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The Potential Surfaces for the Addition Reactions of π-Systems

M. V. BASILEVSKY, V. A. TIKHOMIROV, and I. E. CHLENOV
Karpov Institute of Physical Chemistry, Moscow

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A semi-empirical MO method is used to calculate potential energy surfaces for the addition reaction of methyl radical with ethylene and butadiene and the Diels-Alder reaction (ethylene + butadiene). The heights of the potential barriers found agree well with the experimental activation energy values. The reaction model involves explicit consideration of the hybridization changes of the reaction centre and the changes of the intermolecular bond lengths. Using Diels-Alder reaction as an example a significance of the proper choice of basic hybride AO's is examined in detail. It is stressed that the reaction model is to be chosen accurate enough when complex organic systems are studied with the great number of internal nuclear degrees of freedom.

Zur Berechnung von Potentialhyperflächen für die Anlagerung von Methylradikalen an Äthylen und Butadien und für die Diels-Alder-Reaktion wird ein semiempirisches MO-Verfahren angegeben. Die gefundenen Potentialschwellen stimmen gut mit den experimentellen Aktivierungsenergien überein. Das Modell berücksichtigt explizit die Änderung der Hybridisierung an den Reaktionszentren und die der Bindungslängen. Der Einfluß der Basiswahl wird im Fall der Diels-Alder-Reaktion untersucht. Dabei ergibt sich, daß das Verfahren auch ausreichend genau ist für die Behandlung von Systemen mit mehr Freiheitsgraden.

Une méthode d'O.M. semi-empirique est utilisée pour calculer les surfaces d'énergie potentielle pour la réaction d'addition du radical méthyle à l'éthylène et au butadiène ainsi que pour la réaction de Diels-Alder (éthylène + butadiène). Les hauteurs des barrières de potentiel obtenues sont en bon accord avec les valeurs expérimentales des énergies d'activation. Le modèle de la réaction contient explicitement les variations d'hybridation sur le centre réactif et les variations des longueurs de liaison intermoléculaires. En prenant la réaction de Diels-Alder comme exemple la signification d'un choix approprié des orbitales atomiques hydrides est examiné en détail. Les approximations de la méthode de calcul sont discutées. On souligne que le modèle de la réaction doit être choisi avec suffisamment de précision lorsque l'on étudie des systèmes organiques complexes avec un grand nombre de degrés de liberté nucléaire internes.

1. Introduction

In the previous paper [1] a semi-empirical method of calculating potential energy surfaces for the reactions of conjugated molecules was elaborated. It was based on the refinement of the well known PPP theory for π-electrons: to the energy expression the terms were added which took into account exchange repulsion and electron correlation [2]. A potential surface for the addition reaction $CH_3^{\cdot} + CH_2 = CH_2$ was calculated.

In the present paper we dealt with Diels-Alder reaction. It appeared to be a serious test for the method applied. Firstly, the elementary reaction act involving a cyclic transition state is a much more complex one than that of the radical addition reaction. This results in a complication of the reaction model: the number of geometric parameters increases which is to be taken into account in describing the reaction path. Secondly, the comparison with the experiment is more unique because of the great value of activation energy (~1 eV) which allows a reliable experimental estimation of the potential barrier height.

In connection with these circumstances the calculation method given in the paper [1] was revised. We have additionally studied the influence of C—C bond length changes on the potential surfaces. This new factor has been preliminarily examined for a more simple radical addition reaction. It is more thoroughly described in a special publication [3].

For a Diels-Alder reaction we have found a specific effect. It has proved impossible to determine the hybridization state of four carbon atoms which form a reaction centre by the simple geometric consideration. Hybridization should be varied to obtain an energy minimum for every fixed geometric configuration of the reagents. The situation observed may be described formally in terms of the bent σ-bonds which are being formed in the course of the reaction.

2. Radical Addition Reaction: The Model

The following reactions were studied:

$$\underset{(1)}{CH_3^{\cdot}} + \underset{(2)}{CH_2}{=}\underset{(3)}{CH_2} \rightarrow CH_3{-}CH_2{-}\dot{C}H_2\,, \tag{I}$$

$$\underset{(1)}{CH_3^{\cdot}} + \underset{(2)}{CH_2}{=}\underset{(3)}{CH}{-}\underset{(4)}{CH}{=}\underset{(5)}{CH_2} \rightarrow CH_3{-}CH_2{-}CH{=}CH{-}\dot{C}H_2\,. \tag{II}$$

The figures in parenthesis indicate the numbers of the carbon atoms. The model accepted is shown on Fig. 1 using reaction II as an example. In the initial state, when the intermolecular distance R is great, both reagents have planar structure, the planes being complanar. The direction of C_1—C_2 bond is normal

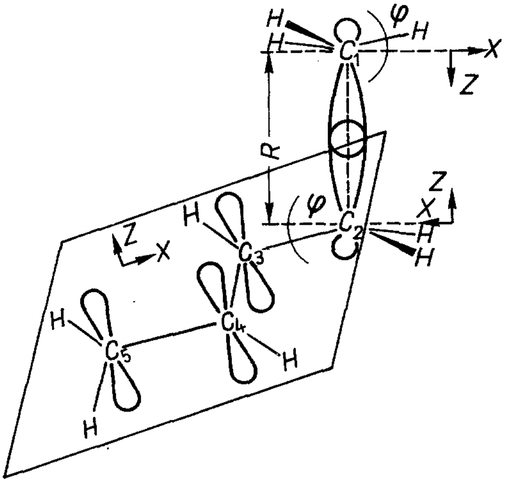


Fig. 1. Reaction model for radical addition reaction

to them. The approaching of the reagents results in the formation of the C_1-C_2 σ-bond, the perturbation of their planar structure and the bond lengths change. The distortion of the reaction centre geometry is described by a single parameter φ – the angle through which the six σ-bonds adjacent to the atoms C_1 and C_2 deflect from their initial directions. When R is small enough a question arises, whether π-electron approximation is permissible. The present calculation is based on an "almost π-electron approximation" [1]. The carbon atoms valence AO's are divided into groups: (a) $2p_z$ AO's of the atoms not involved in reaction centre and hybride ones of the reaction centre atoms, which convert into $2p_z$ AO's in isolated reagents ("π-orbitals"), and (b) the remaining AO's, chosen as hybride ones, three of them for each atom ("σ-orbitals"). The latter are chosen to be directed along the respective σ-bonds. The inverted commas are further omitted.

