rapidly when a 500-W incandescent lamp without filters was employed as a light source. It is believed that the process using fined application in photography will be useful and further examination along this line (including the preparation of the photosensitive plates) is in progress.

Structure of Transition States in Organic Reactions. General Theory and an Application to the Cyclobutene–Butadiene Isomerization Using a Semiempirical Molecular Orbital Method

James W. McIver, Jr.,* and Andrew Komornicki

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214.
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Abstract: A method for locating and identifying transition states for systems with many degrees of freedom is described. The principle feature of the method is the location of saddle points on the potential energy surface by the employment of a generalized least-squares technique to minimize the Euclidian norm of the gradient of the potential energy function. For semiempirical molecular orbital methods the technique is relatively economical to use, thus permitting a variety of organic reactions to be studied. As an example, the transition state for the cyclobutene–butadiene isomerization is calculated using the MINDO/2 molecular orbital method. The results of this study are somewhat unexpected.

A detailed understanding of the dynamics and stereochemistry of organic reactions requires, above all, a knowledge of the many-dimensional potential energy surface. The very dimensionality of this surface, however, precludes its evaluation for all but the simplest systems. The theoretical study of a reaction involving only four atoms, for example, would require a million evaluations of the potential energy function if only ten grid points for each degree of freedom are chosen. To reduce this problem to one of a tractable size, two general approaches have been employed. The first type of approach seeks to reduce the dimensionality of the surface by eliminating certain degrees of freedom. In many cases, for example, the length of carbon–hydrogen bonds can be assumed to remain relatively unchanged throughout the course of the reaction. Thus, the degrees of freedom corresponding to these C–H bond lengths can be eliminated from consideration. However, for most organic reactions, it is unlikely that the dimensionality can be sufficiently reduced to a manageable number of degrees of freedom without placing unrealistically severe constraints on the system. A related technique involves choosing one or two degrees of freedom as independent variables of the potential energy and to allow the system to relax by optimizing the remaining degrees of freedom for each value of the independent variables. This type of approach, however, is computationally expensive, and the resulting surface may very well fail to include the transition state. The second type of general approach involves consideration of all the degrees of freedom of the system but seeks only to locate certain chemically interesting points on the potential energy surface. For a one-step reaction, these points would be the local minima corresponding to the equilibrium geometries of reactants and products and a col or saddle point which separates these local minima. The lowest energy saddle point lying between two such local minima corresponds to the transition state or activated complex for the reaction. The calculation of equilibrium geometries is a relatively straightforward process. It involves only the minimization of the potential energy function with respect to the degrees of freedom of the molecule. Geometries of even moderately large organic molecules can be calculated relatively economically when semiempirical molecular orbital methods are used.[1] Certain types of transition states can also be located using energy-minimization techniques. In reactions for which the reactants and products are identical in structure, intermediate configurations can generally be found which are of a different symmetry. Minimizing the energy within this symmetry will lead to a stationary point which may be a transition state for the reaction. Well-known examples of this are the internal rotations of ethane and ethylene about the C–C bonds and the umbrella inversion of ammonia. Another example is that of the Cope rearrangement, which has been recently studied by Dewar and coworkers.[2] In the general case, however, transition states cannot be determined by minimizing the energy within a given symmetry so that alternative methods of seeking these points must be devised.

The purpose of this article is to describe a valid computational method of locating transition states on the potential energy surface and to apply the method to a simple organic reaction: the isomerization of cyclobutene to butadiene. The semiempirical MINDO/2 molecular orbital method[3] was used for this particular

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(2) A. Brown, M. J. S. Dewar, and W. W. Schoeller, *J. Amer. Chem. Soc.*, **92**, 5516 (1970).
(3) (a) M. J. S. Dewar and E. Haselbach, *ibid.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

example. In the following section we review the characteristics of a transition state and describe the method used to locate and identify it. The formal mathematical and computational aspects are given in the appendices.

The Location and Identification of Transition States

The notation used in this article is as follows: $E(q_1, q_2, \ldots, q_{3N})$ represents the potential energy function as being dependent upon the $3N$ Cartesian coordinates q_i of the N atoms of the system. It is convenient to refer to these coordinates as components of the column vector $\mathbf{q}$. The gradient of the potential energy function is denoted by $\mathbf{g}$, also a column vector. Its components are the partial derivatives of E with respect to each of the coordinates

$$g_i = \partial E(\mathbf{q})/\partial q_i \qquad i = 1, 2, \ldots, 3N \tag{1}$$

The matrix of second partial derivatives of the potential energy (the force constant matrix) is denoted by $\mathbf{A}$

$$\mathbf{A}_{ij} = \partial^2 E(\mathbf{q})/\partial q_i \partial q_j \tag{2}$$

We require that a point $\mathbf{q}^T$ which is a transition state for a reaction meet the following criteria.

(1) $\mathbf{q}^T$ *must be a stationary point.* That is, the gradient of E evaluated at $\mathbf{q}^T$ must be null

$$\mathbf{g}(\mathbf{q}^T) = 0$$

This condition guarantees the topological invariance of transition states in the sense that the above equation holds regardless of the coordinate system used.[4]

(2) *The force constant matrix* $\mathbf{A}^T$ *at the transition state must have one and only one negative eigenvalue.* The eigenvalues of $\mathbf{A}^T$ measure the curvature of the potential energy surface along each of the principal directions corresponding to the eigenvectors of $\mathbf{A}^T$. The requirement that $\mathbf{A}^T$ have a negative eigenvalue is necessary to characterize $\mathbf{q}^T$ as a saddle point. A local minimum in the region of the transition state would have no negative eigenvalue of the force constant matrix and might be labeled a "stable" or "long-lived" intermediate. If there is more than one negative eigenvalue, then it can be shown that a lower energy saddle point exists for which $\mathbf{A}^T$ does have only one negative eigenvalue.[4]

