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Factors that determine the reactivity of reactants in normal and catalysed Diels–Alder reactions

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ABSTRACT. The effects of intermolecular stabilisation, the energies of the reacting bonds, and the geometry of the reactants on their reactivity in normal Diels–Alder reactions and those catalysed by Lewis acids have been analysed. The main causes of the small ($1–10^2$ times) or large ($10^4–10^9$ times) increase in the rate of the process in the presence of catalysts and the conditions for synthesising products which often cannot be obtained when the reaction is carried out in the absence of a catalyst are examined.
The bibliography includes 190 references.

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I. Introduction

The increased interest in the Diels–Alder reaction is due both to the considerable synthetic possibilities of using it to obtain various carbocyclic and heterocyclic compounds[1–22] and the high reliability of the quantitative data obtained, which are used as a basis for establishing and verifying many theoretical concepts in organic chemistry.[14–18]

A large amount of information on the kinetics and thermochemistry of the Diels–Alder reaction and the effect of the medium on the enthalpy levels of the reactants, molecular complexes, transition states, and reaction products has been collected. At the present time it is clear that the activity of the addends in the Diels–Alder reaction cannot be accounted for by relying solely on information about the energy of frontier orbitals, namely, using a simple model of molecular orbital perturbation. A large amount of experimental material on the enthalpy of reaction has been collected. With this it is possible to determine the relationship between the activity of the addends and the stability of the adducts and to select the optimum conditions for concurrent displacement of one of the reactants from the reaction adducts. Furthermore, the difference in enthalpies of molecular Diels–Alder reactions primarily reflects the difference in energies of the reacting π-bonds. From this it is possible to understand many "anomalous" kinetic features of the behaviour of a number of reactants. Only when the energy of the donor-acceptor interaction, the energy of the reacting bonds, and the interatomic distance in the diene ($R_{1,4}$) are taken into joint consideration can there be a quantitative representation of the kinetics for conversion of various reactants, the activity of which may differ by a factor of 10^{20}.

With the use of Lewis acids that form highly reactive *n,v*-complexes with one of the reactants, usually the dienophile, it is possible to increase the rate of reaction by a factor of 10^9 and readily obtain products which are often impossible to synthesise by other methods.[23–25]

At the present time a sufficiently large amount of data has been collected to make it possible to correlate the main mechanisms of the course of these reactions, including those carried out in the presence of catalysts.

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In this review the following notation for the physicochemical characteristics and their dimensions has been adopted:

k_2 is the rate constant of a second-order reaction in l mol^{-1} s^{-1};

K_e is the equilibrium constant of reaction or formation of a 1:1 complex in l mol^{-1} s^{-1};

$\Delta G^{\neq}$ is the free energy of activation, $\Delta H^{\neq}$ is the enthalpy of activation, ΔH_{reac} is the enthalpy of reaction, ΔH_{solut} is the enthalpy of solution, ΔH_{solv} is the enthalpy of solvation, ΔH^0_{IC} is the enthalpy of formation of an intermolecular complex, all in kJ mol^{-1};

$\Delta S^{\neq}$ is the entropy of activation of reaction in J mol^{-1} K^{-1};

I_D is the ionisation potential, E_A is the electron affinity, E_{CT} is the energy of the charge-transfer band maximum in the molecular complexes, all in eV;

[*c*] is the concentration of reactants in mol l^{-1}.

II. Position and role of intermolecular complexes in the reaction

Three main types of reaction have been established: 1) "diene donor, dienophile acceptor", 2) "diene acceptor, dienophile donor", and 3) a neutral type corresponding to the case where introduction of donor and acceptor substituents increase the rate of the process.[5–13,26] The most common is the first type of reaction, in which the activity increases as the donor properties of the diene and the acceptor properties of the dienophile increase.[5–18,26] The intermolecular stabilisation energy of the donor-acceptor pairs assists the formation of charge-transfer complexes.[27–29] As the strength of the complexes between the reactants increases, their reactivity also

usually increases.[30-32] According to the theory of frontier orbital interaction,[18,33-36] the stabilisation energy is given by relationship (1), which includes the contributions of charge and orbital interactions to the stabilisation of the system:

$$E_{ST} = -q_D q_A \gamma/\epsilon + 2(c_D c_A \beta)^2/(I_D - E_A) \quad (1)$$

where q_D and q_A are the charges on the reacting atoms of diene (D) and dienophile (A), γ is the Coulomb integral, ε is the dielectric constant of the medium, c_D and c_A are the coefficients of the frontier orbitals on the reacting atoms of diene and dienophile, β is the interaction integral (the values of the interaction and overlap integrals are assumed to be equal), I_D is the ionisation potential of the diene, and E_A is the electron affinity of the dienophile. For neutral molecules the contribution of the charge interaction is usually ignored,[11,37] so the stabilisation energy is determined by the orbital term, the main contribution being made by interaction of the highest occupied molecular orbital (HOMO) of diene and lowest unoccupied molecular orbital (LUMO) of dienophile.[38,39] The variation in reactivity in a series of dienes or dienophiles is quite frequently determined by the variation in ionisation potential of diene or electron affinity of dienophile. This type of dependence in the reaction of cyanoethylenes with cyclopentadiene and 9,10-dimethylanthracene (Fig. 1) has become a select example of the successful application of frontier orbital theory to represent the activity of reactants in the Diels–Alder reaction.[11,37] Similar linear relationships have also been found for many other series of reactants[6,7] (Fig. 2). They are usually parallel lines on the coordinates $\lg k_2$ and $(I_D - E_A)^{-1}$, displaced relative to each other. The question naturally arises as to the reason why there is no single dependence for different classes of reactants. It is clear that for a general representation of the reactivity of addends in the Diels–Alder reaction it is not sufficient to take into account only donor-acceptor interactions. It is therefore advisable to examine the question concerning the position and role of the intermolecular complexes, whose presence in the reaction mixture has been established many times by various methods.[27-29,40-43] This question has been the subject of active discussion for a number of years.[30-32,44,45]

The representation of the stabilisation energy of intermolecular complexes that is given in one monograph[40] is to a considerable degree similar to the representation of the stabilisation energy of the transition state in the Diels–Alder reaction as reported in several studies.[18,33-36] Two reaction schemes involving an intermolecular complex are possible.

1. The intermolecular complex (IC) lies on the reaction pathway:[30-32]

$$A + B \overset{K_e}{\rightleftarrows} IC \overset{k_1}{\rightarrow} \text{Product}. \quad (2)$$

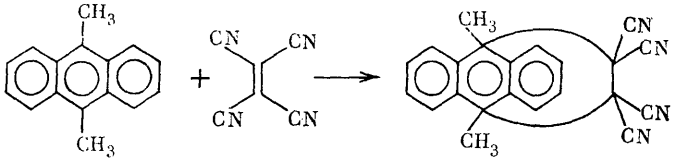
In this case the inherent properties (donor capacity of the diene and acceptor capacity of the dienophile) and the external conditions (solvent and pressure) can equally affect the strength of the complex and the rate of reaction.

2. The intermolecular complex that is formed does not lie on the reaction pathway:

$$IC \overset{K_e}{\rightleftarrows} A + B \overset{k_2}{\rightarrow} \text{Product}. \quad (3)$$

There is thus no similar effect.

It has been found that the donor properties of substituted anthracenes affect in the same way the strength of their molecular complexes with *p*-chloroanils and the rate of reaction with maleic anhydride.[30] Moreover, a similar agreement was noted in a study of the effect of the acceptor properties of a number of *N*-arylmaleimides on the rate of reaction and the stability of their complexes.[31] Thus, by comparing the effect of donor-acceptor properties of the reactants,[30-32] the solvent,[44,46,47] and also the pressure[48,49] on the molecular complex and transition state of the reaction it was possible to conclude that the complexes lay on the reaction pathway.[32] Direct experimental confirmation of this was obtained after determination of the activation parameters of the reaction between the clearly defined donor-acceptor pair—9,10-dimethylanthracene (I_D = 7.04 eV [30]) and tetracyanoethylene (E_A = 2.88 eV [37]):



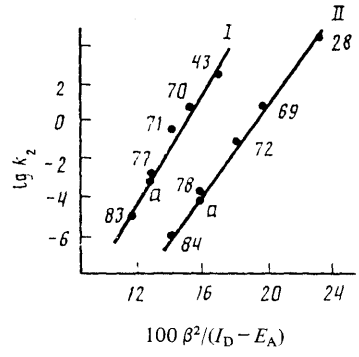


Figure 1. Relationship between the reactivity of cyanoethylenes in the Diels–Alder reaction with cyclopentadiene (*I*) and 9,10-dimethylanthracene (*II*) and the interaction energy of the frontier orbitals of diene and dienophile.[11,37] Point *a* corresponds to the reaction with dinitrilomaleate. Here and in Fig. 2 the value of β is assumed to be equal to 1 eV.

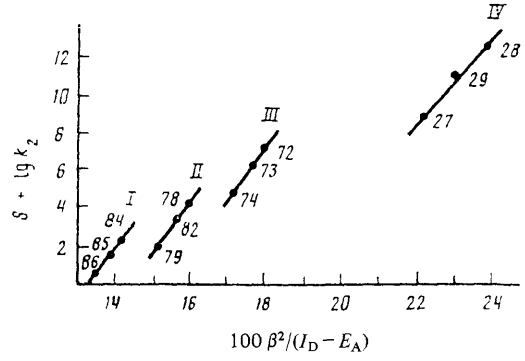


Figure 2. The effect of interaction energies of the frontier orbitals on the reactivity of acrylonitrile (*I*), dinitrilofumarate (*II*), *gem*-dicyanoethylene (*III*), and tetracyanoethylene (*IV*) in reactions with substituted anthracenes.[6,7]

If the reaction occurs in accordance with scheme (2), its rate (v) is given by Eqn. (4)

$$v = k_{exp}[A][B] = k_1[IC] = k_1K_e[A][B]/(1 + K_e[B]), \quad (4)$$

and if it occurs in accordance with scheme (3), v is given by Eqn. (5):

$$v = k_{exp}[A][B] = k_2[A][B]/(1 + K_e[B]), \quad (5)$$

where k_{exp} is the experimentally determined rate constant for reaction, k_1 and k_2 are the rate constants of reaction for formation of product from the molecular complex or from free reactants A and B, K_e is the equilibrium constant of the complex. If $[A] \ll [B]$ and $K_e[B] \ll 1$, the experimentally determined activation parameters include the following parameters for formation of complex:

a) when scheme (2) occurs:

$$\Delta G^{\neq}_{exp} = \Delta G^{\neq}_{real} + \Delta G^{0}_{IC};\ \Delta H^{\neq}_{exp} = \Delta H^{\neq}_{real} + \Delta H^{0}_{IC};\ \Delta S^{\neq}_{exp} = \Delta S^{\neq}_{real} + \Delta S^{0}_{IC}; \quad (6)$$

b) if scheme (3) is true, then:

$$\Delta G^{\neq}_{exp} = \Delta G^{\neq}_{real};\ \Delta H^{\neq}_{exp} = \Delta H^{\neq}_{real};\ \Delta S^{\neq}_{exp} = \Delta S^{\neq}_{real}. \quad (7)$$

Although kinetic schemes (4) and (5) are indistinguishable, their activation parameters differ according to the magnitude of the parameters for complex formation. If the molecular complexes lie on the reaction pathway, for reactants with well-defined donor-acceptor properties a low, zero, or even negative enthalpy of activation can be expected. The results of kinetic measurements (Table 1) are convincing evidence that the geometry of the complex between the reactants corresponds to the structural demands made on the transition state. This assists its formation. The experimentally determined enthalpy of activation contains two components (Fig. 3). If the addends are not capable of intermolecular stabilisation, the energy of activation ($\Delta H_1^{\neq}$) is determined by the distribution of energies of bond cleavage and bond formation. If such a stabilisation takes place (ΔH^{II}_{ST}), formation of the transition state is considerably assisted by using the intermolecular stabilisation energy for expenditure of energy in breaking up the old π-bonds and the apparent energy of activation ($\Delta H^{\neq}_{2,exp}$) is small. When there are considerable intermolecular interactions (ΔH^{III}_{ST}), as a result of such a superposition the energy of activation may be equal to zero and can even acquire a negative value.[50]

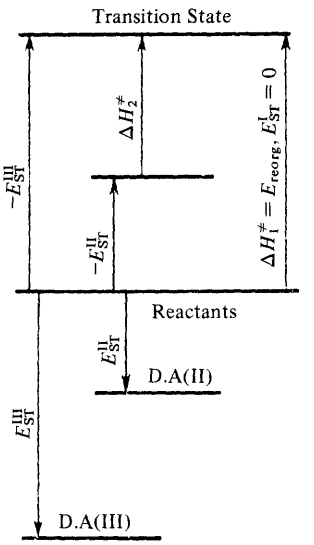


Figure 3. Relationship between the experimental enthalpy of activation ($\Delta H^{\neq}$) and the sum of the contributions from the energy of bond reorganisation (E_{reorg}) and the intermolecular stabilisation energy (E_{ST}).[70]

Since the molecular complex that is formed between the reactants to a considerable extent determines the pathway of the subsequent chemical reaction, the interest shown in studying such complexes

Table 1. Rate constants and activation parameters of the reaction between tetracyanoethylene [TCNE] and 9,10-dimethylanthracene (DMA) in certain solvents when $[TCNE]_0 \gg [DMA]$.[50]

Solvent	$10^4 \times [TCNE]_0$	k_2/T (°C)				$\Delta H^{\neq}$	$-\Delta S^{\neq}$
o-Xylene	10.55	790/13.5	816/14.7	1 050/25	1 605/40.2	18.3	125
Toluene	8.44	2 290/13.5	2 810/25.0	3 790/39.4	3 810/40.2	11.9	138
Benzene	6.56	7 600/13.5	8 480/25.0	10 800/39.4	10 400/40.2	7.2	146
Acetonitrile	8.78	46 500/12.0	43 500/25.1	42 500/40.4	—	—5.0	171
Dichloromethane	6.53	150 000/12.0	136 000/25.3	—	—	—7.5	171
Dichloroethane	4.67	111 000/12.0	110 000/11.8	89 500/40.4	—	—8.1	176
	8.75	102 000/12.9	92 700/24.9	83 000/36.1	—	—8.7	180
	8.90	96 000/12.4	89 000/24.9	83 600/36.1	81 300/43.1	—6.9	171
Chloroform	3.94	290 000/14.0	260 000/24.6	216 000/39.4	—	—11.2	180
	4.20	278 000/12.0	214 000/25.1	185 000/40.4	—	—13.1	186
	4.70	263 000/11.1	226 000/24.8	190 000/42.8	—	—10.2	176
n-Hexane	0.805	14 000/25.0	—	—	—	—	—
Tetrachloromethane	3.34	40 160/25.0	—	—	—	—	—

becomes understandable. There are sufficiently argued proposals for the existence of molecular complexes on the reaction pathway in the acylation of amines,[51,52] electrophilic addition to double bonds,[53,54] and a number of other processes.[27,28,51]

It is important to note that the activity of reactants with different structures cannot be explained solely from the energy of the donor-acceptor interaction, although the difference in reactivity of addends of a single structural type is satisfactorily represented by the change in interaction energy.

