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The Reactivity of Addends in the Diene Synthesis Reaction

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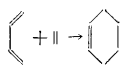
The principal electronic factors determining the reactivity of addends in the diene synthesis reaction are considered. The applicability of the model taking into account both the donor-acceptor properties of the reactants and their relative stabilities with respect to the reaction described by delocalisation energies or reaction enthalpies is demonstrated. The unusual influence of the donor-acceptor interactions between the addends on their selectivity in the Diels-Alder reaction is also demonstrated and the qualitative differences between the effects of the pair interactions of the antisymmetric and symmetrical frontier orbitals are noted.
The bibliography includes 103 references.

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I. INTRODUCTION

The diene synthesis reaction (the diene condensation or the Diels–Alder reaction) occupies one of the most important places in modern organic chemistry, constituting a simple and easy method for the synthesis of a wide variety of carbocyclic and heterocyclic systems containing a six-membered fragment:



The range of transformations embraced by the Diels–Alder condensation involves compounds of various types, starting with the simplest olefins and extending up to complex steroid systems[1].

The Diels–Alder reaction is of considerable theoretical interest. The study of its mechanism has been a long process, reflecting the evolution of theoretical views and experimental approaches in organic chemistry. The advances in the understanding of the mechanism of this reaction have been frequently described in reviews devoted to its various aspects[2].

The knowledge of the factors which determine the reactivity of the addends involved in the cycloaddition has played an important role. The study of the Diels–Alder reaction on the basis of non-empirical[3] and semi-empirical[4] quantum-chemical calculations of the potential surfaces of the reactions does not lead at present to unambiguous results[5] and does not permit broad generalisations based on the extensive experimental data obtained in the study of the reactivities of addends of various types. At the same time the approaches employing model ideas, based on the theory of frontier molecular orbitals[6] and on the concept of localisation[7] and permitting the employment of the experimental characteristics of the reactants and reactions for analysis, have already led to the understanding of many features, sometimes unexpected, which control the interaction of the components of the diene condensation. The present review is devoted to the consideration of the results obtained in this field.

II. THE FRONTIER-ORBITAL APPROACH TO THE PROBLEM OF THE REACTIVITY OF ADDENDS

The Diels–Alder reaction, accompanied by a significant loss of degrees of freedom, is characterised by an appreciable decrease of the entropy of the system. As a rule the entropy of reaction is between −30 and −40 e.u.,[8] which implies that the real processes can be only exothermic. Indeed, even for $\Delta H_0 = 0$ (a thermally neutral process), let alone processes with $\Delta H_0 > 0$, the equilibrium constants cannot exceed 10^{-6} for the entropies indicated[9], which corresponds to a virtually complete shift of the equilibrium towards the starting materials. In conformity with Hammond's postulate[10], the transition state in such real diene condensations should be relatively "early" and should be characterised by a low degree of formation of new bonds. Furthermore, diene synthesis is a reaction of components with relatively similar energies of the interacting orbitals. The set of factors indicated not only permits the classification of this reaction as "frontier-orbital-controlled"[11] but also makes it possible to understand why the theory of frontier molecular orbitals can be applied to the reactivity of the addends in its simplest form, developed by a number of investigators[12,13].

According to the approach investigated, a measure of the relative reactivity of a diene–dienophile system is the stabilisation energy of the transition state (ΔE_{st}) determined by the interaction of the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) of the reacting species:

$$\Delta E_{st} = \Delta E^{\text{LUMO dienophile}}_{\text{HOMO diene}} + \Delta E^{\text{LUMO diene}}_{\text{HOMO dienophile}}, \quad (1)$$

$$\Delta E_{st} \cong K[1/(\epsilon_{\text{HOMO diene}} - \epsilon_{\text{LUMO dienophile}}) + 1/(\epsilon_{\text{HOMO dienophile}} - \epsilon_{\text{LUMO diene}})]. \quad (2)$$

According to Eqn.(2),[13] the quantity ΔE_{st} and hence the relative reactivity of the addends ($\lg k \propto \Delta E_{st}$) depend on the difference between the energies ε of the interacting orbitals. The smaller this difference, the higher the reactivity.

Depending on the different relative dispositions of the interacting orbitals of the diene and dienophile, determined by the structure of the addends, there is a possibility of various types of diene synthesis reactions[14] (Fig. 1). The case where the stabilisation energy is determined mainly by the interaction between the HOMO of the diene and the LUMO of the dienophile (the term $\Delta E^{\text{LUMO dienophile}}_{\text{HOMO diene}}$) because $(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}}) < (\varepsilon_{\text{HOMO dienophile}} - \varepsilon_{\text{LUMO diene}})$ corresponds to the "diene (donor) - dienophile (acceptor)" reaction type. An increase of the reactivity of the system following the introduction of electron-donating substituents into the diene and of electron-accepting substituents into the dienophile is characteristic of reactions of this type in conformity with the influence which these substituents exert on the change of the energies of the orbitals.

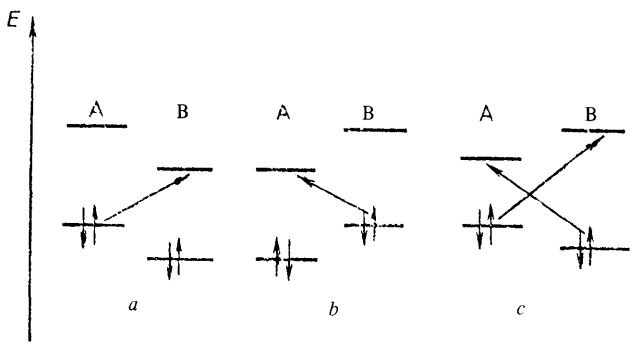


Figure 1. Schematic representation of the relative positions of the frontier orbitals of the addends in the diene synthesis reaction in condensations of the "diene (donor)–dienophile (acceptor)" type (*a*), the "diene (acceptor)–dienophile (donor)" type (*b*), and the "neutral" type (*c*); A = diene; B = dienophile.

Reactions of the "diene (acceptor)–dienophile (donor)" type are characterised by a different relative disposition of the orbitals in the diene and dienophile. In this case the interaction between the HOMO of the dienophile and the LUMO of the diene is decisive because $(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}}) > (\varepsilon_{\text{HOMO dienophile}} - \varepsilon_{\text{LUMO diene}})$. Reaction systems of this type are distinguished by an increase of reactivity following the introduction of electron-accepting substituents into the diene and of electron-donating substituents into the dienophile.

Reactions of these two types were known previously. Thus a theoretical interpretation based on the allowance for the intermolecular donor–acceptor interactions has been achieved for these reactions. However, analysis of the probable situations had led to the conclusion[14] that there is a possibility of the existence of yet another, unknown at the time, type of reaction, called the "neutral" type, where the energies of the pair interactions are comparable: $(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}}) \cong (\varepsilon_{\text{HOMO dienophile}} - \varepsilon_{\text{LUMO diene}})$, whence $\Delta E^{\text{LUMO dienophile}}_{\text{HOMO diene}} \cong \Delta E^{\text{LUMO diene}}_{\text{HOMO dienophile}}$. An increase of the reactivity of the diene–dienophile system should be expected for reactions of this type after the introduction of both electron-donating and electron-accepting substituents into either addend. Subsequent investigations demonstrated the actual existence of reactions of this type (see Section V).

III. REACTIONS OF THE "DIENE (DONOR)–DIENOPHILE (ACCEPTOR)" TYPE

The majority of reactions investigated at the present time belong to this type and one of the first conclusions concerning the electronic nature of the interacting components of diene condensations was that the diene must be an electron donor and the dienophile an electron acceptor[15]. The change in the reactivity of the system as the electronic character of the reactants is altered is consistent with the model considered above.

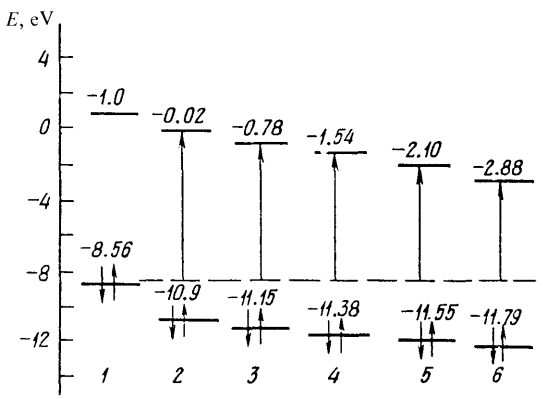


Figure 2. The relative positions of the frontier orbitals of cyclopentadiene (1) and cyanoethylenes: 2) acrylonitrile; 3) maleodinitrile and fumarodinitrile; 4) 1,1-dicyanoethylene; 5) tricyanoethylene; 6) tetracyanoethylene.

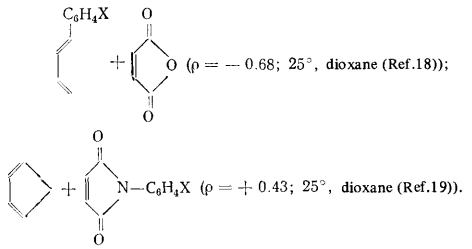
Table 1. The reactivities (k_2, litre mol^{-1} s^{-1}) of cyanoethylenes in the Diels–Alder reactions with cyclopentadiene, 9,10-dimethylanthracene (in dioxane at 20 °C),[13] and 1,3-diphenylisobenzofuran (in dichloroethane at 30 °C).[16]

Dienophile	Cyclopentadiene	9,10-Dimethylanthracene	1,3-Diphenylisobenzofuran
Tetracyanoethylene	480	$1.3\cdot10^{4}$	10^{8}
Tricyanoethylene	4.83	5.88	10^{4}
1,1-Dicyanoethylene	$4.55\cdot10^{-1}$	$1.27\cdot10^{-1}$	$1\cdot10^{3}$
Maleodinitrile	$9.1\cdot10^{-4}$	$1.31\cdot10^{-4}$	1.3
Fumarodinitrile	$8.1\cdot10^{-4}$	$1.39\cdot10^{-4}$	$3.1\cdot10^{-1}$
Acrylonitrile	$1.04\cdot10^{-5}$	$8.9\cdot10^{-7}$	$3.0\cdot10^{-3}$

An example may be provided by the reactions of cyanoethylenes with electron-donating dienes. Table 1 illustrates the influence of the number of CN groups in the dienophile on the reactivity of the system. Fig. 2 illustrates the ratio of the energies of the frontier orbitals of cyclopentadiene and cyanoethylenes[17]. Evidently $(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}}) < (\varepsilon_{\text{HOMO dienophile}} - \varepsilon_{\text{LUMO diene}})$. As the cyano-groups

accumulate, the energy gap between the HOMO of cyclopentadiene and the LUMO of cyanoethylene diminishes and the reactivity increases. Thus the reactivity of the dienophile increases with increase of its electron-accepting character (its electron affinity).