(3) $\mathbf{q}^T$ *must be the highest energy point on a continuous line connecting reactants and products.* This condition is only intended as a device for identifying the reactants and products that are associated with the transition state $\mathbf{q}^T$. In a single-step reaction, the line should be such that the energy along this line decreases monotonically from the transition state value to that of the reactants (or products). In a multistep reaction, the condition serves to identify $\mathbf{q}^T$ as the saddle point of highest energy. The line can, in principal, be constructed in any manner consistent with this condition, so that the line itself is rather arbitrary. In no way should it be interpreted as indicating the stereochemical course of the reaction, which can only be decided from dynamical considerations (although we do, of course, assume that various reactive trajectories will generally pass near the saddle point). A simple method of constructing the line would be to vary the coordinates linearly between their reactant (or product) values and their values at the transition state, and to test the condition by calculating the energy at a number of points along the line. This procedure, however, may not satisfy the condition, and could involve a number of trials, since different choices of a coordinate system would result in different lines. An alternative method might be to use the relaxation technique of Empedocles.[5] This method, when used in conjunction with variational wave functions, can give both an analytical expression for the line *and* the energy at any point on the line, features which could be very useful in connection with dynamical studies. For the present purpose of identifying reactants and products, however, we have found it convenient to simply minimize the energy using $\mathbf{q}^T$ as a starting point, the line being given by the points generated by the minimization. At the saddle point itself, the line must have a nonzero component along the direction of least (most negative) curvature. This direction, which is given as the eigenvector corresponding to the negative eigenvalue of $\mathbf{A}^T$, can be used to initiate the energy minimization: a step along this direction in one sense will lead to reactants, while a step in the opposite sense will lead to products. If the minimization does not converge on the reactants and/or products of interest, then the possibility of the reaction being multistep arises, and further investigation of the intermediate steps will be necessary.

(4) $\mathbf{q}^T$ *must be the lowest energy point which satisfies the above three conditions.* This is, in principle, the most difficult requirement to satisfy since it requires locating all points which satisfy the first three conditions. In practice it will be assumed that the lowest energy $\mathbf{q}^T$ found which satisfies the first three conditions will also satisfy the fourth provided that chemical intuition and such principles as the Woodward–Hoffmann rules[6] are not seriously violated.

The method we use to locate transition states simply involves finding points $\mathbf{q}$ which satisfy condition 1 and then to test them to see if they also satisfy conditions 2 and 3. Figure 1 is a contour map of a hypothetical two-dimensional potential energy surface (generated, in this case, as the product of two ellipses). It might be taken to schematically represent the surface for isomerization of a linear triatomic molecule from A—B═C to A═B—C, where the two interatomic distances r_{AB} and r_{BC} are the horizontal and vertical coordinates of the figure. The points marked R and P correspond to the reactants and products and the saddle point T represents the transition state. Figure 2 is a contour map of the Euclidian norm of the gradient of the potential function of Figure 1

$$\sigma(\mathbf{q}) = \sum_{i=1}^{3N} g_i^2(\mathbf{q}) \tag{3}$$

where the g_i's are the components of the gradient (eq 1). Two important points to note about this function are that it is always positive except at stationary points of E, in which case it is zero, and that it is a sum of squares. Thus, the points R, P, and T of Figure 1 are all local minima with $\sigma = 0$ on the surface of Figure 2. The importance of σ being a sum of squares of functions which is zero at local minima corresponding

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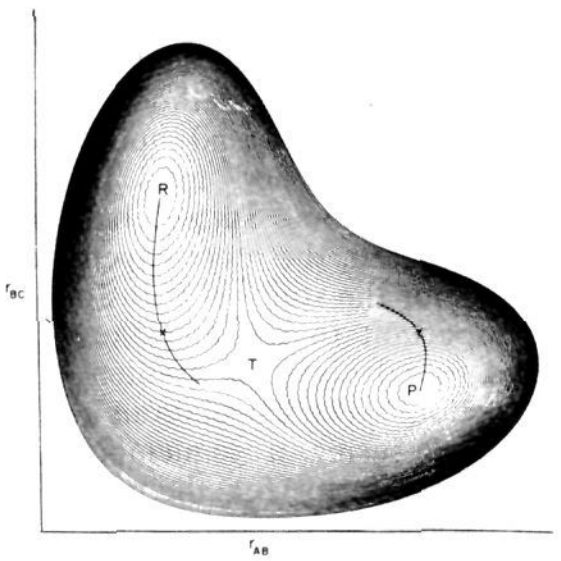

Figure 1. A hypothetical two-dimensional potential energy contour surface illustrating reactants (R), transition state (T), and products (P) and a "path" obtained by optimizing R_{AB} at each value of R_{BC}.

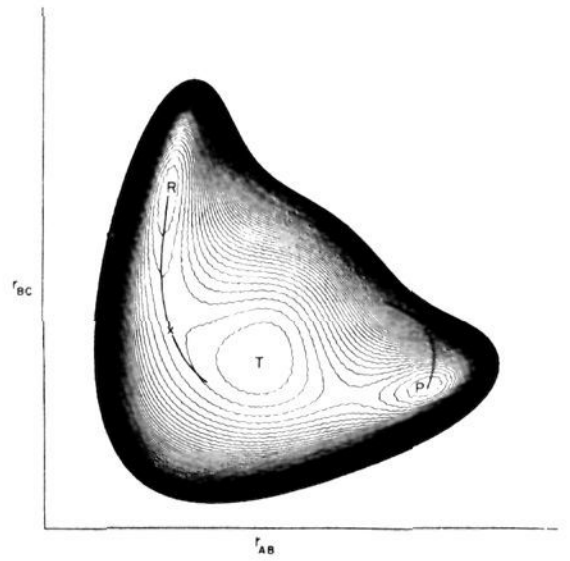

Figure 2. The contour surface obtained as the sum of the squares of the components of the gradient of the surface of Figure 1.

to stationary points of the potential energy is that the very powerful generalized least-squares methods can be used to locate these minima. The particular method we have used for this purpose is described in Appendix A.

