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Application of Quantum-chemical Methods to the Diels-Alder Reaction

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The quantum-chemical reactivity indices, used to estimate the relative reactivities of dienes and dienophiles in the Diels-Alder reaction, are analysed and certain problems associated with the use of quantum-chemical methods for the interpretation of cycloaddition selectivity, the reaction mechanism, and the influence of catalysts are discussed.
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I. INTRODUCTION

One of the most interesting reactions in organic chemistry is the Diels–Alder reaction. Many ideas concerning synthesis and profound theoretical concepts, sometimes going beyond the framework of the description of the reaction itself, are associated with it. Wasserman[1] and Woodward and Hoffmann[2] must be regarded as the founders of the theoretical interpretation of the Diels–Alder reaction. Wasserman's kinetic studies showed that the reaction is characterised by a low enthalpy of activation (less than 105 kJ mol^{-1}) and a negative activation entropy which is fairly large in absolute magnitude (on average $\sim$35 e.u.). These estimates lead to the conclusion that, firstly, in the transition state the initial molecules must retain their configuration and, secondly, that the structure of the transition state must resemble the configuration of the adduct formed. Wasserman suggested for the first time that the bond formed between the diene and dienophile arises as a result of the overlap of the molecular π orbitals in the direction of the terminal fragments of the system and not as a result of the lateral overlap of the corresponding *p* orbitals. Woodward and Hoffmann devised the elegant theory of "symmetry allowed" processes, which makes it possible to predict whether or not concerted reactions have a low or high activation energy at an elevated temperature or on exposure to UV light. Reactions for which a low activation energy has been predicted are symmetry-allowed, while reactions with a high activation energy are forbidden. In terms of this classification, the Diels–Alder reaction is a thermally allowed process; on the basis of the ideas described above, it should be regarded as a stereospecific suprafacial process with a concerted synchronous mechanism.

The use of asymmetric reagents, complex and specific dienes and dienophiles, non-standard reaction conditions, and catalysts led very rapidly to the application of this reaction which was popular even without these factors. More profound and detailed experimental studies demonstrated the possibility of also carrying out processes

which are "not allowed" according to the Woodward–Hoffmann hypothesis[3] and also the possibility of a two-stage mechanism,[4,5] in contrast to the classical single-stage synchronous mechanism. New views, showing that even this elegant theory has specific and relative aspects, have appeared.[6]

Many workers have now analysed various aspects of the Diels–Alder reaction. In particular, we may mention reviews in which the reactivity and reaction mechanism,[7–10] the activity and selectivity ratios,[11] the influence of substituents,[9] the regioselectivity and stereoselectivity,[9,11] the symmetry of the transition state,[7] and the possibility of applying perturbation theory[8,9] and frontier orbital theory[10,12] to the description of the characteristic features of the cycloaddition reaction are discussed.

The aim of the present review is the analysis of various quantum-chemical approaches used to investigate the Diels–Alder reaction and also a survey of the characteristic features of this reaction deduced from calculated data.

II. THE USE OF QUANTUM-CHEMICAL INDICES FOR THE DETERMINATION OF THE REACTIVITY OF DIENES AND DIENOPHILES. ALLOWANCE FOR THE INFLUENCE OF SUBSTITUENTS

The first attempts to use quantum-chemical methods for the quantitative description of the reactivities of dienes were based on Brown's hypothesis.[13–18] Its essential feature is the assumption that, in the formation of an adduct, one π electron is localised at each of two terminal carbon atoms of the diene system having a favourable conformation for the addition of the dienophile. Such localisation is a precondition for the formation of two new σ-bonds. The energy necessary for the localisation of two electrons [the *para*-localisation energy (PLE)] was calculated by the LCAO-MO method and was related to the reactivity of the diene—the lower the value of the PLE, the lower the activation energy for the reaction.

PLE has been calculated by the free electron method for polycyclic aromatic hydrocarbons (28 compounds in all).[19] The values obtained were compared with Brown's data. For all the compounds considered, the predictions by the two methods concerning the ability of aromatic hydrocarbons to combine with maleic anhydride generally agree. In certain cases the course of the reaction is influenced significantly by the steric hindrance due to the substituents. For example, according to Brown's calculation, 1,2,3,4-tetraphenylbutadiene should react with maleic anhydride somewhat more slowly than anthracene; in fact the reaction does not occur at all.[18]

In the case of *o*-benzoquinones, the PLE has been used to characterise their dual ability to react as dienes and dienophiles.[20] It was found that these compounds behave as dienes when the *para*-localisation energy is less than a certain value.

For dienes having several possible addition sites, the Diels–Alder reaction proceeds at sites with the lowest value of PLE[20,21] and the highest localisation of charge.[22] The site at which maleic anhydride adds to Klar's hydrocarbon (centrine) has in fact been determined by calculating the PLE.[21]

On the basis of Brown's idea, Sofer et al.[23] introduced various types of indices (ρ) for dienes and dienophiles: indices of the "ethylene", "butadiene", and "benzene" character, which describe the reactivities of the test systems. For the set of polycyclic aromatic structures, the values obtained are compared with the PLE. It has been found that the character of the correlation between ρ and PLE is different for different types of reaction centre. According to Sofer et al.,[23] this permits conclusions about the reaction mechanism. Indices with the "benzene" character ρ_b were used by the same workers to estimate the relative reactivities of different rings in linear polyacenes.[24] It was assumed that $\rho_b = 1$ for benzene; the value of ρ_b is correlated with the PLE, diminishing with increase in the size of the system. The minimum value ($\rho_b = 0.8$) has been obtained analytically for the middle ring in the infinite polyacene; in practice, it is attained when the number of rings is ten.