III. Kinetic and thermodynamic study of the uncatalysed reaction

Thermochemical enthalpy data assist in establishing the relationship between the activity of the reactants and the stability of the adducts. As will be demonstrated below, when the factors determining reactivity are analysed these data serve as a basis for analysing the change in energy of the reacting bonds in the reactants.

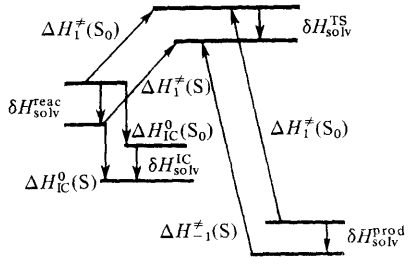


Figure 4. Enthalpies of reactant transfer (δH_{solv}^{reac}), the molecular complex (δH_{solv}^{IC}), the transition state (δH_{solv}^{ST}), and products (δH_{solv}^{prod}) in the Diels–Alder reaction on changing the solvent.[163,164]

1. Effect of solvent

There is a considerable amount of information about the effect of the solvent on the reactivity of the reactants and the stability of the molecular complexes formed by them.[44,46,47,55] However, this does not elucidate the cause of the variation in width of energy gap between the initial and final states of the system. An additional treatment of thermochemical data can be used for such an analysis.[56–58] Examination of the thermodynamic cycle (Fig. 4) shows that the change in enthalpy level of the solvated reactants (δH_{solv}^{reac}) is determined by the difference in enthalpies of solution (ΔH_{solut}^{reac}) in different solvents (S) relative to a given reference solvent (S_0):

$$\delta H_{solv}^{reac} = \Delta H_{solut}^{reac}(S) - \Delta H_{solut}^{reac}(S_0).$$

In order to calculate the change in enthalpy level of the solvated complex (δH_{solv}^{IC}) it is necessary to have data on the enthalpy of formation of the complexes (ΔH_{IC}^0) in different solvents:

$$\delta H_{solv}^{IC} = \Delta H_{IC}^0(S) - \Delta H_{IC}^0(S_0) + \delta H_{solv}^{reac}.$$

Such an analysis was carried out for the first time on complexes formed by the π-donors, mesitylene and benzene, with tetracyanoethylene.[46] The change in transfer enthalpies for mesitylene and benzene was similar to that found for anthracene.[57] A change of medium has a more pronounced effect on tetracyanoethylene than on the π-donors. By using enthalpy of activation data for the reaction of tetracyanoethylene with anthracene in different solvents[55,57] it is possible to calculate the change in enthalpy level of the transition state (ΔH_{solv}^{TS}) relative to cyclohexane chosen as a reference solvent:

$$\delta H_{solv}^{TS} = \delta H_{solv}^{reac} + \Delta H^{\neq}(S) - \Delta H^{\neq}(S_0).$$

The change in enthalpy level of the transition state when the solvent is altered is proportional to the change in enthalpy level of the molecular complex.[46] The type of effect of the medium on the enthalpy levels of solvated reactants and reaction adducts is considerably different from the type of effect of the solvent on the transition state of reaction.[23,46,57] Since a change of solvent leads to a change in enthalpy levels of all states—donor, acceptor, and complex—it becomes obvious that an analysis of the effect of the medium on the enthalpy of formation of the complex based on the change in activity of only one component (usually the acceptor) is not reliable in every case.[59–61]

Table 2. Enthalpy contributions of specific (ΔH_{sol}^{spec}) and nonspecific ($\Delta H_{solv}^{nonspec}$) solvation to the total enthalpy of solvation (ΔH_{solv}) of tetracyanoethylene in given solvents at 22 °C.[23,46]

Solvent No.	Solvent	$[IC]/[TCNE]_0$	K_p	$-\Delta H_{solv}$	$-\Delta H_{solv}^{spec}$	$-\Delta H_{solv}^{nonspec}$	$-\Delta H_{IC}^0$
1	Cyclohexane	0.40	0.072	49.8	1.3	48.5	3.2
2	Tetrachloromethane	0.69	0.217	53.1	4.4	48.7	6.4
3	Chloroform	0.85	0.48	56.9	7.4	49.5	8.7
4	Dichloromethane	0.94	0.98	57.7	10.0	47.7	10.7
5	Benzene	0.96	2.27	66.1	17.3	48.8	18.1

By using information about the equilibrium constants of complexes of tetracyanoethylene with a number of solvents, it is possible to calculate the proportion of specifically solvated acceptor:

$$[IC]/[TCNE]_0 = K_e[S]/(1 + K_e[S]),$$

where [S] is the number of moles of solvent in a litre of solution. By multiplying the proportion of bonded tetracyanoethylene ($[IC]/[TCNE]_0$) by the enthalpy of formation of complex with solvent, it is possible to determine the enthalpy of specific interaction of acceptor with solvent (Table 2). For cyclohexane this interaction proves to be negligible, which is consistent with the results of two studies,[62,63] while on changing to benzene it increases substantially.[46] The contribution of the nonspecific solvation ($\Delta H_{solv} - \Delta H_{solv}^{spec}$) remains constant in this series of solvents.[46] The variation in the enthalpies of solution of tetracyanoethylene (TCNE) in different solvents is virtually the same as the variation in the enthalpies of formation of its complexes with these solvents (Fig. 5).

A similar analysis of the effect of the medium was carried out on n,σ- and π,σ-complexes of iodine with a number of donors using thermochemical solution data[47] and data on the enthalpy of formation of complexes in solution.[59] In these cases also the change

in enthalpy of formation of the complex is determined to a greater degree by the change in solvation of the acceptor—iodine—but the effect of the medium on the enthalpy of formation of the complexes is completely dependent on the change in enthalpy levels of both reactants and the complex. The total enthalpy of solvation of iodine varies mainly as a result of the difference in energy of the specific interaction; consequently, the enthalpy of nonspecific solvation of iodine, as for tetracyanoethylene (see Table 2), does not vary very much in different solvents.[47]

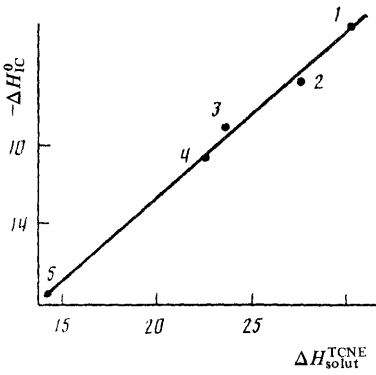


Figure 5. Relationship between the enthalpies of solution of tetracyanoethylene (ΔH^{TCNE}_{solut}) and the enthalpies of complex formation between TCNE and different solvents (ΔH^0_{IC}). The solvents are numbered as in Table 2.

Table 3. Enthalpies of activation for the Diels–Alder reaction between tetracyanoethylene and anthracene ($\Delta H^{\neq}$), enthalpies of solution of tetracyanoethylene (ΔH^{TCNE}_{solut}) and anthracene (ΔH^{An}_{solut}), and the change in enthalpies of solvation of the reactants (δH^{reac}_{solv}) and transition state (δH^{TS}_{solv}) of the reaction at 25 °C.[55,57]

Solvent No.	Solvent	ΔH^{TCNE}_{solut}	ΔH^{An}_{solut}	$\Delta H^{\neq}$	δH^{reac}_{solv}	δH^{TS}_{solv}
1	*o*-Xylene	1.4±0.1	24.0±0.3	51.5	(0)	(0)
2	Toluene	9.4±0.5	24.8±0.8	46.0	9.2	3.6
3	Cyclohexanone	7.6±0.3	20.6±0.6	40.2	2.9	−8.5
4	Benzene	14.9±0.4	24.7±0.4	38.5	14.3	1.2
5	Ethyl acetate	9.2±0.5	25.1±0.2	37.7	8.9	−4.9
6	Chlorobenzene	23.1±0.3	24.6±0.4	31.4	22.3	2.2
7	Methyl acetate	10.5±0.9	25.1±0.2	31.8	10.2	−9.5
8	Acetonitrile	15.2±0.2	28.0±0.3	30.5	17.8	−3.2
9	1,2-Dichloroethane	21.3±0.3	24.9±0.4	26.8	20.9	−3.9
10	Chloroform	24.5±0.3	20.8±0.3	17.6	19.9	−14.0
11	Mesitylene	−2.7±0.4	—	—	—	—

A more extensive analysis of the solvation of the transition state in the Diels–Alder reaction between tetracyanoethylene and anthracene[57] showed that when the solvent was varied there was a change in the enthalpy levels of the reactants and the transition state (Table 3). The considerable increase in the enthalpy of activation on changing to aromatic solvents is due to the sharp decrease in enthalpy level of the reactants with a small change in the level of the transition state. The increased stabilisation of the transition state in chloroform, as noted in a number of studies[44,46,57,58] is due to strengthening of the hydrogen bonds in the activated complex. The kinetics of the reaction between anthracene and tetracyanoethylene in both directions were studied in different solvents.[23] When the large difference in the capacity of tetracyanoethylene and its adduct with anthracene to undergo specific solvation is taken into account, the equal enthalpies of the reactions, calculated from data obtained by direct thermochemical measurement and from the difference in enthalpies of activation for formation and decomposition of the adduct in different solvents, can be taken as proof of the equilibrium solvation of the transition state.[23]

There is a compensating effect between the enthalpies and entropies of activation of this reaction in the given series of solvents (Fig. 6). Consequently, a combined thermochemical and kinetic analysis of the effect of the medium on the enthalpy levels of the reactants and the transition state of the Diels–Alder reaction can explain the change in enthalpy of activation and reactivity as a whole.

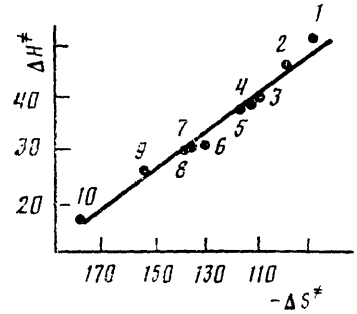


Figure 6. Relationship between the enthalpies and entropies of activation for the reaction of anthracene with tetracyanoethylene in different solvents from published data.[55,57] The solvents are numbered as in Table 3.

Similar studies on solvation effects in the reactions of 9,10-dimethylanthracene with maleic anhydride[64,65] and *trans,trans*-1,4-diphenyl-1,3-butadiene and anthracene with 4-phenyltriazolinedione[58] indicate that in the absence of strong specific interactions between the reactants and the solvent, the effect of the medium on the ground state and transition state is small. Since there is a marked solvent effect on the solvation of the transition state when reactions with effective charge separation are carried out,[66,67] the results of the solvation analysis indicate that the transition state has low polarity.[46,57,58]

2. Main factors determining the reactivity of the reactants

According to the approach of Evans and Polanyi[68] and Semenov,[69] the height of the activation barrier is determined by the distribution of bond cleavage and bond formation energies in the absence of other factors that affect reactivity (Fig. 7). With this approach the enthalpy coordinate of the transition state of reaction is determined

by the relationships:

$$\partial(E_1 + E_2)/\partial R = 0 \quad \text{or} \quad \partial(E_1 + E_3)/\partial R = 0,$$

and the energy of activation is given by the equations:

$$E_{a,4} = (E_1 + E_2)_{R_4} - (E_1 + E_2)_{R_0} \text{ or}$$
$$E_{a,5} = (E_1 + E_3)_{R_5} - (E_1 + E_3)_{R_0},$$

where E_1 is the energy of formation of σ-bonds, and E_2 and E_3 are the energies of cleavage of π-bonds in reactants with a different system of conjugation, R is the reaction coordinate.

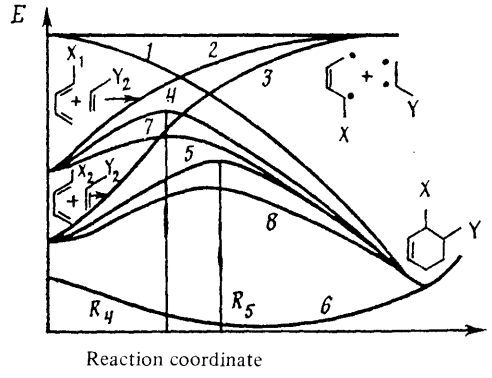
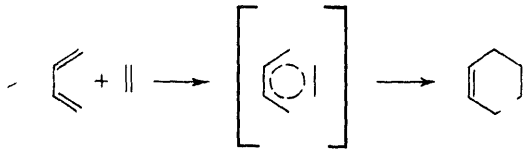


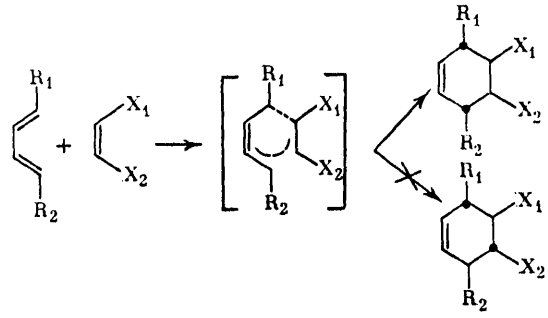
Figure 7. Diagram of energy changes on formation of σ-bonds (*1*) and cleavage of π-bonds in the reactants (*2* for X_1 and Y_1 and *3* for X_2 and Y_2); energies of bond cleavage and bond formation are superimposed (*4* and *5* for a combination of curves *1* + *2* and *1* + *3* respectively), excluding the intermolecular stabilisation energy (*6*) and including it (*7* and *8*).[70]

Since the initial change in energy of cleavage of π-bonds ($\partial E_2/\partial R$ and $\partial E_3/\partial R$) is greater than the change in energy of formation of σ-bonds ($\partial E_1/\partial R$), an activation barrier must occur for exothermic reactions, with a height that increases as the strength of the reacting bonds increases namely with an increase in their conjugation energy [E_3 (Fig. 7, curve *3*)]. If the reactants can undergo intermolecular stabilisation [E_6 (curve *6*)], the compensation of energies of bond cleavage and bond formation must appear at a lower value of the reaction coordinate and hence with lower perturbation energies of the system [E_7 and E_8 (curves *7* and *8*)]. For the Diels–Alder reaction this indicates[70] that both the donor-acceptor stabilisation (E_6) and the energy parameters of the reacting bonds (E_1, E_3, and E_2) affect the height of the activation barrier and the reactivity as a whole. Although the necessity for calculating the energies of cleavage of the reacting bonds in studying the kinetic charactersitics is not in doubt, difficulty arises because there is either no data or insufficient data on these energies and also because there is a wide variety of possible methods of bond cleavage (homolytic, heterolytic with formation of a carbanion, carbocation, etc.).