The problem of selecting a starting geometry for the minimization of σ to a transition state is somewhat more difficult than the analogous problem of selecting an initial geometry for the minimization of E to an equilibrium geometry. In the first place, the minimization of the potential energy will always, by definition, lead to an equilibrium geometry, whereas the minimization of σ can lead to minima, maxima, or saddle points of E. Also, the σ surface may have additional local minima at which σ is not zero. Since the number of minima of σ is much larger than the number of minima of E, the valleys surrounding these minima will generally be smaller than the valleys surrounding the minima of the E surface. The consequence of this is that for a poor choice of initial geometry, the minimization of σ is less likely to lead to the correct local minimum than the minimization of E. Secondly, the rate of convergence of the minimization method will depend rather strongly on how well the initial geometry approximates the true minimum. For equilibrium geometry calculations, an initial geometry can often be taken as the experimental geometry. If this is not known, a good educated guess of the geometry can usually be constructed from an understanding of the nature of chemical bonding. The geometries of transition states, on the other hand, have not been measured directly by experiment, and the inherently unstable nature of the bonding of such species often renders guessing the structure difficult. In such situations the direct, but somewhat clumsy and unreliable, method described below may yield a point in the vicinity of the transition state.

Most reactions involve the breaking or stretching of at least one bond. It may be possible to "force" the reaction to proceed from reactants toward products by varying this bond in small increments from its reactant value to its product value and minimizing the energy with respect to the remaining degrees of freedom at each incremental value of the bond length. Alternatively, a bond angle or dihedral angle can be used. The only nonzero contribution to the Euclidian norm of the gradient at each point obtained by this process will be due to those components of the gradient which correspond to the bond being stretched or angle being bent. If this procedure is to lead to a point in the vicinity of the transition state, σ will initially increase, then pass through a maximum, and finally begin to decrease as the saddle point is approached. The remaining degrees of freedom which have been optimized should change *smoothly* from their reactant values toward their product values. Once the maximum σ is reached, the minimization of σ should lead to the saddle point. This procedure is illustrated in Figures 1 and 2 (which, of course, have been "rigged" for this purpose). The two paths indicated by the solid heavy lines are defined by the locus of points obtained by decreasing r_{BC} in small increments from the point R (the reactant) and optimizing r_{AB} at each increment of r_{BC}. (The same paths are obtained by increasing r_{BC} from the products region.) It is worth pointing out that in this case there is a substantial gap between the two paths and that neither path passes through the transition state. In the intermediate range of r_{BC}, there are two values of r_{AB} which will minimize the energy. If, in proceeding from reactants region, the lowest minimum energy value of r_{AB} is chosen, then at the point marked "X," r_{AB} will "jump" discontinuously to the point marked "Y." In many dimensions, however, it is likely that only a local minimum that is nearest to the previous minimum found will be obtained. If this is the case, then the "jump" in r_{AB} will occur at the end of the path leading from the reactants region. As seen in Figure 2, σ has passed through a maximum at the end of each path so that the minimization of σ should lead to the transition state. This, of course, will depend to a certain extent on the features of the particular minimization method used.

Although we have not yet encountered any difficulties, the procedure described above of "forcing" the reaction into the transition state region may very well fail in some cases. Also, the trial and error nature of selecting the "independent variable" in complicated reactions can lead to the consumption of large amounts of computer time. We are thus investigating alternative methods in an attempt to deal with this potentially serious problem.

Each point located by the procedure of first finding (or guessing) a point in the vicinity of a transition state

and then minimizing σ may satisfy only the first of the above conditions. It must be further tested to see that conditions 2 and 3 are also satisfied. This requires the eigenvalues and eigenvectors of the force constant matrix. The details of the method we use to estimate the force constants and also the harmonic vibrational frequencies, intensities, and normal modes will be given a future publication.[7] The main features of the method, which essentially involves a differencing of the gradient, are given in Appendix B.

Limitations of the Method

The above-described method of locating transition states is in principle applicable to any reaction for which the transition state is well defined by conditions 1–3 of the previous section. For example, the method would fail to locate a transition state that is at a cusp in the potential surface. As the cusp is traversed, the gradient will discontinously change so that there will not be a well-defined valley surrounding the transition state on the σ surface. Cusps of finite energy actually arise from the intersection of two (or more) potential surfaces. The wave function will thus be degenerate at the cusp. Cases in which this degeneracy is due to symmetry can be predicted by the Jahn–Teller theorem.[8] Examples of this would be the degenerate states of the square-planar and tetrahedral configurations of atoms which have been suggested as possible transition states

$$H_2 + D_2 \longrightarrow 2HD \qquad (3)$$

for reaction 3.[9] The intersection of potential surfaces is also known to exist in certain nonsymmetrical cases.[10] Since the definition of the potential energy function arises from the Born–Oppenheimer approximation, the breakdown of this approximation in the vicinity of surface intersections would seem to require a reexamination of the concept of a transition state for reactions involving a surface crossing.

In some cases, an apparent intersection of potential surfaces may appear as an artifact of the method used to calculate the potential energy. Reactions which are predicted to be thermally forbidden by the Woodward–Hoffmann rules necessarily involve a crossing of highest occupied and lowest vacant molecular orbital energy levels.[6] This in turn implies a crossing of potential surfaces calculated with a closed-shell single-determinant wave function. The resulting cusp could lead to the computational difficulties mentioned in the previous paragraph. Pople has recently shown that such cusps are the result of the limited flexibility of the wave function and that they do not appear either if configuration interaction is introduced or if the orbitals in the single-determinant wave function are allowed to become complex.[11] Thus the apparent limitation presented by surfaces involving this orbital crossing exists only for single-determinant wave functions in which the orbitals are restricted to be real.

The computational expense of obtaining the potential energy function and its gradient is potentially the most severe limitation of the method. The magnitude of this cost will largely depend upon the particular quantum mechanical method used to calculate the potential energy function. In general, the more reliable the method used, the more expensive the calculation will be. For the study of transition states, it is particularly important to consider the additional expense required to calculate the gradient of the potential energy function. The calculations reported in this article were made using a semiempirical molecular orbital method primarily for the reasons that such methods can be applied to fairly large molecules and that the additional expense of calculating the gradient is negligible.[1] Since it is clearly desirable to eventually apply the more sophisticated and reliable *ab initio* methods to the study of transition states, it is important to consider the types of methods that would be most economical for this purpose. In this respect, methods for which the Hellmann–Feynmann theorem is satisfied, such as the floating spherical Gaussian method of Frost,[12] deserve serious consideration, since here the gradient is simply obtained as the expectation value of a one-electron operator.

