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Internal and external factors influencing the Diels–Alder reaction

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The internal and external key factors influencing the reaction rates were considered for the Diels–Alder reaction (DAR) with normal electron demand. A simple dependence $\lg k_2 = -28.81 + 316.3/(\mathrm{IP_D} - E_A) - 69.9\, R_{1-4}/(\mathrm{IP_D} - E_A) - 0.054\Delta H_{r\text{-}n}$ for the reaction rate as a function of the ionization potential of π-donor dienes, electron affinity of π–acceptor dienophiles, heat of reaction and diene structure (R_{1-4}) was obtained. This relation allows one to explain the origin of the conventional and 'anomalous' relations between activity and selectivity, and the variety of relationships between the kinetic activity and thermodynamic stability. It helps one to choose the conditions for the directed synthesis of desired products, to explain the acceleration effects in the presence of Lewis acids and to predict the rates of the DAR between the different reagents with C═C bonds not explored earlier. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: Diels–Alder reaction; factors determining reactivity; π,π- and n,v-molecular complexes; catalysis; high pressure effect

INTRODUCTION

The (4+2)-cycloaddition or the Diels–Alder reaction[1–4] (DAR) well known to all chemists is 80 years old. The reaction of the formation of six-member carbo- and heterocyclic compounds has been studied intensively and is currently under study almost in all leading world chemical centers.[5–11] B. Arbuzov, M. Dewar, H. Fujimoto, K. Fukui, R. Hoffman, R. Huisgen, A. Petrov, N. Plate, J. Roberts, V. Tartakovsky, A. Wassermann, R. Woodward, and many other scientists contributed a lot to the development of the pure and applied chemistry of the DAR. During the last decades comprehensive works of Sauer,[12–15] Klärner,[16,17] Houk,[18,19] Sustmann,[20,21] and Jenner[22] have further extended our knowledge in this field.

Initially, the investigations were aimed at the clarification of the possibilities and conditions to involve various substances such as dienes and dienophiles in this reaction and, consequently, to obtain and separate a large number of the new adducts and describe their properties.[1–11] Then the focus of attention shifted to the determination of the regularities of the DAR with the works of K. Alder *et al*. being generally acknowledged. In the numerous papers the reaction rates were shown to differ nearly by the order of 20.[12–21,23–27] The solvent influence, formation of intermolecular charge transfer complexes and effects of catalytic salt additives were studied in detail. Attempts to estimate in general the orbital descriptions of addends, balance of the energies of bond cleavage and formation, and structural characteristics of dienes–dienophile pairs in the transition state were also successful.[23–27] At present, much attention is devoted to the syntheses of biologically active reaction products and the ways of designing desired molecules by the DAR.[7–11] The significant decrease of the formation volume of the cyclic structures opens broad possibilities for the favorable change of the reaction rate and equilibrium under elevated pressures.[16,17,22,28–35]

Currently, there are more than half a million papers in the area of the DAR making the complete analysis of these works impossible. There are many books[6–11] and reviews[16,25–27,30,36,37] dedicated to DARs. Therefore we do not describe in detail all DAR data accumulated up to now. In this paper we concentrate on the review and generalization of the reactivity factors in the DAR with normal electron demand, mainly within the field of our interest and based on our previous publications.

BACKGROUND

The formation of cyclohexene derivatives by diene synthesis had been known before the famous works.[1–4] The dimerization of 1,3-dienes proceeds in a similar manner.[5,6] Few addition reactions of 1,3-dienes with *p*-benzoquinone were described but with erroneous formulas for the products.[5]

At first, it was discovered[38] that the azodicarboxylic acid ester reacts with dienes forming tetrahydropyridazine derivatives. In 1928, Diels and Alder[1–4] have started investigations of the hydroaromatic line of compounds. It was shown that the reaction of diene synthesis proceeds also between hydrocarbons, one being 1,3-conjugated diene, and another having a double or triple bond.

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The importance of researches of Otto Diels and Kurt Alder (the Nobel Prize laureates in 1950) is not limited only to the discovery of the cross combination of different carbo- and heterodienes and dienophiles yielding various cyclohexene derivatives. In their investigations, particularly in the works of Alder *et al.*,[39–43] the main features of the DAR have been revealed and described.

As no other reaction, the DAR gave a powerful impetus to the development of the concept of the stabilization energy during the interaction of the molecular orbitals.[44–53] The observation of the efficient influence of usually electron-donating substituents in the diene and electron-accepting substituents in dienophile on the reaction rate has become an important step in the understanding of the addend activity in the DAR. Sustmann[21] proposed that all kinds of controlling interactions of the molecular orbitals are realizable (Fig. 1).

Orbital-symmetry-allowed reactions with the inverse character of the donor–acceptor properties of the reagents ('diene-acceptor, dienophile-donor', Fig. 1), were found experimentally for the first time by Sauer[54] by the example of changing the activity of dienophiles in the DAR with perchlorocyclopentadiene. For the first time the possibility of the intermediate or 'neutral' variant was confirmed experimentally in the work of Konovalov and Samuilov by the example of the DAR of phencyclones, tetracyclones, and acecyclones.[55]

The elaboration of the DAR mechanism, based on the extensive quantitative experimental data, was discussed in detail in monographs and reviews.[6–12,16,25–27,36,44–53] At present, the DAR is considered to be a concerted process proceeding with the conservation of the orbital symmetry in the transition to the adduct via a cyclic activated complex, in which new bonds are formed simultaneously (a single-stage process). The well-known Woodward–Hoffman rules of the conservation of the orbital symmetry[44,45] are a significant achievement in the theory of cycloaddition reactions. These rules answer the question 'to be or not to be' concerning the reaction occurrence from the point of view of the orbital symmetry. In spite of the principle possibility of its realization according to the orbital characteristics of the reagents, a process may be unfeasible due to the kinetic or thermodynamic reasons. Hence, it is necessary to know what factors control the rate and equilibrium of the DAR.

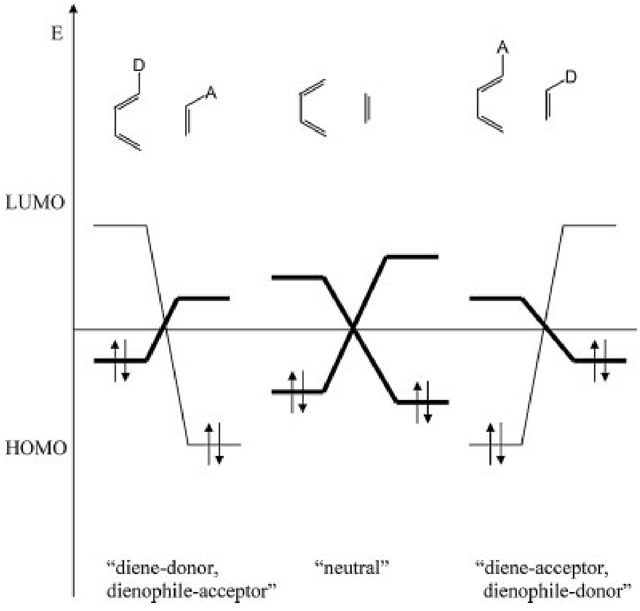


Figure 1. Three variants of controlling interactions of frontier orbitals in the Diels–Alder reaction

FACTORS DETERMINING THE RATE OF THE DAR

The orbital interactions responsible for the formation of molecular π,π-complexes[56] introduce a significant stabilizing contribution into the formation of the activation barrier in the DAR.[47] The relations to calculate the stabilization energy due to the orbital interactions are suggested.[47,56,57] These relations include the difference between the boundary orbital energy of the highest occupied molecular orbital (HOMO) of the π-donor partner and that of the lowest unoccupied molecular orbital (LUMO) of the π-acceptor, $[\beta^2/(\varepsilon_D\text{-}\varepsilon_A)]$, where β is the overlap coefficient of reacting orbitals being a determinant factor.

In the predominant type of the DAR, 'diene-donor, dienophile-acceptor', the interaction of the boundary orbitals of diene and dienophile provides the main stabilizing contribution allowing one to neglect the contributions due to the interaction of the orbitals more separated in energy.[47] Obviously, the stabilization energy characterizes only the change of the activation barrier, but not the value of the activation barrier itself. The dominant contribution of the orbital interaction $[\beta^2/(\varepsilon_D\text{-}\varepsilon_A)]$ can be expressed by the proportional value, $[\beta^2/(\mathrm{IP}-E_A)]$, using the available data on the diene ionization potential (IP) and dienophile electron affinity energy(E_A).[47,56,57]

Within the individual structural type of dienes or dienophiles, a correlation between the lg$k$ and $(\mathrm{IP}-E_A)^{-1}$ is often observed due to the constant β^2 value. However, the stabilization energy is not the only factor determining the reactivity of reagents in the DAR. For example, benzene forms the molecular complexes with many dienophiles, but it does not react in the DAR. To illustrate this, the activity of cyclopentadiene (IP = 8.58 eV) is compared with that of 9,10-dimethylanthracene (IP = 7.04 eV) in the reaction with cyanoethylenes (Fig. 2).[13]

The reaction rates of highly acceptor dienophiles, tri- and tetracyanoethylene, with 9,10- dimethylanthracene are higher than those with cyclopentadiene. In the case of less acceptor dienophiles, such as fumarodinitrile, maleodinitrile, and particularly, acrylonitrile, the reaction rates with cyclopentadiene, a less conjugated diene, are higher than those with 9,10-dimethylanthracene. From the summary data of Table 1 it follows that the kinetic activity of reagents is often not related unambiguously to the thermodynamic stability of the products.

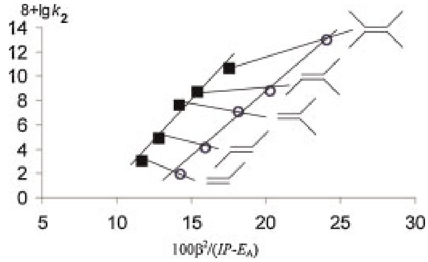


Figure 2. Logarithm of the rate constants (k_2/L/mols) of the Diels–Alder reactions of dienes, cyclopentadiene (■) and 9,10-dimethylanthracene (○) with cyanoethylene; 1,2-*trans*-dicyanoethylene; 1,1-dicyanoethylene; tricyanoethylene and tetracyanoethylene *versus* donor–acceptor properties of the addends $(\beta^2(\mathrm{IP}_D-E_A)^{-1})$

Table 1. Rate constants of the Diels–Alder reactions (k_2/L/mols), ionization potentials of dienes (IP/eV), electron affinity energies of dienophiles (E_A/eV), and the enthalpies of these reactions in solutions ($\Delta H_{r\text{-}n}$/kJ/mol) at 25 °C

