R_1 \rightarrow P_2$ apply only to the first transition state encountered on the way from R_1 to P_1, and the conclusion dealing with $P_1 \rightarrow P_2$ is applicable only at the last transition state.

It should be noted that there are cases in which two or more reactions share a transition state accidentally, i.e., without being compelled to do so by symmetry. Although group theory provides no special guidance in these situations it should be clear from the above discussion that the sharing of a transition state by say $A \rightarrow B$ and $C \rightarrow D$ implies the existence of a lower energy transition state for either $A \rightarrow C$ and $B \rightarrow D$ or for $A \rightarrow D$ and $B \rightarrow C$.

IV. Applications

The practical significance of the theorems derived in the previous section is best illustrated by a series of specific applications. Those discussed below (by no means an exhaustive group) are arranged according to their gradually increasing complexity.

a. Systems with a Threefold Axis. These provide the simplest applications of the theorems. Of the "transition states" discussed below all but the last is forbidden by corollary A of theorem II.

1. The Psuedo-Rotation of Ozone. This reaction, which we used in section IId to illustrate the rotation of reactants into products, was proposed by Berry[11a] in 1960. The D_{3h} structure is clearly a forbidden transition state. Berry actually proposed a direct conversion of one isomer to another via an asymmetric transition state. There is an alternative possibility. Since ozone is isoelectronic with cyclopropane it is not unreasonable to suppose that the D_{3h} structure is a stable intermediate and that the reaction really involves two steps as on the surface shown in Figure 2a. The transition states could then have C_{2v} symmetry. This idea is supported by recent ab initio calculations performed by Hay and Goddard.[11b]

2. The H + H₂ Reaction. It is well established that the transition state for this classic reaction is linear. Several groups, however, have considered the possibility of an isosceles triangle transition state and have investigated apex angles between 180° (linear H_3) and 60° (equilateral H_3, D_{3h} symmetry).[16] The rotation of reactants into products, which is shown below, implies that the equilateral triangle
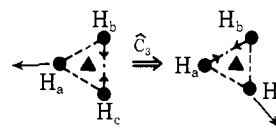

is a forbidden extreme. Actually, it has always been known that the ground state determinantal wave function for the D_{3h} structure would contain a singly occupied degenerate orbital and that this would lead to a Jahn–Teller instability. The equilateral triangle itself, therefore, has never been regarded as a serious candidate for the transition state. What the calculations have shown is that there is no stationary state for any apex angle other than 180°. Isosceles triangles with angles other than 60° would all be symmetry allowed transition states.[17]

As far as theorem IIA is concerned the reaction $H_a^- + H_bH_c \rightarrow H_aH_c + H_b^-$ is exactly analogous to the neutral atom reaction. No more thought is needed to rule out the equilateral triangle in one case than in the other. It turns out that the Jahn–Teller theorem also rules out D_{3h} in this case. Its applicability is less obvious, however, than in the case of the neutral atom reaction. One must make a detailed comparison of electron repulsion terms for the different states in the ground configuration before one can conclude that the state with the Jahn–Teller instability is indeed the ground state of the system.

The contrasting nature of the information provided by IIA and the Jahn–Teller theorem is worth noting. In each of the above examples (O_3, H + H_2, $H^- + H_2$) theorem IIA eliminates the possibility that the D_{3h} structure might be a lowest col connecting reactants and products; the Jahn–Teller theorem, when it is applicable (H + H_2, $H^- + H_2$), implies that the D_{3h} structure cannot even be a stationary point.

3. The Four-Center H₂ + H₂ Reaction. Shock tube studies[18] suggest that this reaction occurs with an activation energy of about 44 kcal. As yet, however, no computed structure has an energy nearly low enough to account for the reaction. Two structures which have been the subjects of extensive calculations[19] could have been eliminated on symmetry grounds. These are the centered equilateral triangle (D_{3h}) and tetrahedral (T_d) complexes. Both contain a threefold axis which rotates reactants into products. (We omit the diagrams since no new principles are involved.) Both also appear to be forbidden by the Jahn–Teller theorem. Although a square (D_{4h}) transition state appears to have excessively high energy it is at least acceptable on symmetry grounds. We reserve its discussion for the next section.

4. The Isomerization of Methylene Cyclopropane. The reaction is shown below.
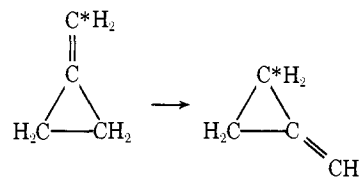
Chesick,[20] who was the first to study the isomerization, suggested that the planar (D_{3h}) structure **1** might serve either
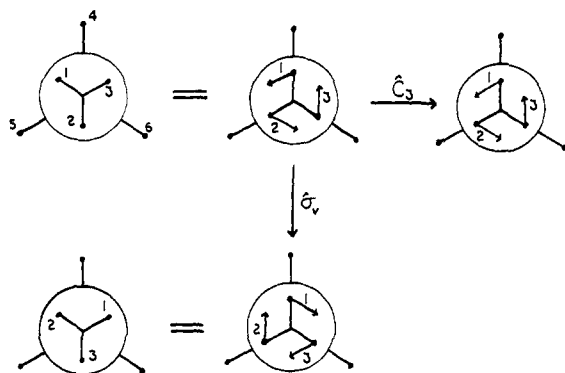

1
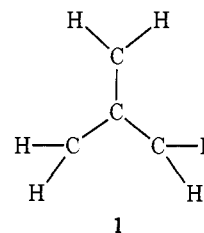
Figure 6. Effect of symmetry operations on the internal rotation of ethane. The figures on the extreme left are ordinary Newman projections of two different rotamers. The immediately adjacent figures show these same rotamers in relation to the staggered (D_{3h}) transition state (see text).

as intermediate or as transition state. This suggestion is no longer in favor.[21] Corollary A rules out **1** as a transition state. One would also expect it to exhibit a Jahn–Teller instability, and this is confirmed by calculations performed by Borden.[22]

5. The Isomerization of (CH)₅⁻. The reaction **2** has been the subject of an extended Hückel calculation by Stohrer

2
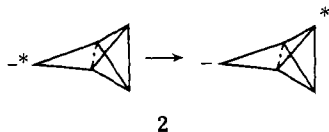
and Hoffmann.[23] Their calculations, which we have repeated and which we illustrate in Figure 1a, seemed to imply that the transition state had a threefold axis of symmetry and occupied the center of a monkey saddle. Since this conclusion was in direct conflict with the claims made herein, we have continued the calculations (still using the Stohrer and Hoffmann method) over a fine grid in the center of the supposed monkey saddle. The results (Figure 1b) show that the symmetric structure corresponds to a potential energy maximum and that there are three equivalent transition states, each noticeably displaced from the central maximum.[24]

6. Internal Rotation in Ethane. It is almost certain that the eclipsed (D_{3h}) structure is the transition state for the conversion of one form of staggered ethane into another. Contrary to what intuition might suggest this does not constitute a violation of corollary A. Since the threefold axis of the transition state is shared with the reactant state it follows that rotation about this axis must leave reactants unchanged. This is verified in Figure 6. On the other hand, the vertical planes of symmetry which are present in both the staggered and eclipsed conformations are not "shared" by these conformations in the special sense defined in section IId. When regarded as covering operations the reflections $\hat{\sigma}_v$ produce different nuclear permutations in the different conformations. One has no reason to conclude therefore that a transition state (eclipsed configuration) $\hat{\sigma}_v$ will leave reactant state displacement vectors unchanged. Figure 6 shows that each transition state $\hat{\sigma}$ actually converts a given staggered conformer into another, i.e., converts torsional reactants into torsional products.

