
**TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY.
A SIMPLE METHOD FOR ESTIMATING THE ACTIVATION ENERGIES
IN PERICYCLIC REACTIONS**

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Received March 28th, 1985

A simple topological model allowing to estimate the activation energies in thermally initiated pericyclic reactions is proposed. The formalism of the model is closely connected with the recently formulated overlap determinant method. Due to its simplicity the proposed model is especially convenient for the semiquantitative estimate of the reactivity, *e.g.* in computer designed synthesis where even the simplest quantum chemical procedures are still too time consuming.

In the last decade the topological approach to chemical reactivity has been the subject of rapidly increasing interest¹⁻¹⁵. This interest, especially in the initial period has been motivated by the effort to disclose the intrinsic topological reasons conditioning the validity of Woodward-Hoffman (W-H) rules¹⁶. Such a qualitative approach starts to be recently extended also for the topological analysis of multidimensional energy hypersurfaces and for the semiquantitative estimate of activation energies^{8,9,13-15}. In this respect the especially fruitful approach is that of Pánčík^{8,9}. His so-called TMO method fulfills all the above criteria with relatively small demands on the extent of necessary calculations.

In an effort to simplify this topological approach even more, we have recently proposed a simple method allowing to formulate the selection rules in chemical reactivity in terms of the so called overlap determinant^{17,18}. The principle of this method has been however shown to be general enough even for a more detailed study of the reaction mechanism¹⁹. In this communication we describe a further extension of the generalised overlap determinant method for the semiempirical estimate of the barrier heights that separate on the potential energy hypersurfaces the reactants and the products. After having presented the principles of the method in an entirely general way the detailed procedure will be documented on a specific example of the cyclisation of 1,3-butadiene to cyclobutene.

THEORETICAL

As a general example of the chemical reaction let us discuss the abstract transformation $R \rightarrow P$ in which the reactant R is converted into the product P . The structure of the reacting molecules is characterised, similarly as in the original overlap deter-

minant method, in terms of bonding functions ϕ_R and ϕ'_P that are constructed in the form of Slater determinant from the individual chemical bonds forming in a reaction the irreducible core¹⁷ (Eq. (1)).

$$\begin{aligned}\phi_R &= |r_1 \bar{r}_1 r_2 \bar{r}_2 \dots r_n \bar{r}_n| \\ \phi'_P &= |p'_1 \bar{p}'_1 p'_2 \bar{p}'_2 \dots p'_n \bar{p}'_n|\end{aligned}\quad (1)$$

After having converted the function ϕ'_P into the modified function ϕ_P the Eq. (2) defines the function $\phi(\varphi)$ describing the structure of the general transient species $X(\varphi)$ in an arbitrary point of the concerted reaction coordinate¹⁹.

$$\phi(\varphi) = \frac{1}{N(\varphi)} \{ \cos \varphi \phi_R + \sin \varphi \phi_P \} \quad (2)$$

On the basis of this generalised bonding function the topological density matrix $\Omega(\varphi)$ is introduced by Eq. (3)

$$\int \phi^2(\varphi) d\xi_1 dx_2 \dots dx_N = \sum_{\mu} \sum_{\nu} (\Omega(\varphi))_{\mu\nu} \chi_{\mu} \chi_{\nu}. \quad (3)$$

The knowledge of this matrix for several different values of the argument φ permits to characterise the reorganisation of the electron density during the chemical reaction. In our previous study¹⁹ a simple method was proposed allowing to describe this reorganisation in terms of occupation numbers of "natural orbitals" diagonalising the topological density matrix $\Omega(\varphi)$. On the basis of this methodology a further generalisation connecting the variations in the values of occupation numbers during the reaction with the energetical requirements of the activation processes is proposed. Such a generalisation is based on Eq. (4) expressing the molecular energy in terms of occupation numbers and "orbital energies" of corresponding natural orbitals ψ_i ^{20,21}.

$$E(\varphi) = \sum_i n_i(\varphi) \varepsilon_i(\varphi) + V_n - E_{rep} \quad (4)$$

By the argument φ an explicit dependence of both occupation numbers and orbital energies ε_i on the magnitude of the angle φ is depicted. Introducing now, similarly as in the original paper by Buenker²¹ a simplifying assumption equating the terms V_n and E_{rep} representing the nuclear and electronic repulsion, the Eq. (4) may be transformed into the form (5) expressing the energy of the arbitrary transient species as a function of the argument φ .