No	Reaction	$8+\log k_2$	IP	E_A	$100/(IP-E_A)$	$-\Delta H_{r\text{-}n}$
Tetracyanoethylene +						
1.	1,3-Diphenylisobenzofuran	16.0	7.62	2.88	21.09	69
2.	9,10-Dimethylanthracene	12.97	7.04	2.88	24.04	88
3.	9-Methoxyanthracene	11.71	7.17	2.88	23.31	61
4.	9-Methylanthracene	11.35	7.17	2.88	23.31	85
5.	9,10-Dimethoxyanthracene	10.94	7.09	2.88	23.75	53
6.	Anthracene	8.48	7.33	2.88	22.47	77
7.	9-Chloroanthracene	7.74	7.39	2.88	22.17	66
8.	2-Methoxy-1,3-butadiene	8.47	8.62	2.88	17.42	159
9.	2,3-Dimethyl-1,3-butadiene	8.40	8.61	2.88	17.45	176
10.	*trans*-1-Phenyl-1,3-butadiene	7.81	8.16	2.88	18.94	142
11.	*trans*-1-Methyl-1,3-butadiene	7.23	8.61	2.88	17.45	163
12.	*trans,trans*-1,4-Diphenyl-1,3-butadiene	6.87	8.09	2.88	19.19	97.0
13.	2-Methyl-1,3- butadiene	6.87	8.89	2.88	16.64	166
14.	1,3-Butadiene	5.23	9.03	2.88	16.26	154
15.	Cyclopentadiene	10.63	8.58	2.88	17.54	113
16.	1,3-Cyclohexadiene	8.14	8.25	2.88	18.62	130
Tricyanoethylene +						
17.	1,3-Diphenylisobenzofuran	12.0	7.62	2.10	18.12	71
18.	9,10-Dimethylanthracene	8.77	7.04	2.10	20.24	90
19.	Cyclopentadiene	8.68	8.58	2.10	15.43	115
1,1-Dicyanoethylene +						
20	1,3-Diphenylisobenzofuran	11.0	7.62	1.53	16.42	77
21.	9,10-Dimethylanthracene	7.10	7.04	1.53	18.15	96
22.	9-Methylanthracene	6.18	7.17	1.53	17.73	93
23.	Anthracene	4.52	7.33	1.53	17.24	85
24.	Cyclopentadiene	7.66	8.58	1.53	14.18	121
Fumarodinitrile +						
25.	1,3-Diphenylisobenzofuran	7.49	7.62	0.78	14.62	82
26.	Cyclopentadiene	4.91	8.58	0.78	12.82	126
27.	9,10-Dimethylanthracene	4.14	7.04	0.78	15.97	101
28.	9-Methylanthracene	3.08	7.17	0.78	15.65	98
29.	9-Methoxyanthracene	2.28	7.17	0.78	15.65	74
30.	Anthracene	1.62	7.33	0.78	15.27	90
31.	9,10-Dimethoxyanthracene	1.08	7.09	0.78	15.85	66
Acrylonitrile +						
32.	1,3-Diphenylisobenzofuran	5.34	7.62	0.02	13.16	87
33.	Cyclopentadiene	3.02	8.58	0.02	11.68	131
34.	9,10-Dimethylanthracene	1.95	7.04	0.02	14.24	106
35.	9-Methylanthracene	1.04	7.17	0.02	13.99	103
36.	9-Methoxyanthracene	0.70	7.17	0.02	13.99	79
37.	Anthracene	-0.07	7.33	0.02	13.68	95
Maleic anhydride +						
38.	1,3-Diphenylisobenzofuran	8.53	7.62	0.97	15.04	85
39.	Cyclopentadiene	6.96	8.58	0.97	13.14	129
40.	9,10-Dimethylanthracene	6.09	7.04	0.97	16.47	104
41.	9-Methylanthracene	4.54	7.17	0.97	16.13	101
42.	9-Methoxyanthracene	3.45	7.17	0.97	16.13	77
43.	Anthracene	2.78	7.33	0.97	15.72	93
44.	9,10-Dimethoxyanthracene	2.49	7.09	0.97	16.33	69
45.	9-Chloroanthracene	2.16	7.39	0.97	15.57	82
46.	2,3-Dimethyl-1,3-butadiene	4.53	8.61	0.97	13.09	194
47.	*trans*-1-Methyl-1,3-butadiene	4.36	8.61	0.97	13.09	179

(*Continues*)

Table 1. (Continued)

No	Reaction	$8+\log k_2$	IP	E_A	$100/(IP-E_A)$	$-\Delta H_{r\text{-}n}$
48.	2-Methyl-1,3-butadiene	4.19	8.89	0.97	12.63	182
49.	*trans*-1-Phenyl-1,3-butadiene	4.05	8.16	0.97	13.91	158
50.	1,3-Butadiene	3.83	9.03	0.97	12.41	170
51.	*trans,trans*-1,4-Diphenylbutadiene	2.47	8.09	0.97	14.04	113
52.	Pentacene	6.13	6.64	0.97	17.64	132
53.	Tetracene	4.88	7.01	0.97	16.55	103
54.	Hexachlorocyclopentadiene	0.06	8.96	0.97	12.56	58
Chloromaleic anhydride +						
55.	1,3-Diphenylisobenzofuran	8.58	7.62	1.08	15.29	82
56.	9,10-Dimethylanthracene	5.81	7.04	1.08	16.78	101
57.	9-Methylanthracene	4.35	7.17	1.08	16.42	98
58.	Anthracene	2.49	7.33	1.08	16.00	90
59.	9-Chloroanthracene	1.83	7.39	1.08	15.85	79
Citraconic anhydride +						
60.	9,10-Dimethylanthracene	3.38	7.04	0.83	16.10	103
61.	9-Methylanthracene	1.93	7.17	0.83	15.77	100
N-(*p*-Nitrophenyl)maleimide +						
62.	1,3-Diphenylisobenzofuran	9.16	7.62	1.01	15.13	96
63.	Pentacene	7.75	6.64	1.01	17.76	143
64.	Tetracene	5.96	7.01	1.01	16.67	124
65.	Cyclopentadiene	7.31	8.58	1.01	13.21	140
66.	9-Methylanthracene	5.23	7.17	1.01	16.23	112
67.	Anthracene	3.93	7.33	1.01	15.82	104
68.	9-Chloroanthracene	2.92	7.39	1.01	15.67	93
N-Phenylmaleimide +						
69.	1,3-Diphenylisobenzofuran	8.57	7.62	0.89	14.86	98
70.	Cyclopentadiene	6.94	8.58	0.89	13.00	142
71.	9,10-Dimethylanthracene	6.48	7.04	0.89	16.26	117
72.	9-Methylanthracene	4.71	7.17	0.89	15.92	114
73.	9-Methoxyanthracene	3.45	7.17	0.89	15.92	90
74.	Anthracene	2.86	7.33	0.89	15.53	106
75.	9-Chloroanthracene	1.45	7.39	0.89	15.38	95
76.	Pentacene	6.98	6.64	0.89	17.39	145
77.	Tetracene	5.34	7.01	0.89	16.34	126
78.	5,11-Dichlorotetracene	4.43	6.81	0.89	16.89	107
Acrolein +						
79.	1,3-Diphenylisobenzofuran	5.92	7.62	0.15	13.39	78
80.	Cyclopentadiene	3.30	8.58	0.15	11.87	122
81.	2-Methyl-1,3-butadiene	0.7	8.89	0.15	11.44	175
82.	1,3-Butadiene	0.0	9.03	0.15	11.26	163
Some additional reactions						
83.	*N*-(*p*-Nitrophenyl)maleimide + 1,3-Diphenylisobenzofuran	9.22	7.62	0.99	15.08	95
84.	*N*-(*p*-Bromophenyl)maleimide + 1,3-Diphenylisobenzofuran	8.87	7.62	0.95	14.99	98
85.	*N*-(*p*-Tolyl)maleimide + 1,3-Diphenylisobenzofuran	8.56	7.62	0.83	14.73	98
86.	*N*-(*p*-Methoxyphenyl)maleimide + 1,3-Diphenylisobenzofuran	8.50	7.62	0.81	14.68	99
87.	*N*-(*p*-Dimethylaminophenyl)-maleimide + 1,3-Diphenylisobenzofuran	8.36	7.62	0.73	14.51	100
88.	Maleodinitrile + 1,3-Diphenylisobenzofuran	8.12	7.62	0.78	14.62	84
89.	Acrylic acid + 1,3-Diphenylisobenzofuran	6.18	7.62	0.09	13.28	84
90.	Methyl acrylate + 1,3-Diphenylisobenzofuran	5.28	7.62	0.19	13.46	85
91.	Acrylic acid + cyclopentadiene	4.77	8.58	0.09	11.78	128
92.	Methyl acrylate + cyclopentadiene	3.51	8.58	0.19	11.91	129
93.	1,3-Butadiene + ethylene	−2.7	9.03	−1.81	9.22	166

The values of the rate constants were taken from References [13,14,23,24,36,58–65]; data on IP, E_A were taken from References [13,18,56,57,59,62,66–69]; data on the enthalpies of reactions were taken from References [24,67,69–72]. The values of enthalpies of reactions 81, 82 93 were calculated (Reference [67]) from the data of the heat of formation of reagents and adducts.

In accordance with the principle of thermochemical kinetics elaborated by Bell,[73] Evans and Polyanyi,[74] the bond breaking energy in reagents and the bond formation energy in products always generate the activation barrier energy. The fraction of the contribution of the bond breaking energy varies from 0 to 1 depending on the contribution of other factors. The contribution of other factors remaining constant, the higher activation barrier should be expected for the conjugated systems with the higher energy of bond cleavage. This idea[73,74] was popularized by Hammond[75] and is more known as the Hammond postulate. In a series of substituted dienes and dienophiles, the difference between the energies of reacting bonds usually exceeds the difference between the energies of resulting single C—C bonds. So the change in the activation energy is probably proportional to the difference in the conjugation energy in the reagents. The complete balance of the bond breaking and formation energies is reflected in the reaction enthalpy in solution. This effect may not necessarily control the change of the reaction rates in a series of substituted reagents, but it always generates the activation barrier. It is clear that the Gibbs energy of reaction is more suitable for such account; however, its determination is connected with serious difficulties. The existing proportionality between the reaction enthalpy and entropy parameters justifies the use of experimental values of the reaction enthalpy.

When the conjugation energy is sharply changed, simple correlations between the reaction rate and stabilization energy of the boundary orbital interaction can be violated even within a single reaction series.[24] For example, due to the enhanced conjugation energy, the exothermic effect of the DAR involving 9-methoxy- and 9,10-dimethoxyanthracene is much lower than that of the reaction with 9-methyl- and 9,10 dimethylanthracenes, which have comparable electron-donating properties (Table 1). It explains not only the low value of the equilibrium constant, but also the lowered reaction rate constant.[64,69] Due to the lower conjugation energy in a series of substituted butadienes, the DAR involving these compounds is much more exothermic than that with substituted anthracenes (Table 1). However, the change of the reaction enthalpy of maleic anhydride with 2,3-dimethylbutadiene (−194 kJ/mol) on going to *trans*-1-phenylbutadiene (−158 kJ/mol) and, particularly, to *trans, trans*-1,4-diphenylbutadiene (−113 kJ/mol) is so high that the orbital properties alone cannot predict the change of the reaction rate correctly without additionally accounting for the contribution of the bond breaking and formation energies (Fig. 3). Similar dependences were observed in the reactions of substituted butadienes and anthracenes with other dienophiles.[24,26,27]

In spite of more favorable π-donor characteristics of anthracene (IP = 7.33 eV) in comparison with 2,3-dimethylbutadiene (8.40 eV), the same reactivity is observed in the reaction with a strong π-acceptor such as tetracyanoethylene ($E_A = 2.88$ eV) due to the substantial difference between the enthalpies of these reactions (−77 and −178 kJ/mol, respectively). The decrease of the stabilization energy on going to the less π-acceptor dienophile, maleic anhydride, ($E_A = 0.97$ eV) provides the activity of anthracene being already 56 times less than that of 2,3-dimethylbutadiene (Table 1). The analysis of the complete data set (Table 1) shows that such 'violations' are quite often. Thus, the 'anomalous' change of the activity of different classes of reagents in the DAR becomes comprehensible under the joint consideration of the influence of the energy of intermolecular interactions and the reaction enthalpy.