As regards the Diels–Alder reaction, the wide variety of experimental data on the structural characteristics of the reaction taking place and adherence to the principle of *cis*-addition,[1,26,71] the data on the kinetic isotope effect,[72–76] and on the effect of the solvent[2,77] and pressure,[48,49] and the results of a number of nonempirical calculations[78,79] are consistent with the proposal of a synchronous mechanism for cleavage and formation of bonds in the transition state:



It is suggested that with an increase in asymmetry of the reacting bonds, the asymmetry of the transition state increases,[14,80,81] but for *cis*-addition to be achieved for donor-acceptor systems, the second bond needs to be "fastened" after a shorter time than the period necessary for a change in geometry of the substituents:



For this reason calculation of the energy of the reacting bonds in the molecular Diels–Alder reaction can be carried out more rigorously using the experimental data.

On the basis of the ideas of Evans and Polanyi[68] and Semenov,[69] Hammond[82] predicted an increase in kinetic activity of the reactants as the exothermicity of the process increases. It was suggested[83] that the bislocalisation energy of the electrons on the reacting atoms should be regarded as an index of the reactivity of addends in the Diels–Alder reaction:



For a number of aromatic dienes the calculated 1,4-bislocalisation energies correlate with the reactivity.[83,84] Since the 1,4-bislocalisation energy of π-bonds in a diene by its very nature corresponds to the energy of cleavage of the reacting bonds, it is obvious that in the given series of dienes—polynuclear hyrocarbons—the variation in bond energy is similar to the variation in their activity. The donor properties of dienes also vary in a similar manner to their activity.[83,84] This led to the mistaken assumption that there was a connection between the bislocalisation energy and the donor-acceptor interaction energy.[22,39] For many dienes and the majority of dienophiles such a relationship does not occur. Thus in a number of cyanoethylenes the activity varies inversely to the change in 1,2-bislocalisation energy.[85] In this case the reactivity is related to the acceptor properties of the cyanoethylenes.[85,86] Thus, in far from every case does an increased stability of adducts correspond to more active reactants in the Diels–Alder reaction. The fact that activity series more often reflect the nature of change of donor-acceptor properties of the reactants and also the difficulties in calculating the

bislocalisation energy for substituted dienes and particularly for dienophiles have meant that less attention has been given to the problem of the effect of the conjugation energy on reactivity.

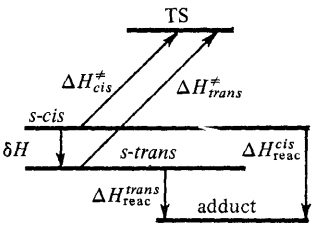


Figure 8. Effect of *trans-cis* conformational change on the enthalpies of activation and reactions of 1,3-butadienes.

Since the cleavage and formation of bonds in the transition state of the Diels–Alder reaction take place according to a concerted mechanism and substituents have a greater effect on the strength of π-bonds than on σ-bonds, the proposal was made[86] that the difference in the enthalpies of reaction reflects the difference in conjugation energies. This proposal is supported by the occurrence of a linear relationship between the change in enthalpy of the reactions of a series of substituted anthracenes with tetracyanoethylene[86] and a series of substituted dienophiles (cyanoethylenes) with 2,5-diphenylisobenzofuran[87] on the one hand and the calculated 1,4- and 1,2-bislocalisation energy on the other hand. These results indicate that the differences in the enthalpies of reaction are due not to steric strain in the adducts formed but to the change in strength of the reacting bonds. The proportional relationship between the enthalpy of reaction and the energy of the reacting π-bonds suggests that there is a small or proportionate change in energy of the σ-bonds formed. To a certain extent data on the change in enthalpy of reaction can provide more information on the reactivity of the reactants in a molecular Diels–Alder reaction than data on the bislocalisation energy. Although the substituents have a greater effect on the strength of the π-bonds than on the strength of the σ-bonds,[88,89] the height of the activation barrier is determined by superimposing the changes in energy of both types of bonds (π and σ) during reaction (see Fig. 7). This effect is reflected in the enthalpy of reaction, whereas the bislocalisation energy in a diene or dienophile only reflects the change in energy of the reacting bonds. Apart from this, the forms of solvation and possible conformational conversions have an effect on the enthalpy of reaction. For example, substituted butadienes mainly have a *trans*-conformation.[84,90] The height of the activation barrier for the reaction of s-*cis*-butadiene is determined by the sum of these factors—the distribution of energies for bond cleavage and bond formation and the donor-acceptor interaction energy (Fig. 8). The experimentally found height of the activation barrier, in addition to the value of $\Delta H^{\neq}_{cis}$ also includes the product of the enthalpy of *trans-cis* conformational change and the proportion of the *trans* form under the experimental conditions (δH). But it is the enthalpies of s-*trans*- and s-*cis*-butadienes and the enthalpies of the reactions involving them which differ by this magnitude of σH. In other words, the enthalpy of the conformational change included in the enthalpy of activation is also included in the enthalpy of reaction.

What results are obtained from a combined calculation of the donor-acceptor interaction energy and the enthalpy of reaction, which reflects mainly the distribution of energies of the reacting bonds, in representing the reactivity of hydrocarbon addends?

By using the enthalpy of reaction as an indicator of reactivity it was possible to account for what appeared at first to be an unusual change in activity of the reactants, occurring sometimes even in the same structural series (Table 4). Thus 9-methoxy- and particularly 9,10-dimethoxy-anthracenes, which exhibit high donating capacity, are appreciably less active when reacting with dienophiles that cannot undergo strong donor-acceptor interaction. The "anomalous" behaviour of these dienes is understandable if the increased conjugation energy (reduced exothermicity of the reaction) is taken into account (Table 4). By calculating at the same time the donor-acceptor interaction energy and the enthalpy of reaction it is possible to determine the overall relationship representing the reactivity of all the reacting pairs of addends. In a number of substituted butadienes the change in donor properties and conjugation energy, which has an opposite effect on the rate of reaction, also results in an "anomalous reactivity" in relation to frontier orbital theory (see Table 4 and Fig. 9).[70] Here also when a combined calculation of both factors is made it is possible to account for the observed activity of the reactants.[70]

Table 4. The reactivity ($8 + \lg k_2$), ionisation potentials (I_D) of dienes, electron affinities (E_A) of dienophiles, characteristics of the donor-acceptor interaction energy [$100\beta^2/(I_D - E_A)$], and enthalpies of Diels–Alder reactions (ΔH_{reac}) at 25 °C.

Reaction No.	Reactants	$100\beta^2/(I_D-E_A)$	$8+\lg k_2$	I_D	E_A	$-\Delta H_{reac}$
	Reactions of dienophiles with 2,5-diphenylisobenzofuran (I_D = 7.62 eV)					
1	Tetracyanoethylene	21.09	16.0		2.88	69
2	Tricyanoethylene	18.12	12.0		2.10	71
3	*gem*-Dicyanoethylene	16.42	11.0		1.53	77
4	Dinitrilofumarate	14.62	7.49		0.78	82
5	Maleodinitrile	14.62	8.12		0.78	84
6	Acrylonitrile	13.16	5.34		0.02	87
7	Maleic anhydride	15.04	8.53		0.97	85
8	*N*-Phenylmaleimide	14.86	8.57		0.89	98
9	*N*-(*p*-Nitrophenyl)maleimide	15.13	9.16		1.01	96
10	*N*-(*m*-Nitrophenyl)maleimide	15.08	9.22		0.99	95
11	*N*-(*p*-Bromophenyl)maleimide	14.99	8.87		0.95	98
12	*N*-(*p*-Methylphenyl)maleimide	14.73	8.56		0.83	98
13	*N*-(*p*-Methoxyphenyl)maleimide	14.68	8.50		0.81	99
14	*N*-(*p*-Dimethylaminophenyl)-maleimide	14.51	8.36		0.73	100
15	4-Phenyltriazolinedione		Very rapid		1.80	104
16	*p*-Benzoquinone	17.01	7.72		1.74	66
17	1,4-Naphthoquinone	16.58	7.03		1.59	58
18	Acrolein	13.39	5.92		0.15	78
19	Acrylic acid	13.28	6.18		0.09	84
20	Methyl acrylate	13.46	5.28		0.19	85
21	Methacrylic acid	—	5.48		—	66
22	Methacrolein	—	5.11		—	62
23	Methyl methacrylate	—	4.32		—	69
24	Methacrylonitrile	—	3.92		—	73
25	Chloromaleic anhydride	15.29	8.58		1.08	82
26	Citraconic anhydride	14.73	5.96		0.83	84
	Reactions of dienes with tetracyanoethylene (E_A = 2.88 eV)					
27	Anthracene	22.47	8.48	7.33		77
28	9,10-Dimethylanthracene	24.04	12.37	7.04		88
29	9-Methylanthracene	23.31	11.35	7.17		85
30	9-Chloroanthracene	22.17	7.74	7.39		66
31	9-Methoxyanthracene	23.31	11.71	7.17		61
32	9,10-Dimethoxyanthracene	23.75	10.94	7.09		53
33	1,3-Butadiene	16.23	5.23	9.03		154
34	2-Methylbutadiene	16.64	6.87	8.89		166
35	2-Methoxybutadiene	17.42	8.47	8.62		159
36	2,3-Dimethylbutadiene	17.45	8.40	8.61		176

Table 4 (contd.).

Reaction No.	Reactants	$100\beta^2/(I_D-E_A)$	$8+\lg k_2$	I_D	E_A	$-\Delta H_{reac}$
	Reactions of dienes with tetracyanoethylene (E_A = 2.88 eV)					
37	*trans*-1-Methylbutadiene	17.45	7.23	8.61		163
38	*trans*-1-Phenylbutadiene	18.94	7.81	8.16		142
39	*trans,trans*-1,4-Diphenylbutadiene	19.19	6.87	8.09		97
40	*trans*-1,2,3-Trimethylbutadiene	—	8.12	—		163
41	*trans,trans*-1-Methyl-4-phenylbutadiene	—	7.66	—		124
42	1,3-Cyclohexadiene	18.62	8.14	8.25		130
43	Cyclopentadiene	17.54	10.63	8.58		113
44	Hexachlorocyclopentadiene	16.53	—	8.93		42*
45	Hexabromocyclopentadiene	—	—	—		29*
46	5,5-Dimethoxytetrabromocyclopentadiene	—	—	—		62*
47	Tetracene	24.21	—	7.01		97
48	5,11-Dichlorotetracene	25.44	—	6.81		78
49	Pentacene	26.59	—	6.64		116
	Reactions of dienes with maleic anhydride (E_A = 0.97 eV)					
50	Anthracene	15.72	2.78	7.33		93*
51	9,10-Dimethylanthracene	16.47	6.09	7.04		104
52	9-Methylanthracene	16.13	4.54	7.17		101
53	9-Chloroanthracene	15.57	2.16	7.39		82*
54	9-Methoxyanthracene	16.13	3.45	7.17		77*
55	9,10-Dimethoxyanthracene	16.33	2.49	7.09		69*
56	1,3-Butadiene	12.41	3.83	9.03		170*
57	2-Methylbutadiene	12.93	4.19	8.89		182*
58	2,3-Dimethylbutadiene	13.07	4.53	8.62		194*
59	*trans*-1-Methylbutadiene	13.09	4.36	8.61		179*
60	*trans*-1-Phenylbutadiene	13.91	4.05	8.16		158*
61	*trans,trans*-1,4-Diphenylbutadiene	14.04	2.47	8.09		113*
62	1,3-Cyclohexadiene	13.74	4.12	8.25		146*
63	Cyclopentadiene	13.14	6.96	8.58		129*
64	Hexachlorocyclopentadiene	12.56	0.06	8.96		58*
65	Hexabromocyclopentadiene	—	0.99	—		45*
66	5,5-Dimethoxytetrabromocyclopentadiene	—	2.38	—		78*
67	Tetracene	16.55	4.88	7.01		103*
68	Pentacene	17.64	6.13	6.64		132*
	Reactions of dienes with tricyanoethylene (E_A = 2.10 eV)					
69	9,10-Dimethylanthracene	20.24	8.77	7.04		90
70	Cyclopentadiene	15.43	8.68	8.58		115
	Reactions of dienes with gem-dicyanoethylene (E_A = 1.53 eV)					
71	Cyclopentadiene	14.18	7.66	8.58		121
72	9,10-Dimethylanthracene	18.15	7.10	7.04		96
73	9-Methylanthracene	17.73	6.18	7.17		93
74	Anthracene	17.24	4.52	7.33		85*
75	9-Methoxyanthracene	17.73	6.16	7.17		69*
76	9,10-Dimethoxyanthracene	17.98	5.64	7.09		61*
	Reactions of dienes with dinitrilofumarate (E_A = 0.78 eV)					
77	Cyclopentadiene	12.82	4.91	8.58		126
78	9,10-Dimethylanthracene	15.97	4.14	7.04		101*
79	Anthracene	15.27	1.62	7.33		90*
80	9-Methoxyanthracene	15.62	2.28	7.17		74*
81	9,10-Dimethoxyanthracene	15.85	1.08	7.09		66*
82	9-Methylanthracene	15.65	3.08	7.17		98*
	Reactions of dienes with acrylonitrile (E_A = 0.02 eV)					
83	Cyclopentadiene	11.68	3.02	8.58		131
84	9,10-Dimethylanthracene	14.24	1.95	7.04		106*
85	9-Methylanthracene	13.99	1.04	7.17		103*
86	Anthracene	13.68	−0.07	7.33		95*
87	9-Methoxyanthracene	13.99	0.70	7.17		79*
	Reactions of dienes with *N*-phenylmaleimide (E_A = 0.89 eV)					
88	9,10-Dimethylanthracene	16.26	6.48	7.04		117
89	9-Methylanthracene	15.92	4.71	7.17		114*
90	Anthracene	15.53	2.86	7.33		106*
91	9-Chloroanthracene	15.38	1.45	7.39		95*
92	9-Methoxyanthracene	15.92	3.45	7.17		90*
93	Tetracene	16.34	5.34	7.01		126
94	5,11-Dichlorotetracene	16.89	4.43	6.81		107
95	Pentacene	17.39	6.98	6.64		145*
96	Cyclopentadiene	13.00	6.34	8.58		142
	Reactions of dienes with *N*-(*p*-nitrophenyl)maleimide (E_A = 1.01 eV)					
97	Cyclopentadiene	13.21	7.31	8.58		140
98	9-Methylanthracene	16.23	5.23	7.17		112
99	Anthracene	15.82	3.93	7.33		104*
100	9-Chloroanthracene	15.67	2.92	7.39		93*
101	9-Methoxyanthracene	16.23	4.43	7.17		88*
102	Tetracene	16.67	5.96	7.01		124
103	Pentacene	17.76	7.75	6.64		143*

Table 4 (contd.).