One can show that the reflection $\hat{\sigma}_h$ also converts reactants into product. The transition vector therefore must be symmetric under $\hat{C}_3$ and antisymmetric under $\hat{\sigma}_v$ and $\hat{\sigma}_h$. This information is sufficient to assign it to the symmetry species A_1''. It is interesting that eclipsed ethane has only
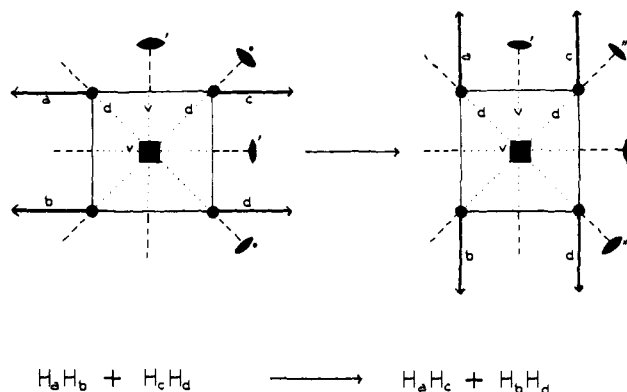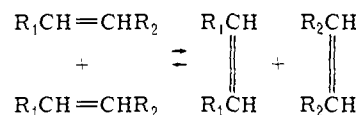
one internal coordinate with this symmetry and that this corresponds to pure internal rotation. The transition vector, in other words, contains no contribution from bond stretching or bending; it is purely torsional.

b. Transition States with a Fourfold Axis. These form an interesting and rather surprising pattern. Each of the "transition states" discussed below is "allowed" as far as symmetry is concerned. In the second and third examples, however, the acceptance of the symmetric structure as the transition state for the reaction of interest implies the existence of a lower energy transition state for a closely related reaction.

1. Square Planar H₄. Figure 7 shows the displacement vectors for reactants and products and also labels the symmetry elements of the supposed D_{4h} transition state. It is relatively easy to see that the reactant vectors are converted into product vectors by $\hat{C}_4^{\pm 1}$ and $\hat{S}_4^{\pm 1}$, by each of the $\hat{\sigma}_d$ reflections and each of the $\hat{C}_2''$ rotations; each set of vectors is left invariant by $\hat{C}_4^2$, by the $\hat{\sigma}_v$'s and $\hat{C}_2'$s, by $\hat{\sigma}_h$ and the inversion $\hat{\imath}$. Taken in conjunction with theorems II and III these symmetry properties imply that the transition vector must belong to the symmetry species B_{1g}. Since square planar H₄ has one internal coordinate with this symmetry the transition state is "allowed".

2. The Olefin Metathesis Reaction. The observed reaction is

$$
\begin{array}{ccc}
R_1CH=CHR_2 & R_1CH & R_2CH \\
+ & \rightleftarrows \quad \| \quad + \quad \| \\
R_1CH=CHR_2 & R_1CH & R_2CH
\end{array}
$$

This takes place in solution with the aid of a complex tungsten catalyst. According to Calderon[25] the most likely mechanism involves the asymmetric absorption of the two olefinic molecules, passage through a symmetric transition state to another asymmetric state, and then desorption of the products. We analyze the reaction under the assumption that the transition state has C_{4v} symmetry. We assume also that this state has higher energy than any transition state blocking the weak attachment of the second olefin once the first is strongly absorbed. Under these assumptions it is legitimate to classify reactants and products as shown in Figure 8.

In contrast to the H₄ reaction there are three distinct product states, each of which can be reached from the square pyramid by a path which is energetically equivalent to one leading back to reactants. One of these products is that for a simple displacement reaction. The other two are intermediates for the metathesis reaction.

Since C_{4v} obviously cannot have a real 1 × 1 representation which is antisymmetric under $\hat{C}_4^2$, the square pyramid

Figure 7. Symmetry elements in a hypothetical D_{4h} transition state for a four-center hydrogen exchange reaction. Planes are indicated by dotted lines, axes by dashed lines and standard point group symbols.

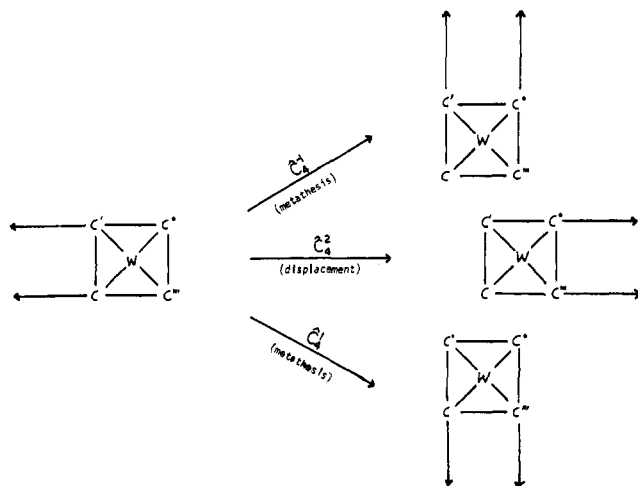$$H_a H_b + H_c H_d \longrightarrow H_a H_c + H_b H_d$$

Figure 8. Symmetry relations between reactants and products in the olefin metathesis reaction.
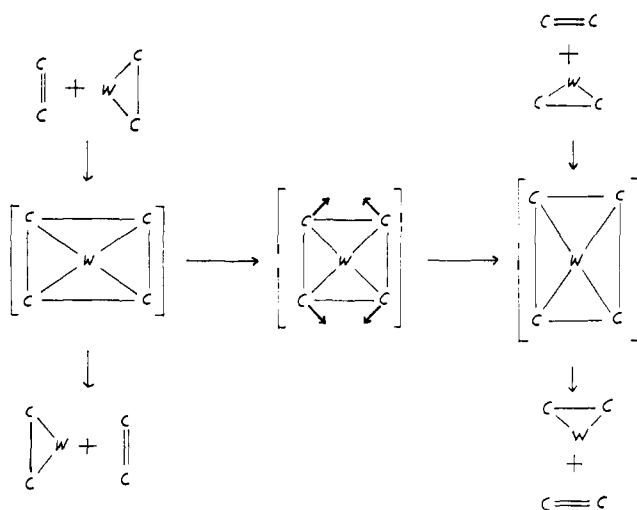