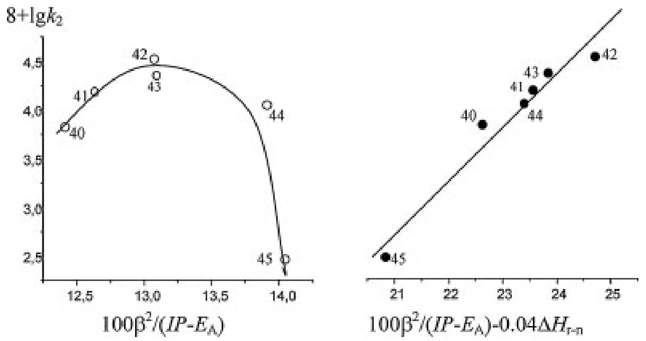


Figure 3. Logarithm of the rate constants (k_2/L/mols) of the Diels–Alder reactions of substituted butadienes with maleic anhydride *versus* donor–acceptor properties of reactants ($\beta^2(\mathrm{IP_D}-E_A)^{-1}$) without (○) and with account (•) of the reaction enthalpies ($\Delta H_{\text{r-n}}$/kJ/mol). The numbering of points corresponds those in Table 1

It was suggested[24,26,27] to take into account three main parameters of the DAR reactivity: (1) the energies of diene and dienophile boundary orbitals; (2) the balance of the bond cleavage and formation energies, and (3) the change in the overlap coefficients of the orbitals basically determined by the difference in the distances between reactive atoms C_1–C_4 in diene (R_{1-4}).

There is a very poor correlation ($r = 0.635$, $n = 93$) between $\lg k_2$ and $(\mathrm{IP}-E_A)^{-1}$ for all reagents of the different structural classes (Table 1) with reaction rates differing by almost 20 orders of magnitude.[24,26] The differences in the bond cleavage and formation energies being taken into account additionally, the complete set of kinetic data for all these reactions transforms into three separate linear dependences (Fig. 4).

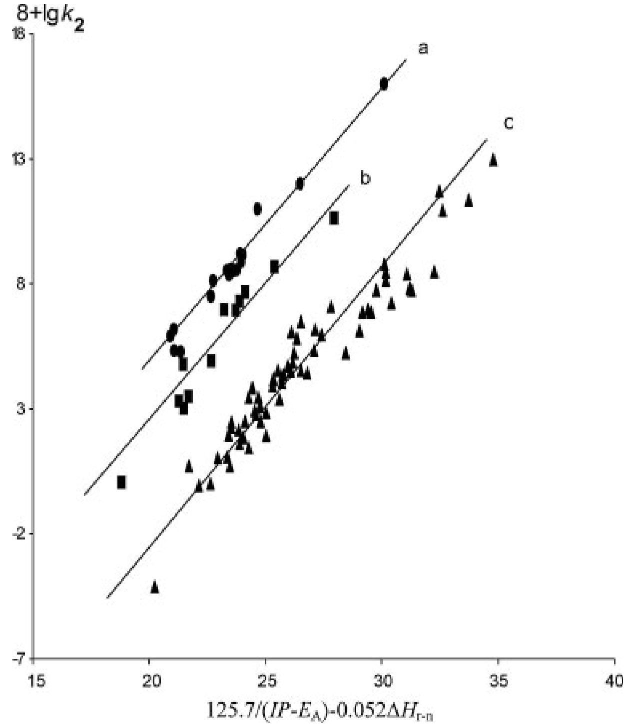


Figure 4. Logarithm of the rate constants (k_2/L/mols) of the Diels–Alder reactions of dienophiles with furan (a); cyclopentadiene (b); anthracene and butadiene (c) derivatives *versus* donor–acceptor properties of reactants ($\beta^2(\mathrm{IP_D}-E_A)^{-1}$) and the reaction enthalpy ($\Delta H_{\text{r-n}}$/kJ/mol) according to the data of Table 1

It can be noted that in the dependence (lgk_2 *vs.* [125.7/(IP$-E_A$)$-$0.052$\Delta H_{\text{r-n}}$] furan derivatives (*a*, Fig. 4) exhibit the enhanced activity in the DAR with dienophiles. The distance between the diene atoms in furan ($R_{1-4} = 2.19$ Å) is shorter than that in cyclopentadiene (2.36 Å), anthracene (2.81 Å), and *s-cis*-butadiene-1,3 (2.90 Å). For reactions with the fixed [125.7/(IP$-E_A$)$-$0.052$\Delta H_{\text{r-n}}$] value, the reaction rates with furan derivatives are 2 orders of magnitude higher (*a*, Fig. 4) than those with cyclopentadiene derivatives (*b*, Fig. 4) and are 6–7 orders of magnitude higher than those with anthracene and butadiene derivatives (*c*, Fig. 4). Sustmann, Bohm, and Sauer[20] have found that the square of the overlap coefficient of reacting orbitals decreases linearly ($r = 0.99$) with the increase of the interatomic distance in diene (R_{1-4}).

$$\beta^2 = \mathrm{a} - \mathrm{b}.R_{1-4} \tag{1}$$

So the contribution of the stabilization energy can be expressed by

$$\frac{\beta^2}{(\mathrm{IP_D} - E_\mathrm{A})} = \frac{\mathrm{a}}{(\mathrm{IP_D} - E_\mathrm{A})} - \mathrm{b}.\frac{R_{1-4}}{(\mathrm{IP_D} - E_\mathrm{A})} \tag{2}$$

The total correlation for the complete data set is observed (Fig. 5) by taking into account all three factors (Eqn (3): $r = 0.972$; SD $= 0.9$; $n = 93$)

$$\lg k_2 = -28.81 + 316.3/(IP_\mathrm{D} - E_\mathrm{A}) - 69.9\,R_{1-4}/(IP_\mathrm{D} - E_\mathrm{A}) - 0.054\Delta H_{\mathrm{r-n}} \tag{3}$$

For a more clear interpretation of these contributions into the DAR rate (lgk_2) (Eqn (3)) it should be mentioned that the effect of the difference in the reaction enthalpies (Fig. 5) is comparable with that of the change in the overlap coefficients of the reacting orbitals of reagents and each of these contributions is twice as less as the effect of the differences in the (IP$-E_A$)$^{-1}$ values.

The relation Eqn (3) allows one to explain the origin of the conventional and 'anomalous' correlations between activity and selectivity, and the variety of relationships between the kinetic activity and thermodynamic stability. It helps one to choose the reagents for directed synthesis of desired products, particularly in competitive processes. It predicts rates of the DAR (lg$k_2 \pm 0.9$) between the different reagents with C=C bonds not explored earlier.

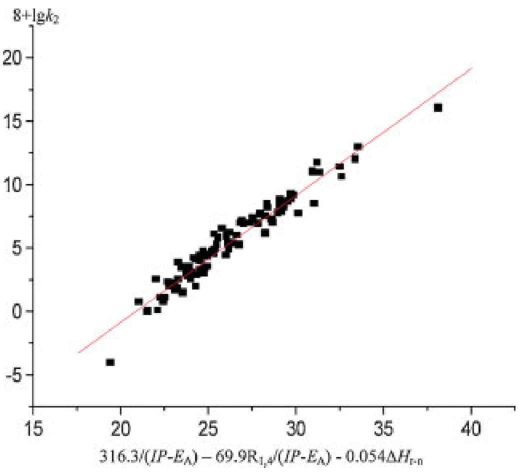


Figure 5. Logarithm of the rate constants (k_2/L/mols) of the Diels–Alder reactions as function of the donor–acceptor properties of reactants (β^2(IP$-E_A$)$^{-1}$), interatomic distance in the dienes (R_{1-4}/Å) and the reaction enthalpies ($\Delta H_{\text{r-n}}$/kJ/mol) according to the data of Table 1

CHARGE TRANSFER COMPLEXES IN THE DAR

Many examples confirm the formation of molecular π,π-complexes between the addends.[23,24,26,57,76,77] The effect of solvent and properties of the substituents in reagents often leads to the proportional change of both the rate constants of the DAR and the equilibrium constants of π,π-complexes. However, this proportionality does not allow solving the problem about the location of molecular complexes in the reaction scheme

$$\mathrm{D} + \mathrm{A} \underset{}{\overset{K_{\mathrm{eq}}}{\rightleftarrows}} \mathrm{MC} \quad \xrightarrow{k_1} \mathrm{P} \tag{4}$$

$$\mathrm{MC} \overset{K_{\mathrm{eq}}}{\rightleftarrows} \mathrm{D} + \mathrm{A} \quad \xrightarrow{k_2} \mathrm{P} \tag{5}$$

When the reaction proceeds under the large excess of one of the reagents (for example, $c_\mathrm{A} >> c_\mathrm{D}$), the observed constant of the reaction rate ($k_{\text{exp.}}$) for the pathway Eqn (4) and the pathway Eqn (5) is described by Eqns (6) and (7), respectively

$$\kappa_{\text{exp.}} = \frac{\kappa_1 K_{\mathrm{eq}}}{(1 + K_{\mathrm{eq}}.c_\mathrm{A})} \tag{6}$$

$$\kappa_{\text{exp.}} = \frac{\kappa_2}{(1 + K_{\mathrm{eq}}.c_\mathrm{A})} \tag{7}$$

The equilibrium constants (K_{eq}) of molecular complexes calculated from the dependence of the reaction rate (1/k_{exp}) on the concentration (c_A) (Eqns (6) and (7)) closely fit the results of direct measurements.[76] Obviously, it is also impossible to choose between the reaction pathways Eqns (4) and (5) on the basis of these data only. If $K_{\mathrm{eq}}\,.c_\mathrm{A} << 1$, then the experimental values of the activation enthalpy for the pathways Eqns (4) and (5) are defined, respectively

$$\Delta H^{\neq}_{\text{exp.}} = \Delta H^{\neq}_1 + \Delta H_{\mathrm{MC}} \tag{8}$$

$$\Delta H^{\neq}_{\text{exp.}} = \Delta H^{\neq}_2 \tag{9}$$

For reagents forming strong molecular complexes, the $\Delta H^{\neq}_{\text{exp}}$ value can be negative only for the pathway Eqn (4) (Eqn (8)), when $|\Delta H^0_{\mathrm{MC}}| > \Delta H^{\neq}_1$. For the DAR between 9,10-dimethylanthracene **1** (IP $= 7.04$ eV) and tetracyanoethylene **2** ($E_\mathrm{A} = 2.88$ eV) in the series of inert solvents the decrease of the reaction rate with the temperature increase was observed.[77] It leads to the negative values of the activation enthalpy observed in acetonitrile, dichloromethane, 1,2-dichloroethane, and chloroform (Table 2, Scheme 1).