Epstein[25] used the orders of the bonds between the carbon atoms in the 1- and 2-positions and 3- and 4-positions in the diene as the static reactivity indices. Benzene, 13 polyacenes containing between two and five condensed rings, 10 even polyenes, and 4 heterocyclic systems were considered. It is stated that a correlation was observed between the bond order and the PLE for each type of molecules listed above, but the correlation breaks down when the molecules of different types are considered jointly. This has also been noted by Raghavan and Narasimhan.[20]

Correlations of different reactivity indices should be treated with caution,[26,27] since they depend on the structure of the compounds, i.e. are functions of the "structural variable" s. Within the limits of a given reaction series, two reactivity indices, say A and B, are functions of s: $A(s)$ and $B(s)$. It would seem at first sight that it is sufficient to eliminate the dependence on s and to find the relations $A = A(B)$. However, this cannot be done because s is not a variable in the fundamental sense but depends in its turn on the nature of the substituent. The correlation of the indices is therefore always some kind of approximation.[26,27] It was shown in the same investigation that the correlation of the reactivity indices is impaired when charge transfer takes place in the transition state between the reactants, which is highly characteristic of the Diels–Alder reaction.[7]

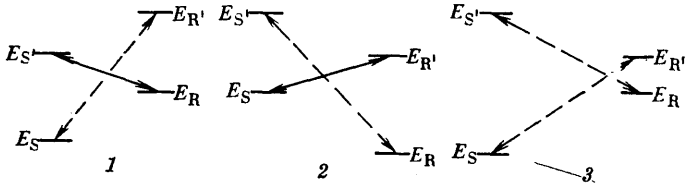
In the PLE, as in other static reactivity indices, no account is taken of the influence of the substituents on the dienophile. Calculation of this kind can then therefore serve only for the description of the relative reactivities of dienes. The change in the π-electron conjugation energy on formation of an adduct from aromatic hydrocarbons has been calculated by the free electron method and related to the relative yields of the reaction products.[28] It was found that a reaction is observed when the losses in the conjugation energy are $< 1.7 \mid \beta \mid$, where β is the resonance integral.

The results of studies on the Diels–Alder reaction involving a series of methyl-substituted 1-ethoxybutadienes (I) and 2-ethoxybutadienes (II) have been analysed.[29] The dienophiles employed were substituted ethylenic compounds $H_2C = CHX$, where X = CHO, CO_2H, $COCH_3$, CO_2CH_3, or CN. Comparison of the experimental data with calculation showed that the logarithms of the rate constants lg k for the reactions considered are linearly correlated with the ionisation potentials of the diene in the series (I) and (II) considered separately. A linear correlation has also been observed between lg k and the electron affinity of the dienophile. The electron density in the frontier MO is also used to account for the reactivity of dienes.[30,31]

We shall consider a series of studies in which account was taken of the influence of substituents.[9,32–35] It is noteworthy that the majority of investigators turn to perturbation theory and to the frontier orbital (FO) approximation in the solution of this problem. Electron-donating substituents increase the energy of both FO's, the energy of the highest occupied molecular orbital E_{HOMO} changing more markedly than the energy of the lowest unoccupied molecular orbital E_{LUMO}. Electron-accepting substituents reduce the energies of both FO's, E_{LUMO} varying more markedly than E_{HOMO}. Depending on the difference between the FO energies of the diene and dienophile, it is formally possible to formulate three types of Diels–Alder reactions: "normal" (*1*), "reverse" (*2*), and "neutral" (*3*) (see Figure).[7,9] The continuous arrow indicates the decisive interaction; such interaction is not observed for reactions of the "neutral" type.

Taking into account the influence of substituents on the FO energy levels in the reactants and the type of decisive interaction, it is possible to predict how these substituents, introduced into the 2π

or 4π system, affect the rate of reaction, since the rate should increase with decrease in the difference between the frontier orbital energies responsible for the interaction.[7,9,32] The theoretical predictions stating that there is a difference between the activation parameters for reactions which obey the forward and reverse Alder rules, that the reactivity of *trans*-disubstituted ethylene, behaving as the dienophile, is higher than that of the *cis*-isomer, and that the introduction of the carbonyl group into the dienophile influences the rate of reaction and predictions concerning the disposition of the orbitals in the reactants, put forward on the basis of calculations by the CNDO/2 method using the perturbation theory, agree with experimental results.[32]



Types of Diels–Alder reactions as a function of the difference between the FO energies of the diene and the dienophile: *1*) "normal" reaction; *2*) "reverse" reaction; *3*) "neutral" reaction; R = diene index; S = dienophile index; E_R, E_S = HOMO energies; E'_R, E'_S = LUMO energies.

The concept of active orbitals has been introduced.[36] Active orbitals comprise the occupied bonding orbital of one of the reactants and the unoccupied antibonding orbital of another. These orbitals describe the bonds formed and broken on cycloaddition. For the "normal" Diels–Alder reaction, the HOMO of the diene and the LUMO of the dienophile are active, whilst the opposite situation obtains for the "reverse" reaction. The experimental activation energy ΔE_{act} obeys the correlation $\Delta E_{act} = \alpha\Delta\varepsilon$, where α is a dimensionless empirical constant for the given reaction (for the Diels–Alder reaction, $\alpha = 0.18$) and $\Delta\varepsilon$ is the difference between the energies of the active orbitals. The quantity $\Delta\varepsilon$ was calculated by the extended Hückel method. The authors[36] believe that the influence of the substituents is associated with the stabilisation and/or destabilisation of the active orbitals.

