Approximate Minimum Energy Reaction Surfaces for the Cyclobutene–*cis*-Butadiene Thermal Isomerization

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A simple procedure is used for obtaining approximate minimum energy sections of potential energy hypersurfaces for reactions of polyatomic molecules. Choice of a couple (*a*,*b*) of internal co-ordinates (bond-angles or -lengths) which undergo large changes from reactants to products allows the calculation for a sufficient number of points of the plane (*a*,*b*) of all the other angles and bond lengths by use of a modified version of Del Re's Criterion of Maximum Localization. This criterion had been previously shown to produce accurate equilibrium (*i.e.* minimum energy) geometries for hydrocarbon molecules. Energies are then calculated for the selected geometries. For the thermal ring-opening of cyclobutene to *cis*-butadiene, approximate minimum energy maps have been drawn for the conrotatory and disrotatory modes. Energies have been calculated simply as sums of contributions due to the localized σ bonds, to the π systems, and to the non-bonded interactions. The two maps are quite different: that of the ' symmetry allowed ' conrotatory mode shows a connection path between the product valley and the reactant valley which corresponds at every point to a minimum potential energy with respect to the perpendicular direction (reaction path), whereas that corresponding to the ' symmetry forbidden ' disrotatory mode does not. The ' forbiddenness ' of the disrotatory mode appears to be due more to this feature than to the fact that the energy barrier is higher than in the favoured mode.

MOST theories of reaction rates explicitly use the so-called potential energy surface if they involve both the assumption of equilibrium between activated complexes and reactants and if they are strictly dynamical theories. Therefore the first problem one has to tackle in the study of a reaction according to those theories is the construction of potential energy surfaces. The latter reduce to the well known Morse-type curves for a reaction between two atoms, but are very complicated hypersurfaces in the general case. In order to represent those hypersurfaces it is necessary to choose pairs of geometrical parameters and to construct maps by drawing appropriate contour lines. In such maps there are usually two or more ' valleys ' which correspond to stability regions for the reactants and the products and which communicate through cols representing the highest potential energy regions which the system must pass in order to go from one valley to the other. One can define a ' minimum energy reaction path ' corresponding to the trajectory of the representative point of the system along the bottom of a valley through the col and into the bottom of another valley.

If one wants to construct a single map, one need select only two variables among all those which are needed to describe the whole potential energy surface. Usually this difficulty has been solved by keeping all the geometrical parameters of the systems under study constant except for two of them. With this procedure, the reaction products are found in a configuration which is not the equilibrium one and one implicitly assumes that the reaction terminates with a vibrational cascade taking the system to its equilibrium configuration. In the present paper we suggest a procedure where one does choose, as is customary, two parameters which are considered to be most significant in connection with the given reaction, but, at variance with other researchers, for every pair of values of these parameters that configuration of the system which minimizes the energy is considered. In this way the map one obtains corresponds to a minimum energy section of the potential energy hypersurface and not to a section obtained by keeping $n - 2$ geometrical parameters constant. This section may be called a reaction surface because the trajectories followed by the individual reactions are expected not to be significantly out of that surface. On it it is also possible to define a minimum energy reaction path and hence a potential energy profile for the reaction.

We present in this paper the construction of maps on these lines for the thermal isomerization of cyclobutene to *cis*-butadiene. This reaction, which was studied by Walters and his co-workers,[1] is a typical unimolecular reaction for which the high pressure rate coefficient is given by equation (1).

$$k/\mathrm{s}^{-1} = 1{\cdot}8 \times 10^{13} \exp\,(-32{,}700/RT) \qquad (1)$$

The selection rules [2-8] indicate that the ring-opening mode, where the methylene planes rotate in the same sense keeping a C_2 symmetry axes for the system, *i.e.* the so-called 'conrotatory mode', is energetically favoured with respect to the disrotatory mode where the two methylenes rotate in opposite senses and a symmetry plane is retained during the whole reaction. The distance between C-1 and C-4 (Figure 1) and the rotation angles of the methylene groups are the most convenient geometrical parameters for describing the evolution of the system from the reactant state to the product state. The carbon atom frame is assumed planar during the whole reaction.