The energies of the orbitals change analogously, but on a smaller scale, under the influence of substituents in the aromatic ring of the diene or the dienophile. In this case reactions of the "diene (donor)–dienophile (acceptor)" type should be characterised by reaction constants $\rho > 0$ when the substituents in the dienophile are varied and $\rho < 0$ when the substituents in the diene are varied. This type of phenomenon does indeed occur, for example, in the reactions of arylbutadienes with maleic anhydride and of cyclopentadiene with *N*-arylmaleimides:

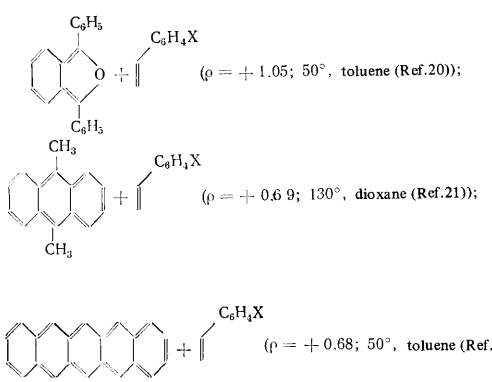


($\rho = -0.68$; 25°, dioxane (Ref.18));

($\rho = +0.43$; 25°, dioxane (Ref.19)).

In conformity with this, the sign of the reaction constants indicates a specific type of reaction and its low absolute value points to a synchronous reaction mechanism. Correlation data are now available for more than 10 reaction series of the "diene (donor) - dienophile (acceptor)" type and some of them have been listed[2].

It is of interest to examine reactions with participation of styrenes as dienophiles. These compounds provide a kind of test for the type of reaction, determined by the electronic character of the diene. Data concerning reactions involving certain electron-donating dienes are presented below:



($\rho = +1.05$; 50°, toluene (Ref.20));

($\rho = +0.69$; 130°, dioxane (Ref.21));

($\rho = +0.68$; 50°, toluene (Ref.22)).

In the last case an estimate of the frontier orbital energies shows (Fig.3*a* presents data concerning pentacene and unsubstituted styrene) that the system should be close to the "neutral type" if not actually of this type (the study was performed in order to detect "neutral" reactions). Nevertheless, a reaction of the "diene (donor)–dienophile (acceptor)" is observed. The possible causes of this phenomenon will be discussed below.

It is noteworthy that the influence of the substituents in the diene is described by the electrophilic constants σ^+; the influence of substituents in the dienophiles containing, apart from these substituents, other groups capable of direct polar conjugation with the +C reaction centre, is described by the Hammett constants σ, while the influence of substituents in styrenes is described by the nucleophilic constants σ^-.

Not all the reaction series obey rigorously the correlations (Table 2) but here too a tendency towards an increase of the reactivity of the system was observed as the electron-donating properties of the diene and the electron-accepting properties of the dienophile are enhanced.

Table 2. The reactivities (k_2, litre mol^{-1} s^{-1}) of acenes in the diene synthesis reactions with *N*-(X-phenyl)maleimides in toluene at 60 °C,[23,24] the ionisation potentials (I_D) of the acenes, and the electron affinities (E_A) of the dienophiles[23,24].

Diene	I_D, eV	X				
		p-$(CH_3)_2N$	*p*-CH_3O	H	*p*-Br	*p*-NO_2
Pentacene	6.64	0.42	0.62	0.75	1.49	3.36
6,13-Dichloropentacene	6.63	$4.30\cdot10^{-2}$	$5.80\cdot10^{-2}$	$5.70\cdot10^{-2}$	$1.00\cdot10^{-1}$	$1.80\cdot10^{-1}$
Tetracene	7.01	$1.65\cdot10^{-2}$	$2.22\cdot10^{-2}$	$2.45\cdot10^{-2}$	$4.62\cdot10^{-2}$	$9.65\cdot10^{-2}$
5,11-Dichlorotetracene	6.81	$3.30\cdot10^{-3}$	$4.00\cdot10^{-3}$	$4.10\cdot10^{-3}$	$7.70\cdot10^{-3}$	$1.16\cdot10^{-2}$
Anthracene	7.40	$1.91\cdot10^{-4}$	$2.46\cdot10^{-4}$	$2.78\cdot10^{-4}$	$4.28\cdot10^{-4}$	$5.79\cdot10^{-4}$
E_A, eV		0.7	0.9	0.9	0.95	1.0

Table 3. The reactivities (k_2, litre mol^{-1} s^{-1}) of substituted butadienes in the Diels–Alder reactions with maleic anhydride (dioxane, 30 °C), tetracyanoethylene (dioxane, 20 °C), and 4-phenyl-1,2,4-triazoline-3,5-dione (benzene, 25 °C) [26,27] and the ionisation potentials (I_D) of the dienes.

Diene	I_D, eV	PTAD	MA	ТЦЭ
2,3-Dimethylbuta-1,3-diene	8.76	183	$3.36\cdot10^{-4}$	$2.43\cdot10^{-1}$
trans-1-Phenylbuta-1,3-diene	8.16	63	$1.12\cdot10^{-4}$	$6.68\cdot10^{-2}$
2-Methylbuta-1,3-diene	9.04	46	$1.54\cdot10^{-4}$	$1.13\cdot10^{-2}$
Buta-1,3-diene	9.07	6.9	$6.83\cdot10^{-5}$	$5.19\cdot10^{-3}$
trans,trans-1,4-Diphenylbutadiene	7.54	5.1	$2.96\cdot10^{-6}$	$8.4\cdot10^{-3}$

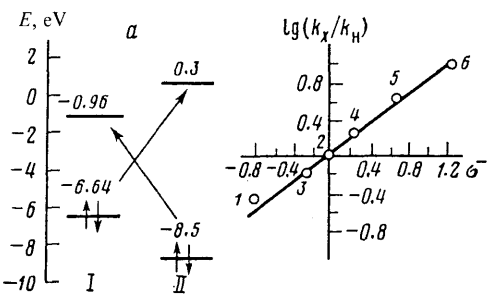


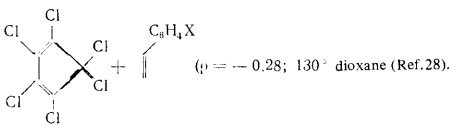
Figure 3. *a*) The relative positions of the frontier orbitals of pentacene (I) and styrene (II); *b*) dependence of the relative reactivities of styrenes [$\lg(k_X/k_H)$] in the diene synthesis reaction with pentacene on the nucleophilic constants of the substituents (toluene, 60 °C). Substituents X in styrenes: 1) *p*-$(CH_3)_2N$; 2) H; 3) *p*-CH_3O; 4) *p*-Br; 5) *m*-NO_2; 6) *p*-NO_2; $\rho = 0.685$; $r = 0.992$.

Finally, one should point out the existence of reaction series in which the variation of the reactivity of the system for a series of related compounds is inconsistent with the variation of the electronic character of the reactant, although there is no doubt about the assignment to a particular type

of reaction [in the given instance to the "diene (donor)–dienophile (acceptor)" type]. Table 3 presents data referring to the reactions of a series of butadienes with tetracyanoethylene (TCE), maleic anhydride (MA), and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). Evidently phenylated butadienes have a reduced reactivity compared with that expected on the basis of their electron-donating properties. The reactivity series of substituted butadienes are found to be different in reactions with different dienophiles. The possible causes of this phenomenon will be examined below (in Section VII).

IV. REACTIONS OF THE "DIENE (ACCEPTOR)–DIENOPHILE (DONOR)" TYPE

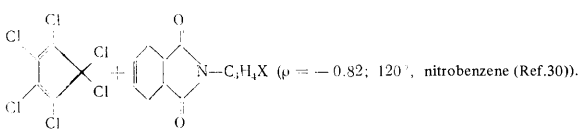
The existence of reactions of this type was first demonstrated as a result of a kinetic study of the reactions of hexachlorocyclopentadiene with styrenes:



($\rho = -0.28$; 130° dioxane (Ref.28).

A conclusion concerning the type of reaction was reached on the basis of the sign of the reaction constant. Examination of the ratio of the energies of the frontier orbitals (Fig.4) confirms that this conclusion is well founded. The stabilisation of the transition state in the given system is due to the preferential interaction of the HOMO of the dienophile with the LUMO of the diene.

Hexachlorocyclopentadiene reacts as an electron-accepting diene also with dienophiles such as the *N*-arylimides of *cis*-4-cyclohexene-1,2-dicarboxylic acid and *N*-arylimides of *endo*- and *exo*-bicyclo[2.2.1]heptene-2,3-dicarboxylic acid[29,30], for example:



($\rho = -0.82$; 120°, nitrobenzene (Ref.30)).

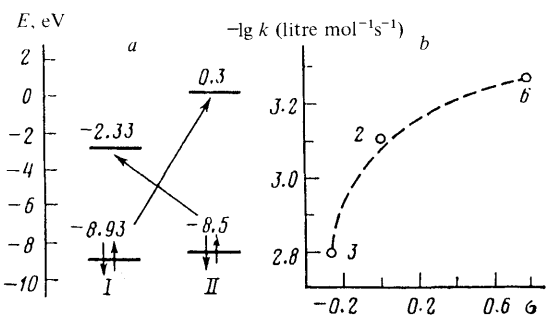
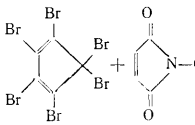


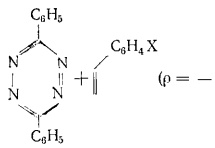
Figure 4. *a*) The relative positions of the frontier orbitals of hexachlorocyclopentadiene (I) and styrene (II); *b*) dependence of the reactivities of styrenes ($\lg k$) in the diene synthesis reaction with hexachlorocyclopentadiene on the Hammett σ constants (dioxane, 130 °C). The numbers of the styrenes correspond to the numbers of the compounds in Fig.3*b*.

It is of interest that the reactions of hexabromocyclopentadiene are of the "diene (acceptor)–dienophile (donor)" type even with electron-accepting dienophiles such as *N*-arylmaleimides:

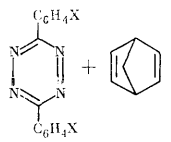


($\rho = -0.28$; 80°, benzene (Ref.31)).

Substituted tetrazines also behave as electron-accepting dienes. The influence of substituents in both the diene and the dienophile has been traced in relation to these compounds:



($\rho = -0.59$; 120°, nitrobenzene (Ref.2));



($\rho = +1.25$; 30°, dioxane (Ref.2)).

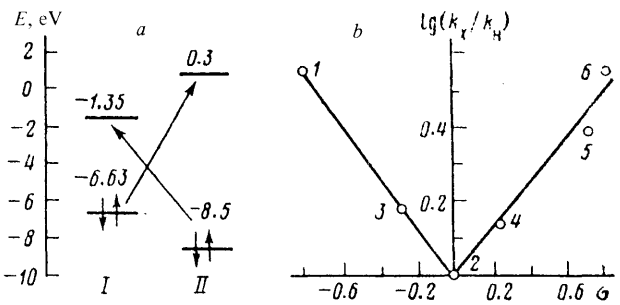


Figure 5. *a*) The relative positions of the frontier orbitals of 6,13-dichloropentacene (I) and styrene (II); *b*) dependence of the relative reactivities of styrenes in the diene synthesis reaction with 6,13-dichloropentacene on the Hammett σ constants (toluene, 50 °C). The numbers of the styrenes correspond to the numbers of the compounds in Fig.3*b*.