Figure 9. A possible reaction scheme for the olefin metathesis reaction and the related catalytic displacement reaction. The heavy arrows in the central figure show a transition vector of B_1 symmetry.

cannot be the transition state for the displacement reaction. Consultation of a set of character tables shows that it *can* be the transition state for formation of the metathesis intermediates and that if it is, then the transition vector must belong to the B_1 representation. A normal mode with this symmetry is indicated in the center of Figure 9. This diagram also shows how a complex which can decompose with equal ease into four different states can be an "allowed" transition state for the interconversion of certain pairs of states, while it is "forbidden" as a transition state for the interconversion of other pairs. This is possible if a path downhill from the complex encounters a forking region beyond which it can pass into either of two equilibrium states. Geometries corresponding to possible forking points are shown on the left and right sides of the diagram. If these forking points exist and have lower energy than the transition state then it will be possible to carry out a displacement reaction (vertical path on the diagram) without going through an energy as high as E_T. It is in this sense that the square pyramid is forbidden as a transition state for the displacement reaction. On the other hand the metathesis reaction requires passage from the left to the right side of the diagram and the transition state is allowed for this process.

Figure 10 shows how the fourfold symmetry of the potential surface about T is consistent with the reaction scheme outlined above. The right side of the diagram shows the po-
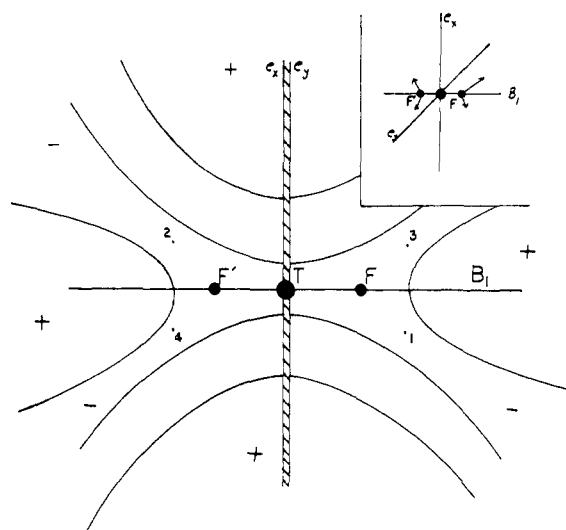

Figure 10. Potential energy surface for the olefin metathesis reaction scheme shown in Figure 9. The forking paths shown in the inset are perpendicular to one another. The right side of the main diagram shows the surface above the e_y-B_1 plane; the left side shows the surface above the e_x-B_1 plane. The forking points F and F' correspond to the rectangular structures in Figure 9.

tential surface above the B_1, e_y internal coordinates; the left side shows the potential surface above the B_1, e_x coordinates. Successive 90° rotations of the displacement vectors for point 1 about the transition state convert them into the vectors for points 2, 3, 4, 1, etc.

3. Methane Substitution. The hot atom reaction

$$T + CH_4 \longrightarrow CH_3T + H$$
$$3$$
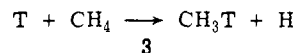
has been the subject of a great many experimental studies. One rather firm conclusion, based on experiments with substituted methane, is that the reaction takes place almost exclusively with retention rather than inversion of configuration.[26] Whether this actually indicates a lower barrier for the retention reaction or whether it requires a dynamic explanation is not completely certain.

Parts of the potential surface for reaction 3 have been studied at the semiempirical (CNDO) level by Weston and Ehrenson[27] and at the ab initio level by Morokuma and Davis[28] and by Ehrenson and Newton.[29]

Our interest lies in the suggestion by Weston and Ehrenson that the transition state for the retention reaction might be a C_{4v} complex. The lower path in Figure 11 shows one retention reaction via this complex. The full reaction scheme shown in Figure 11 is closely analogous to that for the metathesis reaction in Figure 8 and can be analyzed in the same way. The C_{4v} complex is a forbidden transition state for the inversion reaction. It is allowed for either of the configuration retention reactions. However, if it is the transition state for these reactions, then there necessarily exists a lower energy path for the inversion reactions. The obvious route for the lower energy reaction is Walden inver-

$$T + CH_4 \longrightarrow T-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{H}}{C}}-H \longrightarrow TCH_3 + H$$
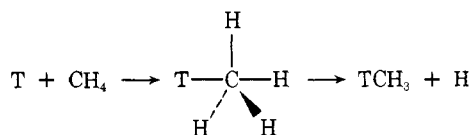
sion. The trigonal bipyramid (D_{3h}) transition states for the Walden inversion could serve as the downhill forking points (compare Figure 9) on each side of the C_{4v} structure. Passage from one forking point to another would then be a typical pentacoordinate pseudo-rotation, and this is exactly what Weston and Ehrenson proposed.
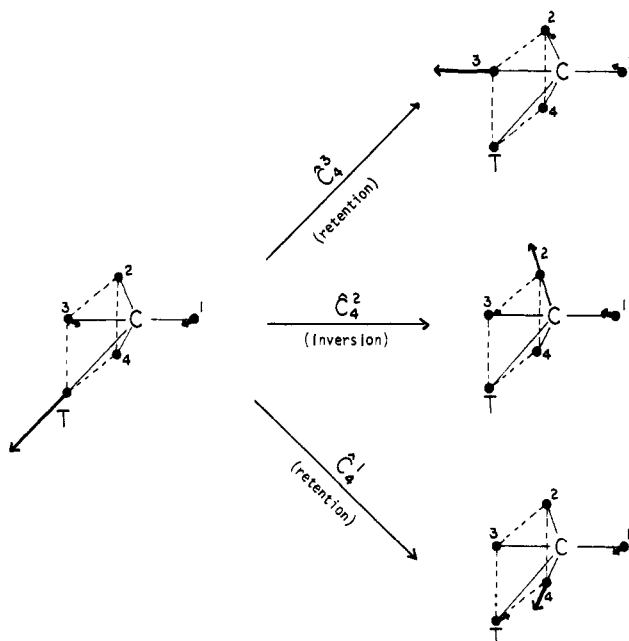
Figure 11. Symmetry relations in the reaction $T + CH_4 \rightarrow H + TCH_3$ via a C_{4v} transition state.
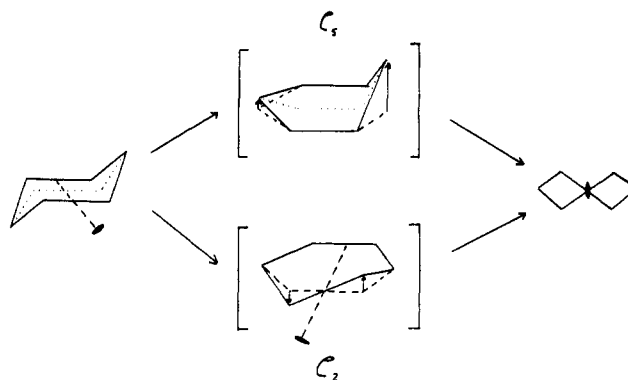