Application to the Cyclobutene–Butadiene Reaction

The method described above was applied to the ring opening of cyclobutene to butadiene. This reaction is a particularly simple example of an electrocyclic process and has been extensively studied both theoretically[13] and experimentally.[14] In the present study, the MINDO/2 molecular orbital method[3] was used to calculate the potential energy function and its gradient. We selected this particular semiempirical method because it is computationally economical and because it has been shown to simultaneously predict equilibrium geometries, heats of formation, and stretching force constants that are in reasonable agreement with experiment for a wide range of molecules.[3a,b] The parameters used are those reported in ref 3b.

As a first step in the study of this reaction, the equilibrium geometries of the reactants and products were calculated. The energy-minimization method described in ref 1 was used for this purpose. The calculated results for cyclobutene, which was optimized in C_{2v} symmetry, are given in Table I along with the experimental values obtained in a recent microwave study.[15] The atom numbering convention is given in Figure 3, which is an ORTEP[16] drawing of the calculated geometry. As seen in Table I, the MINDO/2 geometry is in reasonable agreement with experiment. The most serious discrepancies are the C–H bond lengths, which are predicted to be too long by about 0.1 Å; the C_1–C_4 bond length, which is too short by 0.05 Å;

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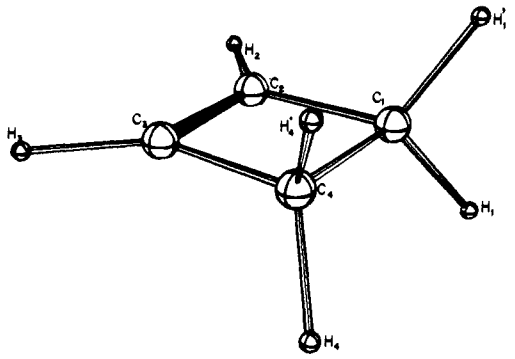

Figure 3. An ORTEP plot of the calculated structure of cyclobutene.

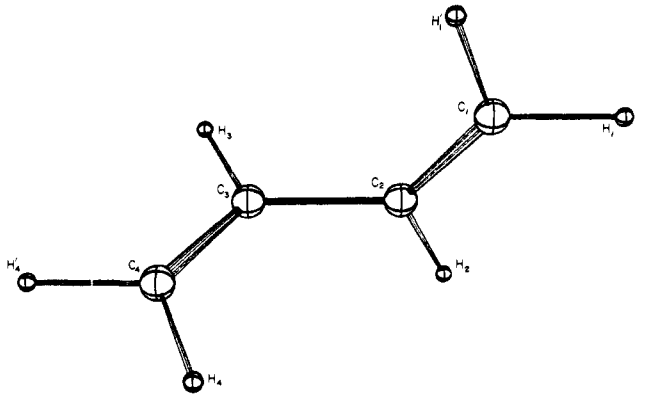

Figure 4. An ORTEP plot of the calculated structure of butadiene.

and the H_1-C_1-H_1' angle, which is about 7° too small. Dewar, *et al.*,[3a] have found that the MINDO/2 method is consistent in predicting C–H bond lengths to be too long by about 0.1 Å. We have found,

Table I. Experimental and Calculated Geometrical Parameters of Cyclobutene

Bond, Å[a]	Exptl[b]	Calcd	Angle, deg	Exptl[b]	Calcd
C_1–C_2	1.517	1.48	C_2–C_3–C_4	94.2	93.6
C_2–C_3	1.342	1.33	C_3–C_4–C_1	85.8	86.4
C_1–C_4	1.566	1.51	H_2–C_2–C_3	133.5	135.6
C_2–H_2	1.083	1.19	H_1–C_1–H_1	109.2	102.1
C_1–H_1	1.094	1.21	H_4–C_4–C_1	114.5	117.6
			α[c]	135.8	132.6

[a] Atom numbering refers to Figure 3. [b] Reference 14. [c] Angle of the C_1–C_4 bond with H_1–C_1–H_1' plane.

from the study of a number of hydrocarbons, that MINDO/2 also consistently predicts C–C single bonds to be too short by a few hundreths of an ångström and H–C–H bond angles to be too small by several degrees.[17]

The calculated geometry of *cis*-butadiene (optimized in C_{2v} symmetry) is given in Table II. Since the

Table II. Experimental and Calculated Geometrical Parameters of *cis*-, *trans*-, and *gauche*-Butadiene

	Exptl[b] trans	Calcd cis	Calcd trans	Calcd gauche
	Bond, Å[a]			
C_1–C_2	1.343	1.32	1.32	1.32
C_2–C_3	1.467	1.46	1.45	1.45
C–H(av)	1.094	1.20	1.20	1.20
	Angles, deg			
C_1–C_2–C_3	122.8	127.1	129.6	126.1
H_2–C_2–C_1	119.5	118.6	119.8	120.2
H_1–C_1–H_1'	121.0	110.8	110.6	110.7
	Dihedral Angles, deg			
C_1–C_2–C_3–C_4	180.0	0.0	180.0	86.9
H_1–C_1–C_2–H_2	0.0	0.0	0.0	0.7
H_1'–C_1–C_2–H_2	180.0	180.0	180.0	179.0

[a] Atom numbering refers to Figure 4. [b] Reference 17.

cis isomer has not been experimentally isolated,[18] we have also calculated the geometry of *trans*-butadiene (in C_{2h} symmetry) in order that a meaningful comparison with experiment could be made. As seen in Table II, the calculated geometries of the cis and trans isomers differ insignificantly, and the calculated geometry of *trans*-butadiene is in reasonable qualitative agreement with experiment. The discrepancies are of the same type noted in the previous paragraph. It might be pointed out that the difference in stability between the two isomers appears to be well accounted for by the MINDO/2 method. On the basis of heat capacity and other thermodynamic data, Aston has concluded that *trans*-butadiene is more stable than *cis*-butadiene by 2.4 kcal.[19] The MINDO/2 calculated value is 2.2 kcal.