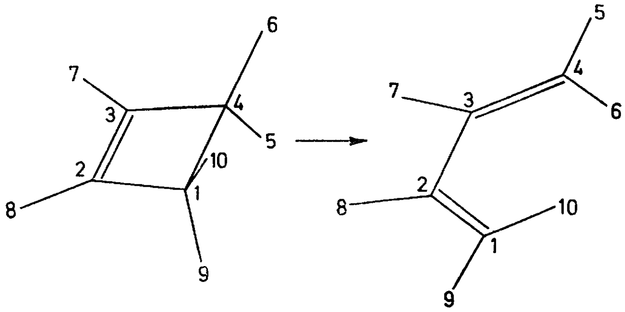

FIGURE 1 Cyclobutene ⟶ *cis*-butadiene

Geometries.—In principle one should optimize the geometry of a molecule in its ground state by looking for the minimum energy. This could be done by an *ab initio* procedure with reasonable success. Every configuration intermediate between cyclobutene and *cis*-butadiene should equally be optimized under the conditions of constant values for $R_{1\text{-}4}$, the distance between C-1 and C-4, and θ, the angle between the planes of the methylene groups and that of the carbon atoms. Such calculation is exceedingly expensive and, as far as is known, cannot provide results of chemical accuracy.[9] Long computing times are also needed by some semi-empirical methods of the CNDO series that aim to reproduce *ab initio* results. Simpler semi-empirical methods, which are essentially equivalent to interpolation procedures, give more satisfactory results. The problem we are studying, which requires the calculation of geometries and energies of a very large number of geometrical configurations, requires that the method of calculation be particularly simple.

There exists a linear relationship between the character of the orbitals which form a bond and the experimental bond lengths. This relationships is particularly accurate for C–C and C–H bonds, which are the only bonds which we need consider in our example. The angles between the bonds can be determined on the basis of orthogonality relations between the orbitals by an 'orbital following' procedure.[10a]

For the determination of the orbitals and the determination of the geometries we have used an iteration method [10b] based on the maximum localization criterion; [11] one starts with the molecular topology and uses the empirical relationships between the character of the orbitals and the bond lengths to determine a first approximate geometry; from this one determines the orbitals according to the criterion mentioned above and calculates a new geometry so that, after few iterations, one obtains stable results which reproduce quite well the experimental data. For geometries intermediate between those of cyclobutene and butadiene we have used the same method imposing, however, the condition that the distance $R_{1\text{-}4}$ and the angle θ should have in any given case values previously chosen and lying between those which correspond to cyclobutene and *cis*-butadiene. In this way for every pair of values of $R_{1\text{-}4}$ and of θ we have obtained a complete geometry of the system; as the maximum localization orbitals are essentially maximum overlap orbitals, it is reasonable to consider the geometries calculated by the above procedure as those which correspond to the minimum energy for every given pair ($R_{1\text{-}4}$, θ), the required assumption being that the overlap integrals are proportional to the corresponding bond energies, an assumption which holds at least to the first order. On the other hand this procedure leads to geometries which match very well with the experimental ones for the equilibrium (*i.e.* minimum energy) configuration.[10a] We have thus realized the conditions for obtaining the minimum energy reaction surface as defined in the introduction.

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Energies.—When we have the geometries the choice of the method for the calculation of energy is only a problem of consistency and of accuracy. With geometries optimized on the basis of a maximum localization criterion it is certainly preferable to carry out a semi-empirical calculation parametrized so as to reproduce the heats of formation of the reactants and of the products, or directly the heat of reaction. The energy in a point of the plane R_{1-4}–θ, referred to the energy of *cis*-butadiene taken as zero point, has been calculated as a sum of two contributions, namely the all-valence electron energy in a Hückel approximation on a basis of hybrid orbitals, and the nonbonded interaction energy. When the calculation is carried out for cyclobutene, $E(R_{1-4}, \theta)$ must coincide with the experimental values of the heat of reaction.

The electronic contribution comes from the solution of the eigenvalue equation (2) where $\mathscr{H}$, $\mathbf{C}$, $\mathbf{S}$, and ε are

$$\mathscr{H}\mathbf{C} = \mathbf{S}\mathbf{C}\varepsilon \qquad (2)$$

respectively the Hamiltonian matrix, the matrix of the coefficients of the molecular orbitals, the overlap matrix, and the diagonal matrix of the orbital energies. By introducing in *cis*-butadiene the $\sigma - \pi$ separation and the approximation of σ bond localization, in agreement with the hybridization procedure, the problem is factorized into very simple problems [equations (3) and (4)]. Then equation (5) applies where $\varepsilon_{\sigma i}$ is the energy

$$\mathscr{H}_{\sigma i}\mathbf{C}_{\sigma i} = \mathbf{S}_{\sigma i}\mathbf{C}_{\sigma i}\varepsilon_{\sigma i} \quad \text{for every } \sigma \text{ bond } i \qquad (3)$$