Figure 12. Probable transition state structures for the conversion of chair cyclohexane into a metastable twist boat. Reactants and products are shown in conventional perspectives which differ from that of the transition states. The symmetry axis shown for the (D_2) twist boat is shared with chair cyclohexane and the C_2 transition state. The symmetry plane of the C_s structure, shown via its intersection with the carbon framework, is shared with the chair.

The above reaction sequence was favored by the Weston–Ehrenson calculations which showed only a very small barrier for the pseudo-rotation. The ab initio calculations on the other hand imply that the energy difference between the D_{3h} and C_{4v} structures is actually quite large ($\sim$30 kcal). Whatever the mechanism or numerical data our conclusions stand. The C_{4v} structure cannot be the lowest barrier for the general displacement reaction; it could be the transition state for the retention reaction.

c. The Inversion of Cyclohexane. It is generally agreed that the interconversion of the two equivalent chair forms of cyclohexane proceeds through an intermediate boat structure. It is also thought that the boat undergoes pseudo-rotation from one stable twist boat (D_2) form to another and that the classical (C_{2v}) boat probably serves as transition state between successive twist forms. What is less certain is the nature of the transition state joining the chair with the twist boat. The two structures currently thought to be acceptable are shown in Figure 12 along with the chair and twist boat forms. Since the chair is invariant to both the reflection $\hat{\sigma}_s$ and the rotation $\hat{C}_2$ it follows that if either of these structures is to serve as chair $\rightarrow$ boat transition state then the transition vector would have to be totally symmetric.

MINDO/2 calculations have recently been carried out on these and other cyclohexane structures.[30] According to MINDO/2 the C_s and C_2 structures have practically the same energy, each is a saddle point with one principal axis of negative curvature, and the transition vectors for the two structures belong to the A_1 representations of their respective point groups. Either, therefore, could serve as transition state. In fact, it was concluded that the entire ridge joining the two states could be regarded for practical purposes as the transition state since the energy was so nearly constant on this ridge.

To what extent these conclusions will hold up on a more accurate potential surface is a matter of speculation. If one adds the implications of theorem IV to those of II and III, however, one can extract information concerning the cyclohexane system which is independent of the quality of the surface.

Suppose that the C_s structure is in fact the transition

state for the chair $\rightarrow$ twist boat reaction. Figure 12 shows that while the chair is invariant under $\hat{\sigma}_s$, the boat is not. One can show that it is converted into the product of a pseudo-rotation reaction. As pointed out above the invariance of the chair under $\hat{\sigma}_s$ requires that the transition vector belong to the A_1 representation of C_s. Theorem IV implies therefore that the barrier to pseudo-rotation (presumably the classical boat) must lie lower in energy than the C_s structure on any surface for which the latter serves as the transition state separating chair from twist boat. The natural expectation then is that the classical boat will correspond to a downhill forking point separating equivalent twist-boat products.

The C_2 structure is less interesting from the present viewpoint. Since the chair and twist boat are both invariant under $\hat{C}_2$ one can draw no conclusions about the pseudo-rotation from a consideration of this structure.

The classical (C_{2v}) boat is somewhat more interesting. Although chemical arguments may make the role implausible it is not obviously impossible for a structure of this symmetry to serve as transition state for the chair to twist boat reaction. If it were of course there would be no need for the twist boat to act as intermediate for the chair inversion. A symmetric continuation of the uphill path from chair to classical boat would provide a downhill path to inverted chair. We can prove more than this, however. By combining theorems III and IV as in the case of the C_s structure discussed above, we can show that if the classical boat were the transition state for the chair to twist-boat reaction then there would exist lower energy transition states for both the chair inversion and the twist-boat pseudo-rotation. The argument follows.

Theorem III allows us to assign the transition vector to the totally symmetric A_1 representation since (1) the $\hat{C}_2$ axis is shared by the classical and twist boats, (2) the chair is invariant to the reflection $\hat{\sigma}_1$ (see Figure 13), and (3) symmetry under the above operations implies symmetry under $\hat{\sigma}_2$. Theorem IV then tells us (1) that there is a lower energy path for the chair inversion since $\hat{C}_2$ and $\hat{\sigma}_2$ both convert chair into inverted chair and (2) that there is a lower energy path for pseudo-rotation of the twist boat since both $\hat{\sigma}_1$ and $\hat{\sigma}_2$ convert one twist boat into another.
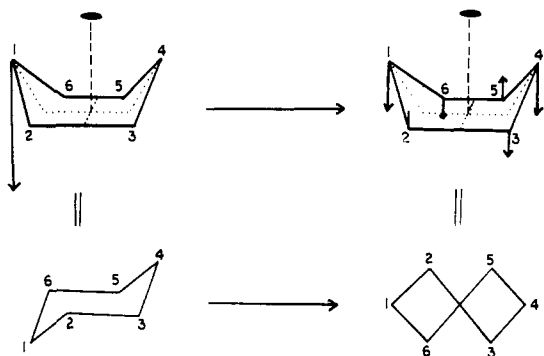
d. The Cope Rearrangement. The Cope rearrangement **4**

4
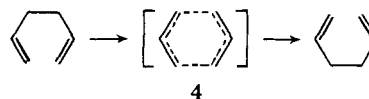
Figure 13. The chair → twist-boat reaction. The upper part of the diagram shows reactants and products in relation to a classical boat "transition state". The lower diagram shows the same structures in conventional perspectives.

is one of a family of closely related isomerizations. In Woodward–Hoffmann[31] terminology the Cope rearrangement itself is a [3,3] sigmatropic shift. The related isomerizations include the [1,3] sigmatropic shift, methylene rotation about one or both double bonds, and rearrangements through intermediates such as bicyclo[2.2.0]hexane.

One can conceive of several symmetrical forms for the transition state in **4**. Traditional opinion, based on the Doering–Roth experiments,[32] has favored a cyclohexane-like chair of C_{2h} symmetry. This conclusion has recently been questioned by Goldstein and Benzon.[33] Our approach is to ask which (if any) of the possible isomerizations of 1,5-hexadiene a given symmetrical structure might serve as transition state and (if it does) which reactions would then proceed by a lower energy path.

