projectile ions are of minor importance for the total cross sections.

**2. Comparison with Thermal Ion Data.** Our data all refer to projectile ions having an average kinetic energy of about 50 eV. Extensive studies of thermal-ion charge transfer with atomic and diatomic projectile ions and diatomic targets have been carried out by Ferguson and coworkers[29] using a flowing-afterglow method and by Warneck[30] using photoionization mass spectrometry. Both workers conclude on the basis of their data that there is no correlation between the energy defect of the reaction and the charge-transfer cross section; *i.e.*, there are no pseudoresonance effects. As mentioned in the introduction, charge transfer may occur by complex formation at thermal ion energies and then resonance effects would not be expected. It is of interest, however, to examine this point in more detail by using a variety of projectile ions spanning a large RE range on the same target. Most thermal ion studies have compared the cross sections for the same ion on different targets.

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# Theoretical Determination of the Reaction Path in the Prototype Electrocyclic Transformation between Cyclobutene and *cis*-Butadiene. Thermochemical Process[1a]

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**Abstract:** A detailed study of the potential surfaces of the cyclobutene and *cis*-butadiene isomers is undertaken with the aim of determining the characteristics of the reaction (minimum energy) path followed by these systems in an electrocyclic transformation which is thermochemically induced. Nonempirical SCF and CI calculations using a large gaussian basis set are employed for this purpose and emphasis is placed upon the inherently nonlinear relationships which exist between the various geometrical quantities as they change from their respective equilibrium values in the two stable end products. As a result of this work it is demonstrated that a stepwise mechanism in which rotation of the methylene groups occurs only *after* the cyclobutene ring has been destroyed is much preferred to a linear procedure in which rotation and bond breaking occur simultaneously. Specifically, it is found that the energy barrier for CC stretch is approximately 1.1–1.2 eV, while that due to *pure* rotation at the optimum intermediate bond distance (4.49 bohrs) is only 0.85 eV; the total barrier for the reaction is thus found to be 0.6 eV above the experimental estimate for this quantity. In obtaining the various potential surfaces emphasis is placed upon the importance of configuration interaction in determining a reliable representation of the wave functions for various intermediate species, particularly for those corresponding to the disrotatory energy maximum and for structures in which the cyclobutene ring bond is partially destroyed. The stepwise mechanism found to be operative in this work indicates that the conrotatory mode is definitely preferred over the disrotatory, in agreement with experiment and with predictions emanating from the Woodward–Hoffmann rules; it is interesting, however, that in both cases quite symmetrical rotational potential curves are obtained. In addition it is found that for certain higher energy paths (involving different models for altering the various geometrical parameters) the disrotatory species is actually preferred, thereby clearly emphasizing the need for determining the *true* minimum-energy interconversion path in order to effect a reliable estimation of the relative stability of the two rotational modes.

The elucidation of the mechanism for electrocyclic reactions[2] is of great importance in theoretical chemistry because it illustrates the utility of the MO theory with regard to the understanding of dynamic processes, as well as for its more common applications in the area of static molecular properties. In the usual case an electrocyclic reaction involves a simultaneous breaking of a CC bond and the rotation of a pair of $CH_2$ groups through 90°; such a transformation takes its stereospecific character from the relative direction in which this rotation occurs, and on the basis of what has been described as the principle of conservation of orbital symmetry,[3] the stereospecific course of a large series of

(1) (a) Parts of this paper were presented at the Joint Conference of the Chemical Institute of Canada and the American Chemical Society, Toronto, May 1970; (b) University of Nebraska; (c) Johannes Gutenberg Universität.
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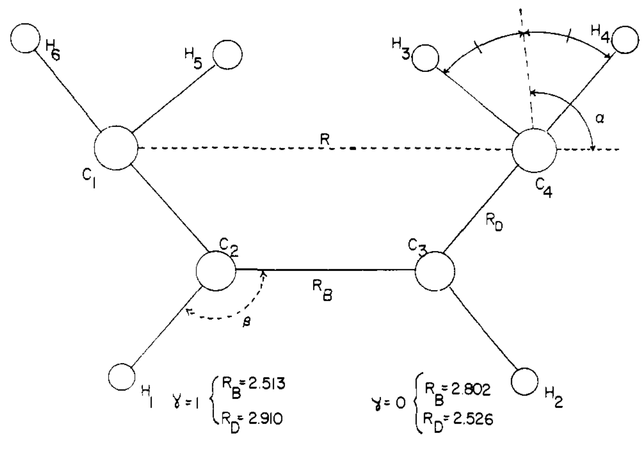


Figure 1. Definition of geometrical parameters for the $C_4H_6$ system.

concerted reactions has been successfully predicted. Originally Woodward and Hoffmann ascribed the origin of this pattern of behavior solely to symmetry characteristics of the highest occupied MO of the open-chain partner,[2] while shortly thereafter Longuet-Higgins and Abrahamson[4] presented a somewhat expanded argument in which the symmetry characteristics of all occupied MO's are taken into account.

Clearly, more information besides the symmetry rules is needed, however, before one can truly state that the reaction mechanism is understood. It is certainly of interest. for example, to determine whether the rotation, in the conrotatory or disrotatory mode,[2] occurs before, after, or during the bond-breaking process; this question seems particularly pertinent because of Hoffmann's finding that in the transformation between *cis*-butadiene and cyclobutene the opposite mode to that favored experimentally is predicted by EHT calculations when rotation is assumed to take place entirely within the *cis*-butadiene framework. More generally, it is obviously desirable to determine the true reaction path, since only then is it possible to calculate the activation energy for this transformation. Another reason for investigating this process in depth is that in the absence of such specific information there is considerable uncertainty as to the true underlying reasons explaining the applicability of the Woodward-Hoffmann rules for determining the stereospecific course in these reactions.

Feler[5] has previously reported some EHT calculations dealing with the reaction path in the isomerization of cyclobutene and butadiene; the work of Clark and Armstrong[6] which employs the *ab initio* SCF method for $C_3H_5^+$ and $C_3H_5^-$ is also a major step toward the determination of a generalized reaction path for electrocyclic transformations. The objective of the present work is to give a thorough examination of the possible mechanisms for electrocyclic reactions in order to deduce the potential surface corresponding to the reaction path. The method chosen employs *ab initio* SCF-MO calculations with large basis sets since such a treatment[7,8] has been successful in the past for similar studies, and the limits to which it may be considered to be adequate are well documented. At the same time it is well to take heed of the work of Longuet-Higgins and Abrahamson[4] and follow the SCF calculations up with a rather extensive CI treatment to take account of the possible changes in correlation energy for the various nuclear conformations encountered throughout the course of a given reaction.

Because of the difficulties accompanying the execution of calculations at this level, the relatively small $C_3H_5$ systems, allyl and cyclopropyl isomers, would seem to be the proper choice for the investigation, but it has been decided to consider instead the $C_4H_6$ systems, *cis*-butadiene and cyclobutene, principally because both of these molecules are well characterized with respect to their equilibrium nuclear geometries. From this experimental information it is possible to judge the success of the present method with respect to its description of the various potential surfaces of interest. Thus the present paper deals exclusively with the problem of defining the stereochemical course of the cyclobutene–*cis*-butadiene transformation; the method involves a rather straightforward attempt to calculate the minimum-energy path in the reaction. Moreover, the calculations to be discussed herein are concerned explicitly only with the thermal isomerization process, and consequently only the ground-state wave function of the various $C_4H_6$ conformations is considered. Subsequent communications in this series will then discuss what effect the reaction mechanism so deduced has upon the formulation of the qualitative rules for determining the stereospecific course for such reactions in general. In addition, a similarly quantitative treatment of the photochemical mechanism of electrocyclic transformations is in progress.