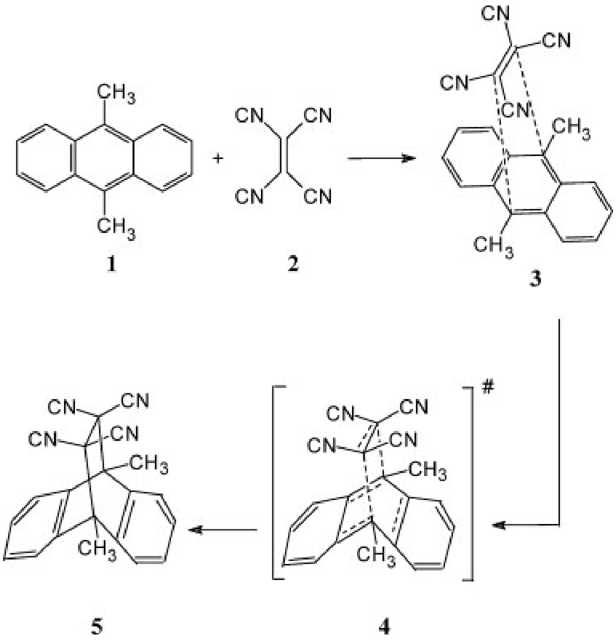
These results correspond to the fact that for the given reaction the structure rearrangement of the molecular complex **3** during its further transformation into the transition state **4** and reaction product **5** (Scheme 1) is not required.[77]

CATALYSIS IN THE DAR

In 1955 it was found that the reactions between anthracene and β-chlorovinylalkyl ketones in toluene occur only in the presence of tin chloride.[78] Yates and Eaton[79] have observed that

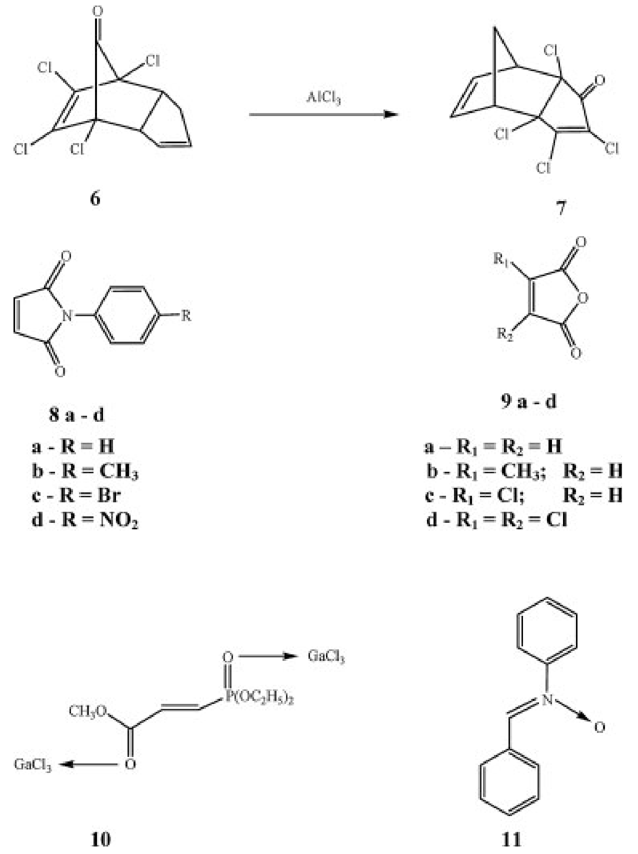
Table 2. Initial concentrations of tetracyanoethylene (C_{TCNE}/mol/L), rate constants (k_2/L/mols), enthalpy ($\Delta H^{\neq}$/ kJ/mol), entropy ($\Delta S^{\neq}$/J/mol K) of activation in the Diels–Alder reaction of tetracyanoethylene with 9,10-dimethylanthracene in some solvents[77]

Solvent	$10^4 C_{TCNE}$	k_2(°C)				$\Delta H^{\neq}$	$-\Delta S^{\neq}$
o-Xylene	10.55	790(13.5)	816(14.7)	1050(25.0)	1605(40.2	18.3	125
Toluene	8.44	2290(13.5)	2810(25.0)	3790(39.4)	3810(40.2	11.9	138
Benzene	6.56	760(13.5)	8480(25.0)	10800(39.4)	10400(40.2	7.2	146
Acetonitrile	8.78	46500(12.0)	43500(25.1)	42500(40.4)	—	−5.0	171
Dichloromethane	6.53	150000(12.0)	136000(25.3)	—	—	−7.5	171
1,2-Dichloroethane	4.67	111000(12.0)	110000(11.8)	89500(40.4)	—	−8.1	176
	8.75	102000(12.9)	92700(24.9)	83000(36.1)	—	−8.7	180
	8.90	96000(12.4)	89000(24.9)	83600(36.1)	81300(43.1)	−6.9	171
Chloroform	3.94	290000(14.0)	260000(24.6)	216000(39.4)	—	−11.2	180
	4.20	278000(12.0)	214000(25.1)	185000(40.4)	—	−13.1	186
	4.70	263000(11.1)	226000(24.8)	190000(42.8)	—	−10.2	176
Hexane	0.805	14000(25.0)	—	—	—	—	—
Carbon tetrachloride	3.34	40160(25.0)	—	—	—	—	—



Scheme 1.

aluminum chloride sharply accelerates the rearrangement of tetrachlorodicyclopentadiene-8-on (**6**) into isomeric ketone (**7**) (Scheme 2):



Scheme 2.

Since the rearrangements of the DARs occur via the mechanism of decomposition and formation, obviously the activity of dienophiles may sharply increase in the presence of Lewis acids. This fact has served as a powerful incentive for a thorough study of the acceleration effect in the DAR. During the last 40 years numerous kinetic data on the acceleration effect of the DAR in the presence of Lewis acids and enthalpy of the *n*,ν-complex formation, enthalpy of catalyzed reaction and the effect of medium on the solvation of reagents, *n*,ν-complexes and transition state of the catalyzed DARs were obtained.[24,80–101] The formation of strong *n*,ν-complexes leads to a sharp (of up to 10^9) increase of the reaction rate involving into the reaction even those reagents which are usually exceedingly inert. It was shown[24] that the acceleration of the catalyzed DAR with normal electron demand in medium rather inert toward Lewis acids (benzene, toluene, dichloromethane, 1,2-dichloroethane) was approximately constant and of about 1, 3, 4, 5, and 6 orders of magnitude in the presence of $SnCl_4$, BBr_3, $GaCl_3$, $AlCl_3$, and $AlBr_3$, respectively (Table 3).

In the reactions with reagents having inverse electron properties, i.e., 'diene-acceptor, dienophile-donor', the coordination of these Lewis acids with the heteroatom of dienes

Table 3. Enthalpy formation of *n,v*-complexes (ΔH_{MC}/kJ/mol), rate constants (k_2/L/mols), enthalpy ($\Delta H^{\neq}$/kJ/mol), entropy ($\Delta S^{\neq}$, J/mol K) of activation and Lewis acids catalytic effects (k_{cat}/k_{noncat}) for some Diels–Alder reactions in benzene solution at 25 °C[24,80–90]

No/No	Reaction	Lewis acid	$-\Delta H_{MC}$	k_2	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	k_{cat}/k_{noncat}
1.	9,10-Dimethylanthracene + methyl acrylate	—	—	$7.8\ 10^{-7}$	63	150	—
2.		$AlCl_3$	—	0.15	31	155	$1.9\ 10^{5}$
3.		$GaCl_3$	52	$3.5\ 10^{-2}$	—	—	$4.5\ 10^{4}$
4.	9,10-Dimethylanthracene + methyl metacrylate	—	—	$1.3\ 10^{-7}$	63	163	—
5.		$AlCl_3$	—	$3.8\ 10^{-2}$	35	155	$2.8\ 10^{5}$
6.	9,10-Dimethylanthracene + dimethyl fumarate	—	—	$6.7\ 10^{-6}$	52	167	—
7.		$AlCl_3$	—	0.43	23	171	$6.4\ 10^{4}$
8.	Anthracene + *N*-(*p*-nitrophenyl)maleimide	—	—	$8.5\ 10^{-5}$	57	129	—
9.		$AlCl_3$	—	8.2	33	113	$9.6\ 10^{4}$
10		$GaCl_3$	48	1.0	—	—	$1.2\ 10^{4}$
11.	Anthracene + *N*-(*p*-bromophenyl)maleimide	—	—	$2.5\ 10^{-5}$	60	129	—
12.		$AlCl_3$	—	2.9	34	121	$1.2\ 10^{5}$
13.		$GaCl_3$	53	0.65	34	135	$2.6\ 10^{4}$
14.	Anthracene + *N*-(*p*-methoxyphenyl)maleimide	—	—	$8.1\ 10^{-6}$	68	112	—
15.		$AlCl_3$	—	1.2	38	113	$1.5\ 10^{5}$
16.	Anthracene +	—	—	$7.3\ 10^{-6}$	68	112	—
17.	*N*-phenylmaleimide	$AlCl_3$	—	1.2	48	105	$1.7\ 10^{5}$
18.		$AlBr_3$	78	5.7	—	—	$7.9\ 10^{5}$
19.		$GaCl_3$	55	0.35	—	—	$4.9\ 10^{4}$
20.	Anthracene +	—	—	$6.8\ 10^{-6}$	68	113	—
21.	*N*-(*p*-tolyl)maleimide	$AlCl_3$	—	1.2	41	105	$1.8\ 10^{5}$
22.		$GaCl_3$	57	0.35	—	—	$5.2\ 10^{4}$
23.	9,10-Dimethylanthracene + *N*-phenylmaleimide	—	—	$3.0\ 10^{-2}$	—	—	—
24.		$SnCl_4$	8	$3.6\ 10^{-2}$	—	—	1.2
25.		$Et_2O{\cdot}BF_3$	5	$3.0\ 10^{-2}$	—	—	1.0
26.	Anthracene +	—	—	$6.0\ 10^{-6}$	65	126	—
27.	maleic anhydride	BCl_3	—	$4.1\ 10^{-2}$	—	—	$6.9\ 10^{3}$
28.		$GaCl_3$	41	0.40	—	—	$6.7\ 10^{4}$
29.		$AlCl_3$	—	1.6	—	—	$2.6\ 10^{5}$
30.		$AlBr_3$	—	7.2	—	—	$1.2\ 10^{6}$
31.	Anthracene +	—	—	$1.8\ 10^{-7}$	66	140	—
32.	1,4-naphthoquinone	$GaCl_3$	54	2.3	34	120	$1.3\ 10^{7}$
33.		$2GaCl_3$	—	600	—	—	$3.4\ 10^{8}$
34.	Anthracene +	—	—	$2.4\ 10^{-6}$	64	123	—
35.	1,4-benzoquinone	$GaCl_3$	53	1.9	—	—	$7.8\ 10^{5}$
36.	1,3-Diphenylisobenzo-furan + O, O-diethyl-β-carbomethoxyvinyl-phosphonate	—	—	$7.0\ 10^{-4}$	—	—	—
37.		$GaCl_3$	90; P=O	0.37	—	—	$5.3\ 10^{2}$
38.	1,3-Diphenylisobenzofuran + O, O-diphenyl-β-carbomethoxyvinyl-phosphonate	—	—	$3.7\ 10^{-5}$	58	121	—
39.		$GaCl_3$	76; P=O	$3.4\ 10^{-2}$	42	121	$9.2\ 10^{2}$
40.	9,10-Dimethylanthracene + O, O-diethyl-β-carbomethoxyvinyl-phosphonate	—	—	8.910^{-10}	90	155	—

(*Continues*)

Table 3. (Continued)