It is convenient to begin with a D_{2h} structure having all carbons coplanar. This could be reached either by a disrotatory or conrotatory twist of the methylenes. Figure 14 shows the symmetry operations which interconvert reactant a and the various products, b, c, and d possible when one assumes that the mechanism is disrotatory. Note that a → b consists of a double rotation about fixed olefinic bonds while a → c and a → d are isotopically distinct Cope reactions. Reactions c → d, b → d, and b → c are similar to a → b, a → c, and a → d, respectively. There are then three different types of reaction which could involve a disrotatory motion through the D_{2h} form shown. Theorem III requires that if this structure is to be the transition state for any of the three reactions then the transition vector must be symmetric under the operation $\hat{\sigma}_{xy}$ which leaves all of the molecules unchanged. This requirement limits the possible symmetry species to A_g, B_{1g}, B_{2u}, and B_{3u} (see Table I). The totally symmetric representation A_g can be eliminated on the basis of II since for each of a → b, a → c, and a → d D_{2h} contains at least one operation which converts reactants into products. Each of the remaining symmetry species is "allowed", but for different sets of reactions. B_{1g}, for example, is allowed for reactions a → b and a → c since the properties of this representation (Table I) are compatible with the requirements of II and III and the transformations are shown in Figure 14. If, however, the D_{2h} structure is actually the transition state for a → b and/or a → c then theorem IV implies the existence of lower energy paths for a → d and b → c. This follows from the fact that B_{1g} is symmetric under the operations $\hat{\imath}$ and $\hat{C}_{2z}$ both of which convert a into d and b into c. This information is summarized in diagram **5**, where we use solid lines to indicate passage through a transition state and dotted lines to indicate lower energy reactions.[34] Similar diagrams result from the analysis of the B_{2u} and B_{3u} possibilities. These are shown in the first line of Table II. (The low energy paths which we show explicitly
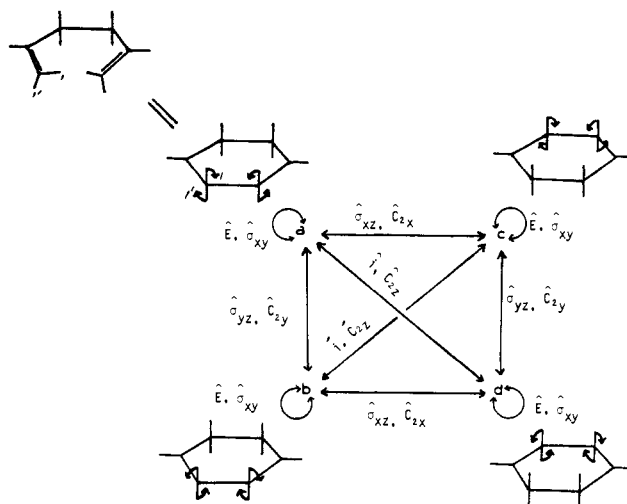

Figure 14. Symmetry interconversion diagram for the disrotatory Cope reaction system.

Table I. Character Table for D_{2h} and Its Subgroups[a]

C_{2h}					$\hat{E}$	$\hat{\sigma}_{xy}$	-	-	$\hat{\imath}$	$\hat{C}_{2z}$	-	-
	D_2				$\hat{E}$	-	-	-	-	$\hat{C}_{2z}$	$\hat{C}_{2y}$	$\hat{C}_{2x}$
		C_{2h}			$\hat{E}$	-	$\hat{\sigma}_{xz}$	-	$\hat{\imath}$	-	$\hat{C}_{2y}$	-
			C_{2v}		$\hat{E}$	$\hat{\sigma}_{xy}$	$\hat{\sigma}_{xz}$	-	-	-	-	$\hat{C}_{2x}$
				D_{2h}	$\hat{E}$	$\hat{\sigma}_{xy}$	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{yz}$	$\hat{\imath}$	$\hat{C}_{2z}$	$\hat{C}_{2y}$	$\hat{C}_{2x}$
A_g	A	A_g	A_1	A_g	+	+	+	+	+	+	+	+
A_u	A	A_u	A_2	A_u	+	-	-	-	-	+	+	+
A_g	B_1	B_g	B_2	B_{1g}	+	+	-	-	+	+	-	-
A_u	B_1	B_u	B_1	B_{1u}	+	-	+	+	+	-	-	-
B_g	B_2	A_g	B_1	B_{2g}	+	-	+	-	+	-	+	-
B_u	B_2	A_u	B_2	B_{2u}	+	+	-	+	-	-	+	-
B_g	B_3	B_g	A_2	B_{3g}	+	-	-	+	+	-	-	+
B_u	B_3	B_u	A_1	B_{3u}	+	+	+	-	-	-	-	+

[a] The axes are those shown in Figure 16. The entries are to be interpreted as ±1.

5
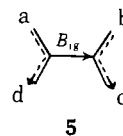
with dotted lines in **5** have been left implicit in Table II.) Note that if one ignores the difference between a → c and a → d and searches simply for the lowest barrier to a disrotatory Cope reaction then only B_{2u} is "allowed". If one is still more restrictive and demands that the transition state be the lowest barrier to any of the hexadiene isomerizations then all three symmetry species are forbidden and so, therefore, is the D_{2h} structure.

A completely analogous argument can be worked out for the conrotatory reactions. The stereochemistry is shown in Figure 15. As in the case of the disrotatory mechanism there are three products which can be reached by a symmetric continuation of the path from reactant to transition state. Reactant a and the double rotation product b are the same as those shown in Figure 14. The new Cope products e

Table II. Diagrammatic Representations of the Cope and Cope-Related Reactions for Which Various Symmetry Species in the D_{2h} Family Are Allowed or Forbidden

