

Volume parameters of some Diels–Alder reactions involving C=C, C=S, and N=N bonds*

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The effect of a hydrostatic pressure of up to 1000 kg cm⁻² on the rate constants of the Diels–Alder reactions of maleic anhydride with 1,2,3,4-tetraphenylcyclopentadiene and with 6,13-dichloropentacene, of 4-phenyl-1,2,4-triazoline-3,5-dione with hexachlorocyclopentadiene, and of thiobenzophenone with isoprene was studied at 25 °C. The volume parameters and ratios of the activation to reaction volumes make it possible to exclude electrostriction of the solvent during transition state solvation in all the reactions studied, which corresponds to the nonpolar nature of the transition state.

Key words: Diels–Alder reactions, activation volumes, reaction volumes.

Elevated pressure facilitates substantially chemical processes if the volume of the system decreases during the reaction. The origin of a volume change is not the main problem for practical purpose. However, the use of volume parameters of the reaction to refine the reaction mechanism requires information on the contributions that form these volume parameters. The factors that affect the activation volume (ΔV^\ddagger) and Diels–Alder reaction volume (ΔV) have been considered earlier.^{1–4} These volume parameters can be determined from the dependence of the rate (k) or equilibrium (K) constant on the pressure (p).

$$(\partial \ln k / \partial p)_T = -1/RT(\partial G^\ddagger / \partial p)_T = -\Delta V^\ddagger / RT \quad (1)$$

$$(\partial \ln K / \partial p)_T = -1/RT(\partial G / \partial p)_T = -\Delta V / RT \quad (2)$$

Real and imaginary changes in the volume parameters should be distinguished. Real values of the volume parameters are caused by the general volume changes in the system (addends, transition state, and solvents) and include changes of the intrinsic (van der Waals, ΔV_W) volumes due to the bond redistribution and changes in intermolecular volumes (ΔV_{sol}) in the solvate shell of the corresponding states (reactants, transition state, products). The reaction volume values can be obtained both by Eq. (2) and directly from the difference between partial molar volumes (PMVs) of the products and reactants. The activation volumes can be calculated only using the dependence (1). If an elevated pressure can induce a change in the properties of the system, which, in turn,

affects the free activation or reaction energy, then the volume parameter values including the imaginary contributions can be obtained from Eqs (1) and (2). With a pressure increase, the rate (k) or equilibrium (K) constants can change due to the energy $p \cdot \Delta V^\ddagger$ or $p \cdot \Delta V$ and pressure-induced changes: in the dielectric constant of the medium,³ concentration of active species in the catalytic process,⁵ and viscosity of the medium to a level of the diffusionaly controlled rate of the process.^{4,6}

Two new C–C bonds are consistently formed in a nonpolar Diels–Alder reaction. However, the values of the activation and reaction volumes can strongly differ (from -15 to -40 cm³ mol⁻¹), depending on the size and structure of the reactants.⁷ The formation of the products from the reactants with elevated packing coefficients ($\eta = V_W/V$) was found⁸ to be usually accompanied by a weak increase in this parameter, while an increase in the packing coefficients on going to the adducts is much higher in the reactions involving "loose" reactants. The observed reaction volume (ΔV) by more than a factor of 2 exceeds the van der Waals reaction volume ΔV_W due to an additional contribution caused by a change in the volume of intermolecular cavities.^{1,2,7,8} This has recently been confirmed experimentally by a comparison of the volumes of several Diels–Alder reactions in the solid phase and in solutions.⁹ The intrinsic volume of the Diels–Alder reaction determined by the difference in the van der Waals volumes V_W of the products and reactants is rather constant (-8 ± 2 cm³ mol⁻¹) for all types of reactants. The contribution of a change in the volume of intermolecular cavities to the observed reaction volume ranges from -10 to -30 cm³ mol⁻¹, *i.e.*, up to 50–75% of the total volume effect.^{1,2,8–10} It is clear that this tendency in changing the

* Dedicated to Academician A. L. Buchachenko on the occasion of his 70th birthday.

packing coefficients and volume parameters should also be observed in reactions with the polar transition state. However, the superimposition of the electrostriction of the solvent and a high sensitivity of the rate of polar and ionic processes to a pressure-induced change in the dielectric constant of the medium considerably impedes this analysis.