The influence of electron-donating and electron-accepting substituents on the energies of the HOMO and LUMO of the diene and dienophile has been examined.[37] The rule has been formulated according to which the maximum increase in the rate of the thermal symmetry-allowed cycloaddition reaction of alicyclic reactants is promoted by the introduction of electron-donating substituents into the reactant molecule having the HOMO with the highest energy. This rule is more general than the familiar Alder rule.

It has been shown[38] that the inertness of certain five-membered cyclic chloro-substituted dienophiles in the reaction with cyclopentadiene is associated with the low electron affinities of the test molecules and the low stabilisation energies of the transition state E_s. It has been suggested that there exists a limiting value of E_s, below which the reaction does not occur. The amount of informa-tion contained in certain quantum-chemical reactivity indices of dienophiles was estimated in the same study. The electron affinities calculated by the simple and extended Hückel methods can be useful in the first stage of the study of the reactivity. The reac-tivities of dienophiles in the Diels–Alder reaction are described more adequately by Dewar's MO perturbation method (MOP) and Salem's intermolecular orbital method (IMO). Fukei's frontier orbital method proved unsuitable for the study of compounds of this series. (The frontier orbital approximation cannot be used for heterodienophiles either.[39]) The dependence of the reactivities of dienophiles (ethylenes, benzoquinones, and naphthoquinones) on the nature of the substituents has been considered in a number of studies.[40,41]

The relative reactivities of heterocyclic compounds, namely furan (III), thiophen (IV), and thiophen 1,1-dioxide (V), have been investigated[43] by a modified CNDO/2 method.[42] The stabilising influence of symmetrical (S_π) and antisymmetric (A_π) orbitals of the heteroatom and the SO_2 group on the S_π and A_π MO of the diene and the product was considered as a perturbation of the diene fragment. In furan the 2*p* AO of oxygen have approximately the same stabilising effect on the MO of the product and the reactant and in this case a thermal reaction is possible. The influence of the 3*d* AO of oxygen in furan is insignificant. On the other hand, in thiophen the 3*d* AO of sulphur exert the greatest influence on the A_π MO of the diene, while their influence on the MO of the product is insignificant and the equilibrium in this reaction is strongly displaced towards the reactant. The stabilisation in compound (V) is less marked than in thiophen and the equilibrium is less displaced towards the reactants. The diene reactivity series (IV) < (V) < (III) has been confirmed experimentally.

III. PREDICTIONS BASED ON CALCULATIONS OF THE SELECTIVITY OF THE CYCLOADDITION

The question of selectivity is very important in the Diels–Alder reaction.[9,11] Three types of selectivity are distinguished: chemoselectivity (competition between processes), regioselectivity (competition between the orientations of the reactant leading to positional isomers), and stereoselectivity (competition between the orientations of the reactants leading to geometrical isomers).[44] Special attention is devoted in the literature to the last two types of selectivity. However, competitive processes, for example [2 + 2]-cycloaddition, Michael addition, and the interaction of functional groups, can also arise with the Diels–Alder reaction. The computational method for the prediction of chemoselectivity in the relevant processes has been used very rarely. The chemoselectivity in the reaction of α-dimethylaminostyrene with various dienophiles has been predicted by the MINDO/3 method.[45] Depending on the polarity of the bond in the reactant (the authors introduced a special parameter, equal to the ratio of the difference between the charges on the bonds involved in the multiple bond to its length), one can establish which reaction takes place: [2 + 2]- or [2 + 4]-cycloaddition or the interaction of the amino-group. On the other hand, if several potentially possible Diels–Alder reactions compete, then the more reactive reactants are found to be more selective. This view, derived from the theory of orbital interaction is opposed to the concept put forward previously stating that the less active reactant is the more selective. This means that the processes in which donor–acceptor interactions play a significant role and the relative reactivity is controlled by the frontier orbital energies constitute exceptions to the general rule.[7,12,39] The chemoselectivities and regioselectivities for the radical-cation cycloaddition reactions have been considered.[46]

A general theoretical approach to questions of regioselectivity and stereoselectivity in the Diels–Alder reaction has been described.[9,47-49] Quantum-chemical methods for the determination of the regioselectivity of the process have been used in Refs.50–72 and those for the determination of stereoselectivity have been used in Refs.73–82.

In order to account for the high regiospecificity in the interaction of asymmetric components, the perturbation energies have been calculated by Dewar's method for substituted butadienes (the 1-methyl, 2-methyl, 1-phenyl, and 2-phenyl derivatives) in their reactions with acrylonitrile, methacrylate, and styrene.[50] The coefficients

of the frontier orbitals of the dienes and dienophiles were calculated in terms of the Hückel approximation. The interaction between the atoms of the reacting molecules was taken into account only in the region of bond formation. The calculated perturbation energies for the *o*-, *m*-, and *p*-derivatives were compared with the relative reaction yields. It thus proved possible to predict the preferred orientation in the addition reaction in all the cases examined.

Calculations have been carried out[51] by the PPP method for methyl vinyl ketone and a series of substituted buta-1,3-dienes: 2-methoxy-1-phenylthiobuta-1,3-diene (VI); 2-methoxyphenylthiobuta-1,3-diene (VII); 2-acetoxy-3-(*p*-hydroxyphenylthio)buta-1,3-diene (VIII); 1-acetoxy-4-phenylthiobuta-1,3-diene (IX), and 3-methoxy-3-(2-pyrimidylthio)-buta-1,3-diene (X). The structures of frontier molecular orbitals have been analysed and the regioselectivity in the Diels–Alder reaction has been investigated on the basis of the MOP theory. For all the dienes examined, the transfer of electron density is determined by the primary interaction of their HOMO with the LUMO of the dienophile. The differences between the HOMO coefficients for the corresponding carbon atoms for compounds (VI) and (VII) are small. The regioselectivity of the addition is therefore determined by the character of the LUMO of these compounds, i.e. by the secondary interaction of the LUMO of the diene and the HOMO of the dienophile. The difference between the HOMO coefficients for compound (VIII) is large and the regioselectivity of its addition to methyl vinyl ketone is determined by the primary interaction, in conformity with experimental data. A characteristic feature of 1-acetoxy-4-phenylthiobuta-1,3-diene is that the weak directing effect of the primary interaction is enhanced by the secondary orbital interaction acting in the same direction.