We believe that the calculated butadiene results of the previous paragraph should be viewed with a certain amount of caution, however, since according to MINDO/2, both the cis and trans isomers are unstable relative to the structure shown in Figure 4. This geometry has C_2 symmetry, approximately perpendicular vinyl groups, and an energy 1.9 kcal below that calculated for the trans structure, but otherwise agrees with both the cis and trans isomers, as can be seen from Table II. Butadiene is almost certainly most stable in the trans configuration, even in the gas phase.[18] It is interesting to note, however, that hexafluorobutadiene is very likely nonplanar.[20] It would thus appear in this case that MINDO/2, as currently parametrized, either overestimates nonbonded repulsion energies, underestimates π-electron delocalization energies, or both.

Once the optimum geometries of the reactant and product were determined, the C_1–C_4 bond of cyclobutene was stretched in 0.05-Å increments and the energy was minimized with respect to all of the remaining degrees of freedom at each incremental value of the C_1–C_4 bond. (It was also necessary to initially destroy the C_{2v} symmetry by moving the methylene hydrogens because the minimization method would otherwise retain this symmetry.[1]) Until a C_1–C_4 bond length of about 2.2 Å was reached, the structures obtained by the minimization resembled that of cyclobutene with the methylene hydrogens slightly twisted in a conrotatory manner. Further stretching of the C_1–C_4 bond resulted in a structure closely resembling that of butadiene. This apparent discontinuity is accounted for by the discussion in an earlier section.

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Table III. Calculated Geometrical Parameters of the Transition State[a]

Bond, Å		Angle, deg		Dihedral angle, deg		Angle with a plane,[b] deg	
C_1–C_2	1.36	C_1–C_2–C_3	102.3	C_1–C_2–C_3–C_4	26.3	(H_4–C_4–H_4')–C_1	133.8
C_2–C_3	1.40	C_2–C_3–C_4	102.3	H_2–C_2–C_3–H_3	54.3	(C_3–C_2–C_1)–H_2	100.9
C_3–C_4	1.36	C_3–C_4–C_1	74.4	H_2–C_2–C_1–H_1	14.7	(H_4–C_4–H_4')–C_3	107.0
C_1–C_4	2.07	H_2–C_2–C_1	127.2	H_2–C_2–C_1–H_1'	140.6		
H_1–C_1	1.20	H_2–C_2–C_3	128.8				
H_2–C_2	1.20	H_1–C_1–H_1'	106.5				
H_3–C_3	1.20	H_4–C_4–C_1	84.6				
H_4–C_4	1.20	H_4'–C_4–C_1	135.4				
		H_4–C_4–C_3	127.4				
		H_4'–C_4–C_3	122.4				

[a] Atom numbering refers to Figure 5. [b] (A–B–C)–D refers to the angle between bond B–D and the plane defined by atoms A, B, and C.

The sum of squares of the components of the gradient, σ, was monitored throughout this process. It was initially zero at the reactants, and it passed through a maximum at a C_1–C_4 distance of about 2 Å. This indicated that the least-squares minimization would lead to a transition state provided that the initial geometry used was chosen to be one of the structures obtained between 2 and 2.2 Å of the C_1–C_4 bond length. An optimum geometry obtained with this bond length slightly less than 2.2 Å used as the initial geometry, and the least-squares minimization was carried out until σ was less than 10^{-3} atomic unit. This ensured that the magnitude of the largest component of the gradient was less than 10^{-4} au (hartree bohr^{-1}) which, in this case, indicated that the Cartesian coordinates of the transition state were determined within 0.01 Å.[1]

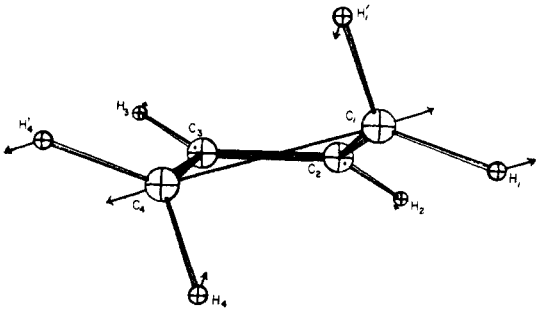

Figure 5. An ORTEP plot of the calculated structure of the transition state.

The small magnitude of the gradient for the structure obtained by the minimization of σ indicates that condition 1 stated earlier was satisfied. In order that this structure could be properly identified as a transition state satisfying conditions 2 and 3, the force constant matrix A was evaluated using the method described in Appendix B. One point on each side of the transition state for each Cartesian coordinate was chosen using an increment of 0.012 Å. This increment was selected on the basis of an extensive error analysis performed on the calculated force constants in smaller hydrocarbons.[7] This procedure resulted in the largest magnitude element of asymmetry of the force constant matrix and the magnitudes of the pure rotational and translational eigenvalues being less than 0.0001 au (hartree bohr^{-2}). On the basis of symmetry, the error in the normalized eigenvectors was less than 0.01. Thus, for the present purposes, we judged the error in the numerical calculation of the force constants to be acceptable. The resulting distribution of eigenvalues of the force constant matrix included a single negative eigenvalue of -0.0876 au, six zero eigenvalues corresponding to pure translations and rotations, and 23 positive eigenvalues ranging from 0.0070 to 1.2659 au.

The geometrical parameters of the calculated transition state are given in Table III. The structure has C_2 symmetry. Figure 5 shows an ORTEP view of this structure along the C_2 axis. The arrows indicate the relative displacements of each atom along the direction of most negative curvature leading toward butadiene. As seen in the figure, this direction is totally symmetric. Starting with the geometry of the transition state and an initial step along this direction, the minimization of the energy led to the butadiene structure of Figure 4. (This is how we actually discovered this butadiene structure.)

The nonplanarity of the carbon skeleton of the transition state is not surprising in view of the calculated butadiene structure. We speculate, however, that the true transition state might actually be more appropriate for the cyclobutene–*trans*-butadiene (rather than *cis*-butadiene) reaction. This, of course, can only be tested by calculations with a method more reliable than MINDO/2. The methylene groups are oriented in a conrotatory manner in accordance with the Woodward–Hoffmann rules.[13a] From Figure 4, however, it would appear that they are oriented in this sense in the calculated product as well. Although quantitative measures are somewhat arbitrary, it seems that the structure of the calculated transition state more closely resembles butadiene than cyclobutene. Thus, the relatively small H_1–C_1–C_2–H_2 dihedral angle of 14° and the C_1–C_2 bond length of 1.36 Å indicate that this fragment and its symmetry equivalent closely resemble the vinyl units in butadiene. Other geometrical parameters, such as the C_2–C_3 bond length and the H–C–H bond angles, are intermediate between their values for reactant and product. The C–H bond lengths are calculated to be the same in all three species.