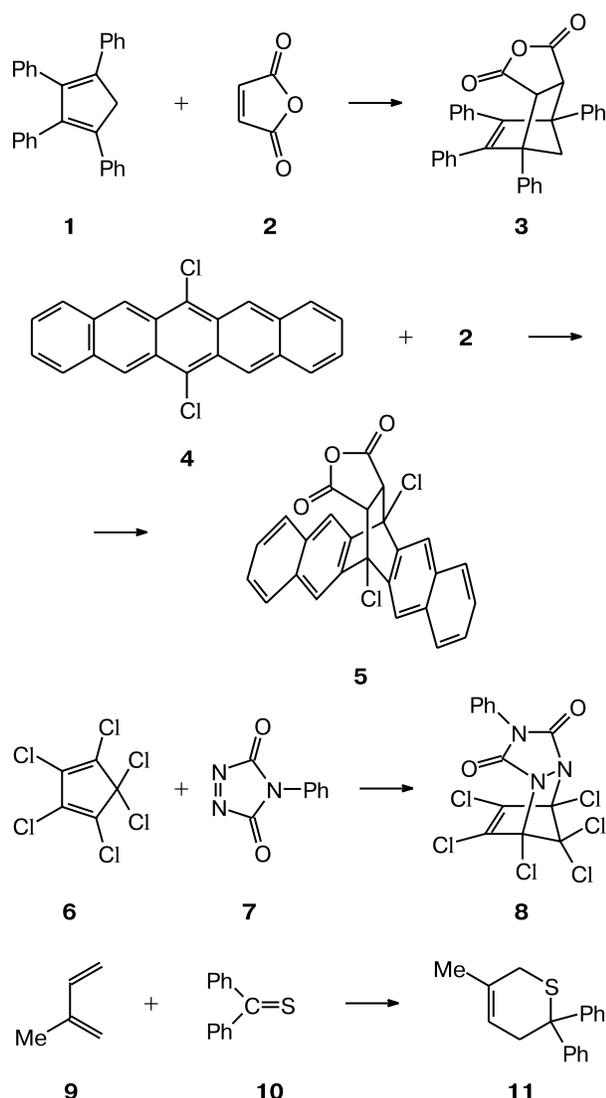
Results and Discussion

In this work, we determined the volume parameters of four Diels–Alder reactions involving dienes and dienophiles of different nature (Scheme 1): π -donor dienes, *viz.*, 1,2,3,4-tetraphenylcyclopentadiene (**1**) and 6,13-dichloropentacene (**4**), with maleic anhydride (**2**); π -acceptor diene, *viz.*, hexachlorocyclopentadiene (**6**), with

4-phenyl-1,2,4-triazoline-3,5-dione (**7**); and isoprene (**9**) with thiobenzophenone (**10**). The data obtained make it possible to monitor changes in the packing coefficients of the addends and their effect on the activation and reaction volumes and the influence of dienophiles with the C=C, N=N, and C=S bonds on the volume parameters in the Diels–Alder reaction.

Reaction of 1,2,3,4-tetraphenylcyclopentadiene (1) with maleic anhydride (2). Tetraalkylcyclopentadienes usually exist as a mixture of isomers of the C=C bond position due to the easy 1,5-hydrogen shift.¹¹ Substituents increasing the conjugation energy facilitate an increase in the fraction of more stable 1,2,3,4-substituted cyclopentadiene. Although the phenyl fragments in diene **1** are shifted from the plane of the cyclopentadiene ring, it can be assumed that its conjugation energy is much higher than that in the unsubstituted cyclopentadiene. The equilibrium constant in the reaction of diene **1** with maleic anhydride is higher and, hence, more difficult for determination. The reaction with the more conjugated dienophile, *viz.*, tetracyanoethylene, in 1,2-dichloroethane at 25 °C is rather fast ($k_2 = 96 \pm 5 \text{ L mol}^{-1} \text{ s}^{-1}$) and equilibrium ($K_{\text{eq}} = 2140 \pm 100 \text{ L mol}^{-1}$). The enthalpy of the reaction of tetracyanoethylene with diene **1** in 1,2-dichloroethane was determined by calorimetric measurements and equals $-57.8 \pm 0.7 \text{ kJ mol}^{-1}$. The calculated entropy of the reaction ($-130 \text{ J mol}^{-1} \text{ K}^{-1}$) is typical of the Diels–Alder reaction. It seems useful to compare the rate constants ($k_2/\text{L mol}^{-1} \text{ s}^{-1}$), equilibrium constants ($K_{\text{eq}}/\text{L mol}^{-1}$), and enthalpies ($\Delta H/\text{kJ mol}^{-1}$) in the Diels–Alder reactions of tetracyanoethylene with several dienes under these conditions (25 °C, 1,2-dichloroethane).

Scheme 1



Diene	k_2	K_{eq}	ΔH
Cyclopentadiene ¹²	$5 \cdot 10^3$	$\geq 10^{12}$	-113
1,2,3,4-Tetraphenylcyclopentadiene	96	$2.1 \cdot 10^3$	-58
Hexachlorocyclopentadiene ¹²	—	~ 4	-42
Isoprene ¹²	0.074	$\geq 10^{20}$	-166

For the reaction of 1,2,3,4-tetraphenylcyclopentadiene with maleic anhydride, the equilibrium constant can be estimated as $3 \cdot 10^6 \text{ L mol}^{-1}$, based on the reaction enthalpy¹² -76 kJ mol^{-1} and with allowance for the reaction entropy $-130 \text{ J mol}^{-1} \text{ K}^{-1}$. The resulting data on the pressure effect on the rate of the reaction of diene **1** with maleic anhydride are given in Table 1.