The orientational phenomena in the Diels–Alder reactions of 2R-butadienes with methyl methacrylate have been investigated by the IMO method. A comparison has been made with other methods: the simple perturbation theory and the FO method.[52] The regioselectivity in the reactions of substituted butadienes has also been investigated in other studies.[29,53,54] Analysis within the framework of the perturbation theory in terms of the approximation of F whose coefficients were calculated by the CNDO/S and the Hückel MO method made it possible to account for the regioselectivity in the reactions of methyl-substituted 1- and 2-ethoxybutadienes with substituted ethylenes.[29]

The mode of cycloaddition to various vinylpyridines[55,56] and oxazoles[56] and also of the cyclodimerisation of vinyl pyridines[57] has been correctly predicted and explained on the basis of the formation energies of the regioisomers. If the vinylpyridines function as the dienes, then in their structures it is possible to distinguish formally two pseudodiene fragments: N=C–C=C and C=C–C=C, which must be taken into account in the calculations.[55,57] The formation energies of the regioisomers were estimated in the above studies from

$$\Delta E_\pi = 2\left[\frac{(C_{R_n}C'_{S_m}\beta_{mn} + C_{R_p}C'_{S_q}\beta_{pq})^2}{|E_R - E_{S'}|} + \frac{(C'_{R_n}C_{S_m}\beta_{mn} + C'_{R_p}C_{S_q}\beta_{pq})^2}{|E_{R'} - E_S|}\right],$$

where C and C' are the coefficients of the atomic orbitals of the directly interacting atoms n and p (diene index R) and m and q (dienophile index S) involved in the corresponding HOMO and LUMO, E_R, $E_{R'}$, E_S, and $E_{S'}$ are the frontier orbital energies of the diene and dienophile, and β_{mn} and β_{pq} are the corresponding resonance integrals of the *mn* and *pq* bonds formed in the combined RS system. The coefficients of the AO and the FO energies were calculated by the MINDO/3 method. The experimental data on the stereochemistry of the reaction of 5-ethoxyoxazole with β-acetylacrylic acid and its ethyl ester as well as the reactions of vinylpyridines with azodicarboxylic acid ester and the cyclodimerisation of vinylpyridines agree with the calculations. Similar studies, demonstrating that the observed changes in the reactivity correspond to the stabilisation energies arising as a consequence of the interaction of the frontier orbitals, have been carried out also for the Diels–Alder reaction of the "neutral" type.[58,59]

The π-electon density at the atoms of 5-ethoxyoxazole and acrylic acid and its ethyl ester has been calculated by the Hückel method taking into account the hyperconjugation effects generated by the methyl group. A two-stage mechanism with charge distribution in the transition state has been proposed on the basis of the results of the calculation and the regioisomer formed has been predicted correctly.[60]

The FO theory has been used to account for the isomeric composition of the products of the Diels–Alder reaction.[61] It was postulated that the reaction takes place in two stages and that a weak bond between centres is formed in the first stage. In the special case where the HOMO energy of one molecule and the LUMO energy of the other are close to the energy of the non-bonding orbital, such centres are atoms with the highest, in terms of absolute magnitude, coefficients of the HOMO of the first molecule and LUMO of the second. More than 100 reactions have been investigated within the framework of the Hückel method with various sets of parameters. In all cases the structure of the main product was predicted correctly.

Summarising, one may say that the regioselectivity of the concerted cycloaddition reactions is determined by the orbital effects favouring the formation of bonds between two atoms, to which correspond the coefficients in the expressions for the FO, and between two atoms for which the coefficients for the FO are minimal.[9] On the other hand, Ioffe et al.[62] believe that the relation between the regioselectivity of the reaction and the structure of its transition state is closer and classify the regioselectivity into short-range and long-range components. It follows from the analysis of the structure of the potential energy surface for a reaction leading to two regioisomeric products that the regioselectivity of such a reaction is determined not only by the relative stabilisation of the transition states but also by the height of the ridge separating two valleys on the potential energy surface. If this ridge is low, then a redistribution of the reaction complexes, in conformity with the relative stabilities, can occur during the reaction. In this case the regioselectivity is of the short-range variety and is high when there are significant differences between the stabilisation energies of the transition states. On the other hand, the existence of a high ridge between the valleys prevents the redistribution of the reaction complexes. In other words, in such reactions the regioselectivity is of the long-range kind and is less pronounced, because it is predetermined already in the early stages where the secondary orbital interactions are insignificant.