$$E(\varphi) = \sum_i n_i(\varphi) \varepsilon_i(\varphi) \quad (5)$$

For such equation to be of practical use it is however necessary to specify at this stage the exact meaning of individual quantities. The situation is relatively clear with the occupation numbers and the principal problem consists thus in determining the orbital energies. Intuitively one feels that they are related in some way to the eigenvectors of the topological density matrix $\Omega(\varphi)$. On the basis of this analogy with elementary MO theory this relation is described by Eq. (6) in which the operator \mathbf{h} denotes an effective one-electron hamiltonian.

$$\varepsilon_i(\varphi) = \langle \psi_i(\varphi) | \mathbf{h} | \psi_i(\varphi) \rangle \quad (6)$$

Because of the lack of the knowledge of this hamiltonian it is apparent that the values of the corresponding matrix elements are to be determined, similarly as in HMO theory, by a proper parametrisation. Such a parametrisation immediately originates from the following simple idea.

Despite of the fact that Eq. (6) defines the values of "orbital energies" for arbitrary value of the argument φ the necessity of confrontation with proper experimental characteristics, which lies in the basis of any parametrisation, restricts the possible choice of the argument φ to $\varphi = 0$ and $\varphi = \pi/2$ since for these two important structures representing the reactant and the product there usually exists a number of convenient experimental characteristics on which the parametrisation may be based. Without going into details let us attempt now to explain the principle of such parametrisation.

In the framework of the topological approach the structure of the reactant and the product is characterised by the density matrices $\Omega(0)$ and $\Omega(\pi/2)$. Owing to one-determinantal form of the bonding functions ϕ_R and ϕ_P the diagonalisation of these matrices results in the disjunct discrimination of the occupation numbers into groups with $n_i = 2$ and $n_i = 0$. The eigenvectors corresponding to eigenvalues 2 are then identical with the bonds r_i , p_j used for the construction of the functions ϕ_R and ϕ_P . Similarly the eigenvectors corresponding to eigenvalue 0 describe the "virtual bonds" differing from the ordinary bonds by the nodal structure, *i.e.* by the change of the sign between the AO on the bonded centers¹⁸. Because of the disjunct character of the distribution of the occupation numbers the Eq. (5) can be simplified and the relation for the molecular energy rewritten in the form of Eq. (7).

$$E_R = E(0) = 2 \sum_i^{\text{bonds}} \varepsilon_i(0) = 2 \sum_i^{\text{bonds}} \langle r_i | \mathbf{h} | r_i \rangle$$

$$E_P = E(\pi/2) = 2 \sum_j^{\text{bonds}} \varepsilon_j(\pi/2) = 2 \sum_j^{\text{bonds}} \langle p_j | \mathbf{h} | p_j \rangle \quad (7)$$

These equations are, however, entirely analogous to the widely used relations describing the molecular energy as a sum of the so-called bonding energies (Eq. (8)).

$$E_R = \sum_i^{\text{bonds}} E_{r_i}$$

$$E_P = \sum_j^{\text{bonds}} E_{p_j} \quad (8)$$

In the light of this analogy the orbital energies $\varepsilon_i(0)$ and $\varepsilon_j(\pi/2)$ can be given a physical meaning of effective bonding energies E_{r_i} , E_{p_j} of the bonds r_i , p_j and in this sense can be regarded as empirically adjustable parameters β_i^r , β_j^p the proper choice of which may compensate the possible imperfections of the simple additive scheme (Eq. (9)).

$$E_{r_i} = 2\varepsilon_i(0) = 2\langle r_i | \mathbf{h} | r_i \rangle = -2\beta_i^r$$

$$E_{p_j} = 2\varepsilon_j(\pi/2) = 2\langle p_j | \mathbf{h} | p_j \rangle = -2\beta_j^p \quad (9)$$

The detailed procedure of determining these parameters is not important at this stage and will be given later during the analysis of concrete examples. For the time being let us assume that the values of these parameters are known. Their knowledge allows us so far to calculate only the energies of the reactant and the product (Eq. (5)). If however one wants to obtain also a certain idea about the energetic aspects of the activation process it is apparent that for calculation the corresponding energies $E(\varphi)$ in a general point of the reaction coordinate a generalization allowing to determine the orbital energies $\varepsilon_i(\varphi)$ for the arbitrary value of the argument φ is necessary. In order to restrict the necessary number of empirical parameters this generalization is to be formulated in a way maximally employing the already known values of bonding energies β without the necessity of introducing any further parameters. For this purpose the transformation will be used converting the eigenvectors of the general density matrix $\Omega(\varphi)$ from the original basis of AO χ (in which they are expressed after the diagonalization) into the basis of "normal" and "virtual" bonds (Eqs (10a, 10b)).