## Definition of Reaction Parameters and Basis Set

In the process of deducing the minimum-energy path in the transformation between the $C_4H_6$ isomers cyclobutene and *cis*-butadiene, it is necessary to take account of 24 free geometrical parameters (*i.e.*, the vibrational degrees of freedom). A full optimization of the geometry of the system at each point in the reaction, however, is quite impractical, and at the same time should not be at all necessary since the great majority of these parameters can be expected to change only slightly from certain equilibrium values as the reaction proceeds. In addition, it can safely be assumed—at least in the study of concerted mechanisms, which are the only processes to which one can reasonably attribute the observed stereochemical behavior—that a certain degree of symmetry is maintained throughout the course of the reaction, thereby causing a considerable reduction in the number of independent geometrical parameters. A diagram showing the $C_4H_6$ system in such a symmetrical conformation is given in Figure 1; all the geometrical parameters to be considered are defined therein.

A decision as to which of the independent geometrical parameters must be optimized explicitly and which can be held fixed throughout the course of the reaction is obviously aided by the experimental knowledge[9] of the

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(5) G. Feler, *Theor. Chim. Acta*, **12**, 412 (1968).
(6) (a) D. T. Clark and D. R. Armstrong, *ibid.*, **13**, 365 (1969); (b) *ibid.*, **14**, 370 (1969).
(7) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **51**, 2528 (1969).
(8) R. J. Buenker and S. D. Peyerimhoff, *ibid.*, **48**, 354 (1968).
(9) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. **18**, M109s (1965), for cyclobutene; A. R. H. Cole, G. M. Mohay, and G. A. Osborne, *Spectrochim. Acta, Part A*, **23** 909 (1967), for butadiene.

equilibrium geometries of the two stable isomers under consideration. Clearly the parameters which change the most as the reaction proceeds, namely the out-of-plane rotation angle $\theta$ of the $CH_2$ groups and the $C_1$–$C_4$ bond distance $R$, must receive careful consideration, while optimization of those which change only slightly, such as the various CH distances and $\angle$HCH for the methylene groups, is considerably less critical. Parameters which exhibit significant but not exceptionally large changes during the isomerization, such as the other CC bond distances $R_B$ (central bond) and $R_D$ (lateral bond), the angle $\alpha$ between the perpendicular bisector of $\angle$HCH and the $C_1$–$C_4$ bond $R$, and also the angle $HC_2C_3$ (referred to as $\beta$), should also be optimized, but it is hoped that in these cases the effect of the energy minimization is not very critical. The distances $R_B$ and $R_D$ can conveniently be defined in terms of an auxiliary parameter $\gamma$ varying continuously from 0 to 1, with the smaller value occurring when $R_B$ and $R_D$ are equal to their equilibrium values for *cis*-butadiene, the larger limit when these distances are those of equilibrium ground-state cyclobutene; for intermediate values $\gamma$ is the fraction of the total distance (between these respective pairs of equilibrium distances) by which $R_B$ and $R_D$ each differ from their respective magnitudes in *cis*-butadiene. Finally, the possibility of intermediate deformations, such as those leading to a nonplanar ring of carbons (described in terms of the angle $\varphi$ between $R_D$ and the plane formed by $C_1$, $C_2$, and $C_3$), should not be overlooked.

The minimization of these geometrical parameters is inherently nonlinear and thus even if the search could safely be narrowed to five or six independent species, the amount of labor involved in deducing the essential characteristics of the reaction path by a *straightforward* energy-minimization procedure would be formidable. It is therefore the aim of some preliminary investigations to define various auxiliary relationships between certain of the critical parameters in order to simplify the optimization procedure sufficiently to make it of practical utility.

A general procedure has thus been adopted whereby the $C_1$–$C_4$ distance $R$ and the methylene rotation angle $\theta$ are treated as the principal independent variables, while several less critical parameters are also varied but are not optimized as thoroughly. The methylene CH distances are held fixed in all nuclear conformations at 1.093 Å, the other CH distances at 1.086 Å, and $\angle$HCH of the methylene groups is assumed to be 114° throughout, roughly the average value of the equilibrium HCH angles in cyclobutene and butadiene; $\beta$ has an initial value of 120°. The optimization of the other geometrical quantities is then carried out by means of energy minimization.

The basis set used is the same as that employed previously for cyclobutadiene[8] and tetrahedrane[10] $C_4H_4$ isomer calculations and consists of ten s and five p gaussian lobe functions on each carbon as well as five s functions of the same type on each hydrogen, grouped in fixed linear combinations of three s and one p function on each of the heavy atoms and one s group on each of the hydrogens; thus 130 primitive gaussians are contracted to 30 grouped species. This basis is sufficient to afford a good approximation to the Hartree–Fock AO's of the constituent atoms of this system. For each $C_4H_6$ nuclear geometry care has been taken to calculate the lowest energy closed-shell state possible; a large series of open-shell states has also been treated for subsequent use in the investigation of the photochemical mechanism for this reaction. The different closed-shell states obtained by these calculations are also necessary in order to compare the present results with the state correlation diagrams introduced by Longuet-Higgins and Abrahamson.[4]

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## Preliminary SCF Potential Curves

**A. Planar and Perpendicular $C_4H_6$ Conformations.** Potential curves for $C_4H_6$ in various conformations described by several combinations of the aforementioned geometrical parameters (Table I) were then calculated using the SCF method, and the results are given in Figure 2. Only $\theta$ values of 0 and 90° are considered in this group of calculations, and $R$ is treated as the independent variable in each case. Comparison between the curves 90 A and 0 C shows that at $R$ = 2.9 bohrs, which corresponds to the approximate cyclobutene equilibrium $C_1$–$C_4$ distance, the energy increase for pure rotation of the methyl groups into the plane of the four carbons is extremely large, on the order of 400 kcal/mol. Rotation through 90° out of the molecular plane in the butadiene equilibrium structure is achieved with an increase of considerably less energy, but the difference in stability is still quite large (>100 kcal/mol). The reason that rotation of the $CH_2$ groups is so much more difficult in the cyclobutene form can be understood from consideration of steric repulsion factors; for small values of the $C_1$–$C_4$ bond distance (Figure 1) repulsion between the inner hydrogen atoms $H_3$ and $H_5$ is much greater for the planar conformation than for the perpendicular. As the $C_1$–$C_4$ distance increases this distinction between the two conformations clearly becomes less significant; thus it can be concluded that the methylene rotation can

**Table I.** Geometrical Data Corresponding to the Various $C_4H_6$ Potential Curves of Figure 2[a]

| $R$ | $\theta$[b] | $\gamma$ | $\alpha$ | $R$ | $\theta$ | $\gamma$ | $\alpha$ | $R$ | $\theta$ | $\gamma$ | $\alpha$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 90 A | | | | 90 B | | | | 90 C | | |
| 2.513 | 90 | 1 | 45 | 2.513 | 90 | 1 | 90 | | | | |
| 2.919 | 90 | 1 | 43 | 2.919 | 90 | 1 | 86 | | | | |
| 3.30 | 90 | 1 | 41.1 | 3.30 | 90 | 1 | 82.2 | | | | |
| 3.70 | 90 | 1 | 39.1 | 3.70 | 90 | 1 | 78.3 | 3.70 | 90 | 0 | 39.9 |
| 4.20 | 90 | 1 | 36.6 | | | | | 4.20 | 90 | 0 | 37 |
| 4.70 | 90 | 1 | 34 | | | | | 4.70 | 90 | 0 | 34 |
| 5.329 | 90 | 1 | 30.5 | | | | | 5.329 | 90 | 0 | 30 |
| | 0 A | | | | 0 B | | | | 0 C | | |
| | | | | | | | | 2.513 | 0 | 1 | 45 |
| | | | | | | | | 2.919 | 0 | 1 | 43 |
| | | | | | | | | 3.30 | 0 | 1 | 41.1 |
| 3.70 | 0 | 0 | 60 | 3.70 | 0 | 0 | 39.9 | 3.70 | 0 | 1 | 39.1 |
| 4.20 | 0 | 0 | 60 | 4.20 | 0 | 0 | 37 | 4.20 | 0 | 1 | 36.6 |
| 4.70 | 0 | 0 | 60 | 4.70 | 0 | 0 | 34 | 4.70 | 0 | 1 | 34 |
| 5.329 | 0 | 0 | 60 | 5.329 | 0 | 0 | 30 | 5.329 | 0 | 1 | 30.5 |

[a] $\varphi$ = 0° and $\beta$ = 120° for all conformations. The specific values for $\alpha$ are chosen in such a way that the bisector of $\angle H_3C_4H_4$ is collinear with either (a) the $C_3$–$C_4$ internuclear distance or (b) the bisector of $\angle C_1C_4C_3$. Throughout this paper, all distances are given in bohrs unless specified otherwise. [b] $\theta$ and $\alpha$ are in degrees.