The dependence of the reaction rate on the external pressure is described (Fig. 1) by the linear equation (3) ($r = 0.9981$; $n = 6$).

$$\ln k_2 = (-8.27 \pm 0.02) + (1.02 \pm 0.01) \cdot 10^{-3} p \quad (3)$$

An additional increase in the reaction rate under an elevated pressure due to an increase in the concentrations in the compressed solvent results in an overestimation (by

Table 1. Effect of the pressure (p) on the rate constant (k_2) of the Diels–Alder reaction of 1,2,3,4-tetraphenylcyclopentadiene (**1**) with maleic anhydride (**2**) in 1,2-dichloroethane at 25 °C

$p/\text{kg cm}^{-2}$	$k_2 \cdot 10^4/\text{L mol}^{-1} \text{s}^{-1}$	$-\ln k_2$
1	2.61	8.25
300	3.39	7.99
350	3.56	7.94
490	4.35	7.74
850	6.17	7.39
1005	7.24	7.23

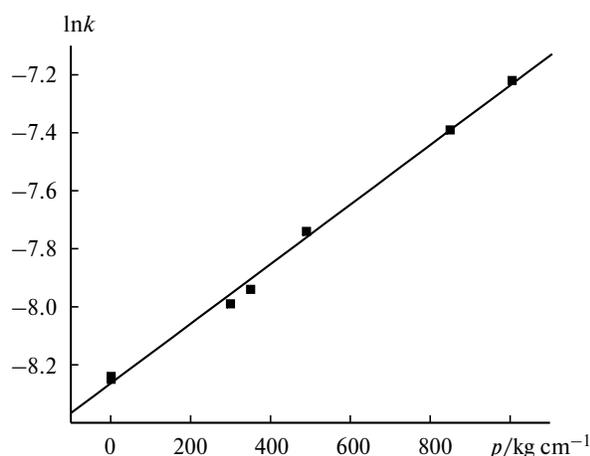


Fig. 1. Plot of $\ln k$ vs. external pressure (p) for the Diels–Alder reaction of 1,2,3,4-tetraphenylcyclopentadiene (**1**) with maleic anhydride (**2**) in 1,2-dichloroethane at 25 °C.

modulus) of the experimental value of the activation volume ($-25.8 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$) by a value of $\Delta n \cdot \beta RT$

$$\Delta V_{\text{corr}}^{\ddagger} = \Delta V_{\text{exp}}^{\ddagger} + \Delta n \cdot \beta RT, \quad (4)$$

where $\Delta n = -1$ is the change in the number of moles during the reaction; $\beta = -7.9 \cdot 10^{-5} \text{ bar}^{-1}$ is the compressibility coefficient of 1,2-dichloroethane;¹³ $R = 84.78 \text{ cm}^3 \text{ kg cm}^{-2} \text{ K}^{-1} \text{ mol}^{-1}$; T/K is temperature. The corrected activation volume in the reaction between reactants **1** and **2** is $-23.8 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$. In the calculation of the reaction volume from the difference between the PMVs of the products and reactants, all errors are summated, which can result in an uncertainty of $\pm(2-3) \text{ cm}^3 \text{ mol}^{-1}$ for the reactions involving large-volume molecules. The kinetic method for determination of the reaction volume by a change in the density of the solution of the reactants needs no data on the PMVs and, therefore, is more exact. The volume of the solution of the reactants can be presented by Eqs (5) and (6)

$$V_t = V_S + (C_A^0 - C_P)V_A + (C_B^0 - C_P)V_B + C_P V_P, \quad (5)$$

$$V_t = [V_S + (C_A^0 V_A + C_B^0 V_B)] + C_P(V_P - V_A - V_B) = V_{t=0} + C_P \Delta V, \quad (6)$$

where $V_{t=0}$ and V_t are the initial and current volumes of the solution of the reactants at the moment t ; V_S is the solvent volume; V_A , V_B , and V_P are the partial molar volumes of the reactants (A and B) and product (P); C_A^0 , C_B^0 , and C_P are the initial molar concentrations of the reactants and the concentration of the reaction product at the moment t ; ΔV is the reaction volume.

Dilatometric measurements of volume changes in time (Eq. (6)) usually need comparatively large volumes of concentrated solutions. To analyze the density data for the reaction in the resonating tube of a precision densimeter, it seems more convenient to transform Eq. (6) into (7).

$$1/d_t = 1/d_{t=0} + C_P \Delta V / 1000 d_{t=0} \quad (7)$$

The reaction volume determined from the difference of the PMVs of adduct **3** ($372.2 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$), diene **1** ($334.8 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$), and dienophile **2** ($72.0 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$) is $-34.6 \pm 1.9 \text{ cm}^3 \text{ mol}^{-1}$. Well reproducible results of the reaction volume with an average value of $-32.9 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ were obtained in three series of measurements of the density of solutions of the reactants in time (Fig. 2).