V. REACTIONS OF THE "NEUTRAL" TYPE

The experimental evidence for the occurrence of reactions of the "neutral" type was first obtained in the study of the interaction of cyclones (phencyclone, tetracyclone, and acecyclone) with styrenes and arylacetylenes[32–35]. According to Sustmann[14], when the arrangement of the frontier orbitals in the addends is nearly symmetrical (the neutrality condition), both electron-donating and electron-accepting substituents increase ΔE_{st} and hence should increase the reactivity of the system; thus the dependence of $\lg k$ on the σ constants of the substituents should be U-shaped. However, for a symmetrical disposition of the frontier orbitals, the differences between the energies of the HOMO and LUMO of the addends may be large and the reactivity of the system is therefore small. For this reason, the closeness of the orbitals in one of the addends must be adopted as the condition for

the occurrence of such reactions (the condition for reactivity). It is more likely that the levels are close to one another in dienes, which are usually more conjugated. Cyclones, which are intensely coloured, satisfy this condition. The "neutral" character of the reactions of cyclones with styrenes has been confirmed in recent studies[36].

The dienes which react with styrenes via a "neutral" mechanism proved to be also 6,13-dichloropentacene, 5,11-dichlorotetracene, and tetrachloro- and tetrabromo-*o*-quinones[25,37,38].

From data for the orbital characteristics of the reactants, it was initially postulated that, among polynuclear hydrocarbons, the diene capable of undergoing "neutral" reactions with styrenes may be pentacene. However, it was found that in this instance a reaction of the "diene (donor)–dienophile (acceptor)" type takes place (see Section III). After the introduction of chlorine atoms in the *meso*-positions (6,13-positions), i.e. after imparting electron-accepting properties to the diene, the "neutral" type of reaction can be observed (Fig.5).

Fig.6*a* presents estimates of the energies of the tetrachloro-*o*-quinone–styrene orbital system, which show that in this case the diene should be an electron acceptor relative to the dienophile; therefore, in formulating these experiments, reactions of the "diene (acceptor)–dienophile (donor)" type were expected. However, it was found that in this case reactions of the "neutral" type actually occur with inversion at the halogen as the substituent in the styrene molecule (Fig.6*b*).

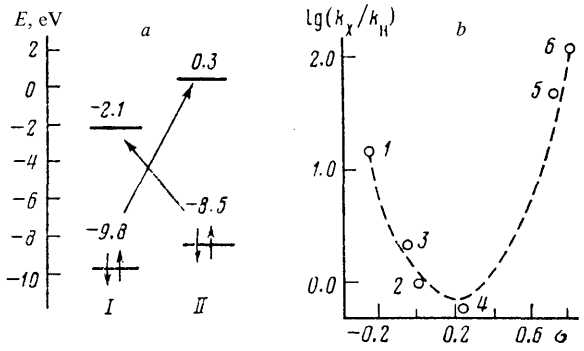
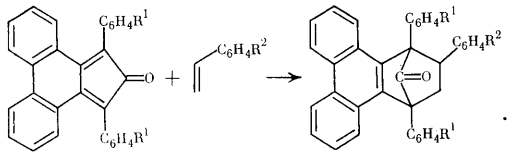


Figure 6. *a*) The relative positions of the frontier orbitals of tetrachloro-*o*-benzoquinone (I) and styrene (II); *b*) dependence of the relative reactivities of styrenes [lg (k_X/k_H)] in the diene synthesis reaction with tetrachloro-*o*-benzoquinone on the Hammett σ constants (dichloroethane, 30 °C). Substituents X in styrenes: 1) *p*-CH_3O; 2) H; 3) *m*-CH_3; 4) *p*-Cl; 5) *m*-NO_2; 6) *p*-NO_2.

A characteristic feature of all the reactions of the "neutral" type investigated is that the diene in these substances is to some extent an electron acceptor relative to the dienophile.

There exist data clearly demonstrating the possibility of transitions between the various types of reactions. Such transitions can be observed within narrow cross reaction series and more effectively when there is a sharp change in the electronic character of the reactants. An example of a transition of the first kind is provided by the change in the reactivity of substituted phencyclones in the Diels–Alder reactions with styrenes[39] (Table 4):



The variation of the reactivity of styrenes in reactions with various cyclones (Table 4) corresponds in all cases to the "neutral" type of reaction, but, on passing from the phencyclone containing the electron-accepting *p*-NO_2 substituents to the phencyclone with electron-donating *p*-CH_3O substituents, the reactivity of styrenes with electron-donating substituents diminishes and that of styrenes with electron-accepting substituents increases with inversion in the region of *p*-bromostyrene.

Table 4. The reactivities (10^3 k_2, litre mol^{-1} s^{-1}) of substituted phencyclones in the Diels–Alder reactions with styrenes (toluene, 40 °C).[39]

R^2	R^1					ρ
	p-NO_2	*p*-Cl	H	*p*-CH_3	*p*-CH_3O	
p-NO_2	6.12	11.7	18.2	22.0	23.2	−0.575
m-NO_2	4.52	7.00	7.90	11.2	9.30	−0.342
p-Br	8.15	8.70	7.50	9.45	7.40	0.008
H	9.40	6.00	4.40	4.10	4.60	0.339
p-CH_3O	40.1	18.5	12.4	13.3	12.0	0.511
p-$(CH_3)_2N$	710	112	74.8	45.5	54.8	1.124

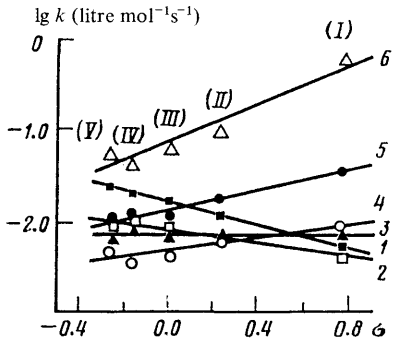


Figure 7. Dependence of the reactivities of the substituted phencyclones (I)–(V) in the diene synthesis reaction with styrenes (lines *1*–*6*) on the Hammett σ constants (toluene, 40 °C). Substituents R^1 in phencyclones: I) *p*-NO_2; II) *p*-Cl; III) H; IV) *p*-CH_3; V) *p*-CH_3O. Substituents R^2 in styrenes: 1) *p*-NO_2; 2) *m*-NI_2; 3) *p*-Br; 4) H; 5) *p*-CH_3O; 6) *p*-$(CH_3)_2N$.

The reactivity of cyclones varies somewhat differently in reactions with different styrenes (Table 4 and Fig.7). The reactions of cyclones with *p*-nitrostyrene are of the "diene (donor)–dienophile (acceptor)" type and the type of reactions remains unchanged but the reactivity and selectivity of the

reactants diminish. The reactions with *p*-bromostyrene are almost insensitive to the influence of the substituents in cyclones[13,14]. The reactions with unsubstituted styrene, *p*-methoxystyrene, and *p*-dimethylaminostyrene are of the "diene (acceptor)–dienophile (donor)" type. In the series of styrenes considered there is an increase of not only the reactivity but also of the selectivity of the reactants. As it were, "macroneutrality" is obtained, i.e. a transition from reactions of one type to another in a number of reaction series, in contrast to the "microneutrality" observed within the limits of a single reaction series.

A transition from reactions of one type to another has also been demonstrated for wider variations of dienes and dienophiles. The change in the type of reaction after the introduction of halogen atoms into the pentacene molecule has already been demonstrated (see Sections III and V); other examples also exist. Thus the reactions of indanocyclones, which have more pronounced electron-accepting properties than phencyclones, tetracyclones, and acecyclones, with styrenes are of the "diene (acceptor)–dienophile (donor)" type[40]; on the other hand, the reactions of cyclones with *N*-arylmaleimides and maleic anhydride–dienophiles with more pronounced electron-accepting properties than styrenes—are of the "diene (donor)–dienophile (acceptor)" type[41,42]. Reactions of an analogous type are observed in systems comprising phencylone and vinyl and isopropenyl dienophiles with electron-accepting substituents[43]. Hexabromocyclopentadiene (Section IV) and tetrabromo-5,5-dimethoxycyclopentadiene react with *N*-arylmaleimides in different ways. In the latter case the reaction of the "diene (donor)–dienophile (acceptor)" type is observed[31].

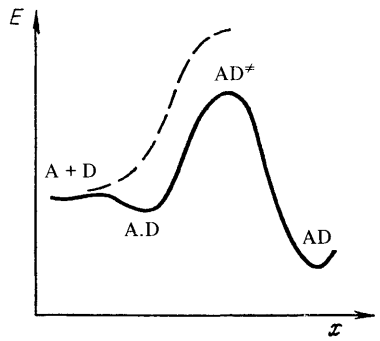


Figure 8. Schematic representation of the energy profile of the diene synthesis reaction proceeding via a charge-transfer complex stage; x = reaction coordinate.

Thus the above discussion demonstrates the applicability of the model based on the frontier-orbital aproach and indicates a significant influence of intermolecular orbital donor–acceptor interactions on the reactivity of diene–dienophile systems.

It is noteworthy that the donor–acceptor interactions between the addends involved in the diene synthesis have already attracted the attention of investigators for a long time. One of the signs of such interactions is the formation of complexes between the diene and the dienophile[44–49], which should be classified as charge-transfer complexes of the π,π-type according to the existing views[50].

The existing data for the relation between the donor–acceptor properties of the addends and the stability of the complexes which they form and the reactivity[51–53], data for the influence of solvents on the diene synthesis and complex formation[54–57], and the characteristic features of the kinetics of certain reactions with a negative temperature coefficient[58] permitted the conclusion that the charge-transfer complexes (CTC) formed between the addends arise in the course of the diene synthesis and are thus prereaction complexes[59]. Donor–acceptor interactions lead to the stabilisation of the system and to a decrease of the potential energy over the entire initial reaction pathway, including the prereaction stage (Fig.8). In this sense the CTC between the addends are prereaction complexes not only as regards their position in the chain of transformations but also as regards their physical nature, while the donor–acceptor interactions are one of the factors determining the reactivity of the system[60]. The formation of the CTC and their characteristics can serve as an indication of the manifestation and intensity of donor–acceptor interactions. According to Markov[61], the elucidation of the role of the CTC is an experimental prerequisite of the application of theoretical approaches based on the consideration of intermolecular orbital donor–acceptor interactions.

One should note that the following scheme is usually postulated for the energy profile of the reaction involving the formation of CTC during diene synthesis:

$$A + D \overset{K}{\rightleftarrows} A.D \overset{k_1}{\rightarrow} AD,$$

where A and D are the free addends (the acceptor and the donor), A.D is the complex, and AD is the adduct. This scheme presupposes that the adduct is formed only from the CTC and that the rate of reaction is proportional to its concentration [A.D]:

$$w = k_1[A \cdot D] = Kk_1[A] \cdot [D]. \qquad (3)$$

According to this scheme and Eqn.(3), on passing from systems forming complexes to those where complexes are not produced, the possibility of the reaction is eliminated ($k_{exp} = Kk_1 \to 0$, since $K \to 0$); however, this conflicts with what is observed in reality.

It is more correct to suppose[59] that in the case of systems with CTC the adduct is formed both from the complex A.D and directly from the free addend A and D. The reaction complex, following the same energy profile of the reaction, then proceeds via the CTC state but without a kinetically independent species being detected.