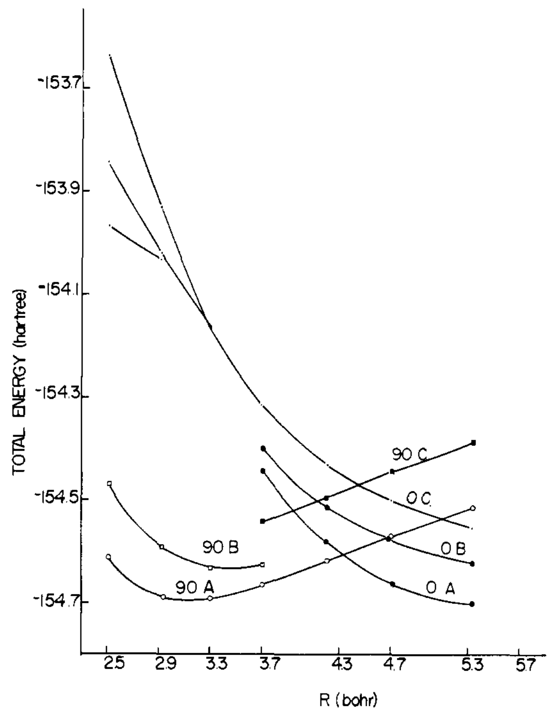


Figure 2. Potential curves for various $C_4H_6$ planar ($\theta = 0$) and perpendicular ($\theta = 90°$) nuclear conformations and different $R_B$, $R_D$, and $\alpha$ values, given in Table I. The different branches of the 0 C curve at small $R$ correspond to three different electronic configurations ($7 \times a_1^2$, $5 \times b_2^2$, $2 \times b_1^2$, $1 \times a_2^2$; $7 \times a_1^2$, $6 \times b_2^2$, $2 \times b_1^2$; $7 \times a_1^2$, $6 \times b_2^2$, $1 \times b_1^2$, $1 \times a_2^2$).

proceed only with the greatest difficulty as long as the carbon ring remains intact.

From Table II it is seen that for a given value of $R$ the $C_4H_6$ conformations corresponding to the curves 90 A and 90 C differ only in the parameter $\gamma$; as expected, the

**Table II.** Geometrical Data Corresponding to the Various $C_4H_6$ Potential Curves of Figure 3 ($\varphi = 0°$)[a]

| $R$, bohrs | 3.70 | 4.20 | 4.70 | 5.329 |
|---|---|---|---|---|
| $\alpha$, deg | 39.1 | 36.6 | 34 | 30.5 |
| $\theta$, deg | 45 | 45 | 45 | 45 |
| $\beta$, deg | 120 | 120 | 120 | 120 |

[a] Data corresponding to curves 90 A and 0 A, respectively, are given in Table I. The electronic configuration for the con- and dis-A states is $8 \times a^2$, $7 \times b^2$ and for the dis-B states $9 \times a^2$, $6 \times b^2$.

cyclobutene equilibrium values for $R_B$ and $R_D$ ($\gamma = 1$) are greatly preferred in the perpendicular arrangement of the methylene groups over the corresponding butadiene values ($\gamma = 0$). An important observation, however, is the fact that these two energy curves are very nearly parallel, thereby indicating that even at larger $C_1$–$C_4$ distances, for which the ring is effectively destroyed, the butadiene bond lengths ($R_B$, single bond and $R_D$, double) are very much less satisfactory than the cyclobutene counterparts ($R_B$, double and $R_D$, single). Furthermore, a similar comparison for 0° structures (0 B and 0 C) shows that (all other quantities being equal) $C_4H_6$ conformations with planar $CH_2$ groups prefer by a substantial margin the butadiene set of internal bond lengths ($\gamma = 0$) to those of cyclobutene ($\gamma = 1$), in contrast to the ordering found in the 90° case; again the two energy curves are very nearly parallel, indicating that the butadiene internal bond lengths are preferred equally well over those of cyclobutene when $\theta = 0°$, even after the $C_1$ $C_4$ distance $R$ has been shortened substantially. These findings taken together suggest a simple relationship between $\theta$ and $\gamma$: $\theta = 0°$ requires that $\gamma = 0$, while $\gamma = 1$ is preferred for $\theta = 90°$. To a first approximation the internal bond lengths $R_B$ and $R_D$ do not change with $R$ (at least for 0 and 90° $CH_2$ orientation) as long as the value of $\theta$ remains constant. It is interesting that such a result is quite consistent with the prescriptions of valence-bond theory which state that the relative orientation of attached methylene groups dictates the type of hybridization preferred by a carbon atom. It remains to be seen, however, if such a simple relationship is also operative for intermediate values of $\theta$.

The role of the in-plane bending angle $\alpha$ can also be seen from Figure 2. According to Table I the potential curves marked 90 A and 90 B differ only in their respective $\alpha$ values; for 90 A the perpendicular bisector of $\angle$HCH also bisects the angle between adjacent CC bonds, while for 90 B it is everywhere collinear with $R_D$. The former choice is much preferred to the latter according to Figure 2, and the energy difference between the curves in question varies rather strongly with $R$ in contrast to the behavior of the 90 A and 90 C curves discussed above. Similar trends are seen in the comparison of the curves 0 A and 0 B, which again differ at a given value of $R$ only in the parameter $\alpha$; it appears that the magnitude of this angle is much less critical for values of $R$ away from the equilibrium disstance. With regard to the objective of determining the reaction surface for the electrocyclic transformation of these two isomers, however, the most pertinent conclusion that can be reached from Figure 2 is that the optimization of $\alpha$ at each value of $R$ and $\theta$ is quite important in the energy minimization.

Neither of the other two subsidiary parameters which seem possibly important in determining the minimal energy surface, namely the angles $\beta$ and $\varphi$, differs much between end products of the reaction; $\varphi$ is 0° in both systems and the value of $\beta$ (around 120°) seems to be less critical since $\beta$ is related to the central carbon atoms, whereas the changes which occur as a result of the reaction take place in the neighborhood of the terminal carbons. More detailed consideration of these parameters will therefore be deferred at this point and attention will be turned instead to $C_4H_6$ conformations in which $\theta$ has an intermediate value between 0 and 90°.

**B. Conformation with $\theta = 45°$.** One question arising after consideration of the potential curves of Figure 2 concerns the relationship between $\theta$ and $\gamma$ and the other parameters for nuclear conformations in which the methylene groups are neither planar nor perpendicular. In this case it is necessary to distinguish between the conrotatory and disrotatory modes of transformation and, as has been pointed out by Longuet-Higgins and Abrahamson,[4] it is also important to consider *several* closed-shell states since in the disrotatory mode a change in electronic configuration of the ground state takes place as the reaction proceeds. Therefore a number of potential curves have been calculated for conformations in which $\theta$ is 45°, these results being given in Figure 3 along with the 0 A and 90 A energy curves of

Figure 2; values for the various other critical geometrical parameters corresponding to the curves in Figure 3 are contained in Table II. Four different sets of nuclear conformations are considered as a function of $R$ corresponding to all possible combinations of dis- and conrotatory modes and $\gamma = 0$ and 1; the disrotatory transformation species are necessarily calculated in two different electronic states.