$$\mathscr{H}_{\pi}\mathbf{C}_{\pi} = \mathbf{S}_{\pi}\mathbf{C}_{\pi}\varepsilon_{\pi} \quad \text{for the 4 } \pi \text{ electron system} \qquad (4)$$

$$E_{\text{electronic}} = \sum_{i} 2\varepsilon_{\sigma i} + 2\varepsilon_{\pi} + 2\varepsilon_{\pi}' \qquad (5)$$

of the lower molecular orbital of the *i*-th bond and ε_{π} and ε_{π}' are the energies of the doubly occupied molecular orbitals of the π-system. Every $\mathscr{H}_{\sigma i}$ is of the second order and contains on its diagonal the energies of the hybrids [12] which form the *i*-th bond and out of the diagonal a quantity proportional to the bond overlap $\mathbf{S}$ of the type $\frac{1}{2}\,\mathrm{K}\mathbf{S}\,(I_1 + I_2)$ where $\frac{1}{2}(I_1 + I_2)$ is the average of the diagonal elements and $\mathrm{K} = 1{\cdot}84$.[13] The σ bonds in *cis*-butadiene are still σ bonds in cyclobutene and so they are considered localized σ bonds all over the plane R_{1-4}–θ, their energies changing with the characters of the orbitals (that influence the valence-state energies I_i) and with variations of the bond overlap (that account also for changes in bond distances). With the reaction proceeding towards cyclobutene, the π system of *cis*-butadiene becomes a *quasi* π system and, at the end, in cyclobutene, gives rise to one σ bond and one π bond; no $\sigma - \pi$ separation is allowed except in cyclobutene, and so these orbitals must be treated as a unique eigenvalue problem in all the plane R_{1-4}–θ; the matrix elements are evaluated in the same way as for the σ orbitals.

The non-bonded interaction energy, E_{nb}, is the sum of the repulsions between the pairs H $\cdots$ H, C $\cdots$ H, C $\cdots$ C of non-bonded atoms; the empirical relations used are (6)—(8).[14] The curve of $E_{\text{nb}}^{\text{CC}}$ *versus* the

$$E_{\text{nb}}^{\text{HH}} = 6591 \times e^{-4{\cdot}08R} - 49{\cdot}2 \times R^{-6} \qquad (6)$$

$$E_{\text{nb}}^{\text{CH}} = 44{,}710 \times R^{-6}\,e^{-2{\cdot}04R} - 124{\cdot}9 \times R^{-6} \qquad (7)$$

$$E_{\text{nb}}^{\text{CC}} = 299{,}300 \times R^{-12} - 325{\cdot}2 \times R^{-6} \qquad (8)$$

distance r_{CC} has been slightly modified so as to obtain for $E(R_{1-4}$–$\theta)$ of cyclobutene the value of 9·4 kcal mol^{-1}, which corresponds to the difference between the heats of formation of cyclobutene and *cis*-butadiene. The heat of formation of *cis*-butadiene had been obtained from the experimental value for butadiene (*trans*-form 26·0 kcal mol^{-1}) by summing the difference in energy of the two isomers (2·17 kcal mol^{-1}). In this way the procedure for the calculation of energy is but an interpolation method for obtaining the energies of all the configurations intermediate between that of butadiene and that of cyclobutene.

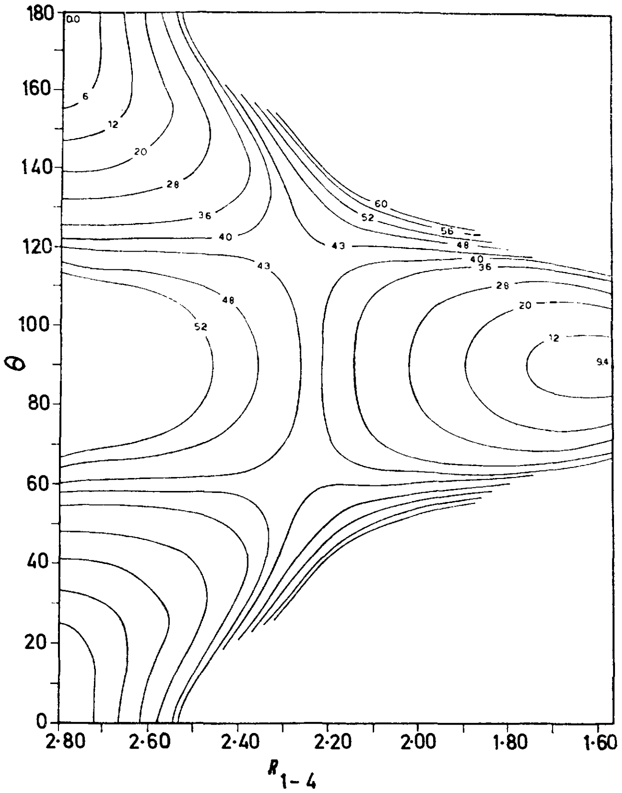

FIGURE 2 Potential energy surface corresponding to minimum energy configurations for given values of the variables R_{1-4} and θ (conrotatory mode)

RESULTS AND DISCUSSION

Figures 2—5 show the potential energy surfaces thus obtained for the conrotatory mode and the disrotatory one.