The interaction energy U of the reagents A and B is equal to

$$U = \Delta_\pi + \Delta_\sigma + \gamma \sum_{\sigma,\pi} S^2, \tag{1}$$

where $\Delta_\pi = E_\pi^{AB} - E_\pi^{A} - E_\pi^{B}$ is the change of π-electron energy of the combined system AB with respect to the isolated reagents (stabilization energy), Δ_σ is the contribution due to the hybridization and bond length changes of σ-bonds and ΣS^2 is the sum of overlap integrals squares including firstly all the intermolecular valence AO interactions and secondly the contribution due to the changes of intramolecular S values for the π-AO's.

Formulae (1) takes into account the exchange repulsion of the valence carbon AO's and the part of attraction due to the π-orbitals. The σ-π and σ-σ resonance is neglected but the selection we accepted for the hybride orbitals minimizes this contribution.

The hydrogen atoms are not considered.

The basis π-orbitals used in calculation of π-energy E^{AB} are of the form

$$\chi_r = a_r(2s)_r + \sqrt{1-a_r^2}\,(2p_z)_r\,. \tag{2}$$

Here $2s$ and $2p_z$ are the respective AO's. For the C atoms of the reaction centre the hybridization parameter is

$$a_r = \sqrt{2}\,\mathrm{tg}\,\varphi_r\,. \tag{3}$$

In the paper [1] the intermolecular bond lengths had been accepted fixed. In this paper the alteration of bond lengths in the course of the reaction was taken into account by means of an empiric relation

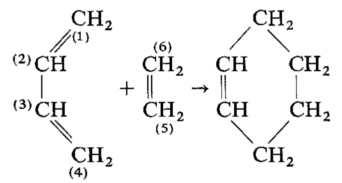
$$l_{rs} = 1.52 - 0.18\,p_{rs}, \tag{4}$$

where l_{rs} and p_{rs} are the bond length in Å and the bond order respectively.

In the energy calculation with R and (for the radical reaction) φ values fixed, an additional selfconsistency was achieved for bond orders according to (4).

3. Diels-Alder Reaction: The Model

The model of reaction



(III)

is shown of Fig. 2. The vector $\boldsymbol{R}$ joins the middles of segments passing through the atoms 5,6 and 1,4. The length R of this vector is one of the geometric parameters of the reaction. The second one is the angle ψ between $\boldsymbol{R}$ and the normal $\boldsymbol{Z}$ to the butadiene plane which is drawn on Fig. 2. The potential surfaces were constructed using coordinates R, ψ. Other geometric parameters were varied keeping these two values constant. The length variation of bonds 1–2, 2–3, 3–4 and 5–6 was accomlished according to (4), the position of vector $\boldsymbol{R}$ and the orientation of molecules being fixed. Hence the reacting system had the symmetry plane passing through $\boldsymbol{R}$ normally to the bonds 2–3 and 5–6.

The condition of sinchronous deflection of three σ-bonds attached to any atom of 1, 4, 5, 6, was retained. Consequently the expression (3) for hybridization parameter is valid. In order to obtain the angle φ_r one should substract $\pi/2$ from the angle between z_r axis, indicating the direction of hybride orbital (2), and the either of the σ-bonds attached to the same atom. The z axes directions are different for all four atoms, however φ and a values differ only for the atoms belonging to different molecules: inside a molecule they are identical due to the symmetry of the system.

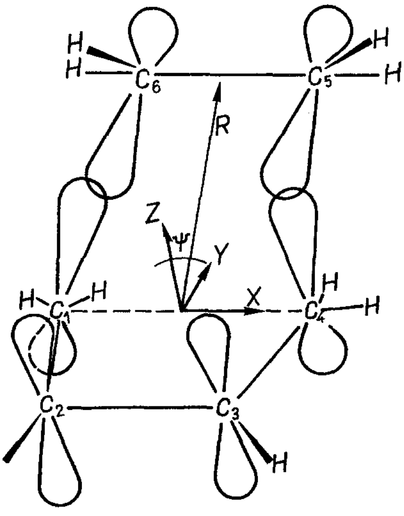


Fig. 2. Reaction model for Diels-Alder reaction

The choice of z directions was specially investigated. The tentative calculations, which assumed z axes to be directed along the respective bonds, were unsuccessful: the potential barrier height obtained (> 2 eV) greatly exceeded the experimental activation energy. In order to make this result more clear one should return to the definition of "almost π-electron approximation". Let the full geometric configuration of the reacting system be given, satisfying the condition of synchronous deflection of σ-bonds. Then the Z directions are completely determined because of the second condition that the σ-orbitals are to be directed along the σ-bonds. Thus any limitation imposed on the Z directions in fact means some additional geometric constraints included in the reaction model. One can introduce new degrees of freedom associated with the motions of hydrogen atoms by varying these directions so as to obtain the minimum of energy U.

In the case of the radical addition in the region of R and φ values investigated, the U minimum seems to be provided by the Z axes directed along the new σ-bonds. Then the maximum absolute values of resonance parameters β for these bonds are obtained. However this conclusion is valid only until the angle φ is small. In reactions I and II we were able to restrict our consideration by φ values $< 10°$. For reaction III with the cyclic transition state the situation is more complicated. If one directs the Z axes along the bonds 1–6 and 5–4, the φ angles will not be small (for example at the saddle point $\varphi_5 = \varphi_6 \approx 18°$). The absolute β values for intramolecular π-bonds are decreasing as φ^2, the formation of a new bond being accompanied with weakening of two such bonds. When R is large and intermolecular β small such choice of hybride orbitals is disadvantageous. The variation of Z axes is necessary in order to obtain a minimum U value (1).

We believe this effect to be of minor significance for the reactions I and II due to the smallness of φ. In this paper it is investigated for reation III only.