The energetics of this reaction are poorly accounted for by the MINDO/2 calculations. The forward reaction (cyclobutene → butadiene) is known to be exothermic by 8.8–8.9 kcal,[21] whereas MINDO/2 predicts the reaction to be *endothermic* by 20.5 kcal. The experimentally determined activation energy from the

(21) This estimate is based on the recent determination of the heat of formation of cyclobutene by Wiberg [K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968)], and the heat of formation of *cis*-butadiene corrected by the difference in stability between the cis and trans isomers.

pyrolysis of cyclobutene is 32.2 kcal.[14a] The calculated value of the barrier height is 49.5 kcal. There are a number of possible reasons for these discrepancies. In the first place, the MINDO/2 method, as currently parametrized, is known to consistently underestimate the energy of strained cyclic hydrocarbons.[3b] This would account for the discrepancy in the heat of reaction. The tendency to underestimate strain energy should also manifest itself for the calculated transition state, so that MINDO/2 would be expected to underestimate the barrier height for the reverse reaction, which it does. It is interesting to note that other zero-differential-overlap methods also tend to favor formation of ring systems in preference to their acyclic analogs.[22] A second possible source of error lies in the fact that the MINDO/2 method, although highly semiempirical, is cast in the framework of single-determinent molecular orbital theory for closed shells. Although correlation effects can be expected to cancel in the enthalpies of certain reactions,[23] it seems likely that they could be important in transition states which involve partially broken bonds. In their extensive *ab initio* study of the cyclobutene–*cis*-butadiene reaction, Hsu, Buenker, and Peyerimhoff[13c] found that correlation effects were indeed important in the region of the partially broken C_1–C_4 bond. A third possible source of error arises from the fact that the activation energy and the potential barrier height are not the same quantity.[24] This, however, is undoubtedly unimportant in the present case compared to the above two sources of error. In view of the large discrepancy between the calculated and observed energies, we would also consider zero-point vibrational corrections to be unimportant here. Finally, we must recognize the possibility that the lowest energy transition state for this reaction was not found, *i.e.*, that condition 4 was not satisfied. However, we find it difficult to conceive of a type of structure for a transition state that is radically different from the one found and which would still obey the Woodward–Hoffmann rules.

Finally, it is interesting, although perhaps not significant, that the *calculated* results are in accord with the Hammond postulate.[25] This postulate essentially states that the structure of the transition state will resemble the product more closely than the reactant for endothermic processes and that the converse is true for exothermic reactions. Of course, if this postulate is generally correct, then some doubt would be cast on the MINDO/2 results for the structure of the transition state since the reaction is, in reality, exothermic.

Conclusions

The method described in this article is both conceptually simple and quite generally applicable to the study of transition states. Its only unique feature is that attention is focused on the gradient of the potential energy rather than the potential energy function itself. The economic feasibility of using such a method will depend on such factors as the computing resources available, the size of the system studied, and the method used to calculate the potential energy function and its gradient. In this latter respect, the use of semiempirical methods appears to be most promising. For example, the entire calculation reported in this article required only 86 min of CDC 6400 central processor time.[26] Dewar, *et al.*, have argued that a method must reliably predict geometries, force constants, and heats of formation in order that structures of transition states can also be reliably predicted.[3a] This in itself, however, is not a sufficient criterion for assessing the accuracy of such calculations by semiempirical methods. Since it is unlikely that the geometries of transition states will ever be determined experimentally, it is important that extensive *ab initio* calculations be performed on such species in order that the reliability of the semiempirical methods can be properly evaluated.

Although semiempirical methods such as MINDO/2 will undoubtedly provide useful information concerning some of the details of chemical tranformations, we do not believe that at present they are of sufficient reliability for kinetic studies. It is hoped, however, that the fact that equilibrium geometries, transition states, and force constants can easily be calculated with such methods would serve as a stimulus for their further development.

Acknowledgments. It is a pleasure to acknowledge many useful discussions with Professor Harry F. King. We also thank Mr. George Guzzardo for computational assistance. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research. Computer time was generously provided by the Computer Center of the State University of New York at Buffalo.

Appendix A. Least-Squares Minimization

We assume that point $\mathbf{q}^0$ in the vacinity of the transition state is known. Expanding $\sigma(\mathbf{q})$ in a Taylor series about $\mathbf{q}^0$ gives

$$\sigma(\mathbf{q}) = \sigma(\mathbf{q}^0) + (\mathbf{q} - \mathbf{q}^0)^\dagger \cdot \mathbf{V}^0 + \tfrac{1}{2}(\mathbf{q} - \mathbf{q}^0)^\dagger \mathbf{B}^0 (\mathbf{q} - \mathbf{q}^0) + \text{higher order terms} \quad \text{(A1)}$$

where $\mathbf{V}_0$ is a column vector whose elements are given as

$$V_i^0 = \left[\frac{\partial \sigma(\mathbf{q})}{\partial q_i}\right]_{\mathbf{q}=\mathbf{q}^0}$$

or, in vector notation

$$\mathbf{V}^0 = (\nabla\sigma)_{\mathbf{q}=\mathbf{q}_0} \quad \text{(A2)}$$

where ∇ is the gradient operator (a column vector). The elements of the matrix $\mathbf{B}$ are given as

$$B_{ij}^0 = \left[\frac{\partial^2 \sigma(\mathbf{q})}{\partial q_i \partial q_j}\right]_{q=q^0}$$

or

$$\mathbf{B}^0 = (\nabla\nabla^\dagger\sigma)_{q=q_0} \quad \text{(A3)}$$

(22) A. Streitwieser, Jr., P. C. Mowery, R. G. Jesaitis, and A. Lewis, *J. Amer. Chem. Soc.*, **92**, 6529 (1970).
(23) W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971), and references contained therein.
(24) M. Menzinger and R. Wolfgang, *Angew. Chem., Int. Ed. Engl.*, **8**, 438 (1969).
(25) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).
(26) The breakdown is: geometry of *cis*-butadiene, 6 min; *trans*-butadiene, 3 min; cyclobutene, 3 min; search for vicinity of transition state, 23 min; minimization of σ, 18 min; calculation of force constants of transition state, 20 min; and minimization of transition state to butadiene, 13 min.