The coefficient θ ($\theta = \Delta V_{\text{corr}}^{\ddagger} / \Delta V = -23.8 / -32.9 = 0.72$) allows one to believe that the transition state vol-

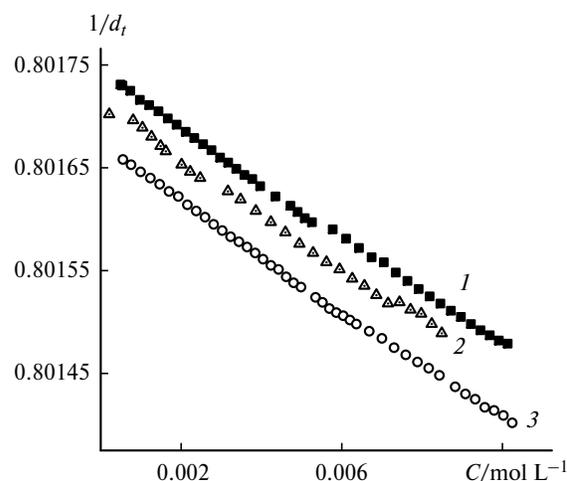


Fig. 2. Anamorphoses of the density of a solution of reactants **1** and **2** during the formation of adduct **3** in 1,2-dichloroethane at 25 °C in measurement series 1–3:

Series	C_1^0	C_2^0	r	$sd \cdot 10^6$	n	ΔV / $\text{cm}^3 \text{ mol}^{-1}$
	mol L ⁻¹					
1	0.01867	0.2116	0.9994	2.6	42	-32.8 ± 0.2
2	0.01826	0.2128	0.9980	4.4	27	-32.9 ± 0.4
3	0.01846	0.2198	0.9993	2.9	44	-33.1 ± 0.2

ume ($383 \text{ cm}^3 \text{ mol}^{-1}$) is closer to the volume of the reaction product **3** ($372 \text{ cm}^3 \text{ mol}^{-1}$) than to that of the reactants ($407 \text{ cm}^3 \text{ mol}^{-1}$). It should be mentioned that the further decrease in the volume of the system, when the transition state moves to the reaction products, is mainly caused by a decrease in the intermolecular cavities. Similar volume parameters were obtained¹⁴ for the reaction of 1,2,3,4-tetrachlorocyclopentadiene with methyl acrylate in 1-chlorobutane at $40 \text{ }^\circ\text{C}$ ($\theta = -24.6/-33.2 = 0.74$).

Reaction of 6,13-dichloropentacene (4) with maleic anhydride (2). The solubility of diene **4** in chlorobenzene at $25 \text{ }^\circ\text{C}$ is higher ($\sim 5 \cdot 10^{-4} \text{ mol L}^{-1}$) than in 1,2-dichloroethane and toluene and is sufficient for monitoring the reaction rate by a change in the diene absorption. The data on the pressure effect on this reaction rate are presented in Table 2.

The dependence of the reaction rate on the external pressure (Fig. 3) is described by Eq. (8) ($r = 0.9955$; $n = 13$).

$$\ln k_2 = (-5.993 \pm 0.013) + (8.872 \pm 0.067) \cdot 10^{-4} p \quad (8)$$

The experimental value of the activation volume ($-22.4 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$) with the correction for a concentration increase with the pressure growth ($\beta RT = 1.9 \text{ cm}^3 \text{ mol}^{-1}$, for chlorobenzene¹³ $\beta = -7.45 \cdot 10^{-5} \text{ bar}^{-1}$) results in the activation volume in the reaction between reactants **4** and **2** equal to $-20.5 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$. A similar activation volume ($-22.7 + 2.5 = -20.2 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$) has been obtained previously¹⁵ for the Diels–Alder reaction between maleic anhydride and 9,10-dimethylantracene in acetonitrile at $25 \text{ }^\circ\text{C}$. The volume of the reaction between reactants **4** and **2** was not determined because of the low solubility of diene **4**. The ratio of the activation and reaction volumes for the reaction of dienophile **2** with 9,10-dimethylantracene ($\theta = -20.2/-23.6 = 0.856$) cor-

Table 2. Effect of the pressure (p) on the rate constant (k_2) of the Diels–Alder reaction of 6,13-dichloropentacene (**4**) with maleic anhydride (**2**) in chlorobenzene at $25 \text{ }^\circ\text{C}$

$p/\text{kg cm}^{-2}$	$k_2 \cdot 10^3/\text{L mol}^{-1} \text{ s}^{-1}$	$-\ln k_2$
1	2.57	5.964
170	2.86	5.857
185	2.91	5.839
250	3.04	5.796
275	3.22	5.738
400	3.52	5.649
470	3.63	5.619
515	4.07	5.504
640	4.40	5.426
640	4.53	5.397
680	4.65	5.371
820	5.14	5.271
900	5.46	5.210