Ioffe et al.[62] note that, although the calculation of the total potential energy surface is extremely complex, the height of the potential barrier for concerted cycloaddition can be estimated from considerations involving orbital symmetry. On the grounds that the regioisomeric adducts are formed in the Diels–Alder reaction from different transition states and interconversion is difficult, the concerted *supra-supra*-cycloaddition is classified as a process with long-range comparatively low regioselectivity. Different methods of predicting regioselectivities have been compared by Chen.[63]

Quantum-chemical calculations which explain the stereoselectivity in the Diels–Alder reaction have been used for the solution of the problem of both the *endo, exo*-specificity and the *syn, anti*-specificity. On the basis of experimental data obtained in the study of the reaction of cyclopentadiene with maleic anhydride, Alder and Stein concluded that differential *endo*-orientation obtains and explained it by the "maximum accumulation of unsaturation".[1] Woodward and Hoffmann[2] explained this rule by the fact that the FO of the secondary centres, i.e. atoms which are not linked to one another in the adduct (the interaction of the orbitals of the secondary centres is

referred to as secondary orbital interaction), may overlap for the *endo*-adduct. This electronic effect lowers the activation energy for the reaction and hence the *endo*-adduct is formed faster. The study of the reaction of cyclopentadiene with various dienophiles within the framework of the Hückel method showed that the delocalisation energy of the *endo*-configuration is always greater than that of the *exo*-isomer,[73,74] which conforms to the Alder–Stein rule. A model calculation for the coplanar *endo*-oriented complex in the reactions of cyclopentadiene with acrolein, crotonaldehyde, butadiene, isoprene, and piperylene has been carried out by the Hückel method including Madelung's correction to the energy.[75] The distance between the plane of the diene and the dienophile was varied in the range 2.6–4.0 Å. It was found that in the range investigated the *endo*-orientation is always energetically more favourable than the *exo*-orientation and that the charge transfer from the diene to the dienophile in the case of the *endo*-orientation exceeds that for the *exo*-orientation.

However, experimental data have shown that the Alder–Stein rule is not absolute. A mixture of isomers is usually formed, their ratio depending on the nature of the initial compounds, the electronic and steric effects, and also the reaction conditions. Under conditions of thermodynamic control, there is a possibility of the preferential formation of the more stable *exo*-adduct. Such uncertainty in the prediction of the expected stereoisomer can be explained by the fact that the secondary orbital interactions responsible for the stereoselectivity have low energies and the influence of other factors is therefore extremely important. For this reason, in contrast to the problem of the regiospecificity of the Diels–Alder reaction, it is much more difficult to solve the problem of the stereoselectivity by computational methods.

Mazzoechi et al.[76] investigated the π-surface stereoselectivity of the cycloaddition of hexachlorocyclopentadiene to 7R-norbornadienes (R = H, t-BuO, $PhCO_2$, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Ph, *p*-FC_6H_4, Cl, CH_3CO_2, or Me). Non-empirical *ab initio* MO calculations have shown that the substituents in the 7-position influence the reorientation of the π-bonds in space, the ease of the displacement of the olefinic protons from the plane, and probably the very planarity of alkenes. The substituents investigated increase the electron density at one of the two bonds of the ring. The dependence of the partial reaction rate factors on the electronegativity ε of the substituent *R* can be satisfactorily explained for *anti, exo*-attack. In the case of *syn, endo*-attack, a significant acceleration of the latter has been demonstrated for 7-t-butoxynorbornadiene. However, the slight variation of the partial rate factor as a function of ε for *syn, endo*- and *anti, endo*-attack could not be fully explained.

In a study of the stereochemistry of cycloaddition to substituted acetylenic and ethylenic compounds,[77] it was found that a dienophile adds stereospecifically to the endocyclic diene fragment of fulvenes from the side opposite the CH_2 bridge. In order to explain this phenomenon, calculations were carried out by the MINDO/3 and INDO methods. On the basis of the perturbation theory, the authors[77] believe that such stereospecificity of the cycloaddition is caused by the fact that, when the dienophile is attacked from the side of the methylene bridge, a strong antibonding interaction takes place between the HOMO of the dienophile and the LUMO of the diene (especially in the *exo*-oriented transition state), because the π orbitals of the terminal atoms of the diene are turned inwards towards the π orbitals of the dienophile. On the other hand, one must take into account the fact that the four-electron four-centre interaction considered weakens under the conditions of the *endo*-attack, since the corresponding π orbitals of the diene fragments are turned away from the dienophile. Analysis of the calculated data and photoeletron spectra also permits conclusions concerning the role of the σ–π interactions of the orbitals in the test systems.

In order to account for the experimental observation of the formation of the *exo* or *endo*-configuration with the *syn*-position of the nitrile group in the reactions of cyclopropenes with various dienophiles, the qualitative perturbation theory has been used.[78] The authors based their conclusions on the fact that the steric structure of the transition state is determined by the maximum overlap of the frontier MO of the adducts.

The study by the INDO method of the influence of the methyl groups on the rate and stereochemistry of the cycloaddition and the use of kinetic data for a series of tricyclo[5.2.1.$0^{2,6}$]decadienes and trienes[34] showed that electronic effects play the main role in determining the selectivity (for the majority of compounds). It is believed[34] that one of the main factors determining the reaction selectivity is the character of the distortion of the MO. For norbornyl-condensed spirocyclic cyclopentadiene systems, the mixing of the σ and π orbitals of the dienes plays the most significant role. It is responsible for minimising the antibonding interactions for the observed stereochemistry of the cycloaddition, which has been demonstrated with the aid of the INDO method.[79] The *syn,anti*-stereoselectivity has been investigated as a function of the geometry of the transition state.[80]

The factors influencing the stereoselectivity of the cycloaddition reactions have been examined in a review.[81] It was concluded that the stereoselectivity is determined mainly by the orbital interaction. The application of perturbation theory to the determination of the selectivity of processes has been discussed in detail in a number of studies.[9,83,84]