$$\psi_i(\varphi) = \sum_{\mu} C_{\mu i}(\varphi) \chi_{\mu} \rightarrow \sum_{\alpha}^{\text{bonds}} R_{\alpha i}(\varphi) r_{\alpha} + \sum_{\beta}^{\text{virt. bonds}} R_{\beta i}(\varphi) r_{\beta}^* \quad (10a)$$

$$\psi_i(\varphi) = \sum_{\mu} C_{\mu i}(\varphi) \chi_{\mu} \rightarrow \sum_{\gamma}^{\text{bonds}} P_{\gamma i}(\varphi) p_{\gamma} + \sum_{\delta}^{\text{virt. bonds}} P_{\delta i}(\varphi) p_{\delta}^* \quad (10b)$$

The argument φ in these equations again denotes that the matrices C , R , and P depend on the magnitude of φ . The transformation is therefore to be performed independently for every value of φ . Combining Eq. (10) with Eq. (6) results in Eq. (11) the form of which clearly suggests the idea of the whole procedure.

$$\varepsilon_i(\varphi) = \sum_{\alpha}^{\text{bonds}} R_{\alpha i}^2 \langle r_{\alpha} | \mathbf{h} | r_{\alpha} \rangle + \sum_{\beta}^{\text{virt. bonds}} R_{\beta i}^2 \langle r_{\beta}^* | \mathbf{h} | r_{\beta}^* \rangle \quad (11a)$$

$$\varepsilon_i(\varphi) = \sum_{\gamma}^{\text{bonds}} P_{\gamma i}^2 \langle p_{\gamma} | \mathbf{h} | p_{\gamma} \rangle + \sum_{\delta}^{\text{virt. bonds}} P_{\delta i}^2 \langle p_{\delta}^* | \mathbf{h} | p_{\delta}^* \rangle \quad (11b)$$

Inspecting these expressions for the matrix elements in the summations over the normal bonds one immediately can see that they are identical with the above introduced bond energies β_i^r , β_j^p . The Eq. (11) requires, however, also the knowledge of the matrix elements in the summations over "virtual" bonds. In order to determine these values we use a simple condition (12) arising from the analogy with elementary MO theory.

$$\langle r_{\alpha} | \mathbf{h} | r_{\alpha} \rangle = -\beta_{\alpha}^r \rightarrow \langle r_{\alpha}^* | \mathbf{h} | r_{\alpha}^* \rangle = +\beta_{\alpha}^r \quad (12a)$$

$$\langle p_{\gamma} | \mathbf{h} | p_{\gamma} \rangle = -\beta_{\gamma}^p \rightarrow \langle p_{\gamma}^* | \mathbf{h} | p_{\gamma}^* \rangle = +\beta_{\gamma}^p \quad (12b)$$

Combining the above equations one may finally express the orbital energies $\varepsilon_i(\varphi)$ in two alternative ways (Eqs (13a, 13b)) the first of which is based on the parametrically determined bonding energies for the reactant and the second for the product. Substituting these values into Eq. (5) one may similarly obtain two alternative expressions for the total molecular energy $E(\varphi)$. Let us attempt now to elucidate the physical meaning of these two alternative relations.

$$\varepsilon_i(\varphi) = \sum_{\alpha}^{\text{bonds}} R_{\alpha i}^2 (-\beta_{\alpha}^r) + \sum_{\beta}^{\text{virt. bonds}} R_{\beta i}^2 (\beta_{\beta}^r) \quad (13a)$$

$$\varepsilon_i(\varphi) = \sum_{\gamma}^{\text{bonds}} P_{\gamma i}^2 (-\beta_{\gamma}^p) + \sum_{\delta}^{\text{virt. bonds}} P_{\delta i}^2 (\beta_{\delta}^p) \quad (13b)$$