No/No	Reaction	Lewis acid	$-\Delta H_{MC}$	k_2	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	k_{cat}/k_{noncat}
41.		$2GaCl_3$	148; 2:1 P=O and C=O	$1.7\ 10^{-2}$	40	140	$1.9\ 10^{7}$
42.	Tetraphenyl- cyclopentadienone + *trans*-stilbene	—	—	$2.8\ 10^{-8}$	70	144	—
43.		$AlCl_3$	39;C=O	$5.6\ 10^{-5}$	39	185	$2.0\ 10^{3}$
44.	Tetraphenyl- cyclopentadienone + norbornadiene	—	—	$6.0\ 10^{-7}$	64	137	—
45.		$AlCl_3$	39;C=O	$5.0\ 10^{-4}$	34	181	$8.4\ 10^{2}$
46.	Tetraphenyl- cyclopentadienone + *N*-phenylmaleimide	—	—	$3.9\ 10^{-5}$	59	120	—
47.		$GaCl_3$	55 imide;	$1.4\ 10^{-4}$	—	—	3.6
48.		$AlCl_3$	-,imide;	10^{-3}	45	137	28
49.		$2\ AlCl_3$	-, both	$4.2\ 10^{-5}$	—	—	1.2
50.	Tetraphenyl- cyclopentadienone + *N*-(*p*-tolyl)maleimide	—	—	$6.3\ 10^{-5}$	57	121	—
51.		$GaCl_3$	57 imide;	$1.5\ 10^{-4}$	—	—	2.4
52.		$AlCl_3$	-, imide;	$7.1\ 10^{-4}$	—	—	11
53.		$2\ AlCl_3$	-, both	$6.5\ 10^{-5}$	—	—	1.0
54.	*C*-Phenyl,*N*-methylnitron + *N*-phenylmaleimide	—	—	$2.0\ 10^{-4}$	—	—	—
55.		$GaCl_3$	55 imide	50	—	—	$2.5\ 10^{5}$
56.	9,10-Dimethylanthracene + acrylonitrile	—	—	$2.2\ 10^{-6}$	63	146	—
57.		$GaCl_3$	51	0.13	36	130	$5.9\ 10^{4}$
58.	9-Methylanthracene + acrylonitrile	—	—	$1.1\ 10^{-7}$	74	122	—
59.		$GaCl_3$	51	$1.7\ 10^{-2}$	42	126	$1.5\ 10^{5}$
60.	Anthracene + acrylonitrile	—	—	$8.6\ 10^{-9}$	76	138	—
61.		$GaCl_3$	51	$5.3\ 10^{-4}$	47	141	$6.2\ 10^{4}$
62.	9-Chloroanthracene + acrylonitrile	—	—	$1.9\ 10^{-9}$	79	140	—
63.		$GaCl_3$	51	$1.6\ 10^{-4}$	49	145	$8.4\ 10^{4}$
64.	9-Methylanthracene + methyl acrylate	—	—	$5.8\ 10^{-8}$	—	—	—
65.		$GaCl_3$	52	$1.3\ 10^{-2}$	—	—	$2.2\ 10^{5}$
66.	9,10-Dimethylanthracene + cyanoacetylene	—	—	$4.0\ 10^{-6}$	—	—	—
67.		$GaCl_3$	—	1.1	—	—	$2.8\ 10^{5}$
68.	9,10-Dimethylanthracene + methyl propiolate	—	—	$2.0\ 10^{-8}$	—	—	—
69.		$GaCl_3$	—	$6.0\ 10^{-3}$	—	—	$3.0\ 10^{5}$
70.	9,10-Dimethylanthracene + maleic anhydride	—	—	$1.2\ 10^{-2}$	43	138	—
71.		$GaCl_3$	41	$2.8\ 10^{2}$	—	—	$2.3\ 10^{4}$
72.		$AlCl_3$	—	$2.0\ 10^{3}$	—	—	$1.7\ 10^{5}$
73.	9-Methylanthracene + maleic anhydride	—	—	$3.4\ 10^{-4}$	53	134	—
74.		$GaCl_3$	41	12.8	27	140	$3.8\ 10^{4}$
75.		$AlCl_3$	—	95.2	—	—	$2.8\ 10^{5}$
76.	9-Chloroanthracene + maleic anhydride	—	—	$1.4\ 10^{-6}$	67	130	—
77.		$GaCl_3$	41	$5.2\ 10^{-2}$	36	153	$3.7\ 10^{4}$
78.		$AlCl_3$	—	0.38	—	—	$2.8\ 10^{5}$
79.	Anthracene + citraconic anhydride	—	—	$1.5\ 10^{-8}$	73	135	—
80.		$GaCl_3$	49	$1.3\ 10^{-4}$	—	—	$9.0\ 10^{3}$
81.		$AlCl_3$	—	$8.3\ 10^{-3}$	32	164	$5.7\ 10^{5}$

(*Continues*)

Table 3. (Continued)

No/No	Reaction	Lewis acid	$-\Delta H_{MC}$	k_2	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	k_{cat}/k_{noncat}
82.	9-Chloroanthracene + citraconic anhydride	—	—	$1.5\ 10^{-8}$	73	135	—
83.		$GaCl_3$	49	$1.3\ 10^{-4}$	—	—	$9.0\ 10^{3}$
84.		$AlCl_3$	—	$8.3\ 10^{-3}$	32	164	$5.7\ 10^{5}$
85.	9-Methylanthracene + citraconic anhydride	—	—	$8.5\ 10^{-7}$	64	135	—
86.		$GaCl_3$	49	$2.0\ 10^{-2}$	41	129	$2.3\ 10^{4}$
87.		$AlCl_3$	—	0.14	28	154	$1.7\ 10^{5}$
88.	9,10-Dimethylanthracene + citraconic anhydride	—	—	$2.4\ 10^{-5}$	45	169	—
89.		$GaCl_3$	49	0.44	31	137	$1.9\ 10^{4}$
90.		$AlCl_3$	—	2.2	29	128	$9.1\ 10^{4}$
91.	Anthracene + chloromaleic anhydride	—	—	$3.1\ 10^{-6}$	62	128	—
92.		$GaCl_3$	40	0.11	—	—	$3.6\ 10^{4}$
93.		$AlCl_3$	—	2.3	—	—	$7.5\ 10^{5}$
94.	9-Chloroanthracene + chloromaleic anhydride	—	—	$6.8\ 10^{-7}$	—	—	—
95.		$GaCl_3$	40	$2.3\ 10^{-2}$	—	—	$3.4\ 10^{4}$
96.		$AlCl_3$	—	0.14	—	—	$2.1\ 10^{5}$
97.	9-Methylanthracene + chloromaleic anhydride	—	—	$2.3\ 10^{-4}$	49	139	—
98.		$GaCl_3$	40	11.9	28	118	$5.3\ 10^{4}$
99.		$AlCl_3$	—	39.7	—	—	$1.8\ 10^{5}$
100.	9,10-Dimethylanthracene + chloromaleic anhydride	—	—	$6.4\ 10^{-3}$	46	118	—
101.		$GaCl_3$	40	$2.4\ 10^{2}$	—	—	$3.8\ 10^{4}$
102.		$AlCl_3$	—	$1.4\ 10^{3}$	—	—	$2.2\ 10^{5}$
103.	Tetracyclone + *N*-(*p*-nitrophenyl)maleimide	—	—	$4.0\ 10^{-5}$	64	100	—
104.		$GaCl_3$	48 imide	$2.8\ 10^{-4}$	—	—	7.1
105.		$AlCl_3$	-, imide	$1.2\ 10^{-3}$	57	96	30
106.	Tetracyclone + *N*-(*p*-bromophenyl)maleimide	—	—	$3.6\ 10^{-5}$	64	100	—
107.		$GaCl_3$	53 imide	$2.2\ 10^{-4}$	—	—	6.2
108.		$AlCl_3$	-, imide	$1.1\ 10^{-3}$	53	111	29.1
109.	Phencyclone + *N*-(*p*-nitrophenyl)maleimide	—	—	2.12	31	133	—
110.		$GaCl_3$	48 imide	36.3	20	135	17.1
111.		$AlCl_3$	-, imide	83.3	—	—	30.3
112.	Phencyclone + *N*-(*p*-bromophenyl)maleimide	—	—	1.42	33	137	—
113.		$GaCl_3$	53 imide	21.0	20	140	14.8
114.		$AlCl_3$	-, imide	51.6	—	—	36.3
115.	Phencyclone + *N*-phenylmaleimide	—	—	0.76	30	146	—
116.		$GaCl_3$	55 imide	9.4	28	121	12.4
117.		$AlCl_3$	-, imide	46.5	14	155	61.2
118.	Phencyclone + *N*-(*p*-tolyl)maleimide	—	—	0.75	34	133	—
119.		$GaCl_3$	57 imide	10.4	24	134	13.9
120.		$AlCl_3$	-, imide	40.1	22	127	53.4
121.	Phencyclone + methyl acrylate	—	—	$1.2\ 10^{-3}$	46	133	—
122.		$AlCl_3$	-,ester	0.63	32	129	$5.5\ 10^{2}$
123.	Phencyclone + methyl acrylate	—	—	$7.5\ 10^{-4}$	46	139	—

(*Continues*)

Table 3. (Continued)

No/No	Reaction	Lewis acid	$-\Delta H_{MC}$	k_2	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	k_{cat}/k_{noncat}
124.		$AlCl_3$	-,ester	0.22	30	144	$2.9\ 10^2$
125.	Phencyclone + dimethyl fumarate	—	—	$4.7\ 10^{-5}$	54	136	—
126.		$AlCl_3$	-,ester	$2.3\ 10^{-2}$	41	126	$4.9\ 10^2$
127.	*trans,trans*-1,4-Diphenyl-1,3-butadiene + *N*-(*p*-tolyl)maleimide	—	—	$9.3\ 10^{-7}$	54	168	—
128.		$AlCl_3$	—	$5.9\ 10^{-3}$	38	148	$6.3\ 10^2$
129.	*trans,trans*-1,4-Diphenyl-1,3-butadiene + *N*-phenylmaleimide	—	—	$1.4\ 10^{-6}$	50	177	—
130.		$AlCl_3$	—	$5.6\ 10^{-3}$	39	143	$3.9\ 10^2$
131.	*trans,trans*-1,4-Diphenyl-1,3-butadiene + *N*-(*p*-bromophenyl)maleimide	—	—	$2.1\ 10^{-6}$	48	180	—
132.		$AlCl_3$	—	$7.1\ 10^{-3}$	—	—	$3.4\ 10^2$

accelerates the reaction as well (Table 3), though in this case the acceleration effect is much less pronounced.[24,88,89]

The observed effects of the DAR acceleration in the case of activated dienophiles are usually explained by the increase in π-acceptor properties of the reacting double bond at the formation of the *n*,*v*–complex.[10,102,103] Quantitative calculations of the catalytic effect in the DAR have limited accuracy.[10] It was found[86–90] that the energy of the maximum of the charge transfer band in π,π-complexes between π-donor, hexamethylbenzene, and *N*-substituted maleimides (MI), activated by the formation of the *n*,*v*-complex with Lewis acid, is much lower than that for the π,π-complex between the same π-donor with non-activated MI (**8**) (Fig. 6, Table 4). For the complexes with the same π-donor, the difference between the charge transfer energies corresponds to the difference between the electron affinities of π–acceptors.[56,57]

Table 4 shows that the differences between the charge transfer energies (E_3–E_4) of π,π-complexes formed by hexamethylbenzene with maleimides (HMB-MI) and activated maleimides [HMB-(MI:$\rightarrow$GaCl$_3$)] are rather large (0.75–1.0 eV).[86–90] When MI are activated by aluminum chloride, the differences between the charge transfer energies are even larger (Table 4).

The comparison of the DAR rate and the charge transfer energy in π,π-complexes formed by hexamethylbenzene with a series of dienophiles showed[24,86] a typical dependence for non-activated and activated MI, which is similar to the widely known linear dependence found for a series of cyanoethylenes (Fig. 7).