4. Results

Figs. 3 and 4 show the potential surface for the radical addition reactions. Reaction I gives 7.5 kcal/mol (without correlation) and 10 kcal/mol (with correlation) for the height of potential barrier. The respective values for reaction II are 6.5 and 9.5 kcal/mol. The experimental activation energies are 8 and 4 kcal/mol [4]. Potential surfaces for Diels-Alder reaction (Fig. 5) give $U = 22$ (without correlation) and $U = 32$ (with correlation) kcal/mol at the saddle point. The experimental estimate is 25 kcal/mol. This figure was obtained after trans-cis isomerisation energy (2 kcal/mol [5]) of trans-butadiene, which is really a substrate of reaction III, was substracted from experimental activation energy [6]. We consider these results as satisfactory, taking into account that the computation was an absolute one, and all parameters used were calibrated to fit the independent spectroscopic and thermochemical data.

We would like to note that the comparison of experimental activation energy and potential barrier height is valid with an uncertainty of order of RT (1–2 kcal/mol). The reliability of such comparison is poor for reactions with low (< 5 kcal/mol) activation energies [7]. Therefore the result for the reaction III is the most convincing one.

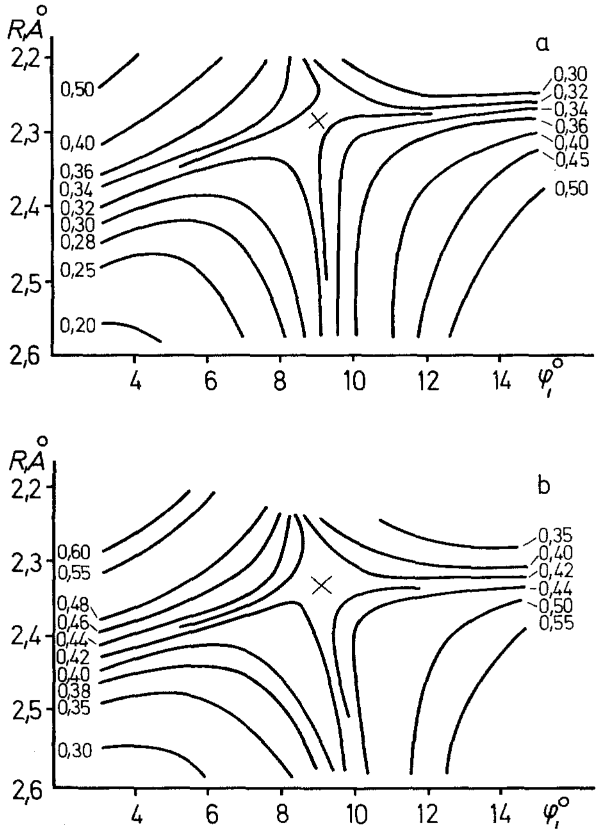


Fig. 3. Potential surfaces for reaction $CH_3 + C_2H_4$; a) without correlation of π-electrons; b) with correlation; energy in eV

Table 1. *Contribution of several terms into interaction energy at the saddle point* (*in* eV)

Energy term	Reaction I		Reaction II		Reaction III	
	with correlation	without correlation	with correlation	without correlation	with correlation	without correlation
$\Delta\pi$	−0.56	−0.67	−0.43	−0.65	−0.63	−0.62
$\gamma\Sigma S^2$ intermolecular	1.11	1.10	0.86	0.97	2.54	2.13
$\gamma\Sigma S^2$ intramolecular	−0.11	−0.10	−0.09	−0.08	−0.35	−0.24
$\Delta\sigma$	0.03	0.0	0.05	0.04	−0.30	−0.30
ΔE_{corr}	−0.05		0.02		0.14	
U	0.43	0.33	0.41	0.28	1.40	0.97
Saddle point Coordinates	$R = 2,3$ Å $\varphi = 9°$	$R = 2,25$ Å $\varphi = 9°$	$R = 2,4$ Å $\varphi = 8°$	$R = 2,35$ Å $\varphi = 8°$	$R = 2,16$ Å $\psi = 30°$	$R = 2,17$ Å $\psi = 28°$

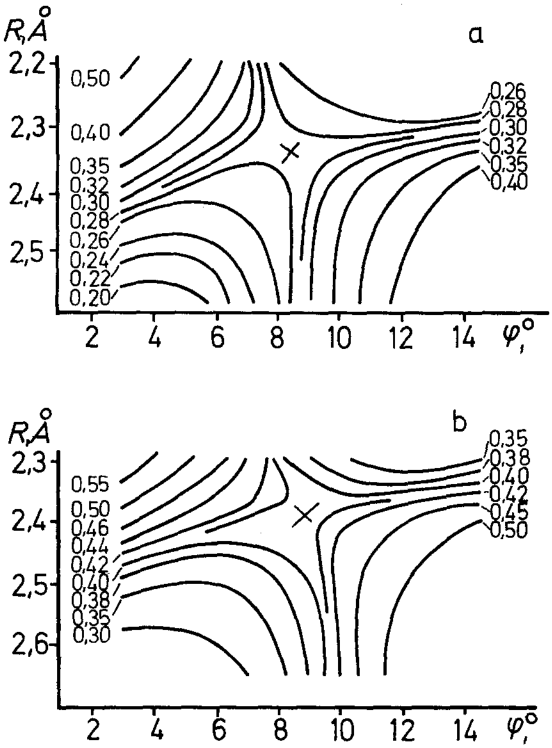


Fig. 4. Potential surfaces for reaction $CH_3 + C_4H_6$; a) without correlation of π-electrons; b) with correlation; energy in eV

In order to make the comparison more precise one should calculate the preexponential factor and absolute rate constant.

It is interesting to estimate the relative importance of several terms contributing into U value. The respective numbers for the saddle points are quoted in Table 1.

For radical reactions the relative contribution of Δ_σ is small as a consequence of variation of bond lengths [3]. Owing to this fact the U values found are insensitive to the selection of empirical parameters which enter into Δ_σ.