In the framework of the model described by Eq. (5) the chemical reaction is regarded as a specific excitation manifesting itself in the variation of the occupation numbers as described by the density matrix $\Omega(\varphi)$. In dependence on whether the forward $R \rightarrow P$ or backward $P \rightarrow R$ reaction is analyzed the formally excited component is either reactant or product. These two alternatives correspond then to the above two mentioned possibilities in calculating the molecular energy. The one using the bond energies β^r corresponds to the situation where the formally excited component is the reactant and the change in the occupation numbers depicts the change in its energy in the course of the reaction. Similarly the second alternative using the product bond energies β^p describes the variation in the energy of the product for the backward reaction $P \rightarrow R$. If the corresponding energies are presented graphically in dependence on the value of φ one obtains a picture of two intersecting curves closely resembling a classical Evans-Polanyi graph^{22,23} (Fig. 1) in which the activation energy is given by the point of intersection of the curves and the reaction heat by the difference $E_p - E_r$.

The above procedure allows thus to determine the principal kinetic and thermodynamic characteristics of a given reaction. The price paid for the simplicity of the approach consists, however, in that these characteristics are not determined absolutely (in contrast to direct quantum chemical procedures) but only relatively in the units of bonding energies β . If such relative values are to be converted into absolute scale it is necessary to determine the values of these empirical parameters. In the following part such a parametrization will be presented in details on a simple example of electrocyclic transformation of 1,3-butadiene to cyclobutene. In agreement with the prediction of W-H rules requiring this reaction to proceed by the conrotatory mechanism, our discussion will be restricted to the detailed analysis of this alternative only.

RESULTS AND DISCUSSION

In the sense of the overlap determinant method the structure of the butadiene and cyclobutene is being described by the functions ϕ_R and ϕ'_P (Eq. (14)).

$$\begin{aligned}\phi_R &= |\pi_{12}\bar{\pi}_{12}\pi_{34}\bar{\pi}_{34}| \\ \phi'_P &= |\pi'_{23}\bar{\pi}'_{23}\sigma'_{14}\sigma'_{14}| \end{aligned} \quad (14)$$

The individual bonds will again be described in terms of usual linear combinations of AO χ and χ' (Eq. (15)).

$$\pi_{12} = \frac{1}{\sqrt{2}}\chi_1 + \frac{1}{\sqrt{2}}\chi_2 \quad \pi'_{23} = \frac{1}{\sqrt{2}}\chi'_2 + \frac{1}{\sqrt{2}}\chi'_3$$

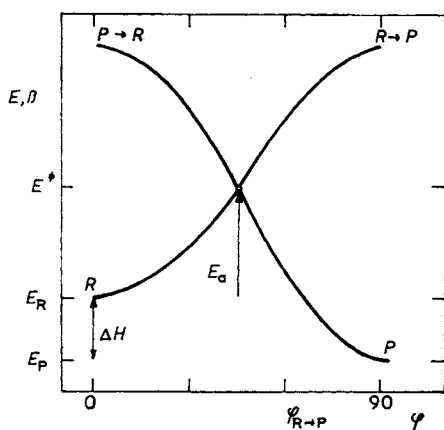


FIG. 1

Schematic visualization of the dependence of the energies of the reactant and the product in reaction $R \rightarrow P$ and $P \rightarrow R$ on the magnitude of the reaction coordinate φ

$$\pi_{34} = \frac{1}{\sqrt{2}} \chi_3 + \frac{1}{\sqrt{2}} \chi_4 \quad \sigma'_{14} = \frac{1}{\sqrt{2}} \chi'_1 + \frac{1}{\sqrt{2}} \chi'_4 \quad (15)$$

The corresponding virtual bonds are then described, in analogy with the elementary MO theory by Eq. (16).

$$\begin{aligned} \pi_{12}^* &= \frac{1}{\sqrt{2}} \chi_1 - \frac{1}{\sqrt{2}} \chi_2 & \pi_{23}^{*'} &= \frac{1}{\sqrt{2}} \chi'_2 - \frac{1}{\sqrt{2}} \chi'_3 \\ \pi_{34}^* &= \frac{1}{\sqrt{2}} \chi_3 - \frac{1}{\sqrt{2}} \chi_4 & \sigma_{14}^{*'} &= \frac{1}{\sqrt{2}} \chi'_1 - \frac{1}{\sqrt{2}} \chi'_4 \end{aligned} \quad (16)$$