Reaction No.	Reactants	$100\beta^2/(I_D-E_A)$	$8+\lg k_2$	I_D	E_A	$-\Delta H_{reac}$
	Reactions of dienophiles with cyclopentadiene (I_D = 8.58 eV)					
104	Acrylic acid	11.78	4.77		0.09	128*
105	Acrolein	11.87	3.30		0.15	122*
106	Methyl acrylate	11.91	3.51		0.19	129*
	Reactions of dienes with chloromaleic anhydride (E_A = 1.08 eV)					
107	9,10-Dimethylanthracene	16.78	5.81	7.04		101*
108	9-Methylanthracene	16.42	4.35	7.17		98*
109	Anthracene	16.00	2.49	7.33		90*
110	9-Chloroanthracene	15.85	1.83	7.39		79*
	Reactions of dienes with citraconic anhydride (E_A = 0.83 eV)					
111	9,10-Dimethylanthracene	16.10	3.38	7.04		103*
112	9-Methylanthracene	15.77	1.93	7.17		100*
	Reactions of dienes with 4-phenyltriazolinedione (E_A = 1.80 eV)					
113	1,3-Butadiene	13.83	8.84	9.03		189
114	2,3-Dimethylbutadiene	14.66	10.21	8.62		213
115	2-Methylbutadiene	14.10	9.66	8.89		201
116	*trans*-1-Phenylbutadiene	15.18	9.80	8.16		177
117	*trans,trans*-1,4-Diphenylbutadiene	15.89	8.71	8.09		132
118	Cyclopentadiene	14.75	12.30	8.58		148
119	Hexachlorocyclopentadiene	14.02	4.92	8.96		77
120	Hexabromocyclopentadiene	—	4.74	—		64
121	5,5-Dimethoxytetrabromocyclopentadiene	—	6.34	—		97
	Other systems					
122	1,3-Butadiene + ethylene	9.22	−4.1	9.03	−1.81	166**
123	1,3-Butadiene + acrolein	11.26	0.0	9.03	0.15	163**
124	Cyclopentadiene + ethylene	9.62	−1.4	8.58	−1.81	126**
125	2-Methylbutadiene + acrolein	11.44	0.70	8.89	0.15	175**

Note. The value of β is assumed to be 1 eV.

* Enthalpy of reaction calculated by Konovalov and Kiselev.[70]
**Calculated from published data[88,89] on the enthalpy of formation.

In the majority of cases the parallel displacement of straight lines relative to each other on the coordinates $\lg k_2$ and $(I_D - E_A)^{-1}$ (see Figs. 1 and 2) is consistent with the variation in the experimentally determined enthalpy of reaction. In this connection attempts were made to represent the activity of different reacting pairs on the basis of the two given factors affecting reactivity.[64,70] The range of reactions to be analysed was restricted to compounds with reacting C=C bonds since for heteroatomic reactants considerable differences in the atomic orbital coefficients and a substantial increase in the contribution of charge interaction to the total stabilisation energy are to be expected[80,81,91] [cf. Eqn.(1)]. A study was made of all reactants for which there existed data on reactivity, ionisation potentials of the diene donors, electron affinities of the dienophile acceptors, and the enthalpy of the Diels–Alder reaction. Known kinetic,[5,11,31,55,87,92–97] thermochemical,[70,86,87,98–102] and orbital data[11,30,31,37,41,70,103–106] are presented in Table 4. It transpired that for all the diene-dienophile hydrocarbon systems there was only a slight tendency towards an increase in reactivity with a rise in donor-acceptor interaction energy (the correlation coefficient r equals 0.635).[70] Analysis shows[70] that calculation of only the stabilisation energy cannot represent the reactivity of all the reactants.

Additional treatment of the data on the enthalpy of reaction does not improve the overall correlation.[70] But a plot of the dependence $\lg k_2 = A/(I_D - E_A) + B\Delta H_{reac}$ shows that the points are grouped

in three distinct regions corresponding to the reactions involving 2,5-diphenylisobenzofuran (Fig. 10, line *I*), cyclopentadiene (Fig. 10, line *II*) and substituted anthracenes and butadienes (Fig. 10, line *III*).

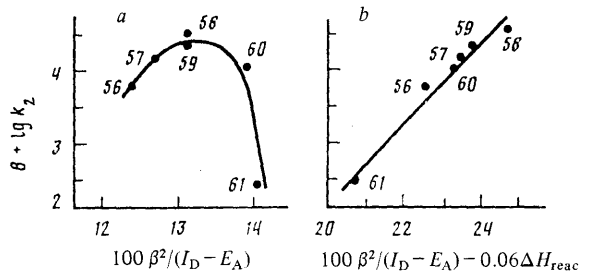


Figure 9. Dependence of the activity of substituted butadienes reacting with maleic anhydride on the intermolecular stabilisation energy excluding (*a*) and with an additional calculation of the change in enthalpy of reaction (*b*). Here and in Figs. 10 and 11 the value of β is assumed to be equal to 1 eV. The reactions are numbered as in Table 4.

It was recently shown[107,108] that the activity of the addends strongly depends on the distance between the reacting diene atoms ($R_{1,4}$). As this distance decreases there is a sharp increase in activity of the dienes. This type of behaviour of dienes in the Diels–Alder reaction can be accounted for[108] by the large variation in overlap of orbitals on the reacting atoms, since there is a proportional dependence $r = 0.999$ [108] between the calculated value of the square of the overlap integral (S^2) and the interatomic distance ($R_{1,4}$) in cyclic 1,2-*bis*-methylenes. In dienophiles the distance $R_{1,2}$ varies insignificantly, although the difference in bond lengths of ethylenic and acetylenic reactants can affect their activity, imparting a higher activity to ethylenic dienophiles when the other conditions are equal.[70]

By arranging the data on the interatomic distance ($R_{1,4}$) in furan (2.19 Å), cyclopentadiene (2.36 Å), anthracene (2.81 Å) and *cis*-1,3-butadiene (2.90 Å) [109] and assuming the corresponding distances in substituted reactants to be unchanged, it was possible to determine the activity of 102 diene-dienophile pairs in relation to the donor-acceptor interaction energy [$\beta^2/(I_D - E_A)$], the enthalpy of reaction (ΔH_{reac}) and the geometrical characteristics of the diene ($R_{1,4}$) [70] (Fig. 11). The significant improvement of the correlation factors ($r = 0.946$, root-mean-square deviation 1.13) achieved by this is shown by the possibility of representing the reactivity of all the pairs of reactants shown in Fig. 11 by a single relationship.

When the proportional relationship identified between the change in the interatomic distance in dienes ($R_{1,4}$) and the square of the overlap integral (S^2) [108] is taken into account, the latter value can be replaced by an experimental factor: $S^2 = A—BR_{1,4}$, where A and B are proportionality coefficients. Then the expression for the stabilisation energy when the resonance integral and overlap integral are equal can be given by the following relationship:

$$E_{ST} = \beta^2/(I_D - E_A) = (A - BR_{1,4})/(I_D - E_A) = A/(I_D - E_A) - BR_{1,4}/(I_D - E_A).$$

The calculated[70] linear regression coefficients lead to the relationship:

$$\lg k_2 = (290 \pm 10)/(I_D - E_A) - (60.8 \pm 2.8)R_{1,4}/(I_D - E_A) - (5.05 \pm 0.39)\Delta H_{reac} - 28.2.$$

The correlation factors in this equation, which has a sounder physical basis, ($r = 0.950$, root-mean-square deviation 1.04) are on the same level as those obtained by Konovalov and Kiselev[70] (see Fig. 11).

It follows from this that calculation of the three main factors that determine reactivity achieves a satisfactory representation of the activity of the compounds, which varies over a wide range (by 10^{20}). Thus, the possibility arises for predicting the reactivity of addends which have not been studied by using the data on donor-acceptor properties of the reactants and the geometric structural features of the diene. In many cases the enthalpy of reaction can be determined from data on the heat effects of other reactions involving the reactants studied.[70] It follows from Table 4 that the low exothermicity of the reaction between hexachlorocyclopentadiene and tetracyanoethylene (–42 kJ mol^{-1}) corresponds to a large displacement of the reaction equilibrium towards the reactants. A similar situation occurs in the reaction of 9,10-dimethoxyanthracene with tetracyanoethylene, the enthalpy of which is equal to –53 kJ mol^{-1}, the equilibrium constant is 6 l mol^{-1}, and the degree of conversion of reactants to adducts under normal conditions does not exceed 2–5%.[86] It is understandable that attempts to obtain an adduct in the reaction between hexachlorocyclopentadiene and tetracyanoethylene at elevated temperatures[110] were not successful.

By using kinetic and thermochemical data it is possible to select reactants for the purpose of liberating concurrently from adducts addends that are difficult to obtain by direct synthesis or from an equilibrium mixture of reactants and also to select addends of equilibrium processes used for the storage of solar energy.[111]

Kinetic and thermochemical studies of the solvation effect in the Diels–Alder reaction[44,57,58] indicate that there is a marked acceleration of the reaction in solvents that form hydrogen bonds with the dienophile. The formation of H-complexes increases the acceptor capacity of the dienophile and consequently its reactivity.[44] Lewis acids form even stronger complexes, which results in a sharp increase in activity of these complexes in the Diels–Alder reaction.

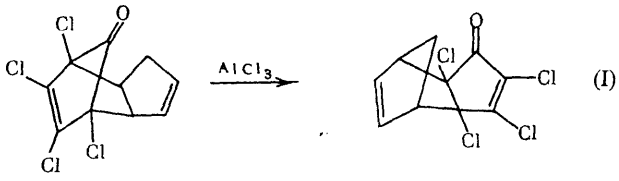
IV. Stoichiometric coordination catalysis

Determination of the factors governing the reactivity of addends does not eliminate the problem concerning the development of methods for involving inactive reactants in the Diels–Alder reaction. The usual methods for accelerating the rate of reaction by increasing the temperature and pressure are not always acceptable because of contamination of the required products with by-products or a displacement of the reaction equilibrium towards the reactants.

1. Catalysts of the Diels–Alder reaction

Data exists on the acceleration of the Diels–Alder reaction by a hydrophobic or cellular effect of the medium.[112–116] However, these only relate to a limited number of compounds, and the rate is not usually increased by more than a factor of 10–10^3.[112–116] A much more marked acceleration effect occurs in the presence of Lewis

acids. The increase in the rate of rearrangement of tetrachlorobicyclopentadien-8-one to tetrachlorobicyclopentadiene-1-one



(I)

in the presence of aluminium chloride[117] served as an impetus for using Lewis acids in the Diels–Alder reaction,[118–129] the ene synthesis,[130–132] [2 + 2]-cycloaddition[130,133] and [2 + 3]-cycloaddition reactions.[134–136] The qualitative prediction of acceleration of the Diels–Alder reaction between anthracene and maleic anhydride in the presence of $AlCl_3$ by a factor of 2×10^5 [118] was recently confirmed by the results of kinetic measurement (acceleration by a factor of 2.60×10^5 found).[137] Such a rapid acceleration of the reaction can be used to obtain adducts at room temperature in a number of minutes. For example, the reaction of anthracene with *p*-benzoquinone to give the bis-adduct in the presence of gallium chloride is complete after 3–5 min.[138] Possibilities arise for the synthesis of carbocyclic and heteroatomic compounds as Diels–Alder adducts which under normal conditions either have a low yield or are not formed at all.[139–141]

Considerable acceleration of the Diels–Alder reaction occurs in the presence of halides of Group II, III, and IV elements of the Periodic Table. The effect of aluminium chloride has been studied