Overall we have a scheme according to which the addends in the initial state are divided, in accordance with the equilibrium constant, into bound (A.D.) and free (A and D). The adduct is formed from both[15,16]:

$$\begin{array}{ccccc} A + D & \overset{K}{\rightleftarrows} & A.D & \overset{k_1}{\rightarrow} & AD \\ \vert & & & & \uparrow \\ \multicolumn{5}{c}{\underline{\qquad\qquad k_2 \qquad\qquad}\vert} \end{array}$$

The rate of the process is then described by the expression

$$w = k_1[A.D] + k_2[A][D] = (Kk_1 + k_2)[A][D]$$

and the quantity

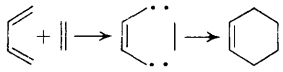
$$k_{exp} = (Kk_1 + k_2) \to k_2 \text{ when } K \to 0$$

corresponds to the transition to systems without CTC mentioned above.

VI. DELOCALISATION ENERGIES. THERMOCHEMISTRY OF THE REACTIONS

The formation of the cycloadduct entails changes in the initial π-electron systems of the diene and dienophile, which correspond to the localisation of two π electrons in the 1,4-positions in the diene and two π electrons in the 1,2-positions

in the dienophile. The corresponding changes in the π-electron energy can be regarded as the 1,4-delocalisation (for the diene) and 1,2-delocalisation (for the dienophile) energies[7]:



Delocalisation is an endothermic process and the differences between the delocalisation energies of dienes and dienophiles characterises the difference between the stabilities of the reactants due to the delocalisation of the electrons. The concept of delocalisation was introduced by Brown[62] ("para-localisation" for polynuclear hydrocarbons as dienes) as the index of the reactivity of these compounds in diene synthesis on the grounds that compounds with a lower delocalisation energy should form more stable (as regards retrodecomposition) adducts, so that these compounds should be more reactive in conformity with the Bell–Evans–Polanyi principle.

The relation between the enthalpy of reaction (stability of the adducts) and the delocalisation energy is illustrated in Fig. 9,[60] according to which the enthalpy of reaction is determined mainly by the delocalisation energies ($L_{1,4}$ and $L_{1,2}$) and also by the energies of formation of new bonds and the energy of rehybridisation in the delocalised states ($E_\sigma + E_S$). If it is assumed that, in a reaction series with the same diene (or dienophile), the 1,4-delocalisation (or 1,2-delocalisation) energy, the energy of formation of new bonds, and the rehybridisation energy are constant, then the differences between the enthalpies of reaction should be determined by the differences between the 1,2-delocalisation (or 1,4-delocalisation) energies. The enthalpy of reaction in a given reaction series can then serve as a measure of the delocalisation energy.

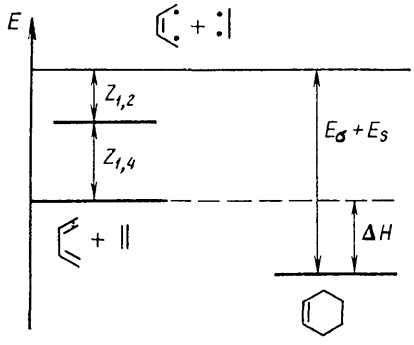


Figure 9. Schematic representation of the relation between the enthalpies of the diene synthesis reaction ΔH and delocalisation energies (for explanation, see text).

Until recently there were almost no literature data for the enthalpies of reaction. They were known for certain reversible reactions because they were determined from the temperature variation of the equilibrium constant[8]. As microcalorimetric methods have developed, the situation has changed, but reliable determinations of such quantities are so far restricted to rapid processes with a very reactive addend as at least one of the components; in particular, tetracyanoethylene and 1,3-diphenylisobenzofuran are used as the dienophile and the diene respectively (Tables 5 and 6).

Table 5. The enthalpies of the reactions[10,64] of various dienes with tetracyanoethylene at 25 °C, the increments in the enthalpies of reaction for the dienes (Δh_{IBF}),[63,64] and the ionisation potentials of the dienes.

Diene	I_D, eV	$-\Delta H$, kcal mol^{-1}	Δh_{IBF}, kcal mol^{-1}
9,10-Dimethylanthracene	7.23	21.1	—4.6
9-Methylanthracene	7.26	20.2	—5.8
Anthracene	7.47	18.5	—2.0
9-Chloroanthracene	7.45	15.3	0.7
9-Methoxyanthracene	7.20	14.6	1.9
9,10-Dimethoxyanthracene	7.09	12.6	3.9
Tetracene	7.01	23.1	—6.6
Pentacene	6.64	27.7	—11.2
5,11-Dichlorotetracene	6.81	18.7	—2.2
6,13-Dichloropentacene	6.63	17.7	—1.2
Buta-1,3-diene	9.03	36.8	—20.3
2-Methylbuta-1,3-diene	8.89	39.7	—23.2
2-Methoxybuta-1,3-diene	8.62	37.9	—21.4
2,3-Dimethylbuta-1,3-diene	8.62	42.0	—25.5
trans-Penta-1,3-diene	8.61	39.0	—22.5
trans-1-Phenylbuta-1,3-diene	8.16	34.0	—17.5
trans, trans-1,4-Diphenylbuta-1,3-diene	8.09	23.2	—6.7
Cyclohexa-1,3-diene	8.25	31.0	—14.5
Cyclopenta-1,3-diene	8.58	26.9	—10.4
1,3-Diphenylisobenzofuran	7.62	16.5	0

Table 6. The enthalpies of the reactions of various dienophiles with 1,3-diphenylisobenzofuran at 25 °C, the increments of the enthalpies of reaction for these dienophiles (Δh_{TCE}),[16,65] and the electron affinities of the dienophiles.

Dienophile	$-\Delta H$, kcal mol^{-1}	Δh_{TCE}, kcal mol^{-1}	E_A, eV
Tetracyanoethylene	16.5	0	2.88
Tricyanoethylene	17.0	—0.5	2.10
1,1-Dicyanoethylene	18.4	—1.9	1.53
Maleodinitrile	20.0	—3.5	0.78
Fumarodinitrile	19.7	—3.2	0.78
Acrylonitrile	20.9	—4.4	0.02
Maleic anhydride	20.4	—3.9	0.97
N-(*p*-Nitrophenyl)maleimide	23.0	—6.5	1.01
N-Phenylmaleimide	23.5	—7.0	0.89
N-(*p*-Dimethylaminophenyl)maleimide	23.9	—7.4	0.79
4-Phenyl-1,2,4-triazoline-3,5-dione	25.0	—8.5	1.80
p-Benzoquinone	15.7	0.8	—
1,4-Naphthoquinone	13.8	2.7	—
Acrolein	18.1	—1.6	—
Acrylic acid	20.1	—3.6	—
Methyl acrylate	20.2	—3.7	—
Methacrolein	14.9	1.6	—
Methacrylic acid	15.9	0.6	—
Methyl methacrylate	16.6	—0.1	—
Methacrylonitrile	17.5	—1.0	—

Analysis of the existing data[63] shows that the enthalpies of the reactions of substituted anthracenes are satisfactorily correlated with the 1,4-delocalisation energies calculated for these reactions (Fig. 10). An analogous correlation has been observed also in a series of dienophiles, as shown in relation to cyanoethylene[16], the difference between the enthalpies of the reactions of tetracyanoethylene and acrylonitrile (4.5 kcal mol^{-1}) corresponding to the difference between the calculated delocalisation energies (4.4 kcal mol^{-1} [63]). The difference between the enthalpies of the reactions of anthracene and tetracene, amounting to 4.65 kcal mol^{-1}, also agrees with the calculated value of 5.5 kcal mol^{-1}.[7] In addition, correlations have been observed between the enthalpies of reactions involving the same compounds in different reaction series. Fig. 11 illustrates the relation between the enthalpies of the reactions of a series of dienes with tetracyanoethylene and 4-phenyl-1,2,4-triazoline-3,5-dione. The slope of the straight line in Fig. 11 is 1.0. These data show that the difference between the enthalpies of the reactions of dienes depends insignificantly if at all on the nature of the dienophile, i.e. are determined mainly by the properties of the diene. On the

other hand, the enthalpies of the reactions of a single dienophile can also differ from those for another dienophile, regardless of the nature of the diene, the difference being fairly constant. Fig.12 confirms this conclusion for other pairs of reactions. Furthermore, such differences are maintained in reactions of different kinds: for (4 + 2)- and (3 + 2)-cycloaddition or (4 + 2)- and (2 + 2)-cycloaddition[67,68].

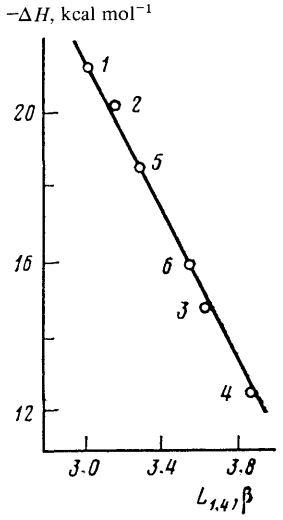


Figure 10. Dependence of the 1,4-localisation energies of substituted anthracene on the enthalpies of the reaction of these dienes with tetracyanoethylene: 1) 9,10-dimethylanthracene; 2) 9-methylanthracene; 3) 9-methoxyanthracene; 4) 9,10-dimethoxyanthracene; 5) anthracene; 6) 9-chloroanthracene; $r = 0.995$.

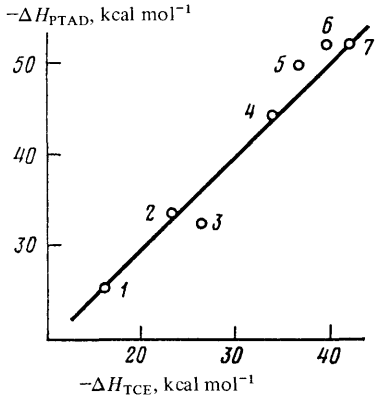


Figure 11. Relation between the enthalpies of the diene synthesis reactions of 4-phenyl-1,2,4-triazoline-3,5-dione (ΔH_{PTAD}) and tetracyanoethylene (ΔH_{TCE}) with various dienes: 1) 1,3-diphenylisobenzofuran; 2) *trans,trans*-1,4-diphenylbuta-2-diene; 3) cyclopentadiene; 4) *trans*-1-phenylbutadiene; 5) butadiene; 6) 2-methylbutadiene; 7) 2,3-dimethylbutadiene.

The results obtained (for a detailed analysis and a broad generalisation, the studies in this field should undoubtedly be continued) already justify the assumption that the differences between the enthalpies of the reactions reflect primarily the difference between the delocalisation energies of the addends, although they also represent an accumulation of other effects, including, for example, the energy of the *s-trans–s-cis* transition in the case of butadienes, etc. This conclusion is important for the understanding of the nature of the phenomenon, bearing in mind the subsequent application of these quantities (Section VII). The "transferability of the differences" makes it possible to estimate the enthalpies of the reactions which cannot be obtained or which have not so far been obtained by direct experimental determinations.