In Table 2 several characteristics of bonds and hybridization parameters at the saddle point are gathered. The new bonds formed ($l \approx 2.3$ Å) and their hybridization parameters ($a \approx 0.2$) are almost identical for the two types of reactions. So we may conclude that the nature of these reactions is similar. Their driving force is a formation of new σ-bonds. The resonance parameter β for these bonds increases along the reaction coordinate. The saddle point location corresponds to the configuration of the reacting system at which the inter- and intramolecular β are approximately equal. For radical addition reactions the permanent configuration of the reaction centre at the saddle point leads to the constancy of intermolecular exchange repulsion per one forming bond (Table 1). As the Δ_σ contribution is neglegibly small, the activation energy is mainly determined by a stabilization energy Δ_π, to which the change of intramolecular exchange repulsion should

Table 2. *Some characteristics of the structure of reacting systems in the initial and transition states*

Reaction	Bond	Bond, length, Å			β, eV			Bond order			Hybridization parameter		
		Initial state	Saddle point		Initial state	Saddle point		Initial state	Saddle point		Atom	Saddle point	
			with correlation	without correlation		with correlation	without correlation		with correlation	without correlation		with correlation	without correlation
$CH_3 + C_2H_4$	1—2	∞	2.30	2.25	0	−2.20	−2.35	0	0.404	0.454	1	0.22	0.22
	2—3	1.34	1.36	1.36	−2.60	−2.43	−2.42	1	0.912	0.888	2	0.22	0.22
$CH_3 + C_4H_6$	1—2	∞	2.40	2.35	0	−1.85	−2.0	0	0.341	0.377	1	0.20	0.20
	2—3	1.35	1.36	1.36	−2.56	−2.44	−2.43	0.944	0.892	0.877	2	0.20	0.20
	3—4	1.46	1.46	1.46	−2.14	−2.13	−2.13	0.329	0.320	0.326			
	4—5	1.35	1.35	1.35	−2.56	−2.56	−2.56	0.944	0.951	0.945			
$C_2H_4 + C_4H_6$	1—6	∞	2.27	2.28	0	−2.00	−1.90	0	0.516	0.477	1	0.20	0.17
	1—2	1.35	1.38	1.38	−2.56	−2.33	−2.37	0.944	0.766	0.792	6	0.20	0.17
	2—3	1.46	1.42	1.42	−2.14	−2.30	−2.28	0.329	0.577	0.546			
	5—6	1.34	1.38	1.37	−2.60	−2.32	−2.37	1	0.808	0.835			

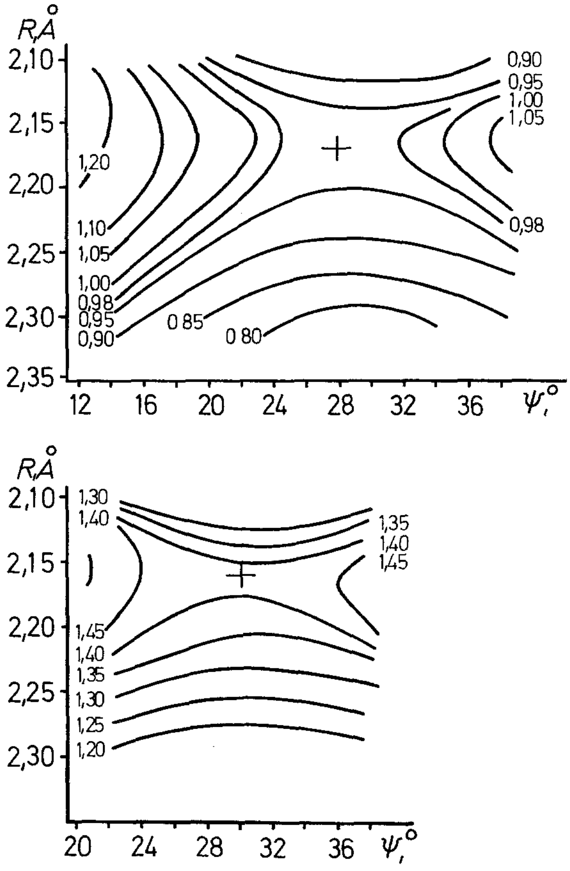


Fig. 5. Potential surfaces for reaction $C_2H_4 + C_4H_6$; a) without correlation of π-electrons; b) with correlation; energy in eV

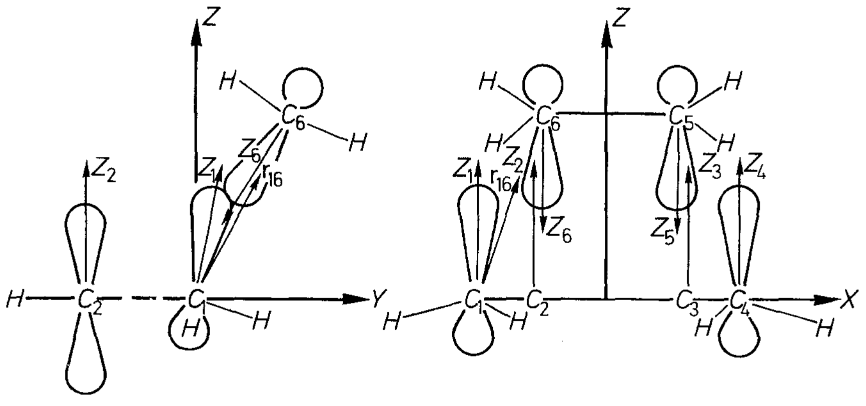


Fig. 6. The hybride orbitals of Diels-Alder reaction at the saddle point: projections on *X*–*Z* and *Y*–*Z* planes

Table 3. *Characteristics of hybride orbitals in the transition state of Diels-Alder reaction (bond 1–6)*

Atom	Direction cosines in XYZ coordinate system (Fig. 2)		Hybridization angle		Angle between z axis and bond vector	Angle $\mathrm{H}\diagdown_{\mathrm{C}}\diagup\mathrm{H}$	Angle $\mathrm{C}\diagdown_{\mathrm{C}}\diagup\mathrm{C}$
	z axis	bond vector r_{16} or r_{61}	z axis directed along the bond	z axis varied			
1	0.056 0.167 0.984	0.313 0.446 0.839	13°18′	6°43′	23°24′	118°39′	103°28′
6	−0.120 −0.472 −0.874	−0.313 −0.446 −0.839	18°14′	6°53′	11°13′	118°36′	108°14′

be added. This conclusion is important for the justification of the reactivity indices method.