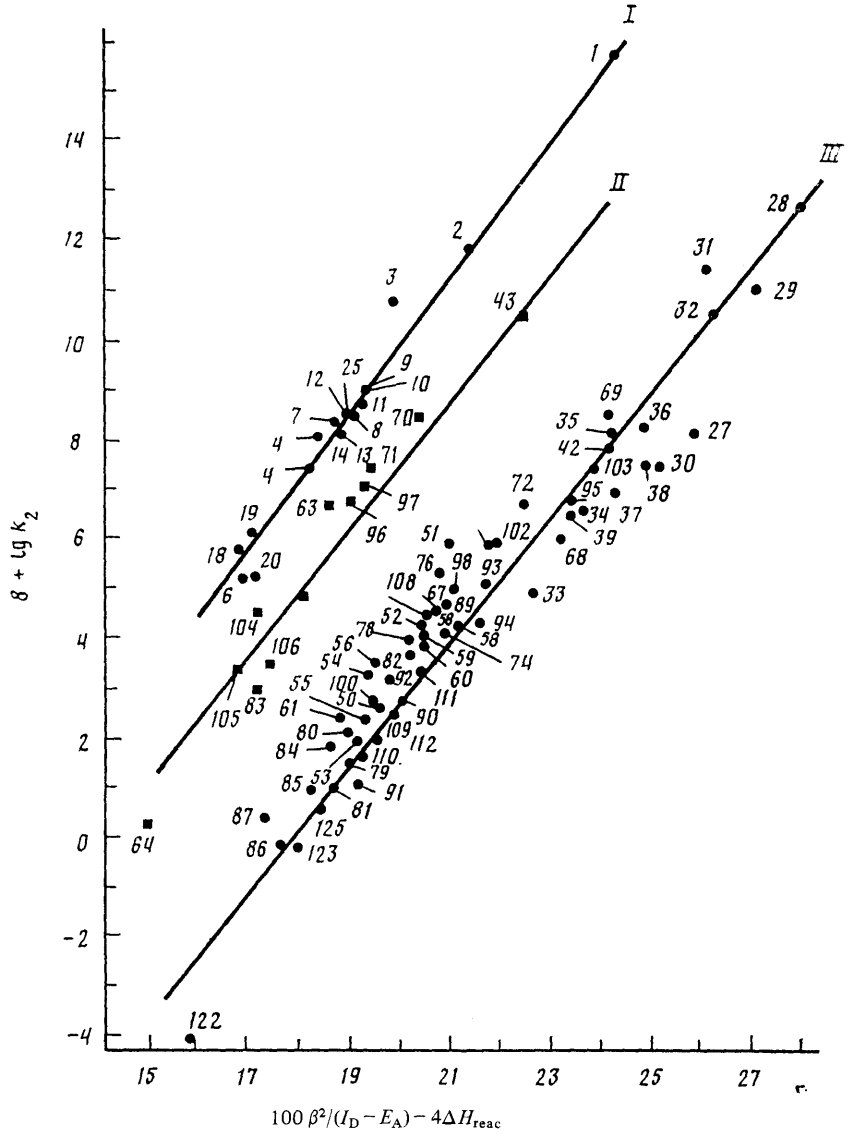
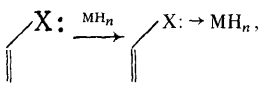


Figure 10. Dependence of the reactivity of reactants in the Diels–Alder reaction on the donor-acceptor interaction energy allowing for the enthalpy of reaction (in eV).

in the greatest detail, but not all reactants are stable in its presence because of the occurrence of polymerisation, isomerisation, or various rearrangements.[118,138,142] The occurrence of these side reactions makes it necessary to find milder Lewis acids and to make a careful selection of solvent and optimum experimental temperature. Traces of moisture in the solvent cause a partial deactivation of the catalyst and the formation of hydrogen halides with side effects that can be avoided in a number of cases by carrying out the reaction in the presence of alkyl halides of metals:[130]

$$RAlCl_2 + HCl \rightleftarrows RH + AlCl_3.$$

Acceleration of the reaction occurs when there are *n*-donor groups in the reactant (usually in the dienophile).[118] It was shown by means of IR, UV, and NMR spectroscopy[43,143–153] that the catalyst interacts with the *n*-donor to form an *n,v*-type molecular complex, which is stabilised by interaction of the unshared electron pair in the functional group of the dienophile with a low vacant orbital of the acceptor:



where X is the dienophile substituent containing a heteroatom with an unshared pair of electrons, M is a Group II, III, or IV element, H is a halogen, alkyl, or aryl.

Organometallic compounds of the type MR_n or MR_mH_{n-m} also form quite strong *n,v*-complexes.

The physicochemical properties of various *n,v*-complexes have been discussed in a review.[43] Analysis of ^{13}C and ^1H NMR spectra indicates that there is a considerable reduction in electron density in complexes of unsaturated esters and primarily on the carbonyl and β-carbon atoms of the *n*-donor.[144–146,154,155]

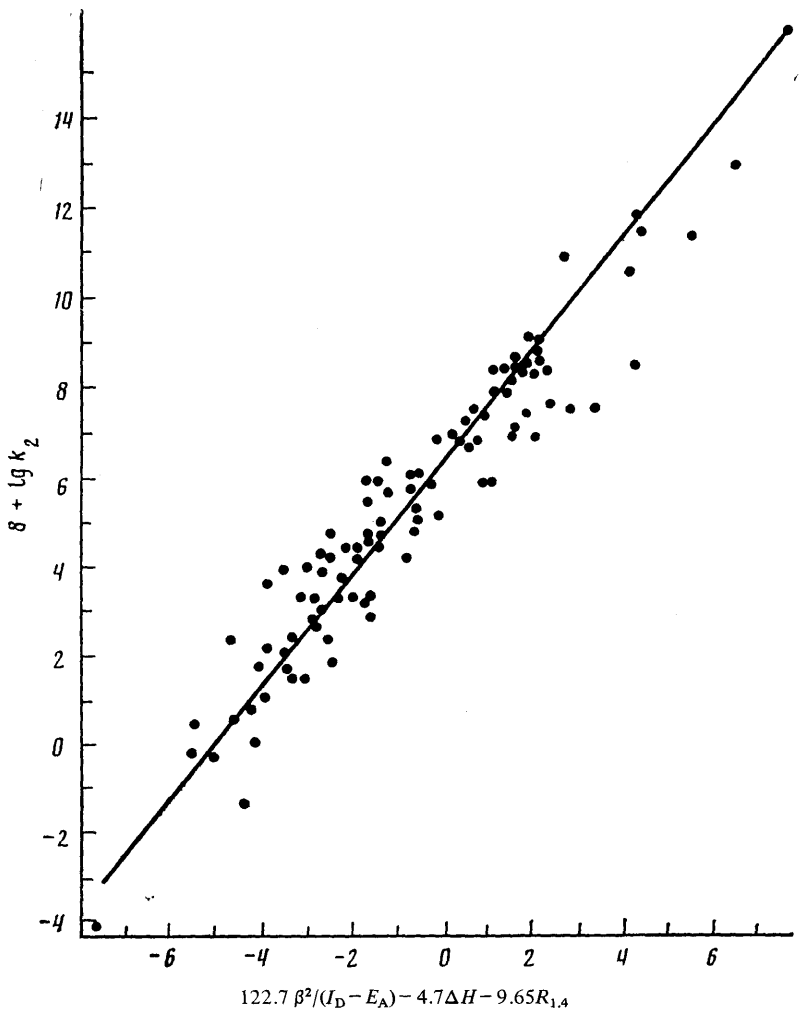
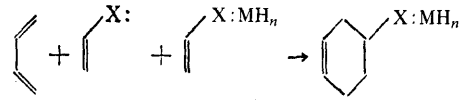


Figure 11. Determination of the reactivity of different compounds in the Diels–Alder reaction by a combined calculation of the donor-acceptor interaction energy, energy of the reacting bonds (from the change in enthalpy of the reactions, in eV) and the distances (in Å) between the reacting atoms in the diene.

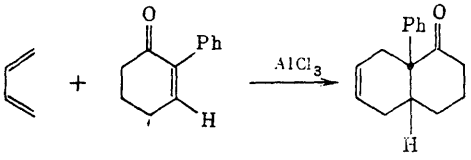
Since *n,v*-complexes of dienophiles with B, Al, and Ga halides are formed almost quantitatively and the acceleration effect on the reaction is quite large (10^4–10^6 times), the rate of reaction between the diene and free dienophile is usually ignored,[23,25] and the diene and *n,v*-complex are regarded as the true reactants.

It was demonstrated by means of thermochemistry[24,138,156] that complexes between the adduct and a Lewis acid does not have inferior stability compared to complexes involving dienophiles:

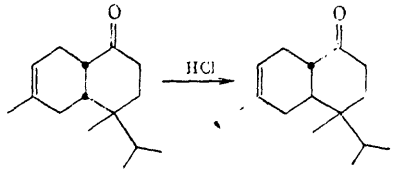


Only when there is a large excess of dienophile relative to the diene and catalyst is there a redistribution of the Lewis acid and its recovery by the dienophile. Only in this case can the reaction strictly be regarded as catalytic, although such a definition has held true for all reactions that occur in the presence of Lewis acids.

A large number of studies have been concerned with the preparation of the necessary adducts in the presence of catalysts and a determination of the structure of the reaction products.[118–130] The main mechanisms of the Diels–Alder reaction—the *cis*-addition principle, steroselectivity, and regioselectivity—are retained in a catalysed reaction. A lack of adherence to the *cis*-addition principle suggests an asynchronous, two-stage formation of bonds in the transition state of the reaction. At the same time, adherence to this principle is not a guarantee of a synchronous mechanism since even in a photochemical [2+2]-cycloaddition the *cis* principle is often fulfilled.[157] Disruption of the orientation of substituents in the adduct of the reaction between 2-phenyl-2-cyclohexen-1-one with butadiene in the presence of aluminium chloride[141] led to the proposal that this reaction had an ionic mechanism:



It was recently shown by ^{13}C NMR that in the presence of trace amounts of hydrogen chloride that develop in the reaction because of the presence of moisture in the solvent, the initially formed adduct with a *syn* configuration of hydrogen atoms rapidly rearranges to a product with an *anti* configuration:[158]



It follows from this that rearrangement occurs after initial formation of an adduct in which the orientation of the substituents is retained.

The conclusion about the asynchronous formation of bonds in the transition state of the reaction between fumaric acid esters and 9,10-dimethylanthracene, catalysed by aluminium chloride, was attributed not to violation of the *cis*-addition principle but to the lack of cooperativity of the asymmetric induction effect.[159] While the existence of the cooperativity of substituents in an uncatalysed reaction can be justified because of the equal effect from the same substituents,[75] in a catalysed reaction the free ester group and the other ester group included in the complex with aluminium chloride can in no way be considered equivalent. The enthalpy of formation of a complex with a 1:1 composition is much higher than half the enthalpy of formation of a complex with a 2:1 composition.[137] Thus the initial condition of cooperativity of the effect is not fulfilled and consequently the proposal about asymmetric formation of bonds in the transition state, despite its attraction, does not have any experimental basis at present.

Since the difference in energies of activation for regioisomers is usually small, formation of an *n,v*-complex between the dienophile and a Lewis acid can lead to both an increase in the difference of the orbital coefficients of the reacting atoms and hence to a predominance of one regioisomer and also to the opposite effect.[160,161] Activation of the dienophile in an *n,v*-complex considerably increases the proportion of *endo* adduct.[121,147]

A study of the kinetics of the Diels–Alder reaction in the presence of catalysts is of particular interest. It should be noted that use of UV spectroscopy, the most common spectrophotometric method for following the course of the reaction, is complicated because during the reaction there is a redistribution of the catalyst between the adduct and the free dienophile, and the *n,v*-complexes between dienophile and Lewis acid are usually brightly coloured.[156,162] Therefore, in the reaction of substituted butadienes with methyl acrylate the relative reactivity was determined from the ratio of adducts of the reaction between two different dienes and the same activated dienophile using GLC.[120–127] However, a more widely used method that has been developed recently is the analysis of kinetic data[156] obtained by following the absorption of *n,v*-complexes and taking into account the redistribution of catalyst.

It is understandable that a marked acceleration of reaction occurs in those solvents which do not form complexes with the catalyst or form complexes that are much less stable than the complexes between catalyst and reactant.[163,164]

In order to determine the true concentration of activated dienophiles it is necessary to know the concentration of catalyst that has lost activity because of the presence of traces of moisture in the solvent. This type of analysis is usually carried out using the data of kinetic or spectrophotometric titration.[156,162,165,166] In Table 5 data on the kientic parameters and the acceleration effect on the Diels–Alder reaction in the presence of a number of Lewis acids have been collected. In all reactions of the type "diene donor, dienophile acceptor" a considerable acceleration effect occurs (10^3–10^9 times) due to a sharp reduction in the enthalpy of activation ($\delta H^{\neq}$ = 30–50 kJ mol^{-1}) with a considerably smaller change in the entropy component of the free energy of activation ($T\delta S^{\neq}$ = 0–10 kJ mol^{-1}).

Although aluminium chloride produces a large acceleration effect on the reaction, a number of dienophiles are oxidised and form tar in its presence. Aluminium bromide accelerates the reaction even more, but kinetic measurements are often complicated by the formation of highly coloured complexes involving hydrogen bromide.[43,156] Boron chloride gives quite strong and active complexes with *n*-donors, and in this case there are only certain disadvantages due to its low boiling point. Boron trifluoride etherate and tin chloride have a weak activating effect because of the low strength of their *n,v*-complexes with dienophiles. Gallium chloride is the most convenient catalyst, and it forms a nondissociated complex which is readily soluble in many inert solvents; its accelerating effect is only slightly less than that of aluminium halides.

Table 5. Enthalpies of formation of *n,v*-complexes (ΔH^0_{IC}), rate constants (k_2), enthalpies ($\Delta H^{\neq}$) and entropies ($\Delta S^{\neq}$) of activation and the apparent acceleration effect in catalysed Diels–Alder reactions (benzene as solvent, 25 °C).