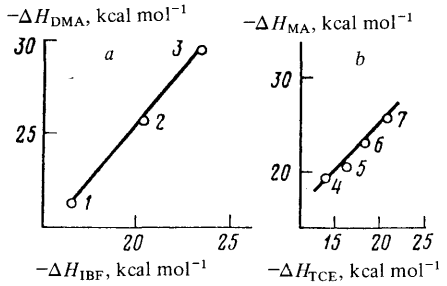


Figure 12. Relations between the enthalpies of the diene synthesis reactions of 9,10-dimethylanthracene (DMA) and 1,3-diphenylisobenzofuran (IBF) with various dienophiles (*a*) and of maleic anhydride (MA) and tetracyanoethylene (TCE) with various dienes (*b*): 1) tetracyanoethylene; 2) maleic anhydride; 3) *N*-phenylmaleimide; 4) 9-methoxyanthracene; 5) 1,3-diphenylisobenzofuran; 6) anthracene; 7) 9,10-dimethylanthracene.

Table 7. The enthalpies of the diene synthesis reactions involving various dienophiles at 25 °C.[64,65]

No.	Diene	Dienophile	$-\Delta H$, kcal mol^{-1}
1	Buta-1,3-diene	PTAD	49.8
2	2-Methylbuta-1,3-diene	PTAD	52.0
3	2,3-Dimethylbuta-1,3-diene	PTAD	52.1
4	*trans*-1-Phenylbuta-1,3-diene	PTAD	44.4
5	*trans, trans*-1,4-Diphenylbuta-1,3-diene	PTAD	33.8
6	Cyclopentadiene	PTAD	32.1
7	Hexachlorocyclopentadiene	PTAD	18.4
8	Hexabromocyclopentadiene	PTAD	15.3
9	Tetrabromo-5,5-dimethoxycyclopentadiene	PTAD	23.1
10	9,10-Dimethylanthracene	MA	25.7
11	Anthracene	MA	23.2
12	9-Methoxyanthracene	MA	19.1
13	9,10-Dimethylanthracene	PMI*	29.4

*N-Phenylmaleimide.

For this purpose, at the present stage of the investigation, having adopted the reaction of tetracyanoethylene with 1,3-diphenylisobenzofuran as the standard, we have listed in Tables 5 and 6 the increments in the enthalpies of the reactions of dienes (Δh_{IBF}) and dienophiles (Δh_{TCE}) which represent the differences between the enthalpies of the reaction of the given diene with tetracyanoethylene or of the given dienophile with 1,3-diphenylisobenzofuran and the enthalpy of the standard reaction [between 1,3-diphenylisobenzofuran (IBF) and tetracyanoethylene (TCE)]. These quantities characterise respectively the relative stabilities of the adducts in the series of dienes and dienophiles considered here. The calculated enthalpy of the reaction of a

given diene (A) and a given dienophile (B) is then equal to the sum of their increments and the enthalpy of the reaction between the tetracyanoethylene and isobenzofuran (−16.5 kcal mol^{-1}):

$$\Delta H^{A+B}\ (\text{kcal mol}^{-1}) = \Delta h^{A}_{IBF} + \Delta h^{B}_{TCE} - 16.5.$$

Comparison of the quantities calculated in this way and the experimental values (Table 7) is illustrated in Fig. 13.

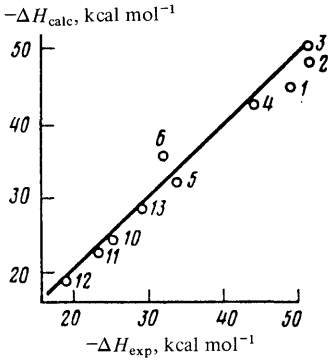


Figure 13. Relation between the experimental (ΔH_{exp}) and calculated (ΔH_{calc}) enthalpies of the diene synthesis reactions; the numbers against the circles correspond to the data in Table 7.

Certain enthalpies of the reactions of dienes, in particular hexachloro- and hexabromo-cyclopentadienes, with tetracyanoethylene have also been estimated from the data obtained. The calculated values are −9.9 and −6.8 kcal mol^{-1} respectively and show that the equilibrium in these reactions should be fully displaced towards the starting materials, i.e. reaction is virtually impossible. This explains the failure of the attempts to obtain the adducts of tetracyanoethylene with the above dienes[69]: it is not the low reactivity of the system but the position of the equilibrium which is responsible for the above phenomenon and, instead of being improved, the situation is actually aggravated by carrying out the reaction at high temperatures. It is indeed known, for example, that the reactions of tetracyanoethylene with 9-chloro-, 9-methoxy-, and 9,10-dimethoxy-anthracenes are reversible[70,71]. In the last instance the equilibrium is almost completely displaced towards the starting materials†. This justifies the assumption that the reactions with $\Delta H \geqslant -15$ kcal mol^{-1} should be reversible while the reactions with $\Delta H \geqslant -12$ kcal mol^{-1} cannot be achieved under the usual conditions.

It is also noteworthy that, according to Tables 6 and 7, in a series of dienophiles belonging to the same reaction series (cyanoethylenes, arylmaleimides, and vinyl and isopropenyl compounds), less stable adducts correspond to more reactive dienophiles in reactions of the "diene (donor)–dienophile (acceptor)" type, in conformity with the hypothesis put forward previously on the basis of model quantum-chemical calculations[60]. This is why the attempts to employ tetracyanoethylene as the competing "displacing" reagent in certain reversible reactions have been unsuccessful[70]. The choice based on the principle of the "reactivity" of the reagent led to an unstable adduct.

† The enthalpy of reaction was determined from data for the retrodecomposition of the adduct by a special method[63].

VII. THE REACTIVITY OF DIENE–DIENOPHILE SYSTEMS

After the qualitative establishment of the fact that the addends in the diene synthesis are of different electronic character, attempts were made to observe correlations between the reactivity of the dienes and dienophiles, on the one hand, and their donor–acceptor characteristics (ionisation potentials and electron affinities), on the other, in order to elucidate the role of the donor–acceptor interactions between the addends reflected in the formation of CTC. It has been shown[16,51,52,60] that such correlations are observed but only within the limits of narrow reaction series. Naturally, the influence of the constant reactant is not then taken into account.

Nevertheless, the model of the interaction of frontier molecular orbitals described in Section II provides a basis for the consideration of the reactivities of diene–dienophile systems with simultaneous allowance for both the electron-donating properties of one addend and the electron-accepting properties of the other. Thus, according to Section II, $\Delta E_{st} \propto$

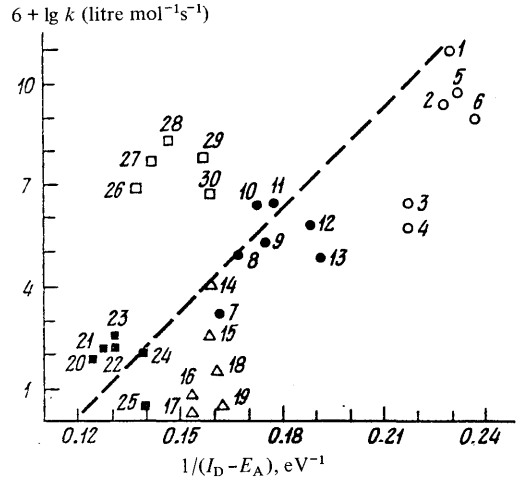


Figure 14. Dependence of the lg k on $1/(I_D - E_A)$ for different diene–dienophile systems. Reactions of tetracyanoethylene with anthracenes: 1) 9,10-dimethylanthracene; 2) 9-methylanthracene; 3) anthracene; 4) 9-chloroanthracene; 5) 9-methoxyanthracene; 6) 9,10-dimethoxyanthracene (dichloroethane, 25 °C [63]). Reactions of tetracyanoethylene with butadienes: 7) buta-1,3-diene; 8) 2-methylbuta-1,3-diene; 9) *trans*-1-methylbuta-1,3-diene; 10) 2,3-dimethylbuta-1,3-diene; 11) 2-methoxybuta-1,3-diene; 12) *trans*-1-phenylbuta-1,3-diene; 13) *trans,trans*-1,4-diphenylbuta-1,3-diene (methylene chloride, 20 °C [74]). Reactions of maleic anhydride with anthracenes: 14) 9,10-dimethylanthracene; 15) 9-methylanthracene; 16) anthracene; 17) 9-chloroanthracene; 18) 9-methoxyanthracene; 19) 9,10-dimethoxyanthracene (dioxane, 30 °C [73]). Reactions of maleic anhydride with butadienes: 20) buta-1,3-diene; 21) 2-methylbuta-1,3-diene; 22) *trans*-1-methylbuta-1,3-diene; 23) 2,3-dimethylbuta-1,3-diene; 24) *trans*-1-phenylbuta-1,3-diene; 25) *trans,trans*-1,3-diphenylbuta-1,3-diene (dioxane, 30 °C [74]). Reactions of 4-phenyl-1,2,4-triazoline-3,5-dione with butadienes; 26) buta-1,3-diene; 27) 2-methylbuta-1,3-diene; 28) 2,3-dimethylbuta-1,3-diene; 29) *trans*-1-phenylbuta-1,3-diene; 30) *trans,trans*-1,4-diphenylbuta-1,3-diene (benzene 25 °C [27]).

$1/(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}})$ for reactions of the "diene (donor)–dienophile (acceptor)" type and, since $\lg k \propto \Delta E_{st}$, it follows that $\lg k \propto 1/(\varepsilon_{\text{HOMO diene}} - \varepsilon_{\text{LUMO dienophile}})$; or, using experimental quantities, namely the ionisation potential I of the electron-donating diene and the electron affinity E_A of the electron-accepting dienophile, $\lg k \propto 1/(I_D - E_A)$.[12,17,72] Comparison of the reactivities of certain diene–dienophile systems with the reciprocals of the differences between the ionisation potentials of the dienes and the electron affinities of the dienophiles shows that in this instance the correlations are limited to individual reaction series[17,72,73] or are not observed at all[74].

The set of data referring to different diene–dienophile systems which can be considered from the above standpoint and discussed further is presented in Figs. 14 and 15#. Evidently, although a definite tendency towards an increase of the reactivity of diene–dienophile systems with decrease of the difference between the ionisation potential of the diene and the electron affinity of the dienophile is on the whole observed, there is no satisfactory correspondence between the quantities compared for the entire set of reactions under consideration. Detailed analysis demonstrates the existence of certain trends which can be explained if it is assumed that the reactivities of the addends are determined by the set of factors stabilising (donor–acceptor interactions) and destabilising (delocalisation) the transition state[60]. As already mentioned, the initial diene and dienophile systems undergo changes during the reaction corresponding to the delocalisation of the electrons in the 1,4-positions in the diene and the 1,2-positions in the dienophile and these changes are manifested in the energy of the transition state. In this connection one may note that, according to *ab initio* calculations for the reaction of butadiene with ethylene, its transition state is characterised by a considerable rearrangement of the initial systems and at the same time a low degree of formation of new bonds[3]. "From the standpoint of delocalisation", the reactivity of addends should be smaller the greater the delocalisation energy, i.e. the greater the energy expenditure required on the decomposition of the initial π-electron systems of the diene and dienophile on formation of the transition state and hence the adduct. Examination of the transition state stabilisation effects based on allowance for the donor–acceptor properties of the initial compounds ignores these differences between the addends. They can be taken into account by considering the enthalpies of the reactions of the diene–dienophile pairs which can serve as a measure of the delocalisation energies of the addends (Section VI).