IV. THE MECHANISM OF THE DIELS–ALDER REACTION

For a long time, the Diels–Alder reaction was assumed to be a concerted suprafacial process with a single-stage synchronous mechanism. This idea was based on the Woodward–Hoffmann theory of orbital symmetry. However, certain experimental and calculated data obtained in recent years make it necessary to consider the following question: is the classical mechanism in the Diels–Alder reaction the rule or an exception. On the basis of the results of kinetic studies by Dewar,[4] one may conclude that the transition state is asymmetric in the reactions of furan derivatives with maleic anhydride. According to the results of the same worker, obtained by the MINDO/3 and MNDO methods, any synchronous processes involving the participation of more than one bond have unduly large activation energies and therefore can hardly occur.[5] Our experimental studies on isoindoles also confirm the possibility of non-synchronous cycloaddition.[85,86]

Nevertheless, from our point of view, the complete neglect of the orbital symmetry theory is unjustified at the present stage. This theory has provided too many explanations for organic chemists to be abandoned without adequate justification. In the general case one must therefore take into account the possibility of both a many-centre synchronous mechanism and a two-stage mechanism with the intermediate formation of a zwitterion or a biradical. A concerted but non-synchronous mechanism, i.e. one where two new bonds are formed at different rates, is also theoretically feasible.

The structure of the transition state of the reaction depends on the proposed mechanism. In the theoretical analysis of this process with the aid of MO methods, one must therefore use different approaches.[87]

Quantum-chemical calculations have been applied most often to the study of the mechanism of the cycloaddition of ethylene to butadiene. It has been demonstrated by the CNDO/2 method that the approach of the ethylene molecule from "above" and not from the plane of butadiene is most favourable.[88] The reaction takes place in such a way that the principle of the maximum overlap of the $2p_\pi$ orbitals of ethylene and the analogous orbitals of the

terminal carbon atoms of butadiene is obeyed. Significant changes in the structure of the reacting molecules, in bond lengths, and in the hybridisation of the atoms take place only when the distance between the carbon atoms of the ethylene and the terminal carbon atoms of butadiene is less than 2 Å. It has been noted that the $\sigma-\pi$ interaction plays a significant role in estimations of the energy characteristics of the reaction. In the case of substituted ethylenes and butadienes,[82] the $\sigma-\pi$ interaction is also very important as a factor controlling the selectivity of the addition.

It has been observed[74] that the stability of the complexes formed between the *cis*-butadiene and dienophile (ethylene or *p*-benzoquinone) components is low if the distance between the components is ~3.0 Å. The stabilisation energy of the charge-transfer complexes in the reaction with ethylene is 16.76 kJ mol^{-1} and that for the reaction with benzoquinone is 37.71 kJ $mole^{-1}$. It has been noted[88,89] that charge transfer takes place from butadiene to ethylene in the course of the formation of the activated complex. It has been demonstrated[90] that, in the analysis of the dependence of the rate of reaction on the nature of the dienophile, it is likewise necessary to take into account the charge transfer between the components of the diene synthesis.

The non-empirical method for the calculation of the reaction pathway in the cycloaddition of ethylene to butadiene within the framework of the Roothaan method makes it possible to establish that during the reaction the planes of the molecules are disposed at an angle of 70° relative to one another.[89] In the same study an attempt was made to determine the heat of reaction and to estimate the electronic and geometrical structures of the transition state. However, it was found that an unsuccessful method had been used for the optimisation of the geometrical parameters.[91]

An interesting method has been proposed[92] for the description of the reactivity (including that in the Diels–Alder reaction), in which the state of each atom involved in the reaction is described by a parameter called the reaction angle. Two computational schemes, based on the PPP and Hückel MO approximations have been developed. The first has been called the method of topological molecular orbitals (TMO) with configuration interaction (TMO-CI) and the second TMO scheme is a simplified version of the first in which the intermolecular repulsion integrals were disregarded. The total energy of the system is described as a function of the reaction angles. This function describes a topological hypersurface; the reaction mechanisms are discussed in terms of stationary points on the hypersurface. A detailed analysis has been carried out for the reaction of butadiene with ethylene.[92] Minima corresponding to the reactants and products (cyclohexene) and two saddle points, corresponding to the *supra, supra-* and supra, antara-cycloadditions were found on the hypersurface for this reaction. However, only the former corresponds to the true activated complex (the gradient at this point is zero and the Hess matrix has only one negative eigenvalue). The activation energy for the reaction, amounting to 101 kJ mol^{-1} (Hückel MO) and 112 kJ mol^{-1} (PPP), was calculated for the *supra, supra*-cycloaddition. An additional saddle point corresponds to the singlet biradical, but the reaction pathway, linking the reactants to this biradical, passes through a stationary point at which Hess's matrix has two negative eigenvalues. The two stage mechanism is therefore prohibited owing to infringement of the Murrell–Laidler rules. On the other hand, the biradical can be obtained from the reaction products. This is a possible mechanism in cases where the stereoselectivity of the reaction diminishes.

The biradical transition state of the Diels–Alder retroreaction cyclohexene → butadiene + ethylene is supported by the results of the study of the fragments of the potential energy surface carried out in terms of the MINDO/3 approximation with full optimisation of the geometry.[93] The calculations were performed taking into account the configuration interaction. The transition state found was consistent with an asymmetric biradical to which corresponds an activation energy of 428.9 kJ mol^{-1} (experimental value 268.8 kJ mol^{-1}). According to the author,[93] the unrestricted SCF method provides a more correct description of potential energy surfaces, making it possible to distinguish two stages in the retroreaction investigated: the first, rate-limiting stage involving the formation of an asymmetric biradical intermediate with an activation energy of 365.4 kJ mol^{-1} and the second stage involving the decomposition of the intermediate to ethylene and butadiene with an activation energy of 79.9 kJ mol^{-1}. The activation entropies for the first and second stages as well as the kinetic isotope effects were calculated and it was concluded that the latter cannot serve as a criterion for the choice between the synchronous and non-synchronous mechanisms of the Diels–Alder reaction.