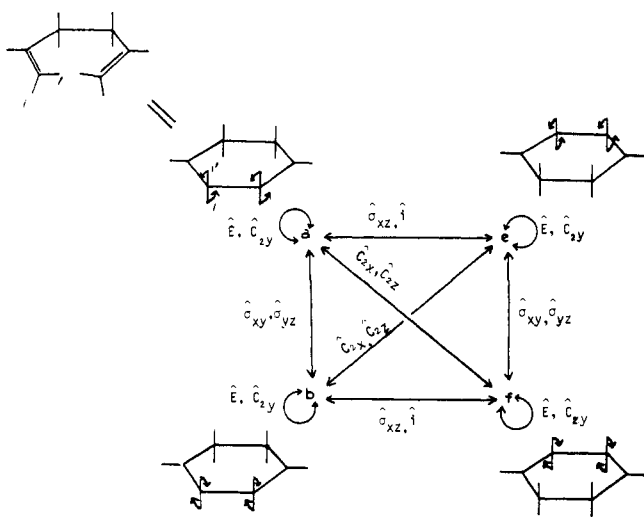| Group	Disrotatory mechanism	Conrotatory mechanism
D_{2h}	$a \xrightarrow{B_{1g}} d$ (b) $a \xrightarrow{B_{2u}} c$ (b) $a \xrightarrow{B_{3u}} d$ (b)	$a \xrightarrow{A_u} f$ (b) $a \xrightarrow{B_{3g}} f$ (b) $a \xrightarrow{B_{2u}} f$ (e)
C_{2v}	$a \xrightarrow{B_2} c$ $b \xrightarrow{B_2} d$	$a \xrightarrow{A_2} f$ (b) $a \xrightarrow{B_2} f$ (e) $a \xrightarrow{B_2} f$ (b)
C_{2h}	$a \xrightarrow{B_g} d$ (b) $a \xrightarrow{A_u} d$ (c) $a \xrightarrow{B_u} d$ (b)	$a \xrightarrow{A_u} e$ $b \xrightarrow{A_u} f$
D_2	$a \xrightarrow{B_1} d$ (b) $a \xrightarrow{B_2} d$ (c) $a \xrightarrow{B_3} d$ (b)	$a \xrightarrow{B_2} f$ $b \xrightarrow{B_3} e$
C_{2h}	$a \xrightarrow{B_u} d$ $b \xrightarrow{B_u} c$	$a \xrightarrow{A_u} f$ (b) $a \xrightarrow{B_g} f$ (b) $a \xrightarrow{B_u} f$ (e)

Figure 15. Symmetry interconversion diagram for the conrotatory Cope reaction system.

and f are distinct from one another and also from c and d. (The transition state is also isotopically distinguishable from that in Figure 14.) The diagrams for the allowed symmetry species are shown in Table II. Once again the B_{2u} species is unique in that it is the only one which is "allowed" for both the Cope reactions.

Many of the symmetrical structures which have been proposed as transition states for the Cope rearrangement have point groups which are subgroups of D_{2h}. These are the C_{2h} chair favored by Doering and Roth, a C_{2v} boat, a D_2 twist boat, and a second C_{2h} structure (call it C_{2h}') in which the carbon atoms are coplanar. Figure 16 shows that each of these structures can be oriented in such a way that its symmetry elements share labels with those of D_{2h}. This perfect correspondence of symmetry elements allows us to superimpose the character tables of the various groups and this has been done in Table I. It also allows us to adapt the interconversion diagrams of Figures 14 and 15 to each of the subgroups of D_{2h}. We need only erase those elements from the diagrams which are absent from the subgroups. Given these interconversions we can then construct the diagrams shown in Table II for each of the subgroups.

Most of the diagrams in Table II differ from those for D_{2h} only in the labeling of the allowed symmetry species. In four instances, however, the reduction of the transition state symmetry from D_{2h} to that of a subgroup splits the forked
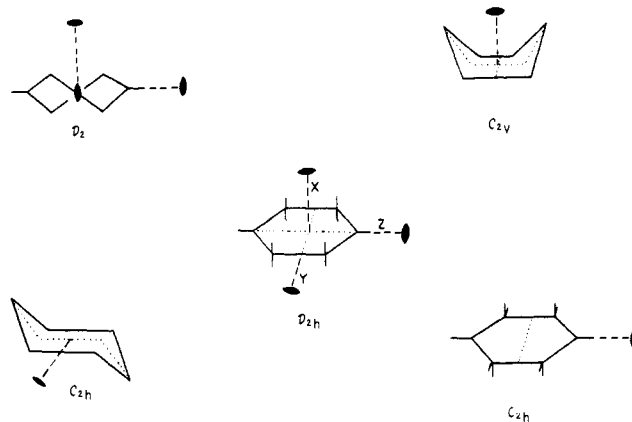

Figure 16. The D_{2h} family of hypothetical transition states for the Cope reaction. The perspective has been modified for the D_2 and C_{2v} structures but orientation of the axes is approximately the same for all structures.

diagram into separate diagrams for uncoupled reactions. In C_{2v}, for example, there is no operation which converts a into anything other than c, or b into anything other than d. Theorem IV, therefore, is inapplicable and the diagrams take on the simple pattern shown in the table.

Goldstein and Benzon, in their elegant scheme for analyzing the kinetics of the sigmatropic shifts of 1,5-hexadiene-d_4, have suggested that the C_{2v}, C_{2h}, D_2, and C_{2h}' structures might serve as transition states for the reactions which we denote as a → c, a → e, a → f, and a → d, respectively. These assignments are consistent with the results of Table II. In fact each assignment corresponds to one of our fork-free diagrams. This means that not only is each assignment allowed in its own right, but also that there is nothing to suggest any mutual incompatibility. (Mutual incompatibility might have occurred if two or more of the diagrams were forked. One might, for example, have had one forked diagram implying that reaction r' went by a lower energy path than reaction r, while the second implied the inverse ordering.) We note in passing that the Goldstein-Benzon analysis does not include a transition state for the direct a → b reaction even though this transformation does occur in the two-step reaction a → e → b. On the other hand they do include the C_{2h}' transition state to account for a → d, a transformation which their analysis implies could occur in three steps. (These would be a → c followed by a two-step c → d double rotation similar to the a → e → b process.) We mention this inconsistency to show that their analysis is somewhat less than exhaustive and the utility of the consideration herein in detecting this.

Whatever the allowedness of a set of transition states one can only substantiate them through computation. An extensive MINDO/2 analysis of the 1,5-hexadiene system will be given in a future publication.[34] We summarize the results. On the MINDO/2 surface the C_{2v} boat and C_{2h} chair are both metastable and must be interpreted as intermediates rather than transition states. Minimizing the energy of C_{2h}' (as IIB allows one to do during the search procedure) produces a collapse into D_{2h} symmetry; moreover, the force constant matrix of the resulting structure has three negative eigenvalues so that both D_{2h} and C_{2h}' can be rejected on the basis of M–L, at least on the MINDO/2 surface. The calculation in D_2 symmetry resulted in two structures (obtained by populating different orbitals), both of which possessed a force constant matrix with a single negative eigenvalue. The higher energy structure had a transition vector of B_1 symmetry. This makes it forbidden for the a → f reaction which the D_2 structure is supposed to serve. The lower
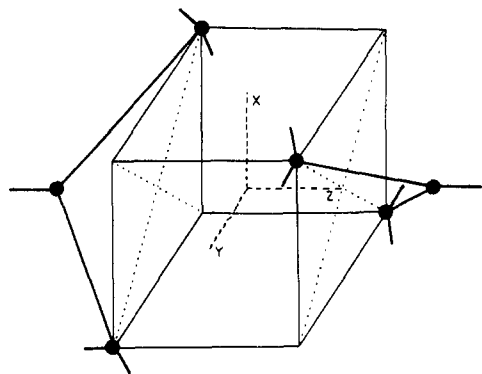
Figure 17. Hypothetical D_{2d} transition state for the Cope reaction.

energy D_2 structure has the B_2 symmetry transition vector required by the theorems. It was also found, however, that there was a lower energy path for this reaction which went through bicyclo[2.2.0]hexane as an intermediate.