The data in Figs. 14 and 15 are presented on the same scale and are comparable. The rate constants for reactions of different series refer to several different temperatures (20°, 25°, and 30 °C), because the activation parameters for the recalculation of the constants in conformity with the Arrhenius or Eyring equation were not available in all cases. There are also differences between the solvents. The calculation performed taking into account the activation parameters for similar reactions and with a known (low) sensitivity of the reaction rate constants to the nature of the solvent have shown that the above differences can lead to differences of the order of 0.3–0.5 in $\lg k$ for different reaction series. This does not exceed the limits of the errors within which the given problem is considered (among all the quantities used for the given study, the electron affinity is determined least accurately). The ionisation potentials and the electron affinities employed are listed in Tables 5 and 6 and were taken from the literature[16,17,25,27,64,65,73,74].

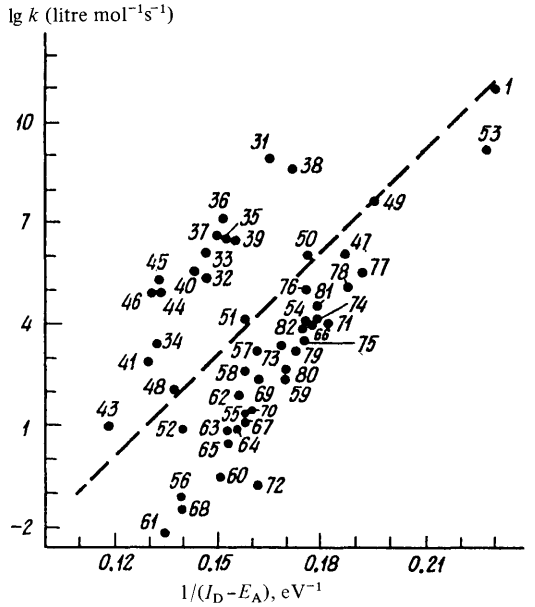


Figure 15. Dependence of $\lg k$ on $1/(I_D - E_A)$ for different diene–dienophile systems. Reactions of 1,3-diphenylisobenzofuran with dienophiles: 31) 1,1-dicyanoethylene; 32) fumarodinitrile; 33) maleodinitrile; 34) acrylonitrile; 35) maleic anhydride; 36) *N*-(*p*-nitrophenyl)maleimide; 37) *N*-phenylmaleimide (dioxane, 30 °C [16]). Reactions of cyclopentadiene with dienophiles: 38) tetracyanoethylene; 39) tricyanoethylene; 40) 1,1-dicyanoethylene; 41) fumarodinitrile; 42) maleodinitrile; 43) acrylonitrile (dioxane, 30 °C [75]); 44) maleic anhydride (dioxane, 30 °C [76]); 45) *N*-(*p*-nitrophenyl)maleimide; 46) *N*-phenylmaleimide (dioxane, 30 °C [19]). Reactions of cyclohexadiene with dienophiles; 47) tetracyanoethylene (methylene chloride, 20 °C); 48) maleic anhydride (dioxane, 30 °C [74]). Reactions of 9,10-dimethylanthracene with dienophiles: 1) tetracyanoethylene; 49) tricyanoethylene; 50) 1,1-dicyanoethylene; 51) fumarodinitrile and maleodinitrile; 52) acrylonitrile (dioxane, 20 °C [75]). Reactions of 9-methylanthracene with dienophiles: 53) tricyanoethylene; 54) 1,1-dicyanoethylene; 55) fumarodinitrile and maleodinitrile; 56) acrylonitrile (dichloroethane, 25 °C [77]); 57) *N*-(*p*-nitrophenyl)maleimide; 58) *N*-phenylmaleimide (dioxane, 25 °C [9]). Reactions of anthracene with dienophiles: 59) 1,1-dicyanoethylene; 60) fumarodinitrile and maleodinitrile; 61) acrylonitrile (dichloroethane, 25 °C [77]); 62) *N*-(*p*-nitrophenyl)maleimide; 63) *N*-phenylmaleimide (dioxane, 25 °C [9]). Reactions of 9-chloroanthracene with dienophiles: 64) *N*-(*p*-nitrophenyl)-maleimide; 65) *N*-phenylmaleimide (dioxane, 25 °C [9]). Reactions of 9-methoxyanthracene with dienophiles: 66) 1,1-dicyanoethylene; 67) 1,2-dicyanoethylene; 68) acrylonitrile (dichloroethane, 25 °C [9]); 69) *N*-(*p*-nitrophenyl)maleimide; 70) *N*-phenylmaleimide (dioxane, 25 °C [9]). Reactions of 9,10-dimethoxyanthracene with dienophiles: 71) 1,1-dicyanoethylene; 72) 1,2-dicyanoethylene (dichloroethane, 25 °C [77]). Reactions of tetracene with dienophiles: 73) maleic anhydride; 74) *N*-(*p*-nitrophenyl)maleimide; 75) *N*-phenylmaleimide. Reactions of pentacene with dienophiles: 76) maleic anhydride; 77) *N*-(*p*-nitrophenyl)maleimide; 78) *N*-phenylmaleimide. Reactions of 5,11-dichlorotetracene with dienophiles: 79) *N*-(*p*-nitrophenyl)maleimide; 80) *N*-phenylmaleimide. Reactions of 6,13-dichloropentacene with dienophiles: 81) *N*-(*p*-nitrophenyl)maleimide; 82) *N*-phenylmaleimide (toluene, 25 °C [25]).

We may draw attention to several phenomena which may be noted in the analysis of the data in Fig.14. The reactivity of butadienes in reactions with all three dienophiles investigated (tetracyanoethylene, maleic anhydride, and 4-phenyl-1,2,4-triazoline-3,5-dione) varies in such a way that the phenylated butadienes are less reactive than might have been expected on the basis of their electron-donating properties and the reactions with these butadienes are less exothermic (Table 5), which indicates higher delocalisation energies (Δh_{IBF} for 2,3-dimethylbuta-1,3-diene, *trans*-1-phenylbuta-1,3-diene, and *trans,trans*-1,4-diphenylbuta-1,3-diene are respectively −25.5, −17.5, and −6.7 kcal mol^{-1}). On the other hand, the differences between the reactivities of the three dienophiles examined are such that they correspond not only to the differences between their electron-accepting properties but also to the differences between the enthalpies of reaction (the Δh_{TCE} are 0, −3.9, and −8.5 kcal mol^{-1} respectively).

It is also striking that the reactivities of anthracenes in reactions with tetracyanoethylene and maleic anhydride (Fig.14) or arylmaleimides (Fig.15) differ very greatly, although the differences between their electron-donating properties are small. Furthermore, 9-methoxy- and 9,10-dimethoxy-anthracenes have particularly low reactivities. Overall, all anthracenes are less reactive than butadienes to a greater extent than might have been expected on the basis of their electron-donating properties. These phenomena are also understandable if account is taken of the observed differences between the enthalpies of the reactions (between the delocalisation energies) of these dienes.

Presumably the sensitivity to changes in the donor–acceptor interactions of the reactants is revealed most correctly in reaction series where the cyanoethylenes are varied. These compounds have very different electron-accepting properties, while the difference between their delocalisation energies is small (Table 6). The correlation straight line in Fig.15 corresponds to the 9,10-dimethylanthracene–cyanoethylenes reaction series. For comparison, it has been transferred to Fig.14 in the form of a dashed line.

Taking into account all the foregoing considerations, an attempt was made to examine the dependence of the reactivity of the same set of diene–dienophile systems on the set of donor–acceptor properties of the addends and their capacity for delocalisation in accordance with the equation

$$\lg k \propto /(I_D - E_A) - p\,\Delta H. \qquad (4)$$

Here both the parameter $1/(I_D - E_A)$ and ΔH reflect simultaneously the properties of both the diene and the dienophile.

According to Eqn.(4), the reactivity of the diene–dienophile system is greater the smaller the difference between the energies of the interacting orbitals ($I_D - E_A$) and the more exothermic the reaction (the higher the absolute value of ΔH).

Fig.16 illustrates the correlation between $\lg k$ and $1/(I_D - E_A) - 0.02\Delta H$§. The results obtained show that there is a large group of reactions (65 points refer to this group in Fig.16) which obey fairly satisfactorily the overall dependence of the reactivity of the diene–dienophile system on the parameters considered and for which the range of variation of the reaction rate constants amounts to 14 orders of magnitude. It includes the reactions of different dienophiles with butadienes and polynuclear compounds as the dienes.

§ In order to employ the experimental quantities directly in the given treatment, the calculation was performed for I_D and E_A expressed in eV and for ΔH expressed in kcal mol^{-1}. The adjustment of the measurements to the same system of units would require a simple alteration of the coefficients.

Compared with this group, an enhanced reactivity (for the same type of variation of the reactivity within the series) is shown in reactions involving cyclopentadiene and 1,3-diphenylisobenzofuran as dienes. This phenomenon can be explained if one takes into account the fact that the C(1)–C(4) distances in the dienes are different and that this influences their reactivity[78,79]; however, these distances are not apparently adequately reflected either in the electron-donating properties of the dienes or in the enthalpies of reaction.

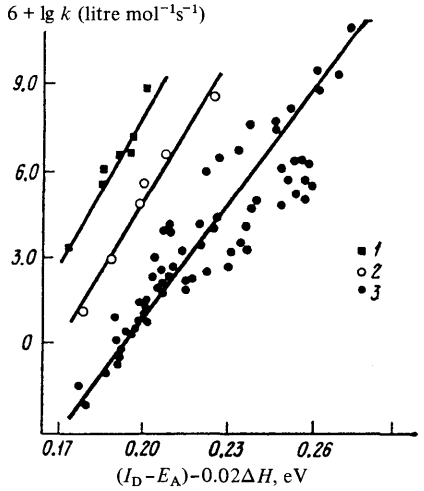


Figure 16. Dependence of the reactivity of addends in the diene synthesis reaction on the reciprocal of the difference between the ionisation potential of the diene and the electron affinity of the dienophile and on the enthalpies of reaction. Dienes employed: 1) cyclopentadiene; 2) 1,3-diphenylisobenzofuran; 3) butadienes and polynuclear compounds.

The view has been expressed that the role of the effects of the donor–acceptor interaction and delocalisation can change as a function of the position of the transition state on the reaction coordinate[80,81,73]:

$$\lg k \propto \alpha[1/(I_D - E_A)] + (1-\alpha)\Delta H,$$

where α varies from 1 to 0 along the reaction coordinate on passing from the starting materials to the products. Accordingly, the data for the reactions presented in Fig.16 were treated in terms of the equation

$$\lg k = 1/(I_D - E_A) - q(I_D - E_A)\cdot\Delta H,$$

according to which the sensitivity to the localisation effects depends on the intensity of the donor–acceptor interaction. The greater this intensity, the smaller the multiplier equal to the difference $I_D - E_A$. In this case the agreement between the calculated and experimental quantities is impaired. At present it would be premature to reach definite conclusions on the basis of these results. It is more correct to regard them as preliminary and to assume that they require further refinement. However, the main conclusion is not subject to any doubt, since both the energies of the donor–acceptor interaction and the delocalisation energies influence the reactivity of the diene–dienophile systems, constituting the principal electronic factors determining the reactivity of the addends.