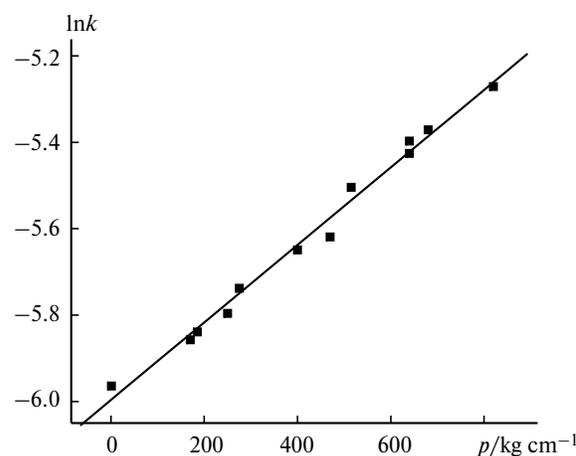


Fig. 3. Plot of $\ln k$ vs. external pressure (p) for the Diels–Alder reaction of 6,13-dichloropentacene (**4**) with maleic anhydride (**2**) in chlorobenzene at $25 \text{ }^\circ\text{C}$.

responds to the Diels–Alder reaction with the nonpolar transition state.¹⁵ Note that the absolute values of the volume parameters of the Diels–Alder reaction of dienophile **2** with "loose" alkylbutadienes are almost twofold higher (-35 – $-45 \text{ cm}^3 \text{ mol}^{-1}$).¹⁴

Reaction of hexachlorocyclopentadiene (6) with 4-phenyl-1,2,4-triazoline-3,5-dione (7). It is known that hexachlorocyclopentadiene (**6**) is a π -acceptor diene and, hence, is more reactive in the reactions with π -donor dienophiles.¹⁶ The rates of the most part of the earlier studied Diels–Alder reactions of diene **6** with acyclic and cyclic dienophiles are rather low. Therefore, the activation volumes were calculated from the data obtained at elevated temperatures (50 – $100 \text{ }^\circ\text{C}$), whereas the reaction volumes were determined^{14,17,18} at $25 \text{ }^\circ\text{C}$. The rate constant and enthalpy for the reaction between reactants **6** and **2**¹² at $25 \text{ }^\circ\text{C}$ are $1.1 \cdot 10^{-8} \text{ L mol}^{-1} \text{ s}^{-1}$ and -58 kJ mol^{-1} , and for reactants **6** and **7**^{12,16} they are $1.84 \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ and -77 kJ mol^{-1} , respectively. For comparison, these parameters at $25 \text{ }^\circ\text{C}$ in the reaction of cyclopentadiene with dienophile **2**¹² are equal to $9.1 \cdot 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ and -129 kJ mol^{-1} , and those in the reaction with dienophile **7**^{12,16} are $2.0 \cdot 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ and -148 kJ mol^{-1} , respectively. It follows¹² from the difference in the enthalpies of the reactions of several dienes with the common nucleophile that the conjugation energy in hexachlorocyclopentadiene is by 71 kJ mol^{-1} higher than that in cyclopentadiene and by 14 kJ mol^{-1} higher than that in 1,2,3,4-tetraphenylcyclopentadiene.

The data obtained for the pressure effect on the reaction rate of reactants **6** and **7** are given in Table 3.

The dependence of the reaction rate on the external pressure (Fig. 4) is described by Eq. (9) ($r = 0.9964$; $n = 9$)

$$\ln k_2 = (-6.29 \pm 0.02) + (1.04 \pm 0.01) \cdot 10^{-3} p. \quad (9)$$

Table 3. Effect of the pressure (p) on the rate constant (k_2) of the Diels–Alder reaction of hexachlorocyclopentadiene (**6**) with 4-phenyl-1,2,4-triazoline-3,5-dione (**7**) in 1,2-dichloroethane at 25 °C

$p/\text{kg cm}^{-2}$	$k_2 \cdot 10^3/\text{L mol}^{-1} \text{s}^{-1}$	$-\ln k_2$
1	1.84	6.30
320	2.55	5.97
410	2.74	5.90
490	3.09	5.78
590	3.51	5.65
705	4.02	5.52
810	4.35	5.44
910	4.58	5.39
950	4.87	5.32

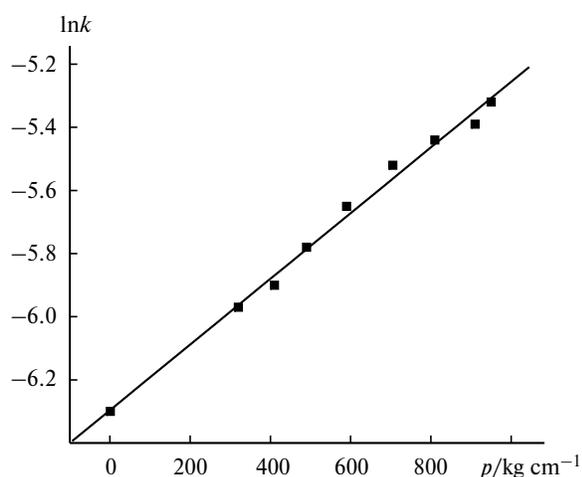


Fig. 4. Plot of $\ln k$ vs. external pressure (p) for the Diels–Alder reaction of hexachlorocyclopentadiene (**6**) with 4-phenyl-1,2,4-triazoline-3,5-dione (**7**) in 1,2-dichloroethane at 25 °C.