The mutual relation of basis sets χ and χ' is given by the so-called assigning tables. Since their construction is sufficiently described in the literature¹⁷ it need not be repeated and we restrict ourselves therefore only to the presentation of the final assignment having in the case of the studied conrotatory cyclization the form (17).

$$\begin{aligned} \chi'_1 &\rightarrow \chi_1 & \chi'_3 &\rightarrow \chi_3 \\ \chi'_2 &\rightarrow \chi_2 & \chi'_4 &\rightarrow -\chi_4 \end{aligned} \quad (17)$$

Using these tables the product bonds are now converted into the basis of unprimed orbitals χ and are given by Eq. (18).

$$\begin{aligned} \pi'_{23} &= \frac{1}{\sqrt{2}} \chi'_2 + \frac{1}{\sqrt{2}} \chi'_3 \xrightarrow{\text{fcon}} \frac{1}{\sqrt{2}} \chi_2 + \frac{1}{\sqrt{2}} \chi_3 \\ \pi_{23}^{*'} &= \frac{1}{\sqrt{2}} \chi'_2 - \frac{1}{\sqrt{2}} \chi'_3 \xrightarrow{\text{fcon}} \frac{1}{\sqrt{2}} \chi_2 - \frac{1}{\sqrt{2}} \chi_3 \\ \sigma'_{14} &= \frac{1}{\sqrt{2}} \chi'_1 + \frac{1}{\sqrt{2}} \chi'_4 \xrightarrow{\text{fcon}} \frac{1}{\sqrt{2}} \chi_1 - \frac{1}{\sqrt{2}} \chi_4 \\ \sigma_{14}^{*'} &= \frac{1}{\sqrt{2}} \chi'_1 - \frac{1}{\sqrt{2}} \chi'_4 \xrightarrow{\text{fcon}} \frac{1}{\sqrt{2}} \chi_1 + \frac{1}{\sqrt{2}} \chi_4 \end{aligned} \quad (18)$$

After this transformation the original bonding function ϕ'_P is converted into the modified function ϕ_P (Eq. (19)).

$$\phi'_P = |\pi'_{23} \bar{\pi}'_{23} \sigma'_{14} \bar{\sigma}'_{14}| \xrightarrow{\text{fcon}} |\pi_{23} \bar{\pi}_{23} \sigma_{14} \bar{\sigma}_{14}| = \phi_P \quad (19)$$

Using this modified function ϕ_P and the function ϕ_R the generalized function $\phi(\varphi)$ can be defined describing the structure of the transient species in a general point of the concerted reaction coordinate. This generalized function then gives the topological density matrix. In our case the form of the matrix $\Omega(\varphi)$ is described by Eq. (20).

$$\Omega(\varphi) = \frac{1}{1 + 0.25 \sin 2\varphi} \left\{ \cos^2 \varphi \begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 \end{pmatrix} + \sin^2 \varphi \begin{pmatrix} 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \end{pmatrix} + \sin \varphi \cos \varphi \begin{pmatrix} 1/2 & 1/2 & 0 & -1/2 \\ 1/2 & 1/2 & 1/2 & 0 \\ 0 & 1/2 & 1/2 & 1/2 \\ -1/2 & 0 & 1/2 & 1/2 \end{pmatrix} \right\} \quad (20)$$

Diagonalizing this matrix for several fixed values of the argument φ the occupation numbers $n_i(\varphi)$ are obtained. Their values are summarized for the illustration in Table I. Similarly the corresponding eigenvectors, expressed in the basis of atomic orbitals χ , are given in Table II. As can be seen these data confirm the expected fact that the eigenvectors corresponding to reactant and product are identical with the vectors of normal and virtual bonds. Using this result the general relation (5) for the molecular energy of the reactant and the product can be converted into the form (21) expressing the molecular energy in terms of two adjustable parameters $\beta_{C=C}$ and β_{C-C} .

$$\begin{aligned} E_R &= -4\beta_{C=C} \\ E_P &= -2\beta_{C=C} - 2\beta_{C-C} \end{aligned} \quad (21)$$

TABLE I

Eigenvalues of the topological density matrix for conrotatory cyclization of the butadiene to cyclobutene

φ	0	30	45	60	90
n_1	2.0	1.882	1.848	1.882	2.0
n_2	2.0	1.882	1.848	1.882	2.0
n_3	0.0	0.118	0.152	0.118	0.0
n_4	0.0	0.118	0.152	0.118	0.0