Reaction	Catalyst	Reaction No.	$-\Delta H^0_{IC}$	k_2	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	Acceleration effect	Refs.
9,10-Dimethylanthracene + methyl acrylate	none	1	—	$7.8\cdot10^{-7}$	63	150		[92]
	$AlCl_3$	2	—	0.15	31	155	$1.9\cdot10^5$	[165]
	$GaCl_3$	3	52	$3.5\cdot10^{-2}$	—	—	$4.5\cdot10^4$	[24]
9,10-Dimethylanthracene + methyl methacrylate	none	4		$1.3\cdot10^{-7}$	63	163		[92]
	$AlCl_3$	5	—	$3.8\cdot10^{-2}$	35	155	$2.8\cdot10^5$	[165]
9,10-Dimethylanthracene + dimethyl fumarate	none	6		$6.7\cdot10^{-6}$	52	167		[92]
	$AlCl_3$	7	—	0.43	23	171	$6.4\cdot10^4$	[165]
Anthracene + *N-p*-nitrophenylmaleimide	none	8		$8.5\cdot10^{-5}$	57	129		[97]
	$AlCl_3$	9	—	8.2	33	113	$9.6\cdot10^4$	[138]
	$GaCl_3$	10	48	1.0	—	—	$1.2\cdot10^4$	[138]
Anthracene + *N-p*-bromophenylmaleimide	none	11		$2.5\cdot10^{-5}$	60	129		[97]
	$AlCl_3$	12	—	2.9	34	121	$1.2\cdot10^5$	[165]
	$GaCl_3$	13	53	0.65	34	135	$2.6\cdot10^4$	[138]
Anthracene + *N-p*-methoxyphenylmaleimide	none	14		$8.1\cdot10^{-6}$	68	112		
	$AlCl_3$	15	—	1.2	38	113	$1.5\cdot10^5$	[165]
Anthracene + *N*-phenylmaleimide	none	16		$7.3\cdot10^{-6}$	68	112		[97]
	$AlCl_3$	17	—	1.2	48	105	$1.7\cdot10^5$	[165]
	$AlBr_3$	18	78	5.7	—	—	$7.9\cdot10^5$	[138]
	$GaCl_3$	19	55	0.35	—	—	$4.9\cdot10^4$	[138]
Anthracene + *N-p*-tolylmaleimide	none	20		$6.8\cdot10^{-6}$	68	113		[97]
	$AlCl_3$	**21**	—	1.2	41	105	$1.8\cdot10^5$	[165]
	$GaCl_3$	**22**	57	0.35	—	—	$5.2\cdot10^4$	[138]
9,10-Dimethylanthracene + *N*-phenylmaleimide	none	**23**	**23**	$3.0\cdot10^{-2}$	—	—		[97]
	$SnCl_4$	**24**	**8**	$3.6\cdot10^{-2}$	—	—	1.2	[25]
	$Et_2O\cdot BF_3$	**25**	**5**	3.0	—	—	1.0	[25]
Anthracene + maleic anhydride	none	26		$6.0\cdot10^{-6}$	65	126		[8]
	BCl_3	27	—	$4.1\cdot10^{-2}$	—	—	$6.9\cdot10^3$	[137]
	$GaCl_3$	28	41	0.40	—	—	$6.7\cdot10^4$	[137]
	$AlCl_3$	29	—	1.6	—	—	$2.6\cdot10^5$	[137]
	$AlBr_3$	30	—	7.2	—	—	$1.2\cdot10^6$	[137]
Anthracene + 1,4-naphthoquinone	none	31		$1.8\cdot10^{-7}$	66	140		[138]
	$GaCl_3$	32	54	2.3	34	120	$1.3\cdot10^7$	[138]
	$2GaCl_3$	33	—	600	—	—	$3.4\cdot10^9$	[138]
Anthracene + *p*-benzoquinone	none	34		$2.4\cdot10^{-6}$	64	123		[138]
	$GaCl_3$	35	53	1.9	—	—	$7.8\cdot10^5$	[138]
2,5-Diphenylisobenzofuran + R	none	36		$7.0\cdot10^{-4}$	—	—		[142]
	$GaCl_3$	37	90	0.37	—	—	$5.3\cdot10^2$	[142]
2,5-Diphenylisobenzofuran + *O,O*-diphenyl vinylphosphonate	none	38		$3.7\cdot10^{-5}$	58	121		[142]
	$GaCl_3$	39	76	$3.4\cdot10^{-2}$	42	121	$9.2\cdot10^2$	[142]
9,10-Dimethylanthracene + R	none	40		$8.9\cdot10^{-10}$	90	155		[142]
	$2GaCl_3$	41	148	$1.7\cdot10^{-2}$	40	140	$1.9\cdot10^7$	[142]
Tetraphenylcyclopentadienone + *trans*-stilbene	none	42		$2.8\cdot10^{-8}$	70	144		[166]
	$AlCl_3^*$	43	39*	$5.6\cdot10^{-5}$	39	185	$2.0\cdot10^3$	[166]
Tetraphenylcyclopentadienone + norbornadiene	none	44		$6.0\cdot10^{-7}$	64	137		[166]
	$AlCl_3^*$	45	39*	$5.0\cdot10^{-4}$	34	181	$8.4\cdot10^2$	[166]
Tetraphenylcyclopentadienone + *N*-phenylmaleimide	none	46		$3.9\cdot10^{-5}$	59	120		[167]
	$GaCl_3$	47	55	$1.4\cdot10^{-4}$	—	—	3.6	[167]
	$AlCl_3$	48	—	$1.1\cdot10^{-3}$	45	137	28	[167]
	$2AlCl_3^{**}$	**49**	—	$4.2\cdot10^{-5}$	—	—	1.1	[167]
Tetraphenylcyclopentadienone + *N-p*-tolylmaleimide	none	50		$6.3\cdot10^{-5}$	57	121		[167]
	$GaCl_3$	51	57	$1.5\cdot10^{-4}$	—	—	2.4	[167]
	$AlCl_3$	52	—	$7.1\cdot10^{-4}$	—	—	11	[167]
	$2AlCl_3^{**}$	53	—	$6.5\cdot10^{-5}$	—	—	1.0	[167]
C-Phenyl-*N*-methylnitrone + *N*-phenylmaleimide	none	54		$2.0\cdot10^{-4}$	—	—		[168]
	$GaCl_3$	55	55	~50	—	—	10^5	[168]
9,10-Dimethylanthracene + acrylonitrile	none	56		$2.2\cdot10^{-6}$	63	146		[92]
	$GaCl_3$	57	51	0.13	36	130	$5.9\cdot10^4$	[24]
9-Methylanthracene + acrylonitrile	none	58		$1.1\cdot10^{-7}$	74	122		[24]
	$GaCl_3$	59	51	$1.7\cdot10^{-2}$	42	126	$1.5\cdot10^5$	[24]
Anthracene + acrylonitrile	none	60		$8.6\cdot10^{-9}$	76	138		[24]
	$GaCl_3$	61	51	$5.3\cdot10^{-4}$	47	141	$6.2\cdot10^4$	[24]
9-Chloroanthracene + acrylonitrile	none	62		$1.9\cdot10^{-9}$	79	140		[24]
	$GaCl_3$	63	51	$1.6\cdot10^{-4}$	49	145	$8.4\cdot10^4$	[24]
9-Methylanthracene + methyl acrylate	none	64		$5.8\cdot10^{-8}$	73	191		[24]
	$GaCl_3$	65	52	$1.3\cdot10^{-2}$	—	—	$2.2\cdot10^5$	[24]
9,10-Dimethylanthracene + cyanoacetylene	none	66		$4.0\cdot10^{-6}$	—	—		[24]
	$GaCl_3$	67	—	1.1	—	—	$2.8\cdot10^5$	[24]
9,10-Dimethylanthracene + methyl propiolate	none	68	—	$2.0\cdot10^{-8}$	—	—		[24]
	$GaCl_3$	69		$6.0\cdot10^{-3}$	—	—	$3.0\cdot10^5$	[24]
9,10-Dimethylanthracene + maleic anhydride	none	70		$1.2\cdot10^{-2}$	43	138		[92]
	$GaCl_3$	71	41	277	—	—	$2.3\cdot10^4$	[137]
	$AlCl_3$	72	—	$2.0\cdot10^3$	—	—	$1.7\cdot10^5$	[137]
9-Methylanthracene + maleic anhydride	none	73		$3.4\cdot10^{-4}$	53	134		
	$GaCl_3$	74	41	12.8	27	140	$3.8\cdot10^4$	[8, 137]
	$AlCl_3$	75	—	95.2	—	—	$2.8\cdot10^5$	[137]
9-Chloroanthracene + maleic anhydride	none	76		$1.4\cdot10^{-6}$	67	130		[137]
	$GaCl_3$	77	41	$5.2\cdot10^{-2}$	36	153	$3.7\cdot10^4$	[8, 137]
	$AlCl_3$	78	—	0.38	—	—	$2.8\cdot10^5$	[137]
Anthracene + citraconic anhydride	none	79		$1.5\cdot10^{-8}$	73	135		[137]
	$GaCl_3$	80	49	$1.3\cdot10^{-4}$	—	—	$9.0\cdot10^3$	[137]
	$AlCl_3$	81	—	$8.5\cdot10^{-3}$	32	164	$5.7\cdot10^5$	[137]
9-Chloroanthracene + citraconic anhydride	none	82		$3.1\cdot10^{-9}$	—	—		[137]
	$GaCl_3$	83	49	$9.5\cdot10^{-6}$	—	—	$3.0\cdot10^3$	[137]
	$AlCl_3$	84	—	$2.9\cdot10^{-3}$	—	—	$9.3\cdot10^5$	[137]
9-Methylanthracene + citraconic anhydride	none	85		$8.5\cdot10^{-7}$	64	135		[137]
	$GaCl_3$	86	49	$2.0\cdot10^{-2}$	41	129	$2.3\cdot10^4$	[137]
	$AlCl_3$	87	—	0.14	28	154	$1.7\cdot10^5$	[137]
9,10-Dimethylanthracene + citraconic anhydride	none	88		$2.4\cdot10^{-5}$	45	169		[137]
	$GaCl_3$	89	49	0.44	31	137	$1.9\cdot10^4$	[137]
	$AlCl_3$	90	—	2.2	29	128	$9.1\cdot10^4$	[137]
Anthracene + chloromaleic anhydride	none	91		$3.1\cdot10^{-8}$	62	128		[137]
	$GaCl_3$	92	40	0.11	—	—	$3.6\cdot10^4$	[137]
	$AlCl_3$	93	—	2.3	—	—	$7.5\cdot10^5$	[137]
9-Chloroanthracene + chloromaleic anhydride	none	94		$6.8\cdot10^{-7}$	—	—		[137]
	$GaCl_3$	95	40	$2.3\cdot10^{-2}$	—	—	$3.4\cdot10^4$	[137]
	$AlCl_3$	96	—	0.14	—	—	$2.1\cdot10^5$	[137]
9-Methylanthracene + chloromaleic anhydride	none	97		$2.3\cdot10^{-4}$	49	139		[137]
	$GaCl_3$	98	40	11.9	28	118	$5.3\cdot10^4$	[137]
	$AlCl_3$	99	—	39.7	—	—	$1.8\cdot10^5$	[137]
9,10-Dimethylanthracene + chloromaleic anhydride	none	100		$6.4\cdot10^{-3}$	46	118		[45, 137]
	$GaCl_3$	101	40	245	—	—	$3.8\cdot10^4$	[137]
	$AlCl_3$	102	—	$1.4\cdot10^3$	—	—	$2.3\cdot10^5$	[137]
Tetracyclone + *N-p*-nitrophenylmaleimide	none	103		$4.0\cdot10^{-5}$	64	100		[167]
	$GaCl_3$	104	48	$2.8\cdot10^{-4}$	—	—	7.1	[167]
	$AlCl_3$	105	—	$1.2\cdot10^{-3}$	57	96	30	[167]
Tetracyclone + *N-p*-bromophenylmaleimide	none	106		$3.6\cdot10^{-5}$	64	100		[167]
	$GaCl_3$	107	53	$2.2\cdot10^{-4}$	—	—	6.2	[167]
	$AlCl_3$	108	—	$1.1\cdot10^{-3}$	53	111	29.4	[167]
Phencyclone + *N-p*-nitrophenylmaleimide	none	109		2.12	31	133		[167]
	$GaCl_3$	110	48	36.3	20	135	17.1	[167]
	$AlCl_3$	111	—	83.3	—	—	39.3	[167]
Phencyclone + *N-p*-bromophenylmaleimide	none	112		1.42	33	137		[167]
	$GaCl_3$	113	53	21.0	20	140	14.8	[167]
	$AlCl_3$	114	—	51.6	—	—	36.3	[167]
Phencyclone + *N*-phenylmaleimide	none	115		0.76	30	146		[167]
	$GaCl_3$	116	55	9.4	28	121	12.4	[167]
	$AlCl_3$	117	—	46.5	14	155	61.2	[167]
Phencyclone + *N-p*-tolylmaleimide	none	118		0.75	34	133		[167]
	$GaCl_3$	119	57	10.4	24	134	13.9	[167]
	$AlCl_3$	120	—	40.1	22	127	53.4	[167]
Phencyclone + methyl acrylate	none	121		$1.2\cdot10^{-3}$	46	133		[167]
	$AlCl_3$	122	—	0.63	32	129	$5.5\cdot10^2$	[167]
Phencyclone + methyl methacrylate	none	123		$7.5\cdot10^{-4}$	46	139		[25, 167]
	$AlCl_3$	124	—	0.22	30	134	$2.9\cdot10^2$	[25, 167]
Phencyclone + dimethyl fumarate	none	125		$4.7\cdot10^{-5}$	54	136		[25, 167]
	$AlCl_3$	126	—	$2.3\cdot10^{-2}$	41	126	$4.9\cdot10^2$	[25, 167]
trans,trans-1,4-Diphenylbutadiene + *N-p*-tolylmaleimide	none	127	—	$9.3\cdot10^{-7}$	54	168		[25]
	$AlCl_3$	128	—	$5.9\cdot10^{-3}$	38	148	$6.3\cdot10^2$	[25]
trans,trans-1,4-Diphenylbutadiene + *N*-phenylmaleimide	none	129		$1.4\cdot10^{-6}$	50	177		[25]
	$AlCl_3$	130	—	$5.6\cdot10^{-3}$	39	143	$3.9\cdot10^2$	[25]
trans,trans-1,4-Diphenylbutadiene + *N-p*-bromophenylmaleimide	none	131		$2.1\cdot10^{-6}$	48	180		[25]
	$AlCl_3$	132	—	$7.1\cdot10^{-3}$	—	—	$3.4\cdot10^2$	[25]
2,3-Dimethylbutadiene + methyl acrylate	none	133		$3.4\cdot10^{-8}$	—	—		[127]
	$AlCl_3$	134	—	$4.2\cdot10^{-2}$	—	—	$1.2\cdot10^6$	[127]
2-Methylbutadiene + methyl acrylate	none	135		$1.9\cdot10^{-8}$	—	—		[120]
	$AlCl_3$	136	—	$1.4\cdot10^{-2}$	—	—	$7.4\cdot10^5$	[120]
trans-1-Methylbutadiene + methyl acrylate	none	137		$1.2\cdot10^{-8}$	—	—		[122]
	$AlCl_3$	138	—	$7.4\cdot10^{-2}$	—	—	$6.3\cdot10^5$	[122]
2-Phenylbutadiene + methyl acrylate	none	139		$2.3\cdot10^{-7}$	—	—		[127]
	$AlCl_3$	140	—	0.11	—	—	$4.7\cdot10^5$	[127]
1,3-Butadiene + methyl acrylate	none	141		$1.0\cdot10^{-8}$	75	151		[123]
	$AlCl_3$	142	—	$1.2\cdot10^{-3}$	44	157	$1.2\cdot10^5$	[123]
2-Chlorobutadiene + methyl acrylate	none	143		$1.3\cdot10^{-8}$	—	—		[127]
	$AlCl_3$	144	—	$6.3\cdot10^{-4}$	—	—	$5.0\cdot10^4$	[127]
2-Trifluoromethylbutadiene + methyl acrylate	none	145		$1.8\cdot10^{-7}$	—	—		[127]
	$AlCl_3$	146	—	$3.7\cdot10^{-4}$	—	—	$2.1\cdot10^3$	[127]
2-Cyanobutadiene + methyl acrylate	none	147		$1.4\cdot10^{-7}$	63	169		[126, 127]
	$AlCl_3$	148	—	$1.2\cdot10^{-4}$	47	169	$8.4\cdot10^2$	[126, 127]
Cyclopentadiene + acrylonitrile	none	149		$3.2\cdot10^{-5}$	—	—		[126, 127]
	$AlCl_3$	150	—	8.99	—	—	$2.8\cdot10^5$	[126, 127]