The saddle point for reaction II relative to reaction I is shifted to the initial state according to Hammond rule. It may be shown that this result is insensitive to the calculational details, being the consequence of extremal properties of the saddle point region [8].

The data presented in Table 3 demonstrate a significance of variation of the Z axes directions for reaction III. The φ values, which determine hybridization state, are very large owing to geometric constraints when these directions are along the new bonds (for ethylene the φ values are almost tetragonal). The variation diminishes φ up to the values which are typical for radical reactions without geometric constraints. The directions found are shown at Fig. 6. They are quite different from the directions of the bond vectors as it is seen from the first two columns of Table 3. The physical meaning of these values is that they determine the configuration of H atoms of terminal CH_2 groups: say, the orientation of planes of $\mathrm{H}\diagdown_{\mathrm{C}}\diagup\mathrm{H}$ angles. The last angles are also presented in Table 3.

5. A Critical Discussion of the Method of Electron Energy Calculation

Our method of calculation of interaction energy is a semiempirical one, hence it is approximate. We would like to discuss briefly the factors which have not been taken into account in the main formula (1).

S^3 *Corrections* [1]

Formula (1) is valid with the accuracy of terms of order S^3, S being the typical value of intermolecular overlap integral [2]. The magnitude of U is of order S^2,

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[1] The extra S^2 order terms also exist generated by the nonorthogonality corrections to β_{rs}. We neglected them in this and preceeding papers. Our recent calculations show that they produce an appreciable energy contribution which can be cancelled by the proper selection of the σ-bonds Morse parameters to give again an acceptable agreement with the experimental activation energies.

thus the relative error is of order S. At the saddle point $S \sim 0.2$ yielding 20% error in the activation energy due to nonorthogonality. This error may be removed only by means of a full Roothaan computation.

Interaction of σ- and π-Electrons

In the basis of optimum hybride orbitals the one particle σ-π interactions become minimum. In more details, rotation of z axes and mixing of $2s$ and $2p$ orbitals decrease the absolute values of one particle matrix elements for intermolecular σ-σ and σ-π interactions and increase them for intermolecular π-π interactions and those inside the σ-bonds. As a result the matrix elements which determine σ-π resonance are small as compared with the energy levels differences of isolated π- or σ-systems. Small are also the a^2 values at the saddle point which determine intramolecular σ-π interactions. These reasons allow us to believe σ-π resonance to be relatively small.

However U is a difference of the two values of the same order: Δ and $\gamma \Sigma S^2$. Provided $|U/\Delta| \ll 1$ even a small error in Δ will be dangerous. For reactions, I, II and III at the saddle point the ratios $|U/(\Delta_\pi + \Delta_\sigma)|$ are equal to 0.5, 0.5 and 0.9 respectively (without correlation), so the situation is rather favourable.

A quantitative estimation of the error discussed cannot be done in the framework of our approach: the complete all valence electrons computation is needed.

Electron Correlation

When π-electron correlation is included in Δ_π, the potential barrier height increases by $\sim 30\%$ making the agreement with the experiment worse[2]. Probably this is due to the fact that we have neglected σ-σ and σ-π electron correlation. Application of hybride orbitals, which increases the relative contribution of the π-π resonance, has a little influence upon the correlation energy, the intermolecular σ-σ and σ-π correlation remaining of considerable magnitude. It seems natural to assume this last contribution as caused mainly by dispersion interactions; then its empirical estimation gives a value of the order of the π-π correlation contribution but with the inverse sign. We conclude that the correlation correction is not a successive element of our procedure. The calculation ignoring correlation completely seems to be more attractive. As an upper bound of the resulting error a difference may be used between this simple calculation and that including π-electron correlation only.

Selection of Parameters

All parameters used (see Appendix) are taken from independent spectroscopic and termochemical data. If these parameters were quite reliable we could consider a degree of disagreement of our calculations with the experiment (20–30%) as a

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[2] Small values of ΔE_{corr} quoted in Table 1 correspond only to the perturbation theory results. The main reason of raising of interaction energy when correlation is involved is the great value of parameter γ.

measure of the errors mentioned above. However the parameters are also opened for criticism.

The most difficult thing is the estimation of energies, Morse constants etc. for σ-bonds. At least two sets of these values are described in literature: namely the data by Lorquet [9] and the recent data by Dewar [10] which are fairly similar, but differ from the previous data by Dewar [11]. We used Lorquet estimations throughout this paper.

The empirical characteristics of σ-bonds were used for interpolation according to (8)–(9) to obtain the energies of the bonds with intermediate hybridization. Such interpolation was not carried out for the constants in (4). Although these values also depend on hybridization, the information of this dependence seems to be absent, especially concerning the factor before the bond order.

A choice of parameters κ in (12) and γ in (1) for intermolecular interactions also should be mentioned. They were supposed to be independent of the intermolecular separation. This assumption is not quite correct, since several terms contributing into β have a different asymptotic behaviour when R is great ($\sim S$ and $\sim S/R$ [3]). Strictly speaking, the absolute values of κ and γ slowly decrease when R increases. Perhaps it is permissible to consider them constant when R varies in a small region around the saddle point. But it is not obvious, whether it is correct to use the values found for $R = 1.4$ Å in this region ($R \approx 2.3$ Å).

At last the parametrization of the coulomb integrals γ_{rs} assumed the same values for $2s$ and $2p$ orbitals ignoring the orientation effects for the latter case as well. This usual semiempirical treatment corresponds to the neglect of multipole contributions and may be partly justified when large interatomic distances (> 2 Å) are considered.

6. Reaction Model as an Important Factor of Potential Surfaces Problem

As pointed above the interaction energy calculation based on the formula (1) in the region of saddle point may result in a 20–30% error, which cannot be controlled. Indeed, one could improve the electron energy calculation. The most necessary refinement – a consideration of all valence electrons – might perhaps be accomplished either in the framework of CNDO type method or by means of non-empirical procedure. Of course, the size of computational labour would increase considerably.