Depending on the relative donor–acceptor interaction and delocalisation energies, there is a possibility of different combinations of the reactions[59,82], which are illustrated schematically in Fig. 17 by energy profiles which refer to the two processes compared and differ only in the dienes or dienophiles; they can model the reaction series. The decrease of the energy in the prereaction state on the profiles corresponds to the donor–acceptor interactions and the relative positions of the final states correspond to the differences between the delocalisation energies of the addends. The combinations of the reactions can be divided into several types.

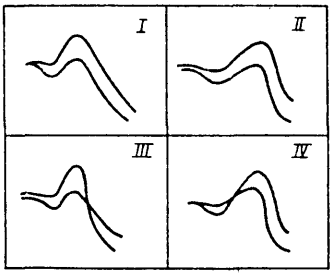


Figure 17. Energy profiles of reactions with different ratios of the donor–acceptor interaction and delocalisation energies (see text).

I. The donor–acceptor interaction and delocalisation energies vary in parallel from the standpoint of the influence on the rate of reaction; the relative reactivity of the addends is controlled by the donor–acceptor interactions. In this case the energy profiles of the reactions do not intersect and the stability of the adducts corresponds to the reactivity of the addends.

II. The donor–acceptor interaction and delocalisation energies vary in parallel, but the relative reactivity of the addends is controlled by delocalisation effects. In this case the energy profiles of the reaction also do not intersect and the stability of the adducts corresponds to the reactivity of the addends.

III. There is an antiparallel variation of the donor–acceptor interaction and delocalisation energies and the relative reactivity of the addends is controlled by the donor–acceptor interactions. In this case the energy profiles of the reactions intersect in the region of energies beyond the activation barrier; the stability of the adducts is inconsistent with the reactivity of the addends.

IV. There is an antiparallel variation of the donor–acceptor interaction and delocalisation energies and the relative reactivity is controlled by delocalisation effects; the energy profiles of the reactions intersect in the range of energies before the activation barrier; the stability of the adducts corresponds to the reactivity of the addends.

Without classifying the entire set of reactions in terms of the types indicated, it is possible to consider certain examples.

Reactions with strongly electron-donating dienes and electron-accepting dienophiles, in particular, the reactions of *meso*-substituted anthracenes with tetracyanoethylene in which the relative reactivity of anthracene corresponds to their electron-donating properties[63] and the "more reactive the reagent the greater its selectivity" rule holds[77] (see Section VIII) can be assigned to type I.

Reactions of type II are difficult to identify definitely. The study of the relation between reactivity and selectivity suggests that this type holds in reactions of arylmaleimides with anthracenes[9].

A striking example of reactions of type III is provided by the interaction of cyanoethylenes with any of the electron-donating dienes (cyclopentadiene, anthracenes, and isobenzofuran). The antiparallel variation of the electron-accepting properties and localisation energies of cyanoethylenes has been demonstrated by both quantum-chemical calculations[60,66] and by experimental data (Table 6). The reactivity of cyanoethylenes corresponds to their electron-accepting properties and increases from acrylonitrile to tetracyanoethylene, while the localisation energies (enthalpies of reaction) vary in the opposite sequence, which is consistent with the variation of the stabilities of the adducts demonstrated in relation to the reactions with 9,10-dimethoxyanthracene[69]. The reactions of butadiene or 1,4-diphenylbutadiene with tetracyanoethylene belong to type III. In this pair of reactions, 1,4-diphenylbutadiene, the more electron-donating diene, is more reactive (Table 3).

The replacement of tetracyanoethylene by maleic anhydride in reactions with the same dienes (butadiene and 1,4-diphenylbutadiene) leads to reactions of type IV. Butadiene, which is less electron-donating but has a smaller localisation energy, is more reactive. When the dienophile is altered, the donor–acceptor interaction energy changes (decreases) and the factor controlling the relative reactivity of the reactant (diene) is changed. Another example of the combination of type IV reactions may be provided by the reactions of butadienes with 4-phenyl-1,2,4-triazoline-3,5-dione compared with the reactions of the same butadienes with tetracyanoethylene. Tetracyanoethylene is more electron-accepting, but it is less reactive for "localisation" reasons. Incidentally, it is of interest also to compare the reactivities of the above dienes (butadiene and 1,4-diphenylbutadiene) in the reactions with 4-phenyl-1,2,4-triazoline-3,5-dione. In this case the reactivities of these dienes are comparable, in conformity with the "intermediate" electron-accepting properties of the dienophile.

Thus the donor–acceptor properties and localisation energies quoted as the two principal electronic factors in the study of the reactivities of addends explain many phenomena which previously appeared obscure.

VIII. THE SELECTIVITY OF ADDENDS IN THE DIENE SYNTHESIS REACTION

The selectivity S in reactivities is understood as the difference between the reactivities ($\lg k$) in the interaction of the given reactant with two others having different reactivities. On the basis of a study by the present author and his co-workers[77], we shall examine the pairs of reactions of two electron donors D_1 and D_2 with two electron acceptors A_1 and A_2. Then

$$S_{D_1} = \lg k_{D_1}^{A_1} - \lg k_{D_1}^{A_2};\ S_{D_2} = \lg k_{D_2}^{A_1} - \lg k_{D_2}^{A_2}$$

and the relative selectivity of the electron donors is described by the expression

$$S_{D_2}^{D_1} = S_{D_1}/S_{D_2} = (\lg k_{D_1}^{A_1} - \lg k_{D_1}^{A_2})/(\lg k_{D_2}^{A_1} - \lg k_{D_2}^{A_2}).$$

Similarly, for electron acceptors we have

$$S_{A_2}^{A_1} = S_{A_1}/S_{A_2} = (\lg k_{D_1}^{A_1} - \lg k_{D_2}^{A_1})/(\lg k_{D_1}^{A_2} - \lg k_{D_2}^{A_2}).$$

We shall assume that the electron-donating properties of D_1 are more prounced than those of D_2 and the electron-accepting properties of A_1 are more pronounced than those of A_2, which implies that $\varepsilon_{D_1}^{HOMO} > \varepsilon_{D_2}^{HOMO}$ (or $I_{D_1} < I_{D_2}$) and $\varepsilon_{A_2}^{LUMO} < \varepsilon_{A_2}^{LUMO}$ (or $E_{A_1} > E_{A_2}$). We shall consider the differences between the reactivities which are due to the differences between the energies of the donor–acceptor interactions [in conformity with the relation $\lg k_D^A \propto 1/(I_D - E_A)$]. Then

$$S_{D_2}^{D_1} = \frac{(I_{D_2} - E_{A_1})(I_{D_2} - E_{A_2})}{(I_{D_1} - E_{A_1})(I_{D_1} - E_{A_2})} ;$$

$$S_{A_2}^{A_1} = \frac{(I_{D_1} - E_{A_2})(I_{D_2} - E_{A_2})}{(I_{D_1} - E_{A_1})(I_{D_2} - E_{A_1})} .$$

For the conditions adopted above, we have the following relations:

$$(I_{D_2} - E_{A_1}) > (I_{D_1} - E_{A_1}); \quad (I_{D_2} - E_{A_2}) > (I_{D_1} - E_{A_2});$$
$$(I_{D_1} - E_{A_2}) > (I_{D_1} - E_{A_1}); \quad (I_{D_2} - E_{A_2}) > (I_{D_2} - E_{A_1}) .$$

Hence

$$S_{D_2}^{D_1} > 1, \quad S_{A_2}^{A_1} > 1 ,$$

i.e. the donor with more marked electron-donating properties and hence the acceptor with more pronounced electron-accepting properties should be more selective. In those cases where the relative reactivity of the addends is controlled by their donor–acceptor properties, this implies that the more reactive reactant should be more selective. This type of relation between reactivity and selectivity has been demonstrated for a whole series of examples of reactions of both the "diene (donor)–dienophile (acceptor)" type[20,24,77] and the "diene (acceptor)–dienophile (donor)" type[40]. Fig.18 presents data referring to the reactions of *N*-arylmaleimides with acenes.

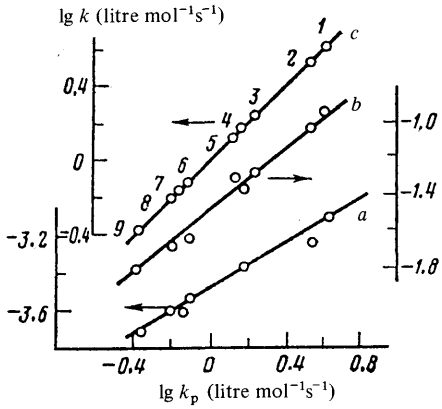


Figure 18. Dependence of the reactivities of *N*-(XC_6H_4)-substituted maleimides [X: 1) *m*-NO_2; 2) *p*-NO_2; 3) *p*-CH_3OCO; 5) *m*-Cl; 6) H; 7) *p*-CH_3; 8) *p*-CH_3O; 9) *p*-$(CH_3)_2N$] in reactions with anthracene (*a*), tetracene (*b*), and pentacene (*c*) on their reactivities in the reactions with pentacene ($\lg k_p$) (toluene, 60 °C).

The rule which states that "the more reactive the reactant the greater its selectivity" holds also in reactions of the "neutral"type in those cases where one of the donor–acceptor interactions between the addends exerts a preferential influence[34,39].

In those reactions where the relative reactivity is controlled by the delocalisation energies of the addends, the relation between reactivity and selectivity may be different, but in this instance too the selectivity of the reactants depends on their donor–acceptor properties. In this connection it is of interest to compare the variation of the reactivities and selectivities of three dienophiles: maleic anhydride, tetracyanoethylene, and 4-phenyl-1,2,4-triazoline-3,5-dione in reactions with buta-1,3-diene, 2-methylbuta-1,3-diene, and 2,3-dimethylbuta-1,3-diene (Fig.19, see also the data in Table 3). Tetracyanoethylene is more reactive and more selective than maleic anhydride. The relative reactivities of these dienophiles are controlled by the effects of the donor–acceptor interactions (tetracyanoethylene is significantly more electron-accepting than maleic anhydride but has a higher delocalisation energy). 4-Phenyl-1,2,4-triazoline-3,5-dione is more reactive than tetracyanoethylene (the relative reactivity is controlled in this instance by the delocalisation energies), but, in conformity with its electron-accepting properties, it occupies an intermediate position as regards selectivity between tetracyanoethylene and maleic anhydride. Another clear example is provided by the reactivities of cyanoethylenes in their interaction with substituted phencyclones (Section IX).

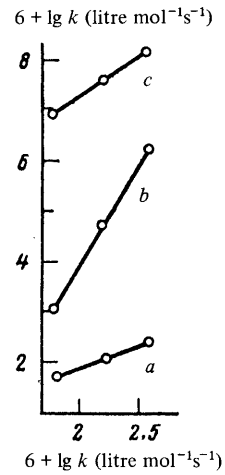


Figure 19. Dependence of the reactivities of maleic anhydride (*a*), tetracyanoethylene (*b*), and 4-phenyl-1,2,4-triazoline-3,5-dione (*c*) in the diene synthesis reactions with a series of dienes [1) butadienes; 2) isoprene; 3) 2,3-dimethylbutadiene] on the reactivities of these dienes in reactions with maleic anhydride ($\lg k_{MA}$).