From the disrotatory potential curves in Figure 3 it is again apparent that energy differences between conformations in this mode with $\gamma = 0$ and 1, respectively, are independent of $R$. The dis-A state correlates with the *cis*-butadiene ground state in $C_s$ symmetry (the common point group), and so it is not surprising that $\gamma = 0$ is the preferred value; in turn the dis-B state correlates with the cyclobutene ground state and again, as expected, prefers the cyclobutene internal bond lengths ($\gamma = 1$). In the conrotatory case one electronic state remains the ground state throughout the transformation, and this fact apparently produces an exception to the previously observed relationship between $\theta$ and $\gamma$; the two conrotatory curves with different $\gamma$ are not parallel, but cross at $R = 4.4$ bohrs. It is interesting, however, that again the $\gamma = 0$ curve is lower at large $R$, while the opposite is true at the smaller values of $R$ preferred by the cyclobutene ground state. The indication is that, even though the electronic configuration in terms of occupied molecular symmetry orbitals does not change in the conrotatory mode with increasing $R$, the constitution of the orbitals themselves does vary, and consequently an adjustment of the internal bond lengths is also effective in lowering the energy in this mode (but less so) as $R$ varies.

One of the most interesting details of Figure 3 is the fact that at a number of $R$ values the disrotatory curves are found to lie below those of the conrotatory mode. As mentioned in the introduction, Hoffmann found this situation to exist within the *cis*-butadiene carbon framework on the basis of EHT calculations; in the present *ab initio* work the lowest lying $\theta = 45°$ state at the equilibrium value for *cis*-butadiene ($R = 5.5$ bohrs) is found to be in the conrotatory mode (with $\gamma = 0$), but the corresponding disrotatory state is more stable than the other conrotatory conformation (with $\gamma = 1$). At rather small values of $R$ ($\leq 3.7$ bohrs) the calculations find the most stable state with $\theta = 45°$ to be disrotatory, however, in contrast to the experimental ordering observed in the *true* reaction path; thus the present SCF calculations confirm that the preference in a given system for one rotational mode over the other depends critically upon the *conditions accompanying* the rotation. Experimentally, of course, the only comparison which is pertinent is that between the two modes of rotation as encountered along the *true* reaction path, emphasizing again the necessity for determining the *minimum*-energy path for this electrocyclic transformation; only with this knowledge can a valid explanation for the observed stereospecifity of this process be obtained.

**C. General Details of the Reaction Path.** The most important result obtained from Figure 3 with regard to deducing the minimum-energy reaction path is clearly the fact that at *every* distance $R$ the lowest energy conformation calculated is either for a planar or a perpendicular conformation, that is, either for $\theta = 0$ or 90°. This observation is moreover entirely consistent with

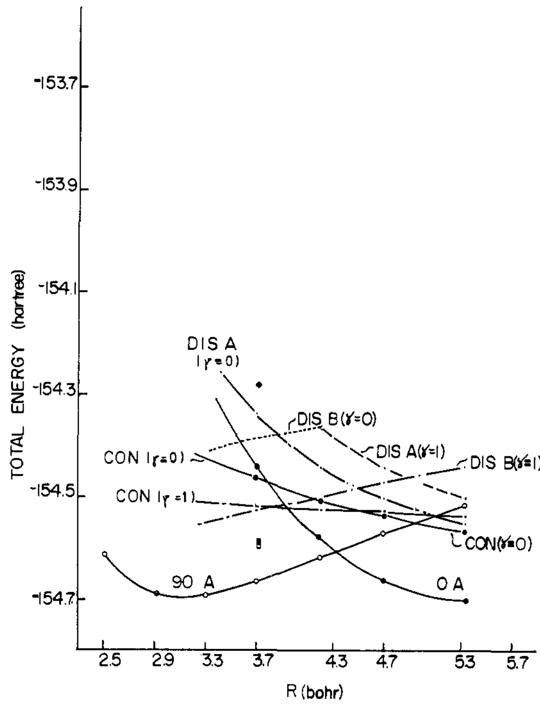


Figure 3. Potential curves for the most stable planar, perpendicular, and con- and disrotatory ($\theta = 45°$) $C_4H_6$ structures. Details of the geometrical parameters are given in Table II. The points □ and ■ give the energy of the con- and disrotatory structure with $R = 3.7$ bohrs, $\theta = 60°$, $\alpha = 49°$, and $\gamma = {}^2/_3$, corresponding to a linear transformation mechanism; ◆ is the energy of the disrotatory $8 \times a^2$, $7 \times b^2$ configuration.

the earlier conclusion drawn from Figure 2 that rotation of the methylene groups requires much more energy than altering the $C_1$–$C_4$ distance $R$. Clearly one could hope to lower the energy of the various 45° conformations by optimization of the other geometrical parameters, but it seems certain that this procedure could *not* be effective enough to overcome the large energy separation shown in the figure; in general, the lowest energy 45° conformation at a given $R$ is some 50 kcal/mol less stable than the corresponding planar or perpendicular structure.

Yet if it is true, as the calculations strongly suggest, that the most stable conformation at any $R$ is either a 0 or 90° species, the question still remains as to how the rotation actually takes place in the course of the reaction. The only reasonable answer seems to be that the methylene rotation takes place *entirely* at the distance $R$ (or at least over a very narrow range of $R$) for which the 0 and 90° conformations have approximately equal energy. The steepness of the 0 A and 90 A potential curves in this region suggests that the *maximum* in the lowest energy rotational surface for $R$ fixed at the crossing point (Figure 3) is lower than the energy value of the *higher* lying of these two curves for distances not far removed from this point; the large energy differences between the 0 and 90° conformations at most $R$ distances indeed make it quite unlikely that any variation of $\theta$ takes place until $R$ assumes a value near the crossing point.

Such a process is quite different from that envisioned by previous authors who generally have assumed that the rotation would take place simultaneously as $R$ varies from its respective equilibrium values for the two end

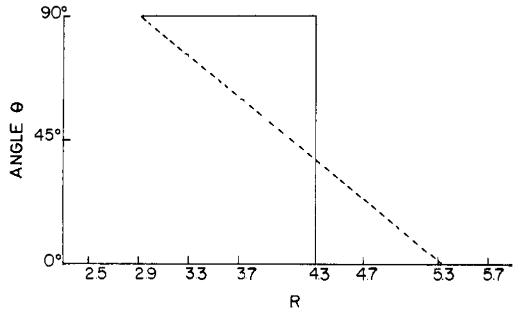


Figure 4. Schematic diagram illustrating the stepwise and the linear mechanisms, respectively, for an electrocyclic reaction as discussed in the text.

products.[11] A schematic representation of the two possible mechanisms is given in Figure 4, in which the *optimum* value for $\theta$ proposed in a given transformation is plotted as a function of $R$. From this viewpoint the mechanism suggested by the present calculations corresponds to a step function, with a break occurring somewhere in the neighborhood of $R = 4.3$ bohrs, whereas that assumed previously[6a] is simply a straight line.

In order to obtain a quantitative comparison of the present step mechanism with that of the linear process, several additional calculations have been carried out corresponding to conformations in which all geometrical parameters are varied linearly one-third of the way from their equilibrium cyclobutene values to those of equilibrium *cis*-butadiene; these structures thus correspond to a value of 60° for $\theta$ in the linear mechanism. The energy of the conrotatory conformation is thereupon found to be 42 kcal/mol *higher* than that of the corresponding 90° conformation at the same value of $R$; the corresponding disrotatory ground state lies 4 kcal/mol above the conrotatory species, a finding which, of course, is consistent with the observed stereospecificity of this transformation. This calculation again clearly indicates that it takes far more energy to alter the $C_1$–$C_4$ bond $R$ (destroy the ring in the cyclobutene structure) *with* simultaneous rotation of the $CH_2$ groups than *without*, and thus that the step-function mechanism is far more realistic than the linear process. Apparently, the ring bond connecting the two methylene groups of cyclobutene must be completely broken before rotation can proceed with a sufficiently small energy increase to be satisfactorily ascribed to a thermal process.