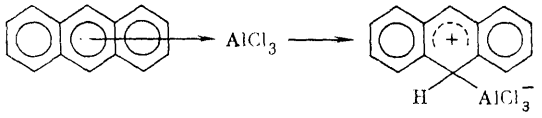
* A 1:1 complex with cyclone.

** A 1:1 complex with imide is formed first, then also a 1:1 complex with cyclone.

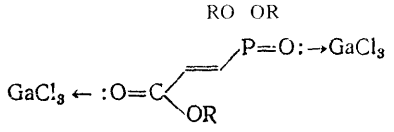
R = *O,O*-diethyl-β-carbomethoxyvinylphosphonate.

In virtually all cases kinetic measurements have been carried out for activated dienophiles in a Lewis acid complex of 1:1 composition. The formation of 2:1 complexes between α,β-dicarbonyl, ester, and

nitrile dienophiles and gallium chloride is usually not quantitative and the free Lewis acid readily gives π- and then σ-complexes with many dienes.[43,153]



In the case of β-carbomethoxyvinylphosphonate a stronger complex involving gallium chloride and the P=O group is mainly formed, and only when the ratio of catalyst to dienophile is higher than 1:1 does the catalyst coordinate also with the β-carbonyl group:[142]



Formation of the first bond P=O·$GaCl_3$ has virtually no effect on the strength of the subsequent complex C=O·$GaCl_3$. Despite the considerably greater strength of the bond between gallium chloride and the phosphoryl group compared to that with the carbonyl group (see Table 5), the acceleration effect on the reaction is greater in the latter case than in the former. By determining the acceleration effect on the reaction from the enthalpy of the *n,v*-complexes formed it was concluded[142] that the action of the catalyst on the system via the phosphorus atom constitutes 30–40% of the effect via the carbonyl carbon atom.

An increased acceleration effect occurs in catalysed reactions involving conjugated acceptor dienophiles such as quinones (see Table 5). It is suggested[169] that on formation of the *n,v*-complex a carbonyl group is excluded from the conjugation system of the quinone.

We shall now examine the factors which determine the acceleration effect in reactions involving a dienophile ligand bonded to a Lewis acid.

2. Solvation effects in a catalysed Diels–Alder reaction

Thermochemical and kinetics methods of approach are the most fruitful in studying the effect of the medium on the enthalpy of solvation of the reactants, *n,v*-complexes, and transition state of a catalysed reaction.[163,164] It follows from the kinetic data that the rate of reaction of tetracyanoethylene, which is an active acceptor dienophile, is substantially reduced in π-donor solvents,[55,57] while the effect of the medium on the rate of reaction of the no less active *n,v*-complexes is small.[163,164] A complete thermochemical analysis of solvation effects in a catalysed reaction requires available data on the change in enthalpy of solvation for each reactant. It follows from Fig. 4 that the change in enthalpy of solvation of an *n,v*-complex is determined by the relationship:

$$\delta H^{IC}_{solv} = \delta H^{A}_{solv} + \delta H^{GaCl_3}_{solv} + \Delta H^{0}_{IC}(S) - \Delta H^{0}_{IC}(S_0).$$

The results of thermochemical measurements made in a series of solvents for the complex of *N*-phenylmaleimide (PMA) with gallium chloride[164] show that the enthalpy of solvation of gallium chloride increases substantially on changing not only to *n*-donor solvents but also to π-donor solvents (Fig. 12). As the enthalpy of solvation of the Lewis acid increases, there is a proportional decrease in the enthalpy of formation of the *n,v*-complex in solution (Fig. 12). The constant enthalpy level of the *n,v*-complex in the series of solvents studied is achieved because the gain in enthalpy of solvation of the reactants in donor solvents is completely balanced by the loss in enthalpy of formation of the complex. This means that on formation of a complex between gallium chloride and imide, which is stronger than a complex with solvent, there is a complete break-up of the weaker complexes. The change in enthalpy of solvation of the reactants (PMA + $GaCl_3$) is mainly determined by the change in enthalpy of solvation of gallium chloride. The constant enthalpy level of the *n,v*-complex of MPA·$GaCl_3$ in the series of solvents indicates that there is approximately the same activation of the dienophile moeity in the complex. This conclusion is consistent with the results of two studies,[43,169] in which cases are noted where the same charge transfer in complexes occurs when there is a different enthalpy of formation of the complexes.

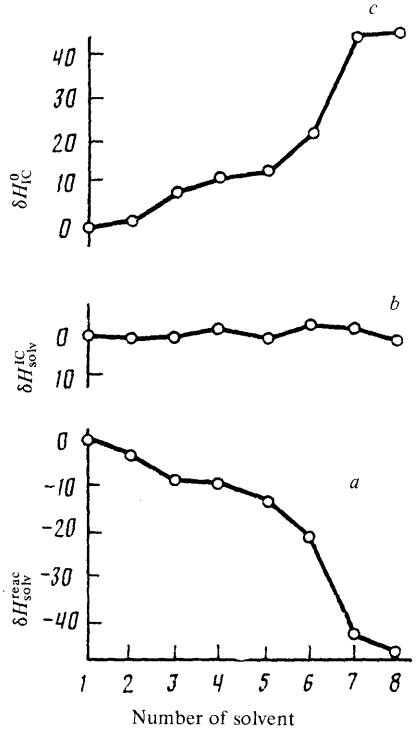


Figure 12. Enthalpies of transfer of the reactants (*a*) and the *n,v*-complex of *N*-phenylmaleimide with gallium chloride (*b*) and also the change in enthalpy of formation of this complex (*c*) in different solvents: *1*, chlorobenzene; *2*, benzene; *3*, toluene; *4*, dichloromethane; *5*, *p*-xylene; *6*, mesitylene; *7*, nitromethane; *8*, nitrobenzene.[163,164]

The insignificant change in enthalpy of solvation of the complex PMA·$GaCl_3$ on changing from nonpolar to polar media is unexpected in view of the high polarity of this complex.[43] A more detailed investigation involving other complexes[170,171] showed that this kind of solvation effect is the rule rather than the exception. More accurate findings on the change in enthalpy of solvation of boron trifluoride etherate[163] are in agreement with this conclusion. The change in enthalpy of solvation of the transition state of a

catalysed reaction[160,163] to a considerable degree corresponds to the nature of the effect of medium on the enthalpy level of a normal reaction involving tetracyanoethylene. The difference in the rate of reactions involving dienophiles that have comparable activity—tetracyanoethylene and imide complexes with gallium chloride—thus becomes clear. The formation of a strong complex between the dienophile and the Lewis acid results in an increase in the rate of reaction by a factor of 10^4, the enthalpy level of this new reactant being insensitive to a change of medium. The complex between tetracyanoethylene and the solvent is less strong, and the specific solvation of this dienophile makes it less active compared to free tetracyanoethylene. In this case the observed rate of reaction is determined mainly by the concentration of free tetracyanoethylene, which varies considerable over a range of π-donor solvents. It is interesting to note that the enthalpy level of a π,π-complex between tetracyanoethylene and a π-donor does not vary very much over this range of solvents.[46]

3. Factors that determine the activity of reactants in a catalysed Diels–Alder reaction

The factors governing the activity of reactants in an uncatalysed Diels–Alder reaction were examined above. In a catalysed process the conversion of the dienophile to an *n,v*-complex only slightly changes the lengths of the C=C bond and hence the magnitude of the overlap integral of the reacting atoms. Thus, the change from ethylene ($R_{1,2}$ = 1.332 Å [172]) to a strong acceptor such as tetracyanoethylene ($R_{1,2}$ = 1.317 Å [173]) is accompanied by only a slight variation in C=C bond length.

Since it is the dienophile and not the diene that forms an *n,v*-complex with the Lewis acid, the value of the ionisation potential of the diene (I_D) and the interatomic distance ($R_{1,4}$) remain constant and do not control the observed acceleration of reaction.[25]

The next factor to affect the reactivity concerns the energies of the reacting bonds, with differences that are reflected in the enthalpy of reaction. This also bears no relation to the observed vigorous acceleration of reaction since the thermochemically determined enthalpies of the reactions with and without involvement of a catalyst differ by not more than 3–5 kJ mol^{-1}.[162]

According to perturbational molecular orbital theory the increase in reactivity of activated dienophiles is due, by analogy with a normal Diels–Alder reaction, to the decrease in energy gap between the HOMO of diene and the LUMO of dienophile.[174,175] In view of the qualitative nature of the calculations carried out, the data obtained by spectrophotometric analysis of *n,v*-complexes containing activated dienophiles[156,176,177] should be considered more reliable. By using the thermodynamic cycle depicted in Fig. 13, it is possible to calculate the change in energy of the LUMO of dienophile on formation of an *n,v*-complex:

$$\Delta E_{LUMO} = E_{CT}^{II}(HMB.(AMA.GaCl_3)) - E_{CT}^{I}(HMB.AMA),$$

where E_{CT}^{II} is the charge-transfer energy in π,π-complexes of hexamethylbenzene (HMB) with *N*-arylmaleimides which are activated due to the formation of an *n,v*-complex with gallium chloride (AMA·$GaCl_3$); E_{CT}^{I} is the charge-transfer energy with unactivated *N*-arylmaleimides.

The formation of π,π-complexes between a π-donor and a π-acceptor which is activated by a Lewis acid is reported in several studies.[144,178,179] A complex between cyclopentadiene and a methyl acrylate–titanium chloride *n,v*-complex has been identified at low temperatures.[179] A large number of ternary complexes of the type B·A·MX_n, where B are π-donors (alkylbenzenes), A are σ-acceptors (acid chlorides) and MX_n are Lewis acids, have been obtained and characterised by IR and NMR spectroscopy.[179] The equlibrium constants and enthalpies of formation of π,π-complexes of styrene and toluene with methyl methacrylate and its *n,v*-complex with tin chloride have been determined.[144]

Hexamethylbenzene is stable in the presence of Lewis acids and has a high π-donor capacity (I_D = 7.85 eV [105]). As the bond energy in the π,π-complex is low, a small perturbation of the HOMO level in the π-donor and the LUMO level in the π-acceptor is to be expected when a complex is formed.[40]

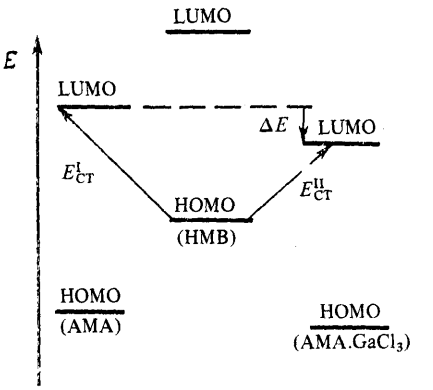


Figure 13. Diagram for determination of the change in energy of the LUMO of *N*-arylmaleimides (AMA) on conversion to an *n,v*-complex with gallium chloride according to the data on the π → π* transfer energy in π,π-complexes with hexamethylbenzene (HMB).[156]

The data from two studies[156,176] (Table 6) indicate an increase in electron affinity of ligands in a complex with gallium chloride (reduction in the LUMO level) by 0.7–1.15 eV. An even larger increase in electron affinity occurs in 1:1 aluminium chloride complexes and 2:1 gallium chloride complexes. The fact that for each group of complexes the difference in energy (ΔE_1 and ΔE_2) is fairly constant is worthy of note. Such a correspondence can occur when the HOMO levels of normal and activated dienophiles vary insignificantly.

The correlation of the acceleration effect on the Diels–Alder reaction with the charge-transfer energy, which is proportional to the electron affinity, is most interesting.[156] The linear nature of such a dependence for the reaction of cyanoethylenes with anthracene has been well established.[11,37] The retention of this type of dependence in the reaction of maleimides activated with Lewis acids (Fig. 14) can serve as experimental evidence that the catalytic effect in a Diels–Alder reaction of the "diene donor, dienophile acceptor" type is due to an increase in orbital interaction because of a significant rise in electron affinity of the dienophile in an *n,v*-complex.[156,165] Moreover, this dependence is regarded as a considerable argument in favour of the invariability of the reaction mechanism.[25] The line for cyanoethylenes is situated below, which is completely consistent with a higher conjugation energy (smaller enthalpy of reaction,

see Table 4) in these compounds compared to maleimides. The values representing the reactivity of all the maleimides activated by gallium or aluminium chlorides lie on a common line which represents the dependence of the reactivity on the three main controlling factors (see Fig. 11).