The minimum point $\mathbf{q}^{min}$ must be a stationary point, so that

$$\nabla\sigma = \mathbf{0} = \mathbf{V}^0 + \mathbf{B}^0(\mathbf{q}^{min} - \mathbf{q}^0) + \text{higher order terms} \quad \text{(A4)}$$

from eq A1. If σ is a pure quadratic function of $\mathbf{q}$, that is, if the higher order terms of eq A1 and A4 are zero, then the minimum point $\mathbf{q}^{min}$ is obtained from eq A4 as

$$\mathbf{q}^{min} = \mathbf{q}^0 - (\mathbf{B}^0)^{-1}\mathbf{V}^0 \quad \text{(A5)}$$

provided that $\mathbf{B}^0$ is positive definite. Otherwise, $\mathbf{q}^{min}$ will be a saddle point or maximum. If σ is not a pure quadratic, then $\mathbf{q}^{min}$ will only be an approximation to the minumum. Equation A5 can then be solved iteratively by replacing $\mathbf{q}^0$ by $\mathbf{q}^{min}$, evaluating the derivatives in eq A2 and A3 at the new $\mathbf{q}^0$ and then substituting into eq A5 and solving for $\mathbf{q}^{min}$ again. This process can be repeated until $(\mathbf{B}^0)^{-1}\mathbf{V}^0 = 0$ within a specified accuracy. This method is known as the generalized Newton–Raphson method. It converges very rapidly in the vicinity of the minimum, but suffers from the disadvantage that both the first and second derivatives of σ are required.

For the location of transition states on the potential energy surface, $\sigma(\mathbf{q})$ is given by eq 3 as the sum of the squares of the components of the gradient of the potential energy

$$\sigma = \mathbf{g}^\dagger\mathbf{g} \quad \text{(A6)}$$

so that

$$\mathbf{V}^0 = \nabla\sigma = 2\mathbf{A}^\dagger\mathbf{g} \quad \text{(A7)}$$

and

$$\mathbf{B}^0 = \nabla\nabla^\dagger\sigma = 2(\mathbf{A}^\dagger\mathbf{A} + \mathbf{C}) \quad \text{(A8)}$$

where $\mathbf{A}$ is the force constant matrix defined in eq 2. Elements of the matrix $\mathbf{C}$ are given as

$$C_{ij} = \sum_K^{3N} g_K \frac{\partial^2 g_K}{\partial q_i \partial q_j} \quad \text{(A9)}$$

which involves the third derivatives of the potential energy. However, at the transition state $\mathbf{C} = 0$ since $\mathbf{g} = 0$, and for points near the transition state $\mathbf{C}$ will be expected to be small compared to $\mathbf{A}^\dagger\mathbf{A}$. Equation A8 can then be approximately written as

$$\mathbf{B}^0 \approx 2\mathbf{A}^\dagger\mathbf{A} \quad \text{(A10)}$$

Equation A10 is the central approximation of the generalized least-squares method. Its significance lies in the fact that the derivatives of $\mathbf{A}$ are no longer needed. Also $\mathbf{B}^0$ is guaranteed to be at least positive semidefinite, so that when it is used in the Newton–Raphson iterative scheme (eq A5) the method will always converge to a minimum point of σ.

The method, as it stands, requires evaluating the force constant matrix $\mathbf{A}$ at each point generated by eq A5. Powell, however, has devised a modification of the least-squares method which largely avoids the expense of calculating $\mathbf{A}$.[27] In Powell's procedure, a general set of linearly independent directions is used which are chosen initially to be the coordinates q_i themselves. The derivatives of $\mathbf{g}$ along these directions become the columns of $\mathbf{A}$ and are initially estimated by differences. By solving an equation similar to eq A5, a new direction is obtained which is used to replace one of the original directions. A new starting point is then determined by searching for a minimum along this new direction. This ensures convergence of the method and also provides an estimate of the derivative of each component of $\mathbf{g}$ along the new direction. These derivatives replace the appropriate column of $\mathbf{A}$ and the new $\mathbf{B}^0$ matrix is constructed using eq A10. The process is repeated until $\mathbf{g} = 0$ within a specified tolerance.

Since the inverse of $\mathbf{B}^0$ is required in eq A5, the method cannot tolerate linear dependencies of q_i. If the $3N$ Cartesian coordinates are used, there will be six linearly dependent directions, three corresponding to pure translation and three corresponding to pure rotation of the system as a whole. These can be eliminated by using six of the q_i's to define a molecule-fixed coordinate system, leaving $3N - 6$ linearly independent degrees of freedom for the minimization of σ. For example, the coordinate system can be chosen such that the first atom (atom number 1) lies on the origin, atom number 2 lies on the z axis, and atom number 3 (not collinear with atoms 1 or 2) lies in the xz plane. Thus $x_1 = y_1 = z_1 = x_2 = y_2 = y_3 = 0$ in this case, and these six coordinates can be eliminated from the list of the $3N$ q_i's in the minimization of σ. The components of the gradient corresponding to these six coordinates can also be eliminated, since, if there are no external forces on the system, they must be zero when the remaining $3N - 6$ components of the gradient are zero. However, our experience with Powell's method indicates that the convergence is dramatically improved when all of the components of the gradient are used. (This, of course, means that $\mathbf{A}$ will have $3N$ rows and $3N - 6$ columns; but $\mathbf{B}_0$ will remain square.) We have also found that the method will occasionally generate a matrix $\mathbf{B}^0$ which is singular and thus cannot be formally inverted. This "accidental" singularity is taken into account by performing the inversion of $\mathbf{B}^0$ in three steps: first by diagonalizing $\mathbf{B}^0$, inverting the eigenvalues, and then back-transforming these inverted eigenvalues with the eigenvectors of $\mathbf{B}^0$ to give $\mathbf{B}^{0-1}$. If one of the eigenvalues is zero (or very small), then the one-dimensional search of the Powell procedure is taken along the direction of the eigenvector of $\mathbf{B}^0$ corresponding to this zero eigenvalue.