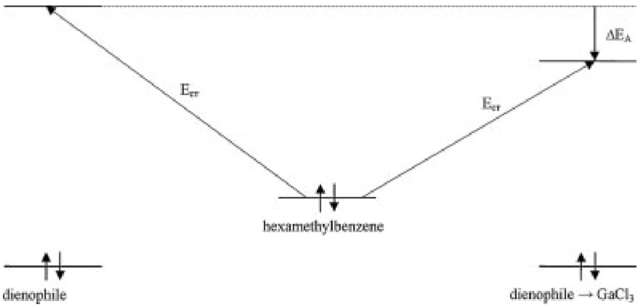


Figure 6. Charge transfer energy (E_{CT}) of $\pi \rightarrow \pi^*$ absorption bands of molecular complexes of hexamethylbenzene with common dienophiles, and with that activated by Lewis acids and the change of electron affinity of dienophiles (ΔE_A)

It follows from these results (Fig. 7) that the mechanisms of the conventional thermal and catalytic reactions should be considered as being the same. It is worth to note that the moderate activity of maleic anhydride and its imides after the formation of the *n*,ν-complex with gallium and, particularly, aluminum halides becomes already comparable with the activity of tetracyanoethylene, and even exceeds it after the formation of the 2:1 complex. By taking into account the change in the electron affinity (E_A) in the catalytic processes, the relation Eqn (3) satisfactorily predicts the rate of the catalyzed process allowing one to choose the reaction conditions.

The effectiveness of carrying out the reaction in the presence of Lewis acids is vividly presented by comparing the reaction rates of the extremely inactive dienophile *O,O*-diethyl-β-carbomethoxy vinylphosphonate **10** in the DAR with those of 9,10-dimethylanthracene **1**.[85] If the DAR of 9,10-dimethylanthracene with vinylphosphonate **10** at 25 °C requires approximately 350 years for the 50% completion, after the coordination of two molecules of gallium chloride with P=O and C=O groups the process rate increases $1{,}9{\cdot}10^7$ times and the half-life of reactions **1** and **10** becomes less than 10 min.[85]

The choice of a solvent is very important for the catalyzed reactions. In the presence of *n*-donor additives the redistribution of the Lewis acid takes place due to its coordination not only with dienophile as the *n*-donors, but also with competitive *n*-donor additives in the solvent. By choosing a proper solvent it is possible to change the catalytic effect of the acceleration reaction in the presence of Lewis acids from its maximum value to full suppression.[100,101]

The changes in the solvation enthalpy of the *n*,ν-molecular complex (MC) in a series of solvents were calculated from the enthalpy cycle using calorimetric measurements[24,80,84–90,100,101] by the difference between the corresponding values of the solution enthalpies of MI, gallium chloride, and enthalpy of the *n*,ν-complex formation (MI:$\rightarrow$GaCl$_3$) in solution

$$\delta H_{MC}(\text{solv.}) = \Delta H^{O}_{MC}(S_i) - \Delta H^{O}_{MC}(S_0) + \delta H_{MI}(\text{solv.}) + \delta H_{GaCl3}(\text{solv.}) \qquad (10)$$

where S_0 is blank solvent. In spite of considerable differences between the solution enthalpy and enthalpy of the *n*,ν-complex formation in a series of solvents, the change in the solvation enthalpy of the *n*,ν-complex is very small (Fig. 8).

Table 4. Maximum (λ/nm) and charge transfer energy (E_{CT}/eV) of $\pi \rightarrow \pi^*$ absorption bands of molecular complexes of hexamethylbenzene with common dienophiles, and with activated by Lewis acids dienophiles, and the increase of electron affinity of dienophiles (ΔE_A/eV)[86,90]

Dienophile	Lewis acid	λ	E_{CT}	ΔE_A
N-Phenylmaleimide **8a**	—	337	3.68	—
	$GaCl_3$	470	2.64	1.05
	$AlCl_3$	481	2.58	1.10
N-(*p*-Tolyl)maleimide **8b**	—	330	3.76	—
	$GaCl_3$	475	2.61	1.15
	$AlCl_3$	488	2.54	1.22
N-(*p*-Bromophenyl)maleimide **8c**	—	345	3.58	—
	$GaCl_3$	470	2.64	0.95
	$AlCl_3$	480	2.59	1.00
N-(*p*-Nitrophenyl)maleimide **8d**	—	365	3.40	—
	$GaCl_3$	464	2.67	0.73
Maleic anhydride **9a**	—	353	3.51	—
	$GaCl_3$	440	2.82	0.69
	$AlCl_3$	470	2.64	0.87
Citraconic anhydride **9b**	—	340	3.65	—
	$GaCl_3$	440	2.82	0.83
	$AlCl_3$	455	2.73	0.92
Chloromaleic anhydride **9c**	—	365	3.40	—
	$GaCl_3$	480	2.58	0.82
	$AlCl_3$	505	2.46	0.94
Dichloromaleic anhydride **9d**	—	388	3.20	—
	$GaCl_3$	500	2.48	0.72

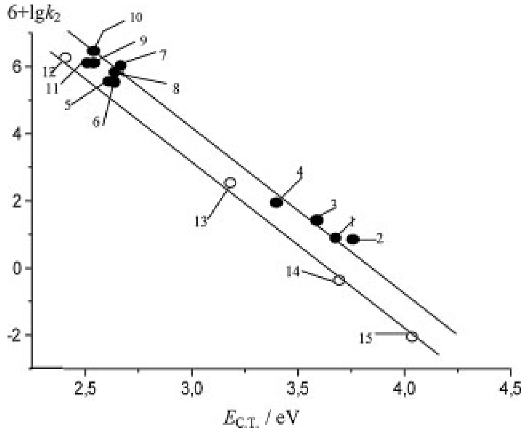


Figure 7. Logarithm of the rate constants (k_2/L/mols) of the Diels–Alder reactions of anthracene **31** with a number of dienophiles *versus* charge transfer energy (E_{CT}/eV) in their π,π–complexes with hexamethylbenzene: 1—**8b**, 2—**8a**, 3—**8c**, 4—**8d**, 5–8—*n,v*-complexes of imides **8a–d** with $GaCl_3$, 9–11—*n,v*-complexes of imides **8a–c** with $AlCl_3$, respectively; 12—tetracyanoethylene, 13—1,1-dicyanoethylene, 14—fumarodinitrile, 15—acrylonitrile

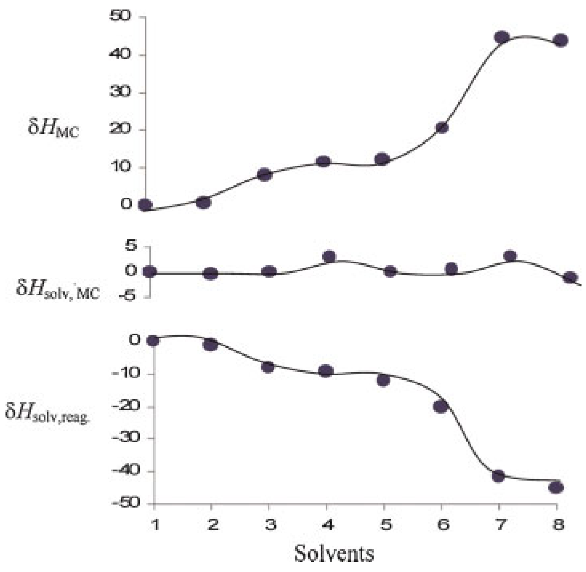


Figure 8. Relative change of the enthalpy of solvation of the reactants (*N*-phenylmaleimide and $GaCl_3$) ($\delta H_{solv,\ reag.}$/kJ/mol), *n,v*-complexes (**32**) ($\delta H_{solv,\ MC}$/kJ/mol), and the enthalpy of formation of this complex (δH_{MC}/kJ/mol) in chlorobenzene, 1; benzene, 2; toluene, 3; dichloromethane, 4; *o*-xylene, 5; mesitylene, 6; nitromethane, 7; and nitrobenzene, 8

It is worth to note that the loss of acceptor properties was observed for the tetracyanoethylene moiety in its complex with π-donors as well.[24]

Salt solution effects on the rate and equilibrium constants in the DAR were widely discussed.[104–113]

DARs UNDER ELEVATED PRESSURE

In all cycloaddition reactions the volume of a reacting system always decreases on going from reagents to the activated complex and to the cyclic adducts. The dependence of the rate and equilibrium constant on the external pressure is described by

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = \frac{-(\partial G^{\neq}/\partial p)_T}{RT} = \frac{-\Delta V^{\neq}}{RT} \qquad (11)$$

$$\left(\frac{\partial \ln K_{eq}}{\partial p}\right)_T = \frac{-(\partial G_{r-n}/\partial p)_T}{RT} = \frac{-\Delta V_{r-n}}{RT} \qquad (12)$$

Here $\Delta V^{\neq}$ and $\Delta V_{r\text{-}n}$ are the activation and reaction volumes, respectively. It follows that for the processes proceeding with the volume decrease, both rate and equilibrium constants increase with the increase of the hydrostatic pressure.[28–35]

The estimation of the solvent effect on the change of the molar volume of reagents, transition states, and products is one of the key tasks in the study of the origin of different pressure effects on the reaction rates and equilibrium in solutions enabling one to analyze the volume activation parameters. In the first approximation, the volume of a diluted solution may be presented by

$$V = V_A N_A + V_S N_S + (V_S^* - V_S)\, n N_A \qquad (13)$$

where V_A, V_S, and V_S^* are the molar volumes of the solute, free solvent, and the solvent in the solvation shell, respectively; n is the number of solvent molecules in the solvation shell; N_A and N_S are numbers of solute and solvent moles, respectively. It follows from Eqn (13) that the partial molar volume of the compound in solution (V_A) is determined by

$$\frac{\partial V}{\partial N_A} = V_A + n\,(V_S^* - V_S) \qquad (14)$$

In the absence of specific interactions in solution ($V_S^* - V_S = 0$), the partial molar volume of the solute may be calculated from the data for the solution density and even using the additive scheme of the chemical bonds or atom increments.[114] If the interaction of the solute with the media is strong, then the additivity rule does not hold due to the large contribution of the solvent volume change at its transition to the solvation shell. In such cases the negative values of the calculated partial molar volumes are not unusual.[115] It is clear that this problem exists for infinitely dilute solutions as well. Since the independent experimental determination of the $n(V_S^* - V_S)$ and V_A values is impossible, all the changes of these values are attributed to the molar volume of the solute (V_A). It is necessary to mention that with the use of such method to determine partial molar volumes of the reagents and products, the difference between partial molar volumes gives correct values of the volume change of the system in solution.

The activation volume can be calculated only from the pressure effect on the reaction rate, by assuming that the change of the reaction rate at elevated pressure (Eqn (11)) is due to the $P \times \Delta V^{\neq}$ contribution.

The reaction volume can be determined from the pressure dependence of the equilibrium constant (Eqn (12)) and, independently, from the difference between partial molar volumes of reagents and products. This allows one to verify the presence or absence of complications in the determination of the volume parameters from the pressure dependence of the equilibrium constant.

It is known that the π-acceptor dienophile, tetracyanoethylene, forms complexes with many solvents.[57,77,116] The partial molar volumes of tetracyanoethylene determined from the density of the dilute solutions are listed in Table 5.[117] Specific interactions of tetracyanoethylene with alkylbenzenes affect proportionally the changes of its solvation enthalpy, partial molar volume, the enthalpy, and free energy of the π,π-complex formation with these solvents and the DAR rate (Table 5).