In both the region of existence of cyclobutene lies at low values of R_{1-4} and at values of θ near 90°, while the

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butadiene valleys lie at values of θ around 180 and 0° and for high values of $R_{1\text{-}4}$.

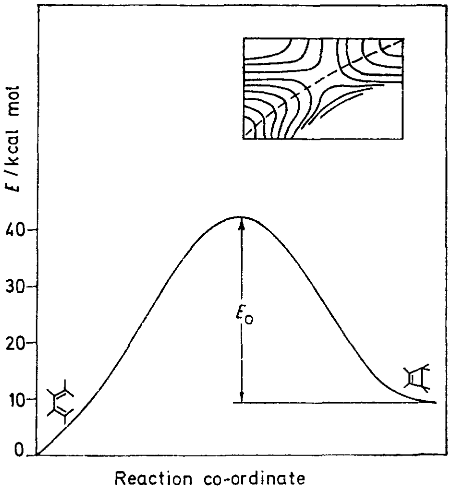

FIGURE 3 Reaction path for the conrotatory mode.

It is very important that in the map of the conrotatory mode there exists a connection path between the product valley and the reactant valley which corresponds in every point to a minimum of potential energy with respect to the perpendicular direction. This path is, by definition, the reaction path on which the reaction co-ordinate must be defined. Figure 3 shows the profile of the potential energy of the reaction along the reaction co-ordinate.

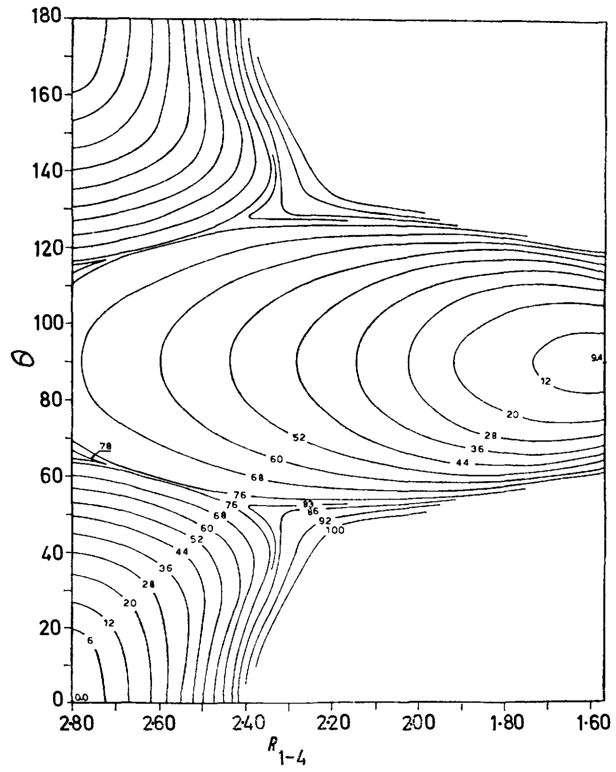

FIGURE 4 Potential energy surface for the disrotatory mode (note that the cyclobutene valley is parallel to the abscissa)

A similar minimum energy path connecting the two valleys does not exist in the disrotatory map. The bottom of the valley of cyclobutene is parallel to the abscissa without ever entering the product valley; this means that in order to react the reaction must follow a path which is energetically unfavourable. This is shown also by Figure 5, where a curve is given which corresponds only formally to a reaction path because the potential energy surface does not allow the choice of a minimum energy path. The section of the surface in Figure 5 has been chosen by cutting the surface with an arbitrary plane. The arbitrariness in the choice does not affect the presence or absence of the peak because the peak would be found anyway for any choice of a ' reaction path ' between the two valleys, owing to the presence of a ridge between them. In conclusion, the most probable reaction mode is certainly the conrotatory one and this is further confirmed by the fact that the potential energy barrier between reactants and products in the conrotatory mode is half that of the disrotatory mode. All this is in full agreement with the Woodward–Hoffmann rules.