The activation volume corrected by the βRT value for the reaction between reactants **6** and **7** is $-24.2 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$.

The reaction volume determined from the difference between the PMVs of adduct **8** ($271.5 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$), diene **6** ($162.1 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$), and dienophile **7** ($131.5 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$), which is equal to $-22.1 \pm 2.5 \text{ cm}^3 \text{ mol}^{-1}$, is inferior in accuracy to the value determined from the dependence of the density of a solution of the reaction mixture on the concentration of the adduct that formed (Eq. (7)). The reaction volumes were calculated using these measurements (Fig. 5).

Based on the obtained values of the reaction volume ΔV , we calculated the ratio of the volume parameters ($\theta = \Delta V^{\ddagger}/\Delta V$) as equal to 0.964.

Two chlorine atoms at the C(5) atom in hexachlorocyclopentadiene (**6**) prevent a dienophile from approaching at the both sides of the diene. We have found¹⁹ a similar effect in the Diels–Alder reaction involving

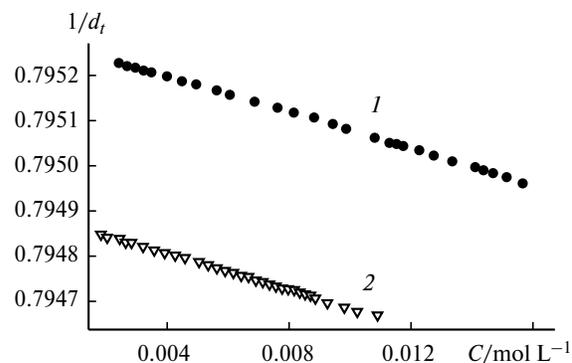


Fig. 5. Anamorphoses of the density of a solution of reactants **6** and **7** during the formation of adduct **8** in 1,2-dichloroethane at 25 °C in measurement series *1* and *2*:

Se- ries	C_6^0	C_7^0	r	$sd \cdot 10^6$	n	ΔV / $\text{cm}^3 \text{ mol}^{-1}$
	mol L^{-1}					
<i>1</i>	0.1633	0.01838	0.9997	2.1	28	-25.0 ± 0.1
<i>2</i>	0.1681	0.01360	0.9993	2.0	32	-25.2 ± 0.2

hexamethylcyclopentadiene. This hindrance is absent in 1,2,3,4-tetraphenylcyclopentadiene (**1**). The activation volumes in the reactions between reactants **1** and **2** ($-23.8 \text{ cm}^3 \text{ mol}^{-1}$) and **6** and **7** ($-24.2 \text{ cm}^3 \text{ mol}^{-1}$) are commensurable. However, the substantial difference between the volumes of these reactions (-32.9 and $-25.1 \text{ cm}^3 \text{ mol}^{-1}$), which considerably exceeds measurement errors, corresponds to a significantly loosened molar volume of adduct **8**, probably, due to steric loads caused by the geminal chlorine atoms at the C(5) atom.

Reaction of isoprene (**9**) with thiobenzophenone (**10**).

The reaction was studied in toluene at 25 °C. The reactivity of the C=S bond in dienophile **10** and the stability of its adducts are much lower than those in the case of the N=N bond in dienophile **7**. Taking into account the asymmetry of the C=S bond, we can assume some asynchronous character for bond formation in the transition state of the reaction. This asymmetry should be manifested in the electrostriction of the solvent and an elevated (by modulus) activation volume, which can be checked experimentally. The data on the pressure effect on the Diels–Alder reaction rate between reactants **9** and **10** are presented in Table 4.

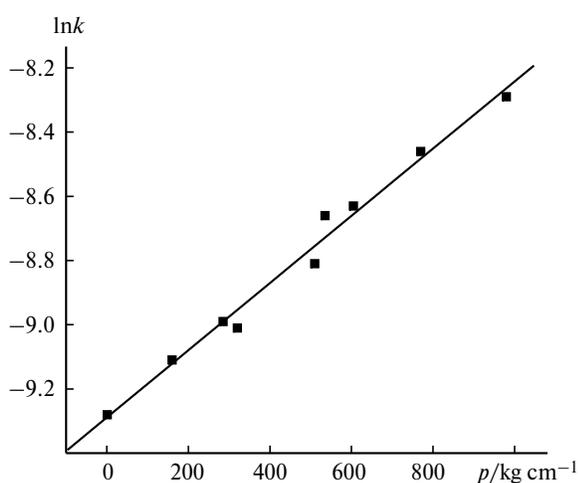
The dependence of the reaction rate on the external pressure (Fig. 6) is described by the linear equation (10) ($r = 0.9921$; $n = 9$)

$$\ln k_2 = (-9.289 \pm 0.027) + (1.050 \pm 0.051) \cdot 10^{-4} p. \quad (10)$$

The experimental activation volume ($-26.5 \pm 1.2 \text{ cm}^3 \text{ mol}^{-1}$) with allowance for the solvent compression (the β coefficient for toluene is equal¹³ to $-8.96 \cdot 10^{-5} \text{ bar}^{-1}$) gives a corrected activation volume in