In this connection it is also interesting to consider the reaction path assumed by Feler[5] in the semiempirical treatment of the electrocyclic transformation between cyclobutene and *cis*-butadiene. In this case EHT calculations were used to find the most stable $C_4H_6$ conformation possible with $\theta$ values of 0, 45, and 90°; then a parabolic fit to the three optimal values for *each* geometrical parameter was calculated, and from these equations the best structural parameters for any other values of $\theta$ were obtained. Aside from certain questions about the reliability of the EHT method in obtaining the optimized geometries at the various values of $\theta$, the main criticism against this approach is again that it assumes without any justification that the rotation of the $CH_2$ groups takes place simultaneously as $R$ is varied. Thus Feler's assumed reaction path again calls for rotation before the cyclobutene ring bond has been destroyed and therefore corresponds to an unnecessarily high energetic route between the two end products of the transformation.

(11) Clark and Armstrong[6] in fact assumed in the calculation of the $C_3H_5^{\pm}$ electrocyclic reactions that $\theta$ (as well as the other geometrical parameters) varies linearly with $R$.

## Geometrically Optimized SCF Potential Curves

**A. Calculation of the Optimum Planar and Perpendicular Conformations.** Further attempts at obtaining the lowest $R$-stretch potential curves for $\theta = 0$ and 90° as well as the distance at which both conformations are equal in energy will continue to employ the results of Figure 2, namely that $\gamma = 0$ is optimum for the planar conformations while $\gamma = 1$ is best for the perpendicular structures. In addition, the data of Figure 2 indicate that the in-plane angle $\alpha$ must be optimized explicitly; the results of this procedure, again making exclusive use of SCF calculations, are given in Table III.[12]

Table III. Optimum Values of $\alpha$ Corresponding to the $C_4H_6$ Potential Curves of Figure 5[a]

| $R$ | $\alpha$ ($\theta$ = 90°), deg | $\alpha$ ($\theta$ = 0°), deg |
|---|---|---|
| 2.513 | 44* | |
| 2.919 | 44* | |
| 3.30 | 44.17 | |
| 3.70 | 44.61 | 55* |
| 4.20 | 44.36 | 57.10 |
| 4.70 | 44* | 59.97 |
| 5.329 | 44* | 57.69 |
| 5.70 | 44* | 60* |

[a] Values marked with an asterisk have been assumed and not determined by direct energy minimization.

The optimum values of $\alpha$ obtained from these calculations are generally around 45° for the perpendicular conformations and 60° for the planar; physically this result means that the perpendicular methylene groups prefer to be directed further away from the center of the system than do their planar counterparts. This effect can be rationalized in terms of valence-bond theory, since there is roughly $sp^3$ hybridization at $C_1$ and $C_4$ (and thus the bisectors of $\angle H_3C_4H_4$ and $\angle C_1C_4H_3$ are approximately collinear, as in propane, for example) for the perpendicular conformation, but $sp^2$ for the planar structures (in which case the bisector of $\angle$HCH is collinear with the adjacent CC double bond). The optimum $\alpha$ is relatively independent of $R$ for a given value of $\theta$, but it changes markedly when $\theta$ is altered; this result means that the $CH_2$ groups bend away from one another as they rotate out of the plane of the carbons.

It can be seen from Figure 5 that the calculated equilibrium distance $R$ for the cyclobutene structure is quite high (3.14 bohrs), 0.22 bohr above the experimental value for this quantity. By contrast the agreement between experimental (5.51 bohrs) and calculated (5.39 bohrs) equilibrium distance $R$ in *cis*-butadiene is quite good. A possible explanation for these discrepancies can be found in the fact that several other geometrical

(12) The total $C_4H_6$ energy has been calculated for from three to five different values of $\alpha$ at each value of $R$ listed in the table in order to find the optimum magnitude for this angle.

parameters have not as yet been optimized, particularly $\angle HC_2C_3$ ($\beta$); a value of 120° has been chosen for this quantity throughout the reaction. In retrospect, however, $\beta$ = 120° seems much more acceptable (on grounds of VB theory) for butadiene than for cyclobutene, and thus several additional calculations have been carried out to investigate the importance of optimizing this quantity. As a result it is found that optimization of $\beta$ can be important for small $R$, causing an energy lowering of about 0.01 hartree for the conformation at $R$ = 2.5 bohrs and $\theta$ = 90°; at smaller distances there is apparently a tendency for the inner CH bonds to assume a collinear position with the perpendicular bisector of $\angle C_1C_2C_3$ and thus the optimum value of $\beta$ increases to approximately 135° in the rectangular cyclobutene conformation. Optimization of $\beta$ is less critical for larger values of $R$, however, and $\beta$ = 120° remains optimum beyond $R$ = 3.0 bohrs for all practical purposes. When this effect is taken into account, a more satisfactory calculated equilibrium value of $R$ is obtained for the cyclobutene form (3.05 bohrs). While this result still represents an overestimation of the experimental quantity, it is well to note that SCF calculations at the level considered in this paper are well known to overestimate such bond distances by 0.10–0.15 bohr, so that there is good reason to believe that further geometrical optimization would not greatly improve the agreement found to this point.

The crossing of the 0 and 90° potential curves in Figure 5 occurs at $R_c$ = 4.32 bohrs. Optimization of $\beta$ should not change this value very much since such a procedure has almost no effect at intermediately large values of $R$, such as $R_c$. The energy barrier between the calculated 90° minimum (cyclobutene in equilibrium) and the crossing point value is quite high (53 kcal/mol) and does, of course, not yet include the energy increase due to actual rotation of the methylene groups (now assumed to occur at $R_c$). Optimization of other geometrical parameters again does not appear to be an effective method for decreasing this barrier; parameters such as CH distances, $\angle$HCH and $\beta$ have already been fixed close to their respective optimal values. Out-of-plane ring deformation could conceivably have some effect, but calculations on the interconversion of *cis*- and *trans*-butadiene indicate that such motion for the cis isomer occurs almost without energy change through the early stages of the rotation and only later on with high energy increase.[13] Thus it seems more likely that the explanation for the rather high energy barrier in Figure 4 lies in the nature of the method of calculation rather than in an inadequate treatment of the possible modes of nuclear motion. It seems quite plausible, for example, that at intermediate values of $R$ the valence electrons tend to become unpaired, *i.e.*, such conformations are less suitably represented as closed-shell systems than are the equilibrium products, and therefore the SCF method is less adequate for describing the system at $R_c$ than in either of the equilibrium forms.

**B. Rotational Potential Curves at $R_c$.** At the crossing point $R_c$ (Figure 5) the values for the various geometrical quantities of the 0 and 90° conformations differ in the majority of instances, as can be seen from Table IV, and therefore the methylene rotation at $R_c$

(13) B. Dumbacher, Ph.D. Thesis, Mainz, June 1970; also see L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, 92, 4786 (1970).

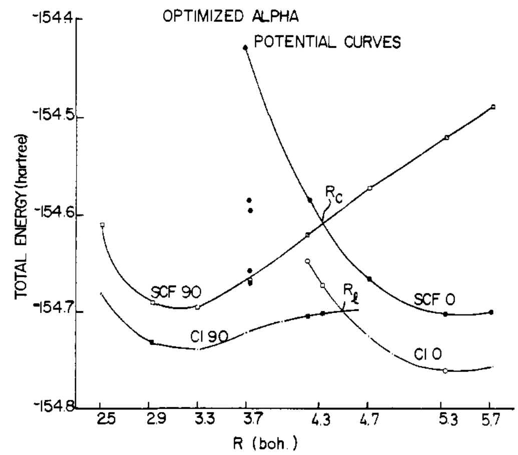


Figure 5. Potential curves for planar ($\theta$ = 0) and perpendicular $\theta$ = 90°) $C_4H_6$ conformations with optimum angle $\alpha$ (see Table III) obtained *via* SCF and CI calculations. The points (:) at $R$ = 3.7 bohrs correspond to the conrotatory (lower energy) and disrotatory structures, respectively, in which the geometrical parameters are scaled linearly ($\theta$ = 60°, $\gamma$ = 2/3, etc.); the lower pair is obtained from CI, the upper pair from the SCF treatment.

must obviously involve more than a continuous change in $\theta$. For the calculation of the angular potential curve at $R_c$, it has been assumed that these parameters vary linearly as a function of $\theta$ between the limiting values, as given in Table IV. It is clear that this approach again can only lead to an upper limit for the real potential curve, but since the various changes in geometry other than in $\theta$ are rather small, the error introduced by this precedure should not be very substantial. The SCF calculations have been carried out at 15° intervals of $\theta$ for the conrotatory ground state and for both important disrotatory closed-shell states; the resulting potential curves are given in Figure 6.