Table 6. Wavelengths (λ) and energies (E) of band maxima for $\pi \rightarrow \pi^*$ transitions of dienophiles (A), their n,ν-complexes with Lewis acids, and π,π-complexes of hexamethylbenzene (HMB) with unactivated and activated dienophiles.[156,176]

Dienophile	Lewis acid	A·MX$_n$			HMB.(A.MX$_n$)		
		λ, nm	E, eV	ΔE_1, eV	λ, nm	E, eV	ΔE_2, eV
N-*p*-tolyl-maleimide	none	260	4.77		330	3.76	
	$GaCl_3$	342	3.63	1.14	475	2.61	1.15
	$AlCl_3$	—	—	—	488	2.54	1.22
	$2GaCl_3$	405	3.06	1.71	593	2.09	1.67
N-Phenyl-maleimide	none	259	4.79		337	3.68	
	$GaCl_3$	332	3.74	1.05	470	2.64	1.05
	$AlCl_3$	—	—	—	481	2.58	1.10
	$2GaCl_3$	390	3.18	1.61	580	2.14	1.54
N-*p*-Bromophenyl-maleimide	none	265	4.68		345	3.58	
	$GaCl_3$	325	3.82	0.86	470	2.64	0.95
	$AlCl_3$	—	—	—	480	2.59	1.00
	$2GaCl_3$	388	3.20	1.48	590	2.10	1.49
N-*p*-Nitrophenyl-maleimide	none	276	4.49		365	3.40	
	$GaCl_3$	330	3.76	0.73	464	2.67	0.73
Maleic anhydride	none	280	4.43		353	3.51	
	$GaCl_3$	328	3.78	0.65	440	2.82	0.69
	$AlCl_3$	—	—	—	470	2.64	0.87
Citraconic anhydride	none	251	4.94		340	3.65	
	$GaCl_3$	315	3.94	1.00	440	2.82	0.83
	$AlCl_3$	—	—	—	455	2.73	0.92
Chloromaleic anhydride	none	246	5.04		365	3.40	
	$GaCl_3$	303	4.08	0.96	480	2.58	0.82
	$AlCl_3$	—	—	—	505	2.46	0.94
Dichloromaleic anhdyride	none	269	4.61		388	3.20	
	$GaCl_3$	322	3.85	0.76	500	2.48	0.72

unsubstituted, 9-methyl-, and 9,10-dimethyl-anthracenes (3.0, 2200, and 93 000 l mol^{-1} s^{-1} respectively) with only a small change in ionisation potential (ΔI_D = 0.29 eV).[30,50,86] It should be noted that with such changes in electron affinity the reactivity in a series of *N*-arylmaleimides only varies by a factor of 10 (see Table 4).

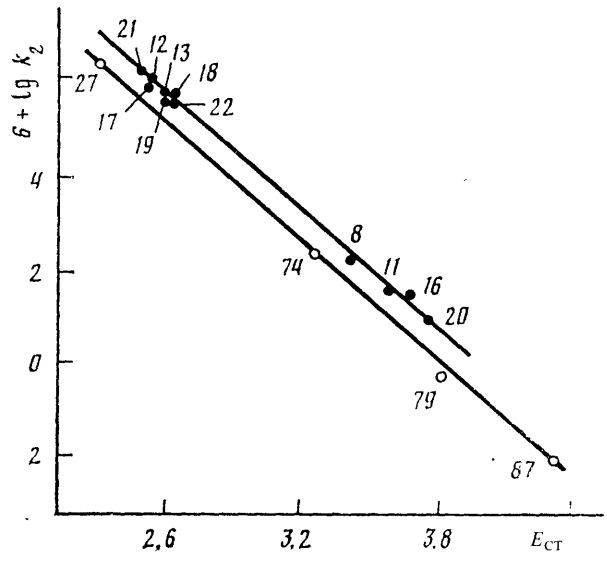


Figure 14. Dependence of the reactivity of anthracene in the Diels–Alder reaction with normal and activated *N*-arylmaleimides on the charge-transfer energy in π,π-complexes with hexamethylbenzene.[25,156] For the numbering of the reactions on the lower line, see Table 4; for those on the upper line, see Table 5.

What is the reason for the differing acceleration of reactions in which the same activated dienophile participates with different dienes?

The Diels–Alder reaction is assumed to be orbital controlled, so that a first-order interaction is usually ignored[11,37] [charge interaction, see, Eqn.(1)]. In a structural series of diene donors and dienophile acceptors the strengthening of donor-acceptor properties of the reactants leads to an increase in nucleophilicity of the reaction centre in the diene and electrophilicity in the dienophile.[180,181] The effective representation of the reactivity of these reactants in terms of frontier orbital interaction energies is possibly due to both types of interaction (charge and orbital) varying in a similar manner.

A combined calculation of the charge and orbital contributions is necessary to elucidate the kinetic mechanisms of reactions involving heteroatomic reactants.[4,80,81,91]

Even in a series of hydrocarbon addends the change in reactivity cannot always be accounted for from a study of the frontier orbital interaction energies. The rate constants of the reaction between 2.5-diphenylisobenzofuran and unsubstituted, methyl-, and dimethylmaleic anhydrides differ considerably (3.36, 9.0 × 10^{-3}, and 1.1 × 10^{-5} l mol^{-1} s^{-1} respectively), whereas the electron affinity remains approximately the same (ΔE_A = 0.30 eV).[137] A substituent effect which is just as marked but works in an opposite direction occurs in the reaction between tetracyanoethylene and

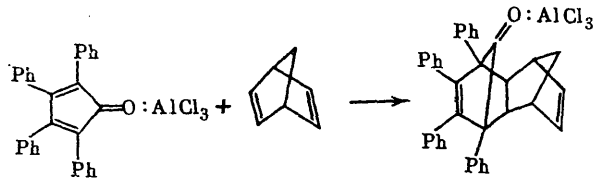
An increase in the charges on the reaction centre in the activated reactants must promote their affect on the reactivity. This effect will be exhibited in those cases where the orbital and charge contributions are not expected to have similar effects.

While in a Diels–Alder reaction of the type "diene donor, dienophile acceptor" the formation of an n,ν-complex with the dienophile leads to a large acceleration due to the increase in electron affinity and electrophilicity of the reacting atoms of dienophile, in reactions of a neutral type and of the type "diene acceptor, dienophile donor" acceleration would be expected when an n,ν-complex was formed with the diene.

Substituted cyclopentadienones—cyclones—can undergo a neutral type of reaction because of the convergence of their HOMO and LUMO levels.[182] An acceleration of the reaction between tetracyclone and alkenes in the presence of aluminium chloride has been recorded.[183] Spectrophotometric measurement showed[166] that tetracyclone forms a strong n,ν-complex with aluminium chloride, which is stable over a period of time and has an intense absorption in the region 800–1000 nm. When stronger Lewis bases are added, the absorption that characterises the free diene is rapidly restored. The enthalpy of formation of the n,ν-complex of tetracyclone with gallium chloride as determined by a thermochemical method

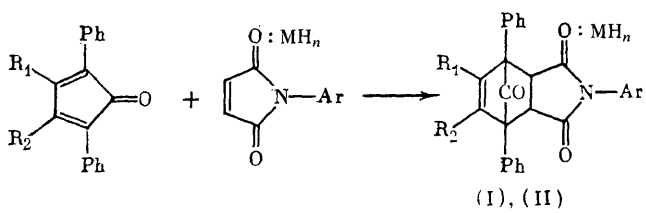
(-39 kJ mol^{-1} [166]) suggests the high strength of the bond in the complex. Phencyclone and indanocyclone decompose even in the presence of gallium chloride.[166]

Dienophiles such as *trans*-stilbene and norbornadiene do not have *n*-donor groups and therefore do not compete with the diene in the formation of a complex:



It is evident from the data given in Table 5 that quite a large acceleration effect occurs in the reaction of alkenes with an activated diene ($\sim 10^3$), but it is noticeably less than the acceleration effect in normal reactions with dienophile activation ($\sim 10^5$).

N-Arylmaleimides form more stable complexes with gallium chloride than does tetracyclone. The results of spectrophotometric titration show that when gallium chloride is added to a solution of tetracyclone and imide, there is no change in the absorption of the diene up to a 1:1 ratio of imide to catalyst. With a further increase in the proportion of Lewis acid an absorption appears in the region 800–1000 nm, which is typical for a complex between the diene and gallium chloride. The Lewis acid bonded to imide in the complex no longer has a destructive effect on cyclones, so it is possible to carry out a kinetic study of the reaction between tetracyclone (I) and phencyclone (II) on the one hand, and a number of dienophiles on the other hand[167] (Table 5):



(I), (II)

I: $R_1 = R_2 =$ Ph; II: $R_1 - R_2 =$ *cis*-*o*,*o*'-biphenylene

The acceleration effect on the reaction of imides in a complex of 1:1 composition with gallium chloride or aluminium chloride is surprisingly small. When aluminium chloride is coordinated with the carbonyl groups of the imide (1:1) and tetracyclone (1:1), the reaction is not accelerated at all (see reactions 49 and 53 in Table 5). Such unusual behaviour of the imides reacting with cyclones cannot be due to the properties of the activated dienophiles. An insignificant acceleration effect also occurs in the reaction of phencyclone with activated esters of unsaturated acids.

V. Conclusion

The considerable progress made in studying the factors that determine the reactivity of compounds in the Diels–Alder reaction has been achieved as a result of involving thermochemical methods. The comprehensive investigation of this reaction using chemical kinetics, spectroscopy, thermochemistry, and structural analysis has led to the identification of three main factors affecting the reactivity: 1) the interaction energy of the frontier orbitals, 2) the energy of the reacting π-bonds, and 3) the interatomic distance in the diene.

The existing data indicate (see Table 4) that the difference in bond energies for dienes (δH_{reac} = 150 kJ mol^{-1}) is greater than for dienophiles (δH_{reac} = 40–50 kJ mol^{-1}). The maximum value of the exothermic reaction between dienophiles and alkylbutadienes corresponds to an increased thermal stability of the addition products. It should be noted that butadiene has the highest interatomic distance $R_{1,4}$ compared to other dienophiles and has a low donor capacity. Since ethylene has the lowest electron affinity, its reaction with butadiene cannot be regarded as a typical example of the Diels–Alder reaction, although it is the simplest for quantum-chemical calculations and therefore a convenient model.

In the series of dienes—isobenzofuran, cyclopentadiene, anthracene, butadiene—the $R_{1,4}$ value increases from 2.19 to 2.90 Å.[109] Taking into account the increasing structural changes which occur when a cyclic adduct is formed with these dienes, a decrease in exothermicity of reaction would be expected if both factors affecting the reactivity ($R_{1,4}$ and E_{C-C}) were interrelated. However, the experimentally found values of the enthalpy of reaction increase in this series of dienes (see Table 4) and hence these factors act independently.

By using reactants that are activated by Lewis acids it is possible to obtain adducts which are difficult to synthesise by other methods.[141,184–187]

The acceleration effect can vary over a very wide range. Thus, in the presence of tin chloride or boron trifluoride etherate the rate of reaction remains virtually unchanged, while in the presence of boron, gallium, or aluminium halides it increases by a factor of 10^4–10^6, and when complexes of composition 2:1 are formed it even increases by a factor of 10^7–10^8 (see Table 5). While, for example, the half-life for formation of an adduct between *O*,*O*-diethyl β-carbomethoxyvinylphosphonate and 9,10-dimethylanthracene at 25 °C and with a concentration of reactants equal to 0.1 mol^{-1} l^{-1} is 350 years, in the presence of two equivalents of gallium chloride only 10 min is needed for this.[142] It is clear that this type of activation, especially in the case of unreactive reagents, is always desirable for the preparation of various cyclic products.

This type of acceleration effect is also possible in other cycloaddition reactions. For example, the rate of addition of a nitrone to an activated dipolarophile approximately increases by a factor of 10^5 (see Table 5).

It follows from an analysis of the spectra of π,π-complexes (see Table 6) that the electron affinity of the dienophile increases in the series of *n*,*v*-complexes with $GaCl_3$, $AlCl_3$, and $2GaCl_3$. In this case the effect of two moles of gallium chloride on the change in electron affinity is considerably less than doubling the effect in a 1:1 complex. These data are consistent with the observed acceleration effect in catalysed reactions (see Table 5).

In reactions of the type "diene donor, dienophile acceptor", activation of the dienophile leads to an increase in stabilisation energy for frontier orbital interaction and a decrease in repulsion energy of the reacting nucleophilic and electrophilic centres in the diene and dienophile. This effect also occurs in a reaction of the type "diene acceptor, deinophile donor" when the diene is activated. In reactions involving dienes that have an acceptor nature (cyclones;[182] 2-cyano- or 2-trifluoromethyl-butadienes[160,161]), the acceleration effect is substantially reduced, possibly because of the increase in repulsion energy between the converging electrophilic atoms in both reactants. The formation of *n*,*v*-complexes by both

partners is clearly unfavourable for reaction (see Table 5). Similar behaviour is noted in the uncatalysed Diels–Alder reaction involving tetracyclone. Here the rate of reaction with tetracyanoethylene is considerably less than with tricyano- and *gem*-dicyano-ethylenes.[182] In a similar manner the rate constant of the reaction between tetracyanoethylene and phencyclone (0.13 l mol^{-1} s^{-1}) is less than the rate constant of the reaction involving *N*-phenylmaleimide (0.76 l mol^{-1} s^{-1}).[182] Since *N*-phenylmaleimide complexed with aluminium chloride has acceptor properties (E_A = 1.99 eV [156]) approaching those of tetracyanoethylene (E_A = 2.88 eV [37]) the small acceleration effect is understandable. The development of various types of acceleration effect has been confirmed experimentally.[117,120–129,142,162,166,167] The kinetic behaviour of normal and activated reactants is consistent with the assumption that there is not always a similar effect from charge and orbital interactions on the stabilisation energy of the transition state of the Diels–Alder reaction.[168,180,181,188–190]

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