Table 4. Effect of the pressure (p) on the rate constant (k_2) of the Diels–Alder reaction of isoprene (**9**) with thiobenzophenone (**10**) in toluene at 25 °C

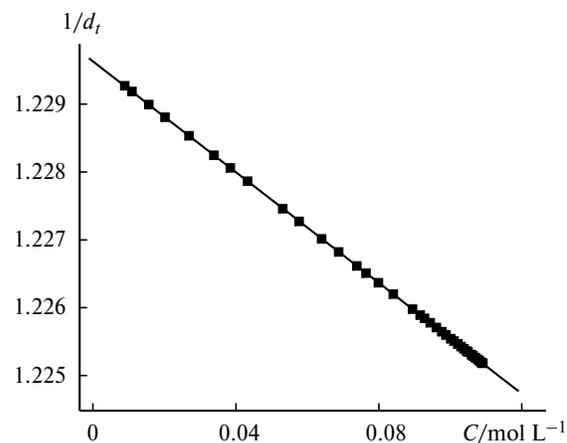
$p/\text{kg cm}^{-2}$	$k_2 \cdot 10^4/\text{L mol}^{-1} \text{s}^{-1}$	$-\ln k_2$
1	0.932	9.28
160	1.10	9.11
285	1.24	8.99
320	1.22	9.01
510	1.49	8.81
535	1.73	8.66
605	1.78	8.63
770	2.11	8.46
980	2.51	8.29

**Fig. 6.** Plot of $\ln k$ vs. external pressure (p) for the Diels–Alder reaction of thiobenzophenone (**10**) with isoprene (**9**) in toluene at 25 °C.

the reaction between reactants **9** and **10** of $-24.3 \pm 1.2 \text{ cm}^3 \text{ mol}^{-1}$. The volume of this reaction determined from the kinetic dependence (Fig. 7) is $-33.2 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$. The reaction volume was also calculated from the data on the density of the reaction mixture obtained at the moment of mixing the reactants and after the reaction was completed, being $-33.8 \text{ cm}^3 \text{ mol}^{-1}$.

* * *

It has previously been shown^{2,8} that the activation volume for the Diels–Alder reaction with consistent bond formation in the cyclic transition state should be by approximately $15 \text{ cm}^3 \text{ mol}^{-1}$ more negative than that of the radical process of successive bond formation (two-step mechanism). The activation volumes obtained in this work for all the four studied Diels–Alder reactions involving C=C, N=N, and C=S bonds of dienophiles with π -donor (**1**, **4**, **9**) and π -acceptor (**6**) dienes are almost equal (Table 5). No correlation is observed, on the one hand,

**Fig. 7.** Anamorphosis of the density of a solution of reactants **9**, **10** during the formation of adduct **11** in toluene at 25 °C, $C_{10}^0 = 0.1099 \text{ mol L}^{-1}$, $C_9^0 = 2.4164 \text{ mol L}^{-1}$, $r = 0.9999$, $sd = 1.1 \cdot 10^{-6}$, $n = 38$, $\Delta V = -33.2 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$.

between changes in the reactivity of the studied series of reactants and the stability of their adducts and, on the other hand, changes in the activation volumes and the reaction volumes. This corresponds to the fact that the energy and volume profiles are formed under the influence of different factors. Even great differences in the energy of orbital interaction of reacting atoms do not

Table 5. Intrinsic (V_W) and partial molar volumes (V) of compounds, their packing coefficients ($\eta = V_W/V$), and activation (ΔV^\ddagger) and reaction volumes (ΔV_W , ΔV) at 25 °C

Com- pound	V_W $\text{cm}^3 \text{ mol}^{-1}$	V $\text{cm}^3 \text{ mol}^{-1}$	η	ΔV_W^a $/\text{cm}^3 \text{ mol}^{-1}$	$\Delta V^\ddagger/\Delta V$
1 ^b	227.3	334.8	0.679	-6.6	$-23.8/-32.9 = 0.72$
2 ^b	48.4	72.0	0.672	-6.6	
3 ^b	269.1	372.2	0.723	-6.6	
6 ^b	101.1	162.1	0.624	-6.8	$-24.2/-25.1 = 0.96$
7 ^b	90.0	131.5	0.684	-6.8	
8 ^b	184.3	272.5	0.676	-6.8	
9 ^c	52.9	100.3	0.528	-6.8	$-24.3/-33.5 = 0.73$
10 ^c	116.9	—	—	-6.8	
11 ^c	163.0	—	—	-6.8	
2 ^d	48.4	70.4	0.687	-8.3	$-20.2/-23.6 = 0.86$
12 ^d	129.6	187.2	0.692	-8.3	
13 ^d	169.7	232.2	0.731	-8.3	

^a The ΔV_W value for the reaction **2** + **4** \rightarrow **5**: $223.8 - (48.4 + 183.8) = -8.4 \text{ cm}^3 \text{ mol}^{-1}$.