However there is a thing which makes doubtful the necessity of such refined calculations, at least at present. We mean the internal degrees of freedom due to the nuclear motion. There are 24, 36 and 42 such degrees of freedom in systems I, II and III respectively. Usually, when bimolecular addition reactions are considered, the single geometric parameter, namely the intermolecular separation R, is varied. As our calculations show the saddle point cannot be obtained at all in this case. The reaction model must be refined. For reactions I and II at least one more parameter, the angle φ, should be added. The variation of bond lengths alters the interaction energy within the same limits of 20–30%, but it changes significantly the relative contributions of various terms [3]. For example, the Δ_σ contribution (obtained by the least reliable empiric procedure) decreases in this case, and the ratio $|U/\Delta|$ increases, diminishing the possible error. Therefore it is desirable to introduce one more variable for reaction I and three more variables for reaction II. In the case of reaction III the variation of bond lengths (three more variables, symmetry being taken into account) is quite important because the bonds change markedly in the saddle point region. At last the variation of z directions (four more degrees of freedom, symmetry again being remembered) reduces the potential barrier height more than twice.

So we have considered explicitly 9 internal degrees of freedom for Diels-Alder reaction. However there are 33 more degrees and we have no guarantee that the interaction energy would not change within 20–30% when one took them into consideration.

The calculation of potential surfaces for chemical reactions is a many particle problem. We can solve it (or, more carefully speaking, we believe in it) at the electron level, but it arises again at the nuclear one. The full solution of the whole problem is still impossible. We must again apply a semi-empirical procedure based on chemical intuition, which postulates the reaction model, i.e. selects the minimal set of specific geometric variables needed for adequate description of the reaction. It seems unreasonable to refine the electron energy calculation until the reaction model is crude. On the other hand, when the model is well detalized, even a simple computational procedure allows to obtain an acceptable result.

Appendix: Calculation Details

Stabilization Energy

The diagonal and nondiagonal matrix elements of the one particle hamiltonian h between AO's (2) are given by formulae (5) and (6)

$$\alpha_r = W_p + a_r^2 (W_s - W_p)\,, \tag{5}$$

$$\begin{aligned} \beta_{rs} = {} & a_r a_s \langle s_r | h | s_s \rangle + \left[a_r \sqrt{1 - a_s^2}\,(\boldsymbol{z}_s, \boldsymbol{r}_{sr}) + a_s \sqrt{1 - a_r^2}\,(\boldsymbol{z}_r, \boldsymbol{r}_{rs})\right] \\ & \times \langle s_r | h | \sigma_s \rangle + \sqrt{1 - a_r^2}\sqrt{1 - a_s^2}\,\{\langle \sigma_r | h | \sigma_s \rangle (\boldsymbol{z}_r, \boldsymbol{r}_{rs})(\boldsymbol{z}_s, \boldsymbol{r}_{sr}) \\ & + \langle \pi_r | h | \pi_s \rangle [(\boldsymbol{z}_r, \boldsymbol{z}_s) + (\boldsymbol{z}_r, \boldsymbol{r}_{rs})(\boldsymbol{z}_s, \boldsymbol{r}_{sr})]\} \end{aligned} \tag{6}$$

$\beta_{rs} = 0$ for nonneighbouring atoms in the same molecule. Here:

W_s and W_p are the energies of $2s$ and $2p$ AO's, s_r, σ_r, π_r – $2s$ and $2p_z$ AO's, the latter two directed along or perpendicularly to the line joining the atoms C_r and C_s; $(\boldsymbol{z}_r, \boldsymbol{z}_s)$, $(\boldsymbol{z}_r, \boldsymbol{r}_{rs})$ – the scalar products of unit vectors $\boldsymbol{z}_r$ and $\boldsymbol{z}_s$, which indicate the directions of AO's χ_r and χ_s, and $\boldsymbol{r}_{rs}$, which is directed from C_r to C_s.

The E^{AB} value is to be calculated with respect to the energies of basis AO's [1]:

$$E_\pi^{\mathrm{AB}} = \varepsilon_\pi^{\mathrm{AB}} - \Sigma \alpha_r\,. \tag{7}$$

For the isolated reagents

$$E_\pi^{\mathrm{A}} + E_\pi^{\mathrm{B}} = E_\pi^0 = \varepsilon_\pi^0 - n W_p\,,$$

where n is the number of C atoms, $\varepsilon_\pi^{\mathrm{AB}}$ and ε_π^0 the total π-energies.

The ε_{π}^{AB} value was calculated using Pople approximation (for radicals it was originated from Roothaan method [12]) with the parameters which are quoted below.

In accordance with (4) the following bond lengths were accepted for the isolated reagents: $l_0 = 1.34$ Å for ethylene and $l_0 = 1.35$–1.46–1.35 Å for butadiene.

The Energy of σ-Bonds

The energy changes of σ-bonds are due to the alteration of their lengths and hybridization. The hybridization change is proportional to a^2 [8]. For the C–H bonds attached to the reaction centre, considering their lengths as equilibrium ones, one obtains

$$\Sigma \varDelta E_{\mathrm{C-H}} = \frac{a^2}{0.25}(3E_{\mathrm{C}_{te}-\mathrm{H}_{\mathrm{prim}}} + 2E_{\mathrm{C}_{te}-\mathrm{H}_{\mathrm{sec}}} - 5E_{\mathrm{C}_{te}-\mathrm{H}}) \tag{8a}$$

(for radical addition)

$$\Sigma \varDelta E_{\mathrm{C-H}} = 2\sum_r \frac{a_r^2}{0.25}(E_{\mathrm{C}_{te}-\mathrm{H}_{\mathrm{sec}}} - E_{\mathrm{C}_{tr}-\mathrm{H}}) \tag{8b}$$

(for Diels-Alder reaction).

The indices *te* and *tr* indicate respectively the tetragonal and trigonal hybridization; prim and sec indicate the primary and secondary atoms.