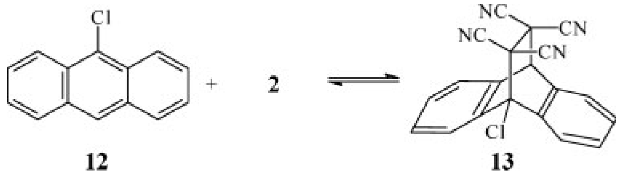
There are a lot of data[28–35] concerning the effect of elevated pressure on the rate of the direct DAR, but there are only few direct measurements of the pressure effect on the equilibrium constant of the reaction.[22,118] The reversible reaction between 9-chloroanthracene and tetracyanoethylene in 1,2-dichloroethane proved to be convenient for such experiments (Scheme 3).[118]

Its reaction volume was determined by three independent methods:[118] first, from the pressure effect on the equilibrium constant ($-20{,}6 \pm 1.5\ \mathrm{cm^3/mol}$); second, from the difference between partial molar volumes of the adduct (**13**) 255,5, 9-chloroanthracene (**12**) 170,7 and tetracyanoethylene (**2**)

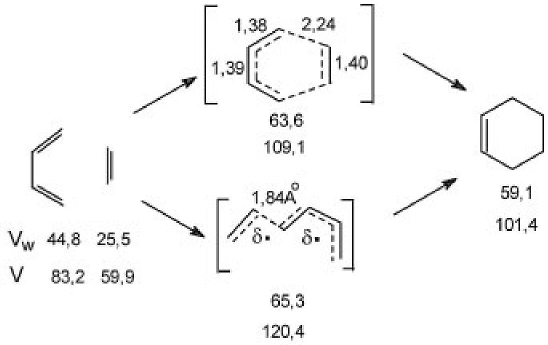
Table 5. Ionization potentials of solvents (IP/ eV), partial molar volume of tetracyanoethylene (V_{TCNE}/cm^3/mol), enthalpy of solution (ΔH_{sol}/kJ/mol) and solvation (ΔH_{solv}/kJ/mol), free energy (ΔG_{MC}/kJ/mol) of π,π-complex formation of TCNE with alkylbenzenes and the rate constants (k_2/L/mols) of the Diels–Alder reaction of TCNE with anthracene at 25 °C[117]

No	Solvent	IP	V_{TCNE}	ΔH_{sol}	$-\Delta H_{solv}$	$-\Delta G_{MC}$[a]	k_2
1	Chlorobenzene	9.10	109.2	23.1	58.1	−0.65	1.82
2	Benzene	9.25	108.4	14.9	66.3	1.72	0.38
2	Toluene	8.82	104.5	9.7	71.5	3.24	0.13
4	*o*-Xylene	8.58	102.1	1.4	79.8	4.81	0.061
5	*p*-Xylene	8.48	101.4	0	81.2	5.04	—
6	Mesitylene	8.14	98.1	−2.7	83.9	7.07	0.010
7	Acetonitrile	12.12	110.0	15.2	66.0	—	2.18
8	Ethyl acetate	9.54	112.1	9.2	72.0	—	0.24
9	Cyclohexanone	9.14	110.4	7.6	73.6	—	0.20
10	1,4-Dioxane	9.13	105.7	4.3	76.9	—	0.34
11	1,2-Dichloroethane	11.12	107.8	21.3	59.9	—	3.82
12	Dichloromethane	11.35	107.5	23.4	57.8	—	4.28

[a] Data from References [116].



Scheme 3.



$$\Delta V_w = 59{,}1 - (44{,}8+25{,}5) = -11{,}2\ \text{cm}^3\ \text{mol}^{-1}$$

$$\Delta V^{\#}_w = 63{,}6 - (44{,}8+25{,}5) = -6{,}7\ \text{cm}^3\ \text{mol}^{-1}\quad \text{(cyclic T.S.)}$$

$$\Delta V^{\#}_w = 65{,}3 - (44{,}8+25{,}5) = -5{,}0\ \text{cm}^3\ \text{mol}^{-1}\quad \text{(biradical T.S.)}$$

$$\delta\Delta V^{\#}_w = -1{,}7\ \text{cm}^3\ \text{mol}^{-1}$$

$$\Delta V_{r\text{-}n} = 101{,}4 - (83{,}2+59{,}9) = -41{,}7\ \text{cm}^3\ \text{mol}^{-1}$$

$$\Delta V^{\#} = 109{,}1 - (83{,}2+59{,}9) = -34{,}0\ \text{cm}^3\ \text{mol}^{-1}\ \text{(cyclic T.S.)}$$

$$\Delta V^{\#} = 120{,}4 - (83{,}2+59{,}9) = -22{,}7\ \text{cm}^3\ \text{mol}^{-1}\quad \text{(biradical T.S.)}$$

$$\delta\Delta V^{\#} = -11{,}3\ \text{cm}^3\ \text{mol}^{-1}$$

Scheme 4.

107,8 cm^3/mol ($-23.0 \pm 2.0\ \text{cm}^3$/mol), and third, from the difference between activation volumes for the direct ($-28.5\ \text{cm}^3$/mol) and reverse reactions ($-6.5\ \text{cm}^3$/mol) giving the same value ($-22.0 \pm 1.5\ \text{cm}^3$/mol).

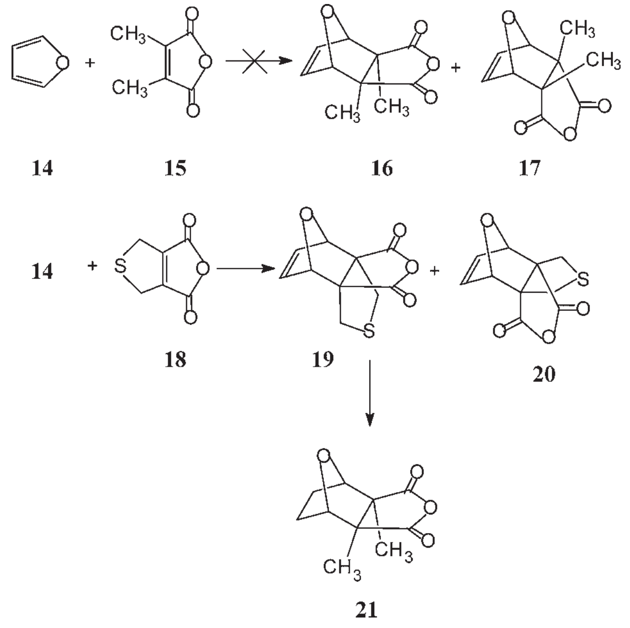
It is interesting to note that the activation of adduct decomposition is often accompanied by the volume decrease. This effect was explained[27,118] by contraction at the transformation of a sterically branched adduct structure in solution to a nearly planar structure of the transition state, in spite of some volume increase due to the loosening of two C—C bonds. The differences in the accessibility of the cavities of these states for the solvents should be taken into account as well.

At present, there exist a lot of papers on the activation volume and the DAR volume.[16,22,28–35,119] The reliability of the quantitative data on the rate and equilibrium of this non-polar process, excluding electrostriction, allows one to note that for the non-polar and isopolar processes the contribution of the intermolecular package sufficiently exceeds the change in the van der Waals volume.[16,30,120] In other words, these volume parameters are formed not only by the changes of the own volume of reagents (the change in the van der Waals volume) during the transition to the activated complex or to the adduct, but also due to the change of the volume of the intermolecular package during the reaction in solution.[30] The van der Waals volume of the DAR is rather constant and equals only -8–$10\ \text{cm}^3$/mol.[16,30,120] As an example, Klärner[16,30] has estimated the changes of the van der Waals volume and partial molar volume in solution for the reagents, transition state, and products for the reaction of ethylene with 1,3-butadiene. As it can be seen (Scheme 4), the van der Waals activation volume differs slightly both for the stepwise and concerted cyclic type of the transition state. In solution, the total change of the volume for the transition state ($\Delta V^{\neq}$) or product ($\Delta V_{r\text{-}n}$) for cyclic structures is much larger than that for acyclic structures.

The change of the volume of intermolecular voids in the course of reaction depends on the difference between the packing coefficients ($\eta = V_{w.}/V$) for the reagents, activated complex, and reaction products. The change in the packing coefficients during the reaction for small reactant molecules is usually higher than that for large molecules.[120,121] Therefore the activation and reaction volumes are more negative for reactions involving small reactant molecules. For reactions of dienophiles with cyclopentadiene and alkylbutadienes, the activation and reaction volumes are about -35–$40\ \text{cm}^3$/mol, while for reactions with anthracene derivatives, these parameters are only -20–$25\ \text{cm}^3$/mol. The reliable kinetic data for non-polar Diels–Alder reactions confirm unambiguously that such difference in the volume parameters is not due to media electrostriction, but is caused by the large difference in the packing coefficients of the reagents. El'yanov[122,123] proposed the valuable semi-empirical relations to recalculate the activation and reaction volumes to the standard temperature and pressure improving the reliability of conclusions about the reaction mechanisms and validity of the predictions of the pressure effect on the reaction rate and equilibrium. All these details should be taken in account when interpreting the reaction mechanism using data on the activation and reaction volumes.

Much experience has been accumulated in the successful application of elevated pressure for the synthesis of a large number of products otherwise difficult to prepare.[16,22,28,124] A typical example is the synthesis of cantharidin **21** (Scheme 5), a compound actively used for treating benign tumors.[124] The seemingly simple route for its synthesis according to the DAR between furan **14** and dimethylmaleic anhydride **15** with the formation of exo-adduct **16** followed by hydrogenation, cannot be implemented without using elevated pressure.

The thing is that the formation rate of the adducts **16** and **17** is extremely low, of about 10^{-10} L/mols at 25 °C.[90] The conventional ways to increase the reactivity are inapplicable in this case: at higher temperature the equilibrium shifts toward the reactants and furan polymerizes in the presence of Lewis acids. The product **16** was obtained in low yield only when the reaction proceeded at about 40 kbar with the increased reaction rate and equilibrium constants.[124] Later, a more convenient method to synthesize cantharidin by the DAR between furan and strained bicyclic dienophile **18** (Scheme 5) was found.[107] The enhanced tension of the double bond in such bicyclic dienophiles leads to a sharp increase of its activity in complete agreement with the relation Eqn (3). For example, the dianhydride of ethylenetetracarbonic acid cannot be isolated as a pure compound, whereas its stable adducts with some dienes are formed easily enough.[125,126] Therefore the reaction rate and stability of the products **19** and **20** appeared to be suitable for the synthesis at even milder conditions.[107]



Scheme 5.

CATALYZED DARs UNDER ELEVATED PRESSURE

Conducting the catalyzed processes at elevated pressure presents a special case. Since catalysis does not affect the process equilibrium, this combined action is fairly desirable for slow reversible reactions.