Since equilibrium geometries can also be determined by minimizing σ, the least-squares method of Powell can be compared to geometry-optimization methods. We have found that this method is comparable in efficiency to the variable metric method we use to calculate equilibrium geometries,[1] the additional expense of the least-squares method being largely due to the initial estimate of the force constant matrix required.

Appendix B. Calculation of Force Constants

Since the force constants are just the second partial derivatives of the energy taken with respect to each nuclear displacement, they may be evaluated using perturbation theory. We have found it both convenient and computationally efficient to evaluate them

(27) M. J. D. Powell, *Comput. J.*, 7, 303 (1965).

numerically using the finite perturbation method,[28] which we review below.

It is clear from eq 2 that an element of the force constant matrix $\mathbf{A}^T$ at the transition state can be written as

$$A_{ij}{}^T = \left[\frac{\partial^2 E(\mathbf{q})}{\partial q_i \partial q_j}\right]_{\mathbf{q}=\mathbf{q}^T} = \left[\frac{\partial g_i(\mathbf{q})}{\partial q_j}\right]_{\mathbf{q}=\mathbf{q}^T} = \left[\frac{\partial g_j(\mathbf{q})}{\partial q_i}\right]_{\mathbf{q}=\mathbf{q}^T} \quad \text{(B1)}$$

Since in the methods we use, the entire vector $\mathbf{g}$ is obtained with the potential energy, it is convenient to consider one column of $\mathbf{A}^T$ at a time

$$\mathbf{A}_j{}^T = (\partial \mathbf{g}/\partial q_j)_{\mathbf{q}=\mathbf{q}^T} \quad \text{(B2)}$$

where $\mathbf{A}_j{}^T$ denotes the jth column of $\mathbf{A}^T$.

In the finite perturbation method, the derivatives in eq B2 are evaluated numerically using finite differences. First g is evaluated at several points symmetrically spaced about $\mathbf{g}^T$ and separated by a fixed increment h in q_j

$$\delta\mathbf{g}_m{}^0(j) = \mathbf{g}(q_1{}^T, q_2{}^T, \ldots, q_j{}^T + mh, \ldots, q_{3n}{}^T) \quad \text{(B3)}$$
$$m = -n, \ldots, -2, -1, 0, 1, 2, \ldots, n$$

where $n > 0$. The increment h is taken to be the same for all j. The derivative eq B2 is then approximated by using the differentiated Newton–Stirling formula[29]

$$h\mathbf{A}_j{}^T = \mu\delta\mathbf{g}_0(j) - \frac{\mu\delta\mathbf{g}_0{}^3(j)}{3!} + \ldots + \frac{(-1)^{n-1}(n-1)!^2}{(2n-1)!}\mu\delta\mathbf{g}_0{}^{2n-1}(j) \quad \text{(B4)}$$

where the mean differences $\mu\delta g_0{}^{2K-1}$ are defined as

$$\mu\delta\mathbf{g}_0{}^{2K+1}(j) = {}^1/_2(\delta\mathbf{g}_1{}^{2K}(j) - \delta\mathbf{g}_{-1}(j)^{2K}) \quad \text{(B5)}$$

The differences $\delta\mathbf{g}_m{}^{2K}(j)$ are calculated from the recursion formula

$$\delta\mathbf{g}_m{}^{2K}(j) = \delta\mathbf{g}_{m+1}{}^{2K-2} - 2\delta\mathbf{g}_m{}^{2K-2}(j) + \delta\mathbf{g}_{m-1}{}^{2K-2}(j) \quad \text{(B6)}$$

where $\delta\mathbf{g}_m{}^0(j)$ is given by eq B3.

The error in using eq B4 to estimate the derivatives will depend on the number of points n on either side of $q_j{}^T$ taken, the magnitude of h, and the accuracy to which $\mathbf{g}$ is calculated. For a given value of n, it has been shown that the magnitude of h can be chosen to minimize the error and also provide an estimate of its magnitude.[28] In the case of force constant calculations, there are two additional means of estimating the error which we have found to be quite reliable. The first is the degre of asymmetry of the force constant matrix. Since this matrix is calculated column by column, $A_{ij}{}^T$ will only be approximately equal to $A_{ji}{}^T$. Thus the largest element of the matrix $|A_{ij}{}^T - A_{ji}{}^T|$ is a rough estimate of the error. Secondly, if the $3N$ Cartesian coordinates are used, $\mathbf{A}^T$ will have six eigenvalues which are zero. The number of decimal places to which these eigenvalues are zero provides another estimate of the error. The corresponding eigenvectors can also be examined to see how accurately they correspond to pure translation and rotation and, if there is any symmetry in the system, the remaining eigenvectors can be examined to see how accurately they transform according to the appropriate irreducible representations.

An important factor which should not be overlooked is the computational expense involved. It is clearly desirable to minimize this expense as much as possible and still maintain a reasonable accuracy in the force constants. In principle, since $\mathbf{g}(\mathbf{q}^T) = \mathbf{0}$, $\mathbf{g}$ will be an odd function of q_j in the harmonic region of the potential surface near the transition state. Thus, from eq B3

$$\delta\mathbf{g}_m{}^0(j) = -\delta\mathbf{g}_{-m}{}^0(j) \quad \text{(B7)}$$

so that only the points for positive (or negative) m need be calculated. This should halve the computational expense of estimating the force constants. In practive we have found that in order that the transition state be located precisely enough to apply eq B7 it is necessary to spend more additional computer time in minimizing σ than what is saved by using eq B7, if sufficient accuracy in the force constants is to be obtained.

(28) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960 (1968).

(29) H. Jeffreys and B. S. Jeffreys, "Methods of Mathematical Physics," Cambridge University Press, Cambridge, England, 1946, p 277.