For C–C bond of the length l the energy change is a sum of (a) the energy of length alteration from l_0 to l the trigonal hybridization being retained, and (b) the energy of alteration of hybridization parameter from 0 to a, the bond length l being retained:

$$\varDelta E_{\mathrm{C-C}} = \frac{a^2}{0.25}[E_\sigma(l)_{\mathrm{C}_{te}-\mathrm{C}_{tr}} - E_\sigma(l)_{\mathrm{C}_{tr}-\mathrm{C}_{tr}}] + E_\sigma(l)_{\mathrm{C}_{tr}-\mathrm{C}_{tr}} - E_\sigma(l_0)_{\mathrm{C}_{tr}-\mathrm{C}_{tr}} \tag{9a}$$

(for radical addition, the square bracket is remained for C_2–C_3 bond only)

$$\varDelta E_{\mathrm{C-C}} = \frac{a^2}{0.25}[E_\sigma(l)_{\mathrm{C}_{te}-\mathrm{C}_{te}} - E_\sigma(l)_{\mathrm{C}_{tr}-\mathrm{C}_{tr}}] + E_\sigma(l)_{\mathrm{C}_{tr}-\mathrm{C}_{tr}} - E_\sigma(l_0)_{\mathrm{C}_{tr}-\mathrm{C}_{tr}} \tag{9b}$$

(for Diels-Alder reaction, ethylene).

For butadiene C–C bonds in Diels-Alder reaction formula (9a) is valid; the square bracket being remained for the terminal bonds.

The total σ-bonds energy change is

$$\varDelta_\sigma = \Sigma \varDelta E_{\mathrm{C-H}} + \Sigma \varDelta E_{\mathrm{C-C}}\,. \tag{10}$$

In calculation Lorquet data [9] were used.

The expression (10) is easily reduced to the sum of atomic contributions:

$$\varDelta_\sigma = \sum_r C_r a_r^2 + A\,. \tag{11}$$

The C_r and A values, which do not depend on hybridization, may be expressed by means of the standart values of bond energies entering the right parts of (8) and (9).

Exchange Repulsion

Intermolecular contribution to the ΣS^2 term including all the carbon valence AO's is invariant relative to the choice of the basic AO's; 2*s* and 2*p* AO's were used in the calculation. The intramolecular contribution is to be calculated for the π-orbitals (2) only; it arises due to the alteration of bond lengths and hybridization.

Parameters

The electron repulsion integrals $\gamma_{rs}(l)$ were those recomended by Goodman [13], their dependence on the type and orientation of AO's being neglected. The AO energies were assumed to be: $W_p = -11.54$ eV, $W_s = -21.34$ eV.

All the values of resonance parameters β including intramolecular ones were assumed to be proportional to overlap integrals S between orbitals (2):

$$\begin{aligned} &\beta_{rs}(l) \equiv \langle \chi_r | h | \chi_s \rangle = \kappa S_{rs}(l) \\ &\beta_{rs}(1.397\ \text{Å}) = -2.37\ \text{eV}, \quad \kappa = -9.19\ \text{eV}. \end{aligned} \tag{12}$$

The value of κ was empirically calibrated using ethylene, butadiene and benzene spectra. Overlap integrals were calculated using Slater AO's with effective charge $Z = 3.18$.

This estimation of β_{rs} is distinct from the choice accepted in [1, 2]. Thus it is necessary to put new γ value into (1) corresponding to the new β_{rs}. These values, determined as described in [2], are:

$\gamma = 8.66$ eV (without correlation of π-electrons),

$\gamma = 10.15$ eV (with correlation of π-electrons).

Optimization of the Hybride Orbitals

The optimal directions are those which minimize the interaction energy U. Let us select several directions considering them as a zero approximation. Among the values contributing into U overlap integrals S, resonance parameters β and hybridization parameters a depend on hybridization. We suppose their changes being small during the variation procedure. This condition may be satisfied by the proper choice of the zero approximation. Then the bond orders calculated in zero approximation may be regarded as constant. We can write, separating the variable part of interaction energy:

$$U = \sum_{\substack{r,s>r \\ \text{(intramolecular)}}} (2p_{rs}\beta_{rs} + \gamma S_{rs}^2) + \sum_{\substack{r,s>r \\ \text{(intermolecular)}}} 2p_{rs}\beta_{rs} + \sum_r p_{rr}\alpha_r + \Delta_\sigma + \text{Const}.$$

The intermolecular part of exchange repulsion is independent of hybridization since all valence electrons are included in it. Application of formulae (5), (7), (11), and (12) yields

$$
\begin{aligned}
U = & \sum_{\substack{r,s>r \\ \text{(intramolecular)}}} \left(2p_{rs} + \frac{\gamma}{\kappa^2}\beta_{rs}\right)\beta_{rs} + \sum_{\substack{r,s>r \\ \text{(intermolecular)}}} 2p_{rs}\beta_{rs} \\
& + \sum_r \left[C_r + (p_{rr}-1)(W_s - W_p)\right] a_r^2 + \text{Const}\,.
\end{aligned} \tag{13}
$$

Now it is necessary to find explicitly the dependence of the variables β_{rs} and a_r on the small variations $\Delta \boldsymbol{z}_r$ of unit vectors $\boldsymbol{z}_r$. It is convenient to represent the respective expressions in a vector notation using unit vectors $\boldsymbol{r}_{rs}$ defined in (6) and vectors $\boldsymbol{R}_r$, which determine the hybridization of atoms r through the relation

$$
a_r = \frac{(\boldsymbol{z}_r, \boldsymbol{R}_r)}{\sqrt{1 - \dfrac{(\boldsymbol{z}_r, \boldsymbol{R}_r)^2}{2}}} \approx (\boldsymbol{z}_r, \boldsymbol{R}_r)\,. \tag{14}
$$

It is easy to verify that $\boldsymbol{R}_r$ vectors coincide with the directions of the C—C σ-bonds attached to the atom and are equal to $\boldsymbol{R}_1 = \sqrt{2}\boldsymbol{r}_{21}$; $\boldsymbol{R}_4 = \sqrt{2}\boldsymbol{r}_{34}$; $\boldsymbol{R}_5 = \sqrt{2}\boldsymbol{r}_{65}$; $\boldsymbol{R}_6 = \sqrt{2}\boldsymbol{r}_{56}$.