TABLE II
 LCAO expansion coefficients of the topological density matrix for conrotatory cyclization of butadiene to cyclobutene

φ	30				45				60				90				
	n_1	n_2	n_3	n_4	n_1	n_2	n_3	n_4	n_1	n_2	n_3	n_4	n_1	n_2	n_3	n_4	
x_1	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	0	0.689	0.158	0.689	0.158	0.271	-0.653	-0.271	0.653	0.158	0.689	-0.158	0.689	0
x_2	0	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	0.689	-0.158	-0.689	0.158	0.653	-0.271	-0.271	0.653	0.689	0.158	0.689	-0.158	$\frac{1}{\sqrt{2}}$
x_3	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	0	0.158	-0.689	0.158	-0.689	0.653	0.271	-0.271	-0.653	0.689	-0.158	-0.689	-0.158	$\frac{1}{\sqrt{2}}$
x_4	0	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	-0.158	-0.689	0.158	-0.689	0.271	0.653	0.271	0.653	0.158	-0.689	0.158	0.689	0

This set of parameters describes, however, not only the energy of the reactant and the product but as Eq. (13) suggests it is sufficient for the complete characterization of the system.

Since the energies $\beta_{C=C}$ and β_{C-C} are regarded as adjustable parameters it is clear that their determination will require the confrontation with two experimental characteristics. The choice of these characteristics is in principle restricted only by the choice of the quantities intended to be determined by the above topological approach. If for example one is interested in determining the activation energy and reaction heat it is natural to base the corresponding parametrization on the comparison with the known experimental values of these characteristics. In the case of our cyclization both these quantities are experimentally available. Thus, *e.g.* the simple estimate of the reaction heat from the experimental heat of formation of butadiene and cyclobutene leads for the forward cyclization of butadiene to cyclobutene to the value roughly 10 kcal/mol²⁴. Using this value and the value of the activation energy for the backward transformation of cyclobutene to butadiene^{25,26} the estimated activation energy for the forward reaction is equal roughly to 42.5 kcal/mol.

In the following part a simple procedure allowing to determine the values of the necessary bond energies $\beta_{C=C}$, β_{C-C} is presented. Before starting the discussion let us rewrite however the energy of the single C—C bond in the form (22)

$$\beta_{C-C} = \beta_{C=C} - k\beta_{C=C} \quad (22)$$

expressing the change against the energy of the double C=C bond by the value of the dimensionless parameter k . The purpose of this formal transformation consists in that all the energetic characteristics can be expressed in terms of only parameter $\beta_{C=C}$. At the same time the parameter k is simply related to the exothermicity of the reaction (Eq. (23))

$$\Delta H \approx E_P - E_R = 2k\beta_{C=C} . \quad (23)$$

After having presented all the basic ideas let us describe now the detailed parametrization in a given reaction. The first step in this procedure consists in calculating numerically the molecular energies $E(\varphi)$ for both $R \rightarrow P$ and $P \rightarrow R$ reactions in dependence on the value of the argument φ . In our case such a dependence is depicted in Fig. 2 in which the curves corresponding to several fixed values of the parameter k model the hypothetical reactions differing in exothermicities ΔH . Activation energies are then simply given by the corresponding differences $E^\ddagger - E_R$ and as can be seen from Fig. 2 they obey the Hammond postulate²⁷ requiring the decrease of the activation energies with the increasing exothermicity of the reaction. If the above qualitative result is expressed more quantitatively in the form of dependence E_a vs k one generally obtains a curve that can be at least in a certain range approximated linearly (Fig. 3). The functional form of this dependence is given by

Eq. (24)

$$E_a \doteq 0.5k\beta + 1.6\beta. \quad (24)$$

Combining this relation with Eq. (23) one finally obtains the relation (25) closely resembling the well known Bell–Evans–Polanyi relation^{22,23} (26)

$$E_a \doteq 0.25\Delta H + 1.6\beta \quad (25)$$

$$E_a = \alpha \Delta H + C. \quad (26)$$

The above procedure can thus be regarded not only as theoretically justifying the existence of BEP relations but moreover it can be used to determine the actual values of the parameters α and C for any concrete reaction. In this connection it would be of course interesting to confront such theoretically determined quantities with experiment but since such a confrontation lies outside the scope of this study we leave it open to some subsequent studies. For the time being we shall come back to the promised parametrization. It is based on solving the system of two simultaneous Eqs (23) and (25) complemented by the corresponding experimental values of E_a and ΔH . Here it should be perhaps stressed that such a procedure is not re-