The enthalpies of the *n*,*v*-complex formation between the dienophiles and Lewis acids in solution were measured using calorimetric methods (Table 3).[24,80,81,84–90,101] It was found[24] that the catalytic effect of the DAR acceleration is proportional ($r = 0.985$) to the enthalpy of the complex formation (kJ/mol) between the dienophile and Lewis acid

$$\ln(k_{\text{cat.}}/k_{\text{noncat}}) = 0.19\Delta H_{\text{MC}} \qquad (15)$$

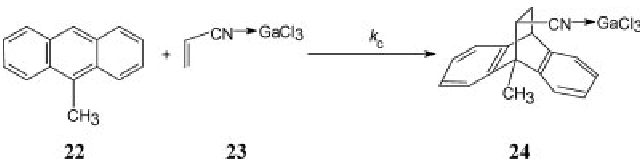
Due to the extremely high sensitivity of the acceleration effect in the catalytic reaction to the change in the bonding energy in the *n*,*v*-complex (Eqn (15)), it is the most convenient model for testing the possible changes of the bonding energy in this *n*,*v*-complex at elevated pressure. It should be noted that due to the high acceleration effect, the contribution of the reaction between diene and non-activated dienophile into the total reaction rate is usually substantially less than 1%. If the energy of the dienophile bonding with a Lewis acid at elevated pressure is increased, then the acceleration of the reaction will be caused not only by the $P\Delta V^{\#}$ contribution, as for the reaction without the Lewis acid, but additionally, by the increase of the dienophile activity in the *n*,*v*-complex at elevated pressure. It follows from the relations Eqns (11) and (15) that the growth of the bonding energy in the complex by only 1.0 kJ/mol at the pressure of 1 kbar is related to the additional change in the rate of the catalyzed reaction under pressure $[k_{\text{cat}}(p)/k_{\text{cat}}(p = 1)]$ equivalent to an additional decrease in the apparent value of the activation volume by 5 cm^3/mol. The modern barostats with direct monitoring of the reaction rate under pressure allow one to determine the activation volumes with an error of less than ±1 cm^3/mol.[30] The results of such measurements may serve as the experimental base for discussing the transformation or conservation of bonds in the activated complex due to elevated pressure. The interpretation of the rates of catalyzed reactions in *n*-donor solvents (e.g., acetonitrile, diethyl ether) is hampered by the redistribution of catalysts between the *n*-donor centers of the solvent and dienophile. Recently, it was shown[127] that the addition of only 0.5% (v/v) of dibutyl ether to a solution of reactants in 1,2-dichloroethane can suppress the $AlCl_3$-catalyzed DAR between 9,10-dimethylanthracene and maleic anhydride almost completely. This happens due to the catalyst being bound almost entirely into a complex with the ether, which is in large excess. Data on the influence of π- and *n*-donor solvents on the properties of π- and *v*-acceptors are given in Table 6.[128]

Data listed in Table 6 indicate that the π-donor solvents have an almost similar effect on the change of the partial molar volume and solvation enthalpy of a *v*-acceptor, gallium chloride, and a π-acceptor, tetracyanoethylene, but the interaction of gallium chloride with *n*-donor solvents is undoubtedly much stronger. These results (Table 6) show a weaker interaction of gallium chloride with benzene, toluene, and 1,2-dichloroethane. The pressure effect on the DAR rate between 9-methylanthracene **22** and acrylonitrile in the presence of gallium chloride **23** in toluene has been studied[129] as well (Scheme 6).

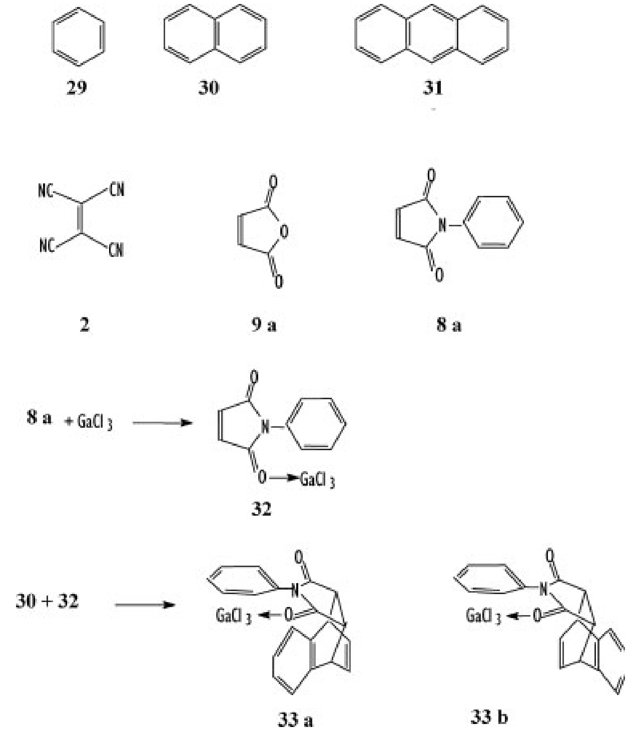
The activation volume of the catalyzed reaction was -16.9 ± 1.0 cm^3/mol.[129] The activation volume of the non-catalyzed process between acrylonitrile and 9,10-dimethylanthracene is -18.0 ± 1.0 cm^3/mol.[130] The same activation volumes for the conventional and catalyzed processes imply that the pressure

Table 6. Partial molar volumes (V/ cm^3/mol) and enthalpy of solution (ΔH_{sol}/kJ/mol) of gallium chloride ($GaCl_3$) and tetracyanoethylene (TCNE) in some solvents[128]

Solvent	$VGaCl_3$	$\Delta H_{\text{sol,GaCl3}}$	V_{TCNE}	$\Delta H_{\text{sol, TCNE}}$
Benzene	74.8 ± 0.1	9.6 ± 0.6	108.4 ± 0.3	14.9 ± 0.4
Toluene	68.7 ± 0.1	2.5 ± 0.6	104.5 ± 0.4	9.7 ± 0.5
o-Xylene	67.1 ± 0.1	−0.8 ± 0.4	102.1 ± 0.3	1.4 ± 0.1
Mesitilene	64.8 ± 0.4	−7.1 ± 0.6	98.1 ± 0.2	−2.7 ± 0.4
1.2-Dichloroethane	73.4 ± 0.4	5.1 ± 0.6	107.8 ± 0.2	21.3 ± 0.3
Ethyl acetate	60.7 ± 0.3	−65.7 ± 2.1	112.1 ± 0.1	9.2 ± 0.5
Acetonitrile	61.9 ± 0.3	−71.1 ± 2.0	110.0 ± 0.1	15.2 ± 0.2
1,4-Dioxane	61.5 ± 0.5	−74.0 ± 2.0	105.7 ± 0.2	4.3 ± 0.2



Scheme 6.



Scheme 7.

increase of up to 1 kbar does not lead to the bond strengthening in the *n,v*-complex formed by the dienophile and gallium chloride. These data can be regarded as an experimental proof that the bond character in the transition state of the reaction does not change upon the pressure increase of up to 1 kbar.

The same activation volumes are in line with the absence of solvent electrostriction that excludes the polar type of the transition state in the catalytic process.

It is interesting to note that the effect of the solvent electrostriction parameter $\partial(1/\varepsilon)/\partial p$ on the change of the partial molar volume of isolated ions of lithium perchlorate[131] is very large and exceeds the electrostriction effect of an ionic pair by more than 20 times.[131,132] For the DAR the electrostriction effect is close to zero.

CAUSE AND EFFECT

The quantitative consideration of the factors determining the reactivity of the addends in the DAR with normal electron demand (Eqn (3)) allows one to predict the rates of unstudied DARs, e.g., benzene (**29**) and naphthalene (**30**) with such dienophiles as tetracyanoethylene **2**, maleic anhydride **9a** and *N*-phenylmaleimide **8a** (Scheme 7). The enthalpy of these reactions can be estimated from the heat of 1,4-dihydroaddition to dienes **29** and **30,** all other parameters in Eqn (3) being known. As follows from the results of calculations presented in Table 7, DARs of these dienophiles with benzene are impossible due to kinetic and thermodynamic reasons, since their half-life is more than 300 years and the equilibrium adduct concentration is less than 10^{-3}%. The sufficiently larger rate and product yield should be expected for the reaction between naphthalene and *N*-phenylmaleimide.[133,134]

It is impossible to carry out this reaction (**30**+**8a**) at ambient temperature and pressure due to the very slow reaction rate ($\tau_{1/2} \sim$ 30 years, Table 7). However, in the presence of gallium chloride this reaction could be successfully carried out within a week.[133] In the catalyzed reaction (**30**+**8a**) at ambient temperature and pressure the only adduct with m.p. 206–208 °C (decomp.) was isolated. According to the X-ray analysis, it was the *exo*-isomer (**33b**, Fig. 9).[134]

Under elevated pressure[134] (8 kbar, 100 °C, 80 h) the reaction (**30**+**8a**) occurs with the formation of a mixture of *endo*- and *exo*-isomers (**33a**:**33b**) in the ratio of 30:70. In the reaction (**30**+**9a**) of naphthalene with maleic anhydride (7–11 kbar,

Table 7. Calculated parameters of Diels–Alder reactions of benzene (**29**), naphthalene (**30**), and anthracene (**31**) with tetracyanoethylene (**2**), maleic anhydride (**9a**), and *N*-phenylmaleimide (**8a**): enthalpies of reactions ($\Delta H_{\text{r-n}}$/kJ/mol), rate constants (k_2/L/mols), equilibrium constants (K_{eq}/L/mol), half-time of the reaction ($\tau_{0.5}$/s) at the initial concentrations of the reactants 0.5 and 5 mol/L and equilibrium conversion (α_{eq}, %) at 25 °C[134]

Reaction	$\Delta H_{\text{r-n}}$	$\lg k_2$	$\lg K_{eq}$	$\tau_{0.5}$	α_{eq}
29+**2**	$+17 \pm 4$	-10.8 ± 0.9	-10.6 ± 1.0	$9 \cdot 10^{9}$	$1 \cdot 10^{-(8\pm1)}$
29+**9a**	$+1 \pm 4$	-13.9 ± 0.9	-7.9 ± 1.0	$1 \cdot 10^{13}$	$6 \cdot 10^{-(6\pm0.5)}$
29+**8a**	-12 ± 4	-13.7 ± 0.9	-5.6 ± 1.0	$7 \cdot 10^{12}$	$(1\text{–}3) \cdot 10^{-3}$
30+**2**	-14 ± 4	-5.2 ± 0.9	-5.3 ± 1.0	$2 \cdot 10^{4}$	$2 \cdot 10^{-(3\pm0.5)}$
30+**9a**	-30 ± 4	-10.4 ± 0.9	-2.5 ± 1.0	$3.5 \cdot 10^{9}$	4 ± 2
30+**8a**	-43 ± 4	-9.9 ± 0.9	-0.3 ± 1.0	$1 \cdot 10^{9}$	70 ± 20
31+**2**	-77^{a}	0.48^{a}	5.5 ± 1.0	0.05	>99.9
31+**9a**	-93^{a}	-5.22^{a}	8.3 ± 1.0	$2.3 \cdot 10^{4}$	>99.9
31+**8a**	-106^{a}	-5.14^{a}	10.5 ± 1.0	$1.9 \cdot 10^{4}$	>99.9

[a] Experimental data from Table 1.

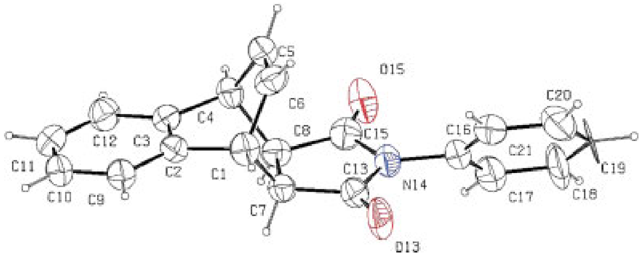


Figure 9. ORTEP structure of *exo*-adduct **33b** of naphthalene with *N*-phenylmaleimide

100 °C, 22 h, $CDCl_3$) two adducts were described as *endo*- and *exo*-isomers with the ratio of 35:65.[135]

CONCLUSIONS

Hence, in 80 years of the development of the DAR the significant progress in the elucidation of the factors determining the reactivity of the reagents and stability of the reaction products was achieved. The DAR has become a powerful method of synthesis of the valuable carbo- and heterocyclic products. The unambiguity of its behavior, availability, and reliability of the quantitative experimental data allowed finding a series of valuable regularities, which control the rate and equilibrium of the conventional and catalyzed processes at ambient and elevated pressure. These regularities provide a deeper understanding of the special features of this reaction and other processes in organic chemistry.

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