In addition to the D_{2h} family of structures one can conceive of other families based on hypothetical, high symmetry transition states. The D_2 structure of Figure 16 can be reached from D_{2h} by twisting the allyls *out* of plane. If one continues twisting the allyls until their planes are perpendicular to one another one comes to the D_{2d} structure shown in Figure 17. One could then reduce the symmetry to D_4 by twisting the methylene groups. Rather than attempt a complete analysis of this system we confine ourselves to the parent D_{2d} structure. The most interesting feature of this structure is that it can decompose into products of a [1,3] sigmatropic shift as well as into the [3,3] shift and double rotation products discussed above. We ask if the D_{2d} structure can serve as transition state for a [3,3] shift.

Table III, taken from Wilson, Decius and Cross,[35] shows the correlation between the symmetry species of D_{2d} and its subgroup D_2. If D_{2d} were to be the transition state for a conrotatory [3,3] shift the symmetry species of the transition vector would have to correlate with the species allowed for the subgroup D_2. Table II shows this D_2 species to be B_2. Since B_2 correlates only with the twofold degenerate E representation of D_{2d} we can rule out (theorem I) D_{2d} as a transition state for the conrotatory [3,3] shift. D_{2d} is forbidden on similar grounds for the disrotatory [3,3] shift which we have labeled a $\rightarrow$ d. It is allowed, however, for the reaction a $\rightarrow$ c. There are in fact two possibilities. The transition vector can belong to either the A_2 or B_2 representations of D_{2d}, both of which correlate with the B_1 representation of D_2. These possibilities, which are suggested by Tables II and III, can be confirmed with the aid of transformation diagrams similar to Figures 14 and 15. On the other hand there are several reactions associated with these symmetry species which IV implies would take place by lower energy paths. These include the Cope reaction a $\rightarrow$ d and also two [1,3] sigmatropic shifts for each of the A_2 or B_2 symmetry species.

V. Concluding Remarks

One common feature among the reactions we have been discussing is the possibility of reaching three or more distinct equilibrium states by equivalent downhill paths from the transition state. In dealing with reactions of this nature some authors have assumed that the transition state rested on a monkey saddle, i.e., that the various reactant and product valleys merged in a common point. Others (M–L) have argued that the transition vector was necessarily degenerate and that the proposed transition state was thereby forbidden. We have shown that neither of these conclusions is justified. The D_{2h} "transition state" for the Cope reaction is

Table III. Correlation between the Symmetry Species of D_{2d} and D_2

D_{2d}	A_1	A_2	B_1	B_2	E
D_2	A	B_1	A	B_1	$B_2 + B_3$

particularly interesting in connection with the M–L argument. In this example we had four equivalent decomposition products (a, b, c, d or a, b, e, f) and yet the group in question was one which did not possess a degenerate representation!

One elementary conclusion which one can draw from the existence of a multiplicity of equivalent decomposition paths is that the transition state is forbidden for some of the associated reactions. The use of forking diagrams to demonstrate the plausibility of this result is another concept which one can introduce without the need for formal group theory. Murrell and Pratt, for example, used forking diagrams for just this purpose. The real necessity for group theory arises in our opinion when one is trying to decide precisely when a given transition state is forbidden or allowed for a *specific* reaction. In answering these questions we do not believe there is at present any broadly applicable alternative to the use of theorems I–IV.

Appendix

Proof of Lemma in Section II. In a principal axes coordinate system eq 1 takes the form

$$E_Q = E_T + \frac{1}{2}\sum k_i q_i^2 + \frac{1}{2}\epsilon_Q s_Q^2 \qquad (A1)$$

We rewrite this as

$$E_Q = E_T + \frac{1}{2}(e_Q^{(2)} + \epsilon_Q)s_Q^2 \qquad (A2)$$

where

$$e_Q^{(2)} = \sum k_i (q_i/s_Q)^2 \qquad (A3)$$

$$= -|k_0|(q_0/s_Q)^2 + \sum_{i>0} |k_i|(q_i/s_Q)^2 \qquad (A4)$$

As the point Q moves toward T along the reaction path (call it p) shown in Figure 3 the quantity $e_Q^{(2)}$ approaches a definite limit $e_T^{(2)}$. This limit is the (vertical) curvature of the surface at T in the direction of the reaction path. Since E_T is a proper maximum on the reaction we are guaranteed that $e_T^{(2)}$ is nonpositive. We will in fact take it to be negative:

$$e_Q^{(2)} \xrightarrow[Q \to T]{} e_T^{(2)} < 0; \, Q \in p \qquad (A5)$$

The reason is that a path of zero curvature (this would be tangent to the contours $E = E_T$) can always be lowered to a path of negative curvature (a path between the contours) as long as k_0 does not vanish. (We omit the proof of this point.)

Since $e_Q{}^{(2)}$ approaches $e_T{}^{(2)}$ as Q moves along p toward T and since E_Q approaches zero as s_Q approaches zero along any path it follows that the hypercircle C can be assigned a sufficiently small but nonzero radius that

$$\left| e_Q{}^{(2)} - e_T{}^{(2)} \right| < \tfrac{1}{2} \left| e_T{}^{(2)} \right| \tag{A6}$$

for all Q on p that lie inside C, and such that

$$\left| \epsilon_Q \right| < \tfrac{1}{2} \left| e_T{}^{(2)} \right| \tag{A7}$$

for any point within C whether it lies on p or not.

Now let X be a point on the line joining A to B. We wish to show that

$$E_X - E_T < 0 \tag{A8}$$

for all X. Since $e_X{}^{(2)} \le e_A{}^{(2)}$ it follows that

$$E_X - E_T \le (e_A{}^{(2)} + \epsilon_X) s_X{}^2 \le \{ e_T{}^{(2)} +$$
$$\left| e_T{}^{(2)} - e_A{}^{(2)} \right| + \left| \epsilon_X \right| \} s_X{}^2 \tag{A9}$$

The desired result (A8) follows from (A9) after the introduction of the inequalities (A6) and (A7). This completes the argument.