While variating $\boldsymbol{z}_r \to \boldsymbol{z}_r + \Delta\boldsymbol{z}_r$, $a_r \to a_r + \Delta a_r$ and $\beta_{rs} \to \beta_{rs} + \Delta\beta_{rs}$. For small $\Delta\boldsymbol{z}_r$ values we find with the help of (14) and (6)

$$
\begin{aligned}
\Delta a_r &= (\Delta\boldsymbol{z}_r, \boldsymbol{R}_r)\,, \\
\Delta\beta_{rs} &= (\Delta\boldsymbol{z}_r, \boldsymbol{T}_{rs}) + (\Delta\boldsymbol{z}_s, \boldsymbol{T}_{sr})\,.
\end{aligned}
$$

Vectors $\boldsymbol{T}_{rs}$ are defined by relations

$$
\begin{aligned}
\boldsymbol{T}_{rs} = {} & \boldsymbol{R}_r\left[(\boldsymbol{z}_s, \boldsymbol{R}_s)\langle s_r|h|\, s_s\rangle + (\boldsymbol{z}_s, \boldsymbol{r}_{sr})\langle s_r|h|\,\sigma_s\rangle\right. \\
& \left. + \boldsymbol{r}_{rs}[(\boldsymbol{z}_s, \boldsymbol{R}_s)\langle s_r|h|\,\sigma_s\rangle + (\boldsymbol{z}_s, \boldsymbol{r}_{sr})(\langle\sigma_r|h|\sigma_s\rangle + \langle\pi_r|h|\pi_s\rangle)\right] + \boldsymbol{z}_r\langle\pi_r|h|\pi_s\rangle
\end{aligned}
$$

$\boldsymbol{T}_{sr} = 0$ for nonneighbouring atoms inside a molecule. Let us accept following abbreviations:

$$
\begin{aligned}
A_{rs} &= p_{rs} + \frac{\gamma}{\kappa^2}\beta_{rs} && \text{(intramolecular)}, \\
A_{rs} &= p_{rs} && \text{(intermolecular)}, \\
\boldsymbol{S}_r &= \sum_{s \neq r} A_{rs}\boldsymbol{T}_{rs} + [C_r + (p_{rr}-1)(W_s - W_p)](\boldsymbol{z}_r, \boldsymbol{R}_r)\boldsymbol{R}_r && (r = 1, 4, 5, 6), \\
\boldsymbol{S}_r &= 0 && (r = 2, 3)\,.
\end{aligned}
$$

After a number of simple transformations we obtain

$$
\Delta U = 2\sum_r (\Delta\boldsymbol{z}_r, \boldsymbol{S}_r)\,. \tag{15}
$$

The variations $\Delta\boldsymbol{z}_r$ are supposed to be independent in formula (15). This does not hold virtually since the normalization condition of $\boldsymbol{z}_r$ puts a restriction on $\Delta\boldsymbol{z}_r$. The last condition is satisfied with the accuracy of order of $(\Delta\boldsymbol{z}_r, \Delta\boldsymbol{z}_r)$ if the vectors z_r and Δz_r are orthogonal. Therefore we orthogonalize S_r and z_r:

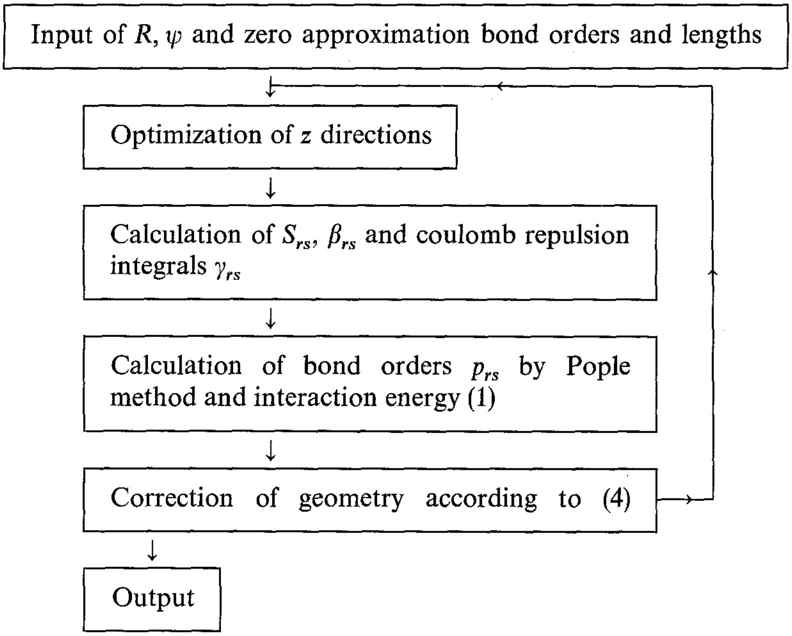
$$S'_r = S_r - (z_r, S_r)\, z_r$$

and obtain a final expression, which contains no restrictions for Δz_r:

$$\Delta U = 2 \sum_r (\Delta z_r, S'_r)\,. \tag{16}$$

The last formula is an approximate one since we have supposed the bond orders to be constant (the first order of perturbation theory) and used the approximation (14) which holds with the accuracy of order of a_r^2.

Optimization of U was carried out by means of a steepest descent method. As a zero approximation z axes were assumed which were directed along the bonds 1–6 and 4–5. The directions of Δz_r were estimated by the relation $\Delta z_r = -\lambda S'_r$. Then the minimum of (13) was sought for numerically with respect to the step λ, this procedure producing λ value. The new vectors z_r were used to calculate new a_r and β_{rs} and the new vectors S'_r. This procedure was repeated until selfconsistency was obtained. The general block-scheme of U calculation with the parameters R and ψ fixed is quoted below:



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Dr. M. V. Basilevsky
Karpov Institute of Physical Chemistry
Moscow B-120, ul. Obukha, 10
USSR