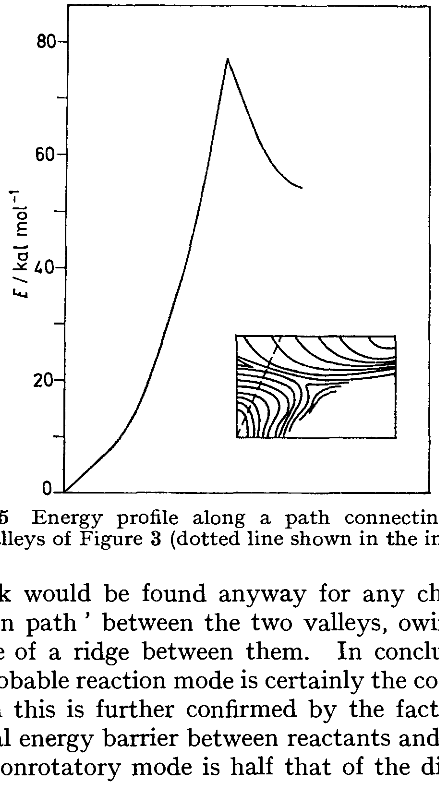

FIGURE 5 Energy profile along a path connecting the two valleys of Figure 3 (dotted line shown in the insert)

As far as the actual value of E_0 and the details of the forms of the maps are concerned, we must point out that large simplifications have been introduced, both in the calculations and in the assumption of a planar carbon atom frame and symmetric structure throughout the reaction. However, the iterative hybridization procedure we have used for calculating bond angles and bond lengths cannot produce asymmetries whereas it can lead to non-planar carbon atom frames. For the conrotatory mode, we have done some test calculations in the region of the saddle point for configurations in which the C-1 and C-4 atoms were shifted from the plane by +5 and −5° respectively and we have found that the energies increase by about 0·5—1 kcal mol^{-1} and that the form of the map does not change appreciably.

The calculation of the potential energy surfaces is the most serious difficulty in the evaluation of the rate coefficient. Therefore, once it has been overcome, one can try to calculate those coefficients. As an example we have carried out an approximate calculation of the rate constant according to the activated state theory. This calculation is only possible if one assumes that the reaction takes place at a sufficiently high pressure, for only in those circumstances is the unimolecular reaction a first-order elementary process, and the activated complexes are in equilibrium with the reactants, a necessary condition for the application of the theory. The rate coefficient is given by relationship (9) where

$$k = L\frac{k_BT}{h}\frac{Q^\ddagger}{Q_A}\,\mathrm{e}^{-E_0/RT} \qquad (9)$$

$Q^\ddagger$ and Q_A are the partition functions for the activated complex and cyclobutene, respectively; E_0 is the difference between the zero-point levels for the initial and activated states at 0 K and L is the statistical factor ($L = 2$ in our case).

If the zero-point energies of the activated complex and of the reactant are approximately the same, a reasonable assumption given the strict structural similarity of the two states, E_0 can be evaluated directly from the potential energy profile along the reaction coordinate as given by Figure 3.

For the calculation of the partition function ratio we use equation (10) where the Q_r terms are rotational contributions to the partition functions and the I terms are moments of inertia. The simplification comes from

$$\frac{Q^\ddagger}{Q_A} = \frac{Q_r^\ddagger}{Q_{rA}} = \frac{I_1^\ddagger \cdot I_2^\ddagger \cdot I_3^\ddagger}{I_{1A} \cdot I_{2A} \cdot I_{3A}} \qquad (10)$$

the fact that the electronic contribution to the partition functions is unity, the ratio between the translational contributions is unity, and also the ratio between the vibrational contributions should not be much different from unity because the structure of cyclobutene and of the activated complex are similar to each other and the frequency to be subtracted in the calculation of $Q^\ddagger$ is probably of the order of 1000 cm^{-1}.[15]

For the rate coefficient we have obtained the expression (11). As a test we have calculated the activation

$$k = 0{\cdot}51T10^{11}\,\mathrm{e}^{-32{,}600/RT} \qquad (11)$$

energy E_a. As E_0 depends on the temperature only for some termolecular reactions or some liquid-phase reactions,[16] we have calculated the Arrhenius activation energy directly from relationship (12) where n is the

$$E_a = E_0 + nRT \qquad (12)$$

temperature exponent of the pre-exponential factor, which is equal to 1 in our case from relation (11). The calculated value of E_a is 33·44 kcal mol^{-1}, a value very close to that of 32·7 kcal mol^{-1} obtained experimentally by Hauser and Walters.[1]

[1/1989 *Received, 27th October*, 1971]

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