IX. CYANOETHYLENES IN THE DIENE SYNTHESIS REACTION. QUALITATIVE DIFFERENCES BETWEEN THE EFFECTS OF THE INTERACTION OF ANTISYMMETRIC AND SYMMETRICAL FRONTIER ORBITALS

As mentioned above (Sections III and VII), the reactivities of cyanoethylenes in reactions with typical electron-donating dienes vary in accordance with their electron-accepting properties (electron affinities). It has been found that this

behaviour of cyanoethylenes is not always observed. Interesting data have been obtained in the study of their reactions with substituted phencyclones[83,84]:

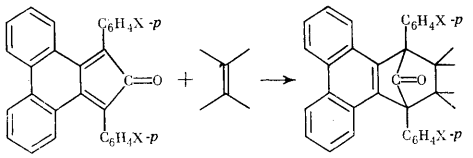


Fig. 20, which presents the corresponding correlation plots, shows that the variation of the reactivities of substituted phencyclones in reactions with each cyanoethylene is described satisfactorily by the Hammett σ constants (r varies from 0.993 to 0.999) with $\rho < 0$. In conformity with the conclusions reached in Section VIII, the absolute value of ρ (the selectivity) is then greater the more pronounced the electron-accepting properties of the cyanoethylene (Fig. 21), which indicates that the reaction is of the "diene (donor)–dienophile (acceptor)" type.

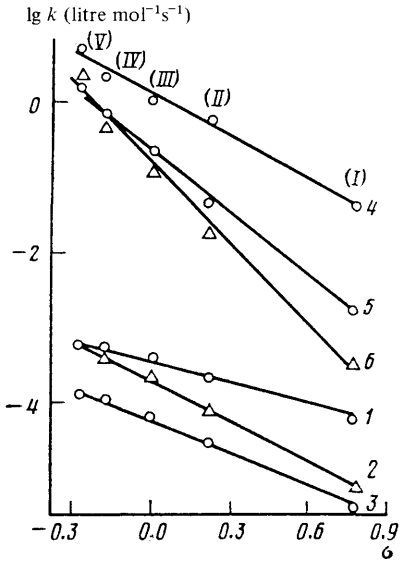


Figure 20. Dependence of lg k for the substituted phencyclones (I)–(V) in the reactions with cyanoethylenes (lines *1*–*6*) on the Hammett σ constants (chlorobenzene, 30 °C). Substituents X in phencyclones: I) p-NO_2; II) p-Cl; III) H; IV) p-CH_3; V) p-CH_3O. Cyanoethylenes: 1) acrylonitrile; 2) maleodinitrile; 3) fumarodinitrile; 4) 1,1-dicyanoethylene; 5) tricyanoethylene; 6) tetracyanoethylene.

On the other hand, the relative reactivities of cyanoethylenes in the reactions with each phencyclone vary in an unusual manner. The reactivities do not correspond explicitly to one particular reaction type and depend on the electron-accepting character of the substituent in the cyclone. The possible causes capable of giving rise to this phenomenon have been analysed[83,84]. The behaviour of cyanoethylenes becomes understandable if it is assumed that their reactivites are determined not only by the electron-accepting properties but also by the delocalisation energies.

Table 8 presents equations describing the variation of the reactivities of cyanoethylenes taking into account their electron affinities and localisation energies in reactions with each phencyclone investigated. It is striking that, on passing from the phencyclone containing the electron-donating CH_3O substituent to one with the electron-accepting NO_2 substituent, the sensitivity of the diene to the localisation effects of the dienophiles increases. Taking into account the fact that the phencyclone containing the carbonyl group exhibits electron-accepting properties, the general conclusion that an enhancement of the electron-accepting properties of the dienes entails an increase of their sensitivity to the effects of the localisation of the dienophiles becomes apparent.

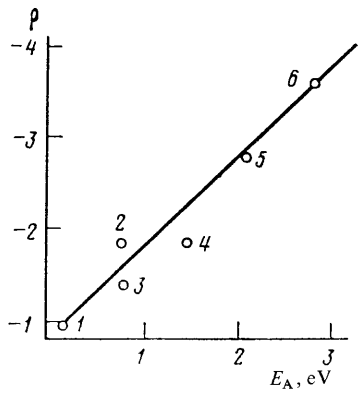
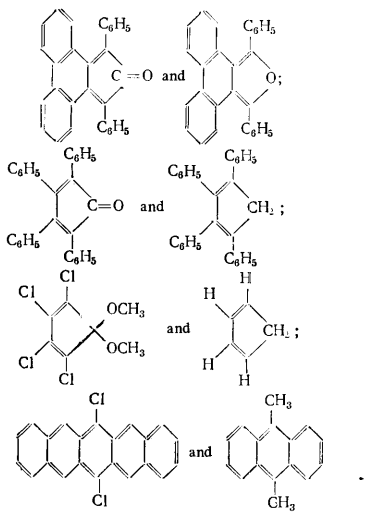


Figure 21. Dependence of the reaction constants for the reactions of substituted phencyclones with cyanoethylenes on the electron affinity of the dienophiles (chlorobenzene, 30 °C). The numbering of the dienophiles is the same as in Fig. 20.

The validity of this conclusion is demonstrated by the results of the study of the reactivities of cyanoethylenes with respect to the following pairs of dienes, having similar structures but differing in their electronic properties[83–88]:



The variation of the reactivities of cyanoethylenes in reactions with electron-donating dienes is determined by the electron-accepting properties of the dienophiles. In the reactions with electron-accepting dienes account must be taken of their localisation properties. A similar behaviour has been observed also in the reactions of substituted phencyclones with arylmaleimides and maleic anhydride[89].

Table 8. Correlation between the reactivities of cyanoethylenes as dienophiles in reactions with substituted phencyclones (k, litre mol^{-1} s^{-1}), and the electron affinities (E_A, β) and localisation energies (L, β) of the dienophiles (β is the resonance integral).

Substituent X in phencyclone	Equation	r
p-CH_3O	$\lg k = 30.16\,E_A - 6.64\,L + 33.39$	0.992
p-CH_3	$\lg k = 28.31\,E_A - 6.51\,L + 32.30$	0.986
H	$\lg k = 27.91\,E_A - 6.70\,L + 32.45$	0.986
p-Cl	$\lg k = 28.30\,E_A - 7.08\,L + 33.93$	0.986
p-NO_2	$\lg k = 27.03\,E_A - 7.54\,L + 33.78$	0.984

For further study, it is important to note that, according to the data in Section V, in reactions of the "neutral type" the dienes are as a rule electron-accepting in relation to the dienophiles (cyclones, dichloroacenes, and halogeno-*o*-quinones in reactions with styrenes). This makes it necessary to suppose that the interactions of the HOMO of the diene with the LUMO of the dienophile and of the HOMO of the dienophile with the LUMO of the diene are non-equivalent. The interaction of the HOMO of the diene with the LUMO of the dienophile is seen to be preferred.

On the basis of a theoretical analysis, it has been suggested[90,91] that there are fundamental differences between the interactions of the HOMO of the diene and the LUMO of the dienophile (antisymmetric orbitals), on the one hand, and of the HOMO of the dienophile and the LUMO of the diene (symmetrical orbitals), on the other. In the former case the electron density is concentrated between the reaction centres, ensuring conditions for the formation of the chemical bond. A change in the coordinates of the atomic nuclei promotes the reaction (Fig. 22). In the latter case, as a consequence of the resolution of the cross-overlapping, the electron density is concentrated in the central part of the intermolecular space and the changes in the coordinates of the atomic nuclei are not favourable for the reaction. Therefore, even in those cases where the interaction of the symmetrical orbitals predominates, the authors[90,91] believe that the interaction of the antisymmetric orbitals is responsible for the occurrence of the reaction (i.e. for the formation of new bonds). The interaction of symmetrical orbitals promotes the stabilisation of the prereaction charge-transfer complex (and to some extent of the transition state), but requires the localisation of the electrons on the reaction centres for the reaction to occur.

This approach explains also the characteristic features of reactions of the "neutral type" and of the more pronounced dependence of the reactivity of the addends on the delocalisation effects when the electron-accepting character of the diene becomes more marked, as well as the observed antiparallel variation of the stabilities of the charge-transfer complexes between the addends and their reactivities in reactions of the "diene (acceptor)–dienophile (donor)" type[92], in contrast to the parallel variation of these properties in reactions of the "diene (donor)–dienophile (acceptor)" type (Section V).

It is noteworthy that, when the interaction of the symmetrical orbitals predominates in the Diels–Alder reaction, the mechanism of the latter can change. Whereas the interaction of the antisymmetric orbitals promotes a synchronous reaction, the dominant interaction of symmetrical orbitals can lead to a two-stage reaction with formation of an intermediate. The available data, indicating the infringement of the "*cis*-principle" in reactions involving electron-accepting dienes such as hexahlorocyclopentadiene[93], acridizinium ions[94,95], and phenyldiazenium salts[96] provide an example of such behaviour. Despite the symmetry of the reactants, instances of the breakdown of the "*cis*-principle" have not so far been observed in reactions of the "diene (donor)–dienophile (acceptor)" type[1,97].

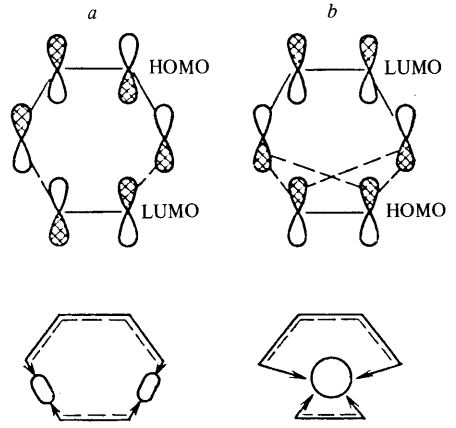


Figure 22. Schematic representation of the interaction of antisymmetric (a) and symmetrical (b) frontier orbitals of the addends in Diels–Alder reactions.

The change in the electronic character of the reactant and the associated change in sensitivity to the localisation effects can alter also the periselectivity of the reaction. It is well known that electron-donating dienes react with tetracyanoethylene at a carbon–carbon bond[98–100]. However, this dienophile reacts with electron-accepting dienes under mild conditions to form products of addition to the cyano-group[101,102]. Acrylonitrile behaves analogously[103]. Such behaviour corresponds to the lower stability (lower delocalisation energy) of the C≡N bond compared with the C=C bond.

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The above discussion shows that many characteristic features of the reactivities of the addends in diene synthesis can be explained if the donor–acceptor properties and stabilities of the reactants, described by the delocalisation energies or enthalpies of reaction, are adopted as the principal electronic factors determining the reactivities of dienes and dienophiles. The enthalpies of reaction make it possible to take into account also the differences between the energies of the *s-trans–s-cis* conformational transitions, which influence the reactivities of open-chain dienes. On the other hand, the

geometrical factor, such as the 1,4-distances in dienes, needs to be taken into account as well. It is noteworthy that the above conclusion has been reached on the basis of the study of reactions of the "diene (donor)–dienophile (acceptor)" type. In order to answer the question to what extent this conclusion is valid for reactions of other types, special studies are necessary. Data indicating the possible qualitative differences between the effects of the interaction of the antisymmetric and symmetrical orbitals make it particularly necessary.

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