Bazilevskii[26] and Tikhomirov[27] suggested that corrections be introduced into the semiempirical π-electron PPP theory in order to take into account the non-orthogonality of the basis AO and the electronic correlation. The correction for the non-orthogonality (exchange repulsion) together with allowance for the Coulombic interaction of the atoms leads to the appearance of a new contribution in the expression for the energy of the system. The potential surface for the Diels–Alder reaction in the ethylene–butadiene system is constructed taking into account this contribution and using the hybrid orbitals. It has been noted that, for a fixed method of calculation of the energy taking into account an incomplete set of degrees of freedom (which is frequently done), one can obtain only the upper limit to the activation barrier (because the crossing point is an extremum).

The results of calculations of the energy of π electrons in terms of the PPP approximation established that the pathway involving the consecutive formation of σ-bonds requires a higher activation energy.[94] The reaction of butadiene with ethylene has been investigated also in other studies,[95–98] whose results do not conflict with these ideas. The possibility of a single-stage mechanism with a pericyclic transition state and of a two-stage mechanism with the intermediate formation of a biradical has been discussed.[99]

Thus one may conclude that the results of quantum-chemical calculations for the forward Diels–Alder reaction between butadiene and ethylene indicate a single-stage synchronous mechanism with the intermediate formation of a charge-transfer complex. However, the retroreaction is characterised by a two-stage mechanism with the intermediate formation of a biradical (or by a single-stage mechanism with a biradical transition state).

A number of studies have been devoted to the mechanism of the reactions of substituted butadienes and ethylenes. The parameters of the transition states for the Diels–Alder reactions of 1- and 2-ethoxybutadienes with acrolein have been calculated by the MINDO/2 method for two reaction mechanisms: the concerted synchronous mechanism and a non-synchronous mechanism.[98] The geometrical parameters were optimised by minimising the energy using Rinaldi's method. The calculated potential barriers to the reaction led to the conclusion that 2-ethoxybutadiene reacts preferentially via the concerted mechanism, while 1-ethoxybutadiene reacts via a non-synchronous mechanism. The calculated activation energies (163 and 119.5 kJ mol^{-1} respectively) agree with the observed rate constants for the reactions of these isomers with acrolein at 65 °C.[98] Evidence supporting the single-stage mechanism for substituted butadienes has also been obtained in other studies.[29,100]

Calculations for the transition state[101] in a reaction involving the cyclodimerisation of buta-1,3-diene to 4-vinylcyclohexene by various methods, (FO, MINDO/3 and *ab initio* SCF MO) showed that the activation energy is reduced when a radical-cation is formed as an intermediate, which is inconsistent with the synchronous mechanism. The authors[101] suggest that the Diels–Alder reaction between

buta-1,3-diene and the butadiene cation proceeds in accordance with a concerted but non-synchronous mechanism via a bisallyl radical-cation in which the pericyclic interaction is relatively weak.

We shall now return to the study mentioned previously[29] in which the mechanism of the reaction of ethoxybutadienes with various dienophiles is discussed (see above). The calculations were performed within the framework of the perturbation theory in terms of the FO approximation and the frontier orbital coefficients were calculated by the CNDO/S and the Hückel MO methods. Comparison of the calculated interaction energies of the frontier orbitals with the logarithm of the reaction rate constant with the aid of correlation analysis leads to the conclusion that a synchronous mechanism operates in the series of compounds II and a non-synchronous mechanism in the series of compounds I. However, the CNDO/S and Hückel MO methods yield opposite answers to the question as to which of the two bonds is formed earlier.

An interesting approach to the study of the reaction mechanism has been proposed.[102] On the basis of the FO theory, the role of the donor–acceptor interaction in two systems is considered qualitatively: (1) with the diene as the donor and the dienophile as the acceptor; (2) with the dienophile as the donor and the diene as the acceptor. The objects of study are not specified exactly. It follows from the analysis in the above investigation[102] that the simultaneous formation of two bonds is possible if the interaction between antisymmetric MO predominates. On the other hand if the interaction between symmetrical MO is decisive, the probability of the formation of a cyclic transition state diminishes.

In relation to the interaction of cyclopentadiene with various dienophiles and of maleic anhydride with various dienes, it has been shown[74] that the diene and the dienophile are charged positively and negatively respectively in the intermediate complex. The degree of polarisation is correlated with the delocalisation energy of the corresponding complex, which is linearly related to Brown's *para*-localisation energy.[74]

The distribution of electron density in the π-complexes between the diene and the dienophile, which have been identified with the activated complexes in the Diels–Alder reaction to simplify the procedure, has been studied with the aid of a modified version of the Hückel method.[103] The π-complexes of cyclopentadiene with ethylene, acroleine, *p*-benzoquinone, and 1,4-naphthoquinone and the π-complexes of maleic anhydride with benzene, napthalene, anthracene, phenanthrene, pyrene, benzanthracene, dibenzanthacene, benzophenanthrene, pentacene, and hexacene were examined. The distance between the molecular planes was assumed to be 1.87 Å. The resonance integrals arising when the molecular interaction was considered were assumed to be proportional to the overlap integrals. In all the π complexes investigated, the diene component is the electron donor. The magnitude of the transferred charge increases with increasing delocalisation of the π complex. It was found that the degree of conjugation in the π complexes corresponding to the endothermic reactions is greater than in the π complexes in the exothermic reactions.