**Table IV.** Geometrical Parameters Corresponding to the Rotational Potential Curves at $R_c$ = 4.32 Bohrs of Figure 6 ($\varphi$ = 0°, $\beta$ = 120°)

| $\theta$, deg | $R_B$ | $R_D$ | $\alpha$, deg | $\gamma$ |
|---|---|---|---|---|
| 0 | 2.80232 | 2.52641 | 57 | 0 |
| 15 | 2.75416 | 2.59037 | 55 | 1/6 |
| 30 | 2.70600 | 2.65434 | 53 | 1/3 |
| 45 | 2.65784 | 2.71830 | 51 | 1/2 |
| 60 | 2.60969 | 2.78227 | 49 | 2/3 |
| 75 | 2.56153 | 2.84624 | 46 | 5/6 |
| 90 | 2.51337 | 2.9102 | 44 | 1 |

The first point to be noted in these results is that the (SCF) crossing point was determined quite accurately; the calculations at $R_c$ in fact find a discrepancy between the energies of the planar and perpendicular structures of only $3.0 \times 10^{-4}$ hartree, or less than 0.2 kcal/mol. The next point of interest is the fact that the conrotatory mode is now indicated to be substantially favored over the disrotatory mode, although one must accept this result with a certain amount of caution because of the change in ground-state electronic configuration throughout the rotation in the disrotatory process. The conrotatory curve is fairly symmetrical, with a maximum occurring at $\theta$ = 51°, in rather strong contrast to the results of Feler obtained *via* EHT calculations for a continuous rotational process; the barrier height is

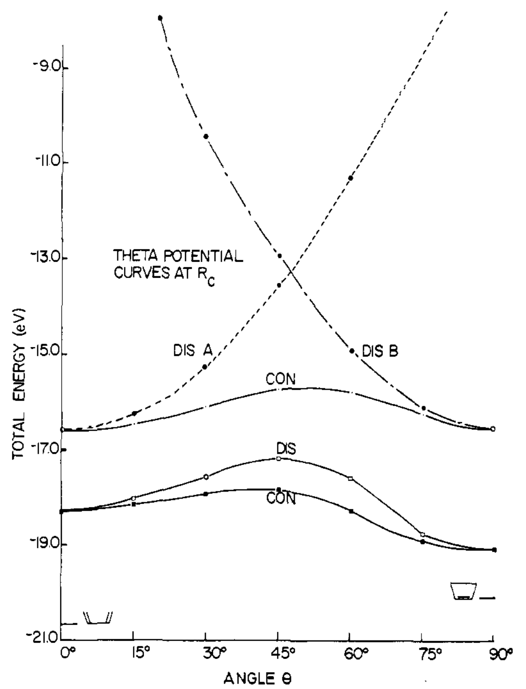


Figure 6. Total energy for the con- and disrotatory $C_4H_6$ structures as a function of the rotation angle $\theta$ at $R = R_c$; the upper curves are obtained *via* SCF, the lower *via* CI calculations. The CI energies for the cyclobutene and *cis*-butadiene structure are also given. (Zero of energy is $-154.0$ hartrees.)

found to be 20 kcal/mol. The crossing point of the two disrotatory energy curves occurs at 47°, but again this result is not particularly significant because of the limitations of the SCF treatment; it is obviously necessary to employ CI techniques, as Longuet-Higgins and Abrahamson[4] have pointed out, in order to obtain reliable potential curves in this case. Although the deficiencies of the SCF method are much more apparent in this example than in the description of the $R$-stretch potential curve discussed above, an overall lowering of the reaction barrier height is expected to result from a CI treatment, and this possibility will also be investigated quantitatively in the next section.

## Effect of CI on the Barrier Height

**A. Details of the CI Method.** One problem with applying the CI technique to chemical problems is, of course, a certain ambiguity in selecting the various excited configurations which are to be mixed in an optimum manner with the ground state (or excited state in the general case). The selection is necessary since a calculation involving all configurations (obtained by exchanging occupied for unoccupied orbitals in the ground state determinant) which can be constructed from a given AO basis is of impractical size. For investigations of potential surfaces there is definite merit in requiring that all configurations considered explicitly in the calculations have a common core of MO's; for even though the major portion of the correlation energy is due to the core orbitals of the system, it is reasonably safe to assume that this energy error is constant for all geometries. Recent exploratory calculations[14] on ammonia support this conclusion quite well. In other words, a limited CI treatment which utilizes a fixed core of orbitals (in general the most stable species) can be quite effective in correcting errors in potential surfaces calculated by SCF methods, errors which are caused by the simple fact that not all conformations assumed from beginning to end in a given process are treated equally well by a single configuration calculation.

The CI treatment employed in the present investigation makes use of a fixed core of the lowest lying 11 doubly occupied MO's in a given conformation, selected on the basis of orbital energy. The remaining four doubly occupied SCF MO's and the four most stable virtual MO's are then selected for variable occupation. In a further attempt to keep the magnitude of the calculation down to practical size it was decided to restrict the list of configurations considered to between 255 and 260, these corresponding to all single and double, most triple, and a few selected quadruple excitation species; selection of the triple and quadruple excitation configurations is based on diagonal energy. The restriction that the order of the resultant secular equation be a maximum of 260 should have a negligible effect on the total energy since triple and higher excitation species excluded are quite ineffective in mixing with the ground state because of the orthogonal MO basis set employed. Details of the method employed are given elsewhere.[15]

**B. CI at $R_c$.** The CI calculations are carried out at the $C_1$–$C_4$ separation $R_c$ as a function of $\theta$. The main objective of this treatment, of course, is to obtain a realistic potential curve for the disrotatory mode, and the results are contained in Figure 6; in addition to achieving this objective, however, the CI calculations provide several other interesting findings. The first is the rather large magnitude of the energy lowerings obtained relative to the SCF values, in some cases as much as 2.5 eV; the second result is that the energy lowering is by no means independent of the rotational angle $\theta$, instead becoming generally greater with increasing $\theta$. Therefore the 0 and 90° CI energy values at $R_c$ are no longer equal, the 90° value being the lower by 0.78 eV. Even though the energy difference between the conrotatory and disrotatory barrier heights is now reduced to the rather small value of 0.6–0.7 eV, this result is still somewhat unsatisfactory because of the differences in the energy values for the 0 and 90° conformations at $R_c$.

Evidently the crossing point of the optimum CI curves for planar and perpendicular conformations differs from that found from the SCF calculations alone. In order to investigate this deviation more explicitly, analogous CI calculations have been carried out for the two structures at equilibrium (cyclobutene and *cis*-butadiene at their respective experimental distances $R_{eq}$), and from these energies and the corresponding calculated values at $R_c$ and $R = 4.2$ bohrs, CI potential curves for planar and perpendicular $R$ stretch are constructed by interpolation.[16] From these curves, also contained in Figure 5, it is seen that the two crossing points do indeed occur at different values of $R$, with the CI value $R_I$ of 4.49 bohrs being somewhat closer to $R_{eq}$ for *cis*-butadiene than is $R_c$ (4.32 bohrs). More signif-

(14) A. Pipano, R. R. Gilman, and I. Shavitt, *Chem. Phys. Lett.*, 5, 285 (1970).

(15) R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta*, 12, 183 (1968).