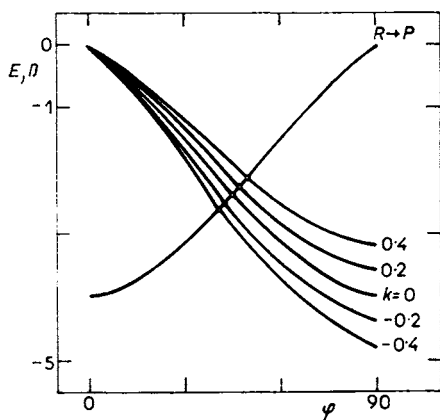


FIG. 2

Calculated dependence of the reactant and product energies on the magnitude of the reaction coordinate φ for thermally initiated conrotatory cyclization of butadiene to cyclobutene. The curves corresponding to different k values describe the hypothetical reactions differing in exothermicities ΔH

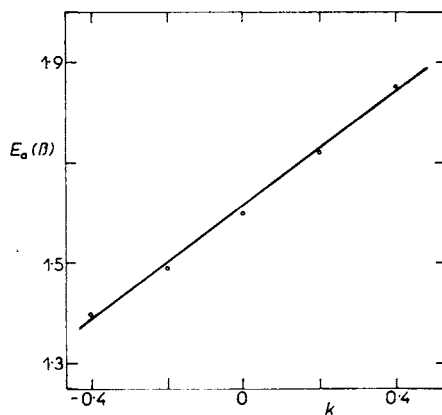


FIG. 3

Evans–Polanyi graph for thermally initiated conrotatory cyclization of butadiene to cyclobutene

stricted only to the above studied cyclization of butadiene but it can be used in an entirely general way for the arbitrary pericyclic reaction the course of which can be characterized by two parameters. In our case the above procedure leads to the values of the parameters β and k given in Eq. (27)

$$\begin{aligned}\beta_{C=C} &\doteq 25 \text{ kcal/mol} \\ k &\doteq 0.2 .\end{aligned}\tag{27}$$

By substituting these values into Eqs (23) and (25) it can be easily verified that the above set of parameters β and k reproduces the values E_a and ΔH . Such a result itself would not be very useful if these parameters were not transferable also to other related reactions. Such a transferability is not, however, apparent *a priori* and should be verified since only this verification gives the presented method the predictive power that opens its applicability for the calculation of E_a and ΔH even in cases for which there are no experimental data available. One of the possibilities to check such a transferability in our case represents an independent calculation of the activation energy for the thermally forbidden disrotatory cyclization and its comparison with available experimental and quantum chemical estimates. For the sake of brevity we shall not repeat the whole procedure in details but we restrict ourselves only to the presentation of the most important differences. These differences manifest themselves on the values of occupation numbers that in the case of forbidden disrotatory reaction indicate the splitting of one of the electron pairs with the subsequent formation of biradical structures. This leads to the increase in the energetical demands of the activation process in comparison with the allowed conrotatory cyclization. The magnitude of this difference can be simply estimated on the basis of comparison of the corresponding BEP relation (28) with the relation (25)

$$E_a^{\text{dis}} \doteq 0.25\Delta H + 2.0\beta .\tag{28}$$

The form of this equations suggests that the difference between the allowed conrotatory and forbidden disrotatory cyclization manifests itself above all in the vertical shift of the corresponding BEP lines. The magnitude of this difference amounts roughly to 0.4β which corresponds to the difference in the activation energies roughly 10 kcal/mol. This quantity nicely agrees with both experimental estimate²⁸ ($\delta \Delta H \doteq 11$ kcal/mol) and with the results of recent *ab initio* calculations²⁹.

We are of course aware of the fact that such an ideal coincidence may not be regarded as absolutely decisive but we intuitively believe that it sufficiently supports the desired transferability of parameters β and k at least in a class of structurally related reactions. This would then open the possibility for a wider use of the proposed

topological model, *e.g.* for the study of regioselectivity and substituent effect in pericyclic reactions as well as for the semiquantitative estimate of the activation energies in computer designed synthesis where the existing direct quantum chemical approaches are still too time consuming.

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Translated by the author.