References and Notes

(1) (a) Canisius College; (b) State University of New York at Buffalo.
(2) (a) J. H. Murrell and K. J. Laidler, Trans. Faraday Soc., 64, 371 (1968); (b) J. H. Murrell and G. L. Pratt, ibid., 66, 1680 (1970).
(3) A preliminary account of this work has appeared in the form of a communication. See J. W. McIver, Jr., and R. E. Stanton, J. Am. Chem. Soc., 94, 8618 (1972).
(4) J. W. McIver, Jr., J. Am. Chem. Soc., 94, 4782 (1972).
(5) L. Salem, Acc. Chem. Res., 4, 322 (1971); L. Salem, J. Durup, C. Bergeron, D. Cazes, X. Chapuisat, and H. Kagan, J. Am. Chem. Soc., 92, 4472 (1970).
(6) (a) J. W. McIver, Jr., and A. Komornicki, Chem. Phys. Lett., 10, 303 (1971); (b) J. Am. Chem. Soc., 94, 2625 (1972).
(7) J. N. Murrell, J. Chem. Soc., Chem. Commun., 1044 (1972).
(8) It should be recognized, however, that an infinitesimal displacement will not be sufficient to move the system from a stationary point of forbidden symmetry to a stationary point of allowed symmetry.
(9) D. S. Schonland, "Molecular Symmetry", Van Nostrand, New York, N.Y., 1965, pp 117 and 118.
(10) R. McWeeny, "Symmetry, An Introduction to Group Theory and Its Applications", Macmillan, New York, N.Y., 1963, pp 144 and 145.
(11) (a) R. S. Berry, Rev. Mod. Phys., 32, 447 (1960); (b) P. J. Hay and W. A. Goddard, Chem. Phys. Lett., 14, 46 (1972). See also J. S. Wright, Can. J. Chem., 51, 139 (1973).
(12) Reference 10, pp 145 and 146.
(13) Reference 10, pp 111 and 112. The relevant theorem is given in eq 5.2.2. The criterion stated above follows from this theorem once one notices that no unitary transformation can convert a nonunitary representation of a group into a unitary representation.
(14) The rejection of a "transition state" takes place when one proves the existence of a lower energy path from reactants to products. The existence of this path is independent of the coordinate system used to describe it.
(15) V. Heine, "Group Theory in Quantum Mechanics", Pergamon Press, New York, N.Y., 1960, pp 234 and 235.
(16) E.g., I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, J. Chem. Phys., 48, 2700 (1968); H. Conroy and B. L. Bruner, ibid., 42, 4047 (1965); R. N. Porter and M. Karplus, ibid., 40, 1105 (1964); J. D. Hirschfelder, ibid., 6, 795 (1938).
(17) This conclusion is not quite trivial. There is no problem when one assumes that the apex atom is bound in both the reactant and product states. The analysis is more complex if the atom labeled H_a in the text occupies the apex position. One can then show from theorem IV that the isosceles transition state is allowed only if it is one of a pair joining reactant and product through a metastable intermediate. [We omit the detailed proof since it would trespass on later portions of this paper.] Since equilateral H_3, the only plausible intermediate, has a Jahn–Teller instability one can for all practical purposes treat the transition state as forbidden. See H. Eyring, H. Gershinowitz, and C. E. Sun, J. Chem. Phys., 3, 786 (1935), for an interesting confirmation of this point.
(18) S. H. Bauer and E. Ossa, J. Chem. Phys., 45, 434 (1966); A. Burcat and A. Lifshitz, ibid., 47, 3079 (1967).
(19) C. W. Wilson, Jr., and W. A. Goddard III, J. Chem. Phys., 51, 716 (1969).
(20) J. P. Chesick, J. Am. Chem. Soc., 85, 2720 (1963).
(21) W. von E. Doering and H. D. Roth, Tetrahedron, 26, 2825 (1970).
(22) W. T. Borden, Tetrahedron Lett., 259 (1967). See also M. J. S. Dewar and J. D. Wasson, J. Am. Chem. Soc., 93, 3081 (1971).
(23) W.-D. Stohrer and R. Hoffmann, J. Am. Chem. Soc., 94, 1661 (1972).
(24) These calculations made use of the program OPTMO (Program 217, Quantum Chemistry Program Exchange, Indiana University, 1972) written by A. Komornicki.
(25) N. Calderon, Acc. Chem. Res., 5, 127 (1972).
(26) M. Henchman and R. Wolfgang, J. Am. Chem. Soc., 83, 2991 (1961); G. F. Palino and F. S. Rowland, J. Phys. Chem., 75, 1299 (1971).
(27) R. E. Weston and S. Ehrenson, Chem. Phys. Lett., 9, 351 (1971).
(28) K. Morokuma and R. E. Davis, J. Am. Chem. Soc., 94, 1060 (1972).
(29) S. Ehrenson and M. D. Newton, Chem. Phys. Lett., 13, 24 (1972).
(30) A. Komornicki and J. W. McIver, Jr., J. Am. Chem. Soc., 94, 4782 (1972).
(31) R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 2511 (1965).
(32) W. von E. Doering and W. R. Roth, Tetrahedron, 18, 67 (1962).
(33) M. J. Goldstein and M. S. Benzon, J. Am. Chem. Soc., 94, 7149 (1972).
(34) A. Komornicki and J. W. McIver, Jr., to be published.
(35) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955, p 338.

The Qualitative Behavior of Vibrational Excitation in Polyatomic Molecules

Yves Jean, Xavier Chapuisat, and Lionel Salem*

Contribution from the Laboratoire de Chimie Théorique, Université de Paris-Sud, Centre d'Orsay, 91405 Orsay, France. Received October 21, 1974

Abstract. The vibrational excitation of polyatomic molecules by an atomic collider is studied in a simple static model (zero impact parameter, no rotational excitation). A general expression is derived for the external force F_i acting on the normal coordinate Q_i of the molecule. The behavior of F_i with angle(s) of approach is determined. Excitation of any of the three vibrational modes of a symmetric linear triatomic molecule XY_2 is shown to involve a nontrivial blind angle, for which $F_i = 0$ and vibrational excitation vanishes. The same is true for the A' mode (two blind angles) and one E' mode (one blind angle) of an equilateral symmetric triangular molecule X_3 approached in a plane perpendicular to the molecular plane. The theoretical and experimental implications on vibrational energy transfer are discussed.

The primary microscopic event in almost any reaction is that where the reactant acquires vibrational, rotational, and translational energy through collision with other molecules in the reactant vessel (whether they be other identical molecules, reactant partners, or solvent molecules). The greater part of the energy is acquired via vibrational excitation.

The collisional excitation of vibrations in a polyatomic molecule by an external atom is an extremely complex problem. The quantitative transition probabilities into the different sublevels of the various vibrational modes of the molecule depend on a vast number of factors:[2] (a) static factors such as the intermolecular potential function, and