(16) In this interpolation scheme the CI energy lowering relative to the corresponding SCF energy has been assumed to vary linearly with $R$ for each value of $\theta$.

icant, however, is the fact that the CI calculations find a substantially *lower* barrier to $R$ stretch than do their SCF counterparts, since the CI is much more effective in the region of intermediate $R$ than for the cyclobutene equilibrium structure.

The rather substantial changes observed in the various potential curves upon introduction of CI suggest that it would be worthwhile to also reconsider the question of whether rotation of the methylene groups can best occur at one distance $R$ (specifically $R_1$ of Figure 5) or continuously with a variation of $R$, as other authors[5,6] have suggested. To this end the analogous CI treatment has been carried out for the 60° structures, at $R$ = 3.7 bohrs, discussed earlier; these results are also plotted in Figure 5 and show that the present 90° structure has a lower CI energy than the conrotatory 60° species by some 34 kcal/mol, so that once again the linear mechanism appears to be much less satisfactory than the one in which $R$ stretch is accomplished both before and after rotation, but *not during* this process.

**C. CI at $R_1$.** It is possible to obtain an *estimate* of the rotational potential surface at the $C_1C_4$ separation $R_1$ under the assumption that at this CI crossing point the energies of the planar and perpendicular conformation are exactly equal, and that the magnitude of the energy lowering relative to the former rotational curve calculated at $R_c$ varies linearly between the two extreme values calculated for 0 and 90°. This procedure has been carried through, and the ensuing results are given in Figure 7 along with the analogous estimates for the SCF curves at this separation.

In order to check the accuracy of the various extrapolations, explicit SCF and CI calculations have been carried out at $R_1$ for $\theta = 0°$ ($\gamma = 0$) and $\theta = 90°$ ($\gamma = 1$) as well as for both rotational modes at the 45° position. The calculated values agree in all cases (at least for the CI curves, which are the only data of significance at this point) with the extrapolated results to within 0.10 eV, suitably close to justify taking the estimated rotational potential curves as the final results. It is thus found that both disrotatory and conrotatory potential surfaces are quite symmetrical, with their respective maxima close to 45°; the conrotatory species lies below the disrotatory curve in the entire region, in agreement with experiment, the energy separation between them being 0.6 eV (14 kcal/mol) at the maximum. The symmetrical nature of these curves is in marked contrast to that of the corresponding curves determined by Feler[5] *via* EHT calculations and, most significantly, by assuming a linear transformation mechanism. The asymmetric shape of the SCF curves at $R_1$ is also of interest and provides a dramatic illustration of the inadequacy of the single-configuration method in describing general potential surfaces and of the importance of improving upon this technique through the use of configuration-interaction techniques.

From a quantitative point of view the present SCF and CI calculations predict an energy barrier of 1.1–1.2 eV (25–28 kcal/mol) caused by $R$ stretch out of the cyclobutene equilibrium structure to the intermediate distance $R_1$; in addition, the calculations predict that rotation of the methylene groups at this distance requires a minimum energy increase of 0.85 eV (19 kcal/mol). The total barrier height for combined stretching and rotation, calculated in this stepwise concerted mechanism, is thus approximately 2.0 eV as compared with an experimental estimate[17] for this process of 1.4 eV. By contrast, the SCF barrier height calculated at $R_c$ is over twice as large as this experimental value.

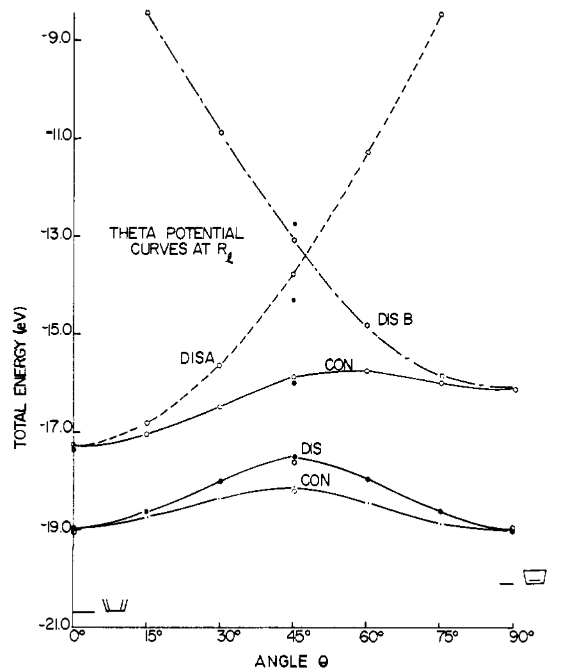


Figure 7. Total extrapolated energy for the con- and disrotatory $C_4H_6$ structures as a function of the rotation angle $\theta$ at $R = R_1$; the upper curves correspond to the SCF, the lower to the CI treatment. Calculated CI energy for equilibrium cyclobutene and *cis*-butadiene is also given. The points (○) close to the CI curves are calculated values; the same holds for the points (■) close to the SCF curves. (Zero of energy is −154.0 hartrees.)

## Tabulation of Energy Values and Conclusion

While the calculations discussed in this paper have been rather complicated in terms of geometrical structures considered and methods employed, their results can be summarized rather succinctly in terms of the quantities $R$, $\theta$, and energy for various geometrical conformations. Table V collects this information for convenient reference; details of the various calculations described therein can be found in earlier sections of this paper.

The evaluation of the results can be divided into two parts, dealing, respectively, with equilibrium conformation calculations and with potential curve crossing point data. With respect to the equilibrium conformations it can be pointed out that for *cis*-butadiene agreement between the calculated and experimental values for $R_{eq}$ (equilibrium structure) is relatively good, both for SCF and CI treatments; in particular, the energy difference (CI value) between the conformations at experimental and calculated $R_{eq}$ is only 0.01 eV, so that the deviation of 0.12 bohr from the measured bond distance can be considered as minor. For cyclobutene two sets of results are given, one before and the other after optimization (the values in parantheses) of the HCC angle $\beta$. The value of $R_{eq}$ is also overestimated, but the discrepancy is larger than for *cis*-butadiene; clearly, optimization of $\beta$ is important and re-

(17) W. Cooper and W. D. Walter, *J. Amer. Chem. Soc.*, **80**, 4220 (1958).

Table V. Tabulation of Pertinent Calculated Energy Values (Zero of Energy Is −154.00 Hartrees)

| | | $R$, bohrs | $\theta$, deg | $E$, eV |
|---|---|---|---|---|
| | | (a) SCF Values | | |
| Cyclobutene | $R_{eq}$(calcd) | 3.14 | 90 | −18.97 |
| | [$R_{eq}$(calcd)][a] | (3.05)[a] | 90 | (−19.07)[a] |
| | $R_{eq}$(exptl) | 2.919 | 90 | −18.79 (−18.93)[a] |
| Butadiene | $R_{eq}$(calcd) | 5.42 | 0 | −19.12 |
| | $R_{eq}$(exptl) | 5.51 | 0 | −19.11 |
| Crossing point | $R_c$ | 4.320 | 0 and 90 | −16.57 |
| Conrotatory mode | Max | 4.320 | 51 | −15.71 |
| Disrotatory mode | Max | 4.320 | 47 | −13.58[b] |
| | | (b) CI Values | | |
| Cyclobutene | $R_{eq}$(calcd) | 3.26 | 90 | −20.10 |
| | [$R_{eq}$(calcd)][a] | (3.12)[a] | 90 | (−20.20)[a] |
| | $R_{eq}$(exptl) | 2.919 | 90 | −19.87 (−20.01)[a] |
| Butadiene | $R_{eq}$(calcd) | 5.39 | 0 | −20.70 |
| | $R_{eq}$(exptl) | 5.51 | 0 | −20.69 |
| Crossing points | $R_c$ | 4.320 | 0 | −18.30 |
| | $R_c$ | 4.320 | 90 | −19.08 |
| | $R_l$(estd)[c] | 4.494 | 0 and 90 | −19.01 |
| | $R_l$(calcd) | 4.494 | 0 | −19.06 |
| | $R_l$(calcd) | 4.494 | 90 | −18.91 |
| Conrotatory mode | Max(estd)[c] | 4.494 | 45 | −18.17 |
| | Max(calcd) | 4.494 | 45 | −18.15 |
| Disrotatory mode | Max(estd)[c] | 4.494 | 45 | −17.52 |
| | Max(calcd) | 4.494 | 45 | −17.56 |

[a] Values with optimized $\beta$. [b] Value too high, since SCF method for this case not applicable; see text. [c] Values estimated from the extrapolated potential curves.

duces the difference between CI and experimental values of $R_{eq}$ to 0.20 bohr, although the energy difference remains fairly substantial (0.15 eV).