The reactivity of dienophiles having different structures in their reactions with cyclopentadiene has been investigated by the method of intermolecular orbitals (IMO) using a coplanar model of the transition state (TS).[104] Such calculation presupposes the equality of the overlap integrals between different atoms. The interaction energy E_{in}, equal to the stabilisation energy, is used as a characteristic of the of the reactivity for various kinds of mutual approach of the molecules. Within the limits of three reaction series of dienophiles (A—cyanoethylenes, B—maleic anhydride derivatives, C—quinones), the values of E_{in} were calculated for two types of coplanar TS: *endo* and *exo*. It was shown that the IMO method is applicable to the description of the reactivities of symmetrical dienophiles (series B and C), and leads to unsatisfactory results for asymmetrical dienophiles (series A). The authors[104] therefore suggest that the IMO-2 method, in which it is assumed that the primary overlap integrals are not equal, be used. The E_{in} surface, plotted in terms of the coordinates of the overlap integrals, has a saddle point at the origin of coordinates. On the basis of this approach (IMO-2), the authors introduced a new reactivity index, equal to the maximum positive curvature of the interaction energy surface (f_{max}), whose value is independent of hypotheses concerning the structure of the transition state (the TS can be non-coplanar). In the same study, it was also shown that in many instances the index f_{max} contains more information than E_{in}. In particular, the use of this index makes it possible to describe satisfactorily both symmetrical and antisymmetric TS (for example in the reactions of cyclopentadiene with series A dienophiles).

The transition states in the reactions of butadiene with ethylene, cyclopropene, and cyclopropenone have been investigated by the IMO-2 method.[94] The molecular geometry was assumed to be unchanged during the reaction. Variation of the geometrical parameters characterising the mutual disposition of the molecules and the structure of different sections of the potential surface for the reaction led to the conclusion that the non-coplanar mutual approach of the molecule is preferred. It was shown that the molecular planes of the diene and the dienophile in the TS are disposed at an angle whose value is intermediate between the angles in the coplanar model and in the adducts. The use of the IMO-2 method also leads to more correct results in the study of the reactivity of the dienophiles, of the *endo*/*exo* ratio for the products, and of other features of the Diels–Alder reaction.

The calculation of the stabilisation energy of the transition state has been used to characterise the reactivity.[105] The application of the extended Hückel method to the determination of the TS energies in the reaction of maleic anhydride with cyclopentadiene yields a correct view of the relative reaction rates, in agreement with experimental data.

Calculations have been performed[106] for the π-complexes of maleic anhydride with various polycyclic aromatic compounds (32 structures in all). The complex of maleic anhydride with naphthalene was chosen as the model. It was shown that the overlap integral $2p_\pi$–AO for σ interactions passes through a maximum with decrease in the distance R between the diene and the dienophile, which corresponds to a minimum on the potential curve for the two π-systems. The value of R corresponding to the minimum potential energy (R_0) depends on the effective charges at the ends of the diene system of the polycyclic hydrocarbon. It has been suggested that the formation of the π-complex determines the rate of the diene synthesis. For many of the systems considered, the delocalisation energy of the π-complexes is correlated with the PLE.

The stabilisation energy of the transition state has been calculated also in other studies.[31,107,108] The influence of energetic, geometrical, and electronic characteristics on the cycloaddition mechanism has been discussed.[109] The mechanisms of cycloaddition have been described in terms of orbital symmetry.[110–114]

V. EXAMPLES OF THE STUDY OF CATALYTIC REACTIONS

Computational methods have also been applied to the study of catalytic Diels–Alder reactions.[30,44,57,98,99] It has been noted[51] that catalysis by Lewis acid diminishes the role of the secondary orbital interaction involving participation of the LUMO of the diene, which reduces the selectivity of the reactions of methyl vinyl ketone with thio-derivatives of buta-1,3-diene. The experimental data on the regioselectivity of the thermal and catalytic addition of 2-methoxy-1-phenylthio- and 2-methoxy-3-phenylthio-buta-1,3-dienes confirm this conclusion. The boundary electron densities of isoquinolinequinone and of its complexes with BF_3 and acids have been calculated by the

MNDO method; the regioselectivity in the Diels–Alder reaction with asymmetric dienophiles has been predicted.[115]

It has been noted[69] that protonation reduces the LUMO energy of acrolein, which should increase the interaction energy of the frontier orbitals and increase the rate of reaction. Furthermore, the reaction of acid catalysts increases the difference between the LUMO coefficients of the corresponding carbon atoms, which increases the process selectivity, since the latter becomes more marked with increasing difference between these coefficients (other conditions being equal).

The potential barriers and the charge distribution have been calculated by the MINDO/3 method for the Diels–Alder reaction between 1-hydroxybutadiene and acrolein and a study has been made of the influence of catalysts on this reaction.[108] In the case of a non-catalytic reaction, the activation energies for *o*-endo-, *o*-exo-*m*-endo-, and *m*-exo-additions are respectively (in kJ mol^{-1}) 124.15, 124.28, 205.6 and 207.74. In the presence of BF_3 and NH_4^+, the activation energy for the *m*-addition decreases slightly (by 25 to 42 kJ mol^{-1}), whereas the activation energies for the *o-endo-* and *o-exo*-additions are respectively 62.77 and 64.57 (in the presence of BF_3) and 46.93 and 52.04 (in the presence of NH_4^+). These data explain the experimentally observed influence of Lewis acids on regioselectivity and stereoselectivity. The transition state corresponds to the most pronounced charge transfer from the diene to the dienophile and from the reactants to the catalysts. Other studies have also been devoted to the regioselectivity and stereoselectivity in catalytic Diels–Alder reactions.[117,118]

It is noteworthy that calculations for the catalytic cycloaddition reactions are undoubtedly more complex and that a correlation between the presence of a catalyst and change in process selectivity does not always occur.

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