The CI calculations thus predict an energy difference between the two end products of 0.50 eV (employing the calculated equilibrium value of $R$) as compared to the corresponding experimental quantity of 0.40 eV. All these results taken together indicate that the overall treatment is somewhat more accurate for the *cis*-butadiene structure than for cyclobutene, but the energy error is obviously small compared with the total reaction barrier height occurring in the electrocyclic transformation of these two substances. It is not clear at this time whether this difference is caused by the inadequacy of the method of calculation employed or by the failure to satisfactorily optimize all geometrical parameters. In spite of these deficiencies, however, it seems quite safe to accept the major conclusion resulting from the calculations, namely that cyclobutene at equilibrium is much more resistant to methylene rotation than it is to $R$ stretch. Furthermore, even if the 90° potential curve of Figure 5 were universally lower by 0.15 eV, the new crossing point would differ from $R_l$ by less than 0.05 bohr (toward larger values than $R_l$); it is extremely doubtful that this change would have any significant effect on either the rotational potential surface or the barrier height calculated in this work.

The other entries in Table V contain information relative to the various crossing points $R_c$ and $R_l$, and the energy differences of greatest interest which can be obtained from these data are summarized in Table VI. The most striking feature of this table is the extreme overestimation of the various barrier heights by the SCF method; as discussed in the previous section, this result points up the inadequacy of the SCF method by itself for studying this reaction. Consequently, one also has to consider the possibility that the SCF calculations used in the preliminary investigations leading to the prediction of the stepwise mechanism for this reaction were misleading. Recalling the arguments which led to the stepwise mechanism, however, there seems to be little doubt that the actual rotation takes place over a narrow range of $R$. The CI results at $R$ = 3.7 bohrs show, for example, that the $\theta$ = 60° structure (linear variation of all geometrical parameters) is less stable than the corresponding perpendicular conformation ($\theta$ = 90°) by 34 kcal/mol, so that there is no indication that the prediction of an energetically favorable stepwise reaction path would have to be altered had the preliminary investigations been carried out with the CI method rather than by means of SCF calculations.

Table VI. Energy Differences Related to the Height of the Various Reaction Barriers

| | | |
|---|---|---|
| | (a) SCF Values | |
| $E$ (conrotatory max), eV | −$E$ ($R_{eq}$(calcd), 90°) | 3.26 (3.36)[a] |
| | −$E$ ($R_{eq}$(calcd), 0°) | 3.41 |
| | −$E$ ($R_c$, 0° and 90°) | 0.86 |
| | −$E$ (disrotatory max) | −2.13 |
| | (b) CI Values | |
| $E$ (conrotatory max), eV | −$E$ ($R_{eq}$(calcd), 90°) | 1.95 (2.05)[a] |
| | −$E$ ($R_{eq}$(calcd), 0°) | 2.55 |
| | −$E$ ($R_l$, 0° and 90°) | 0.86 |
| | −$E$ (disrotatory max) | −0.59 |

[a] Values obtained with optimized $\beta$.

On the other hand, the fact that the CI barrier height is roughly 0.6 eV higher than that found experimentally might well be an indication that adequate geometrical optimization for the intermediate conformations has not yet been attained. Several possibilities to remedy this situation present themselves: one already alluded to suggests that the use of *CI optimization* of the various geometrical parameters could change the value of $R$ for which optimum 0 and 90° potential curves cross and thus could suceed in lowering the part of the barrier height which is due to $R$ stretch; another concerns the fact that energy minimization with respect to the out-of-plane deformation angle has never been considered explicitly. Correcting this deficiency might well help to lower the purely rotational part of the barrier height since such out-of-plane deformations are much more likely for partially rotated intermediates than for either perpendicular or planar structures. In general it is certainly not surprising that the present treatment overestimates the barrier height, since much more is known about the two equilibrium structures than about the intermediate conformation corresponding to the energy maximum of the reaction path.

Finally, while it is extremely difficult to quantitatively fix the details of the reaction surface, it is much easier to obtain a good qualitative picture of the operative mechanism in the thermochemically induced transformation of the two $C_4H_6$ isomers discussed in this paper. Instead of a linear process involving simultaneous rotation of $CH_2$ groups and stretching of the $C_1$–$C_4$ bond $R$, the reaction apparently involves a stepwise mechanism in which $R$ is first varied to some intermediate value (about 60% of the way from its equilibrium cyclobutene value to its *cis*-butadiene counterpart), at which point rotation of the methylene groups then takes place without further change of $R$; thereafter $R$ continues its variation toward the equilibrium value of the product species. The fact that rotation takes place only at a particular $R$ value (or over a very narrow range of $R$ in this region) indicates that it is at this distance that one should calculate orbital and state correlation diagrams for comparison with the qualitative theory given by Woodward and Hoffmann and by Longuet-Higgins and Abrahamson. Especially since the mode of rotation preferred is actually dependent on the reaction path taken, it seems of interest to construct such diagrams for the preferred stepwise mechanism considered in the present work.

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# Kinetics of the Gas-Phase Unimolecular Decomposition of the Benzoyl Radical[1a]

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**Abstract:** The formation of CO has been measured volumetrically in the gas-phase PhCHO–$I_2$–PhCIO–HI system over the temperature range 341–394°. The rate of formation is associated with the unimolecular decomposition of the benzoyl radical as the rate-determining step: $Ph\dot{C}O \rightarrow Ph\cdot + CO$ (3). In the pressure range 24–460 Torr, reaction 3 appears to be in the pressure-dependent region. Despite appreciable scatter in the data (±50%), it is possible to obtain reasonable Arrhenius parameters for $k_3$. Assuming a collisional efficiency of 1.0, the application of both RRK and RRKM unimolecular reaction theories is shown to yield the same high-pressure Arrhenius parameters, $\log (k_3, \sec^{-1}) = (14.6 \pm 0.5) - (29.4 \pm 1.8)/\theta$, where $\theta = 2.303RT$ kcal/mol. After correction to 298°K, this activation energy (29.2 kcal/mol) is in good agreement with the heat of reaction ($\Delta H_{298} = 27.5$ kcal/mol) and a back activation energy for addition of a phenyl radical to carbon monoxide of 2.3 kcal/mol. Reducing the collisional efficiency to 0.1 has the effect of decreasing the Arrhenius activation energy to 28.6 kcal/mol and, hence, $E_{3(298)}$ and $E_{-3(298)}$ to 28.4 and 1.5 kcal/mol, respectively.

The unimolecular decomposition of the benzoyl radical to a phenyl radical and carbon monoxide has received little attention. The formation of carbon monoxide in small quantities has been observed when benzoyl radicals were generated from the reaction of benzoyl peroxide with benzaldehyde at 80°[2] and from the photolytic decomposition of azodibenzoyl, both neat at 100° and as a 1% benzene solution at 80°.[3] These systems are complex and no quantitative rate data could be obtained.

The formation of benzoyl radicals in the gas phase has been measured from the pyrolysis of benzophenone,[4] benzil,[5] benzoyl chloride,[6a] and benzoyl bromide.[6b] In each case, the PhCO–R bond scission is much slower than the decomposition of the benzoyl radical and rates cannot be obtained for the secondary process.

The analogous unimolecular decompositions of the formyl and acetyl radicals have been much more extensively studied.[7] These reactions were in the pressure-

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