^b In 1,2-dichloroethane.

^c In toluene.

^d The data¹⁵ for the reaction of maleic anhydride (**2**) with 9,10-dimethylanthracene (**12**) with formation of cycloadduct **13** in acetonitrile. The volume of this reaction calculated by the difference between the PMVs is $-25.4 \pm 2.5 \text{ cm}^3 \text{ mol}^{-1}$, and that calculated from a change in the solution density in time is $-23.6 \pm 0.16 \text{ cm}^3 \text{ mol}^{-1}$.¹⁵

determine volume changes in the reaction. This agrees completely with the conclusion² that the increase in the absolute value of the activation volume over the reaction volume ($\theta = \Delta V^\ddagger/\Delta V > 1$) cannot be explained by the energy of interaction of secondary orbitals. The van der Waals reaction volumes reflecting the change in the system volume upon the formation of new bonds are almost the same for all reactions (see Table 5) and do not exceed 27% of the reaction volume. A great difference in the volume parameters is caused by different changes in the packing coefficients ($\eta = V_W/V$) during the reaction. It should be assumed that the molar volume of the transition state can be smaller than the molar volume of the adduct ($\theta = \Delta V^\ddagger/\Delta V > 1$) despite partial bond formation only because of a more compact parallel arrangement of the molecules. This is confirmed by examples of negative activation volumes for the reactions of adduct decomposition.^{3,18} Note that a more exact determination of the volume parameters (the same temperature, solvent, introduction of corrections for compressibility, kinetic method of determination of the reaction volume) decreases considerably the number of these examples ($\theta > 1$) but does not exclude them completely.

Based on the obtained values of the volume parameters, we cannot assume that the mechanism of the Diels–Alder reaction involving the N=N and C=S bonds differs from the concert mechanism in the Diels–Alder reaction involving the C=C bonds.

Experimental

Reagents and solvents. Hexachlorocyclopentadiene (Aldrich) was purified by distillation *in vacuo* (118 °C (2 kPa), $n_D^{20} = 1.5660$; *cf.* Ref. 20: $n_D^{20} = 1.5652$). 1,2,3,4-Tetraphenylcyclopentadiene (Aldrich) was recrystallized from a benzene–ethanol (1 : 4) mixture, m.p. 178–179 °C (*cf.* Ref. 21: m.p. 178 °C). 6,13-Dichloropentacene (m.p. 297–300 °C; *cf.* Ref. 22: m.p. 300 °C) was used without additional purification. 4-Phenyl-1,2,4-triazoline-3,5-dione (**7**) was synthesized by a known method²³ and purified by sublimation at 100 °C (20 Pa), m.p. 180 °C (decomp.) (*cf.* Ref. 23: m.p. 180 °C). The spectral purity of dienophile **7** was checked from the absence of the final absorption of its solution after the end of the reaction with excess *trans,trans*-1,4-diphenylbutadiene and from the absorption coefficient of sublimed dienophile **7** (186.2 at 527 nm, dioxane, 25 °C). Thiobenzophenone (**10**) was synthesized by a known method²⁴ and purified by distillation *in vacuo* at 100 Pa, m.p. 51–53 °C (*cf.* Ref. 24: m.p. 53 °C). Maleic anhydride was distilled and additionally purified by recrystallization from a benzene–hexane (1 : 6) mixture. Solvents were purified according to known procedures.²⁵

Kinetic measurements. The reaction rates of formation of adduct **3** were monitored by a change in the absorption (SF-46 and Specord UV–VIS spectrometers) of diene **1** at 400–420 nm, $C_0 (1–3) \cdot 10^{-3} \text{ mol L}^{-1}$; adduct **5**, from a change in the absorption of diene **4** at 565–570 nm, $C_0 (1–2) \cdot 10^{-4} \text{ mol L}^{-1}$; adduct **8**, from a change in the absorption of dienophile **7** at

565–585 nm, $C_0 (1–2) \cdot 10^{-2} \text{ mol L}^{-1}$; and adduct **11**, from a change in the absorption of dienophile **10** at 620–660 nm, $C_0 (1.0–1.5) \cdot 10^{-2} \text{ mol L}^{-1}$. The other components of the reactions were transparent in these spectral regions.

Kinetic measurements under an elevated pressure were carried out in a high-pressure temperature-controlled optical cell placed in the cell compartment of a Specord UV–VIS spectrophotometer. In all measurements, more than a 20-fold excess of an optically transparent reactant was used. Isooctane was used as the pressure-transmitting medium. The apparatus and procedure for measuring reaction rates at an elevated pressure have been described earlier.³

Apparent molar volumes (φ_A) of the compounds in a solution were calculated using the equation (11)

$$\varphi_A = 1000(d_0 - d)/m_A \cdot d \cdot d_0 + M_A/d, \quad (11)$$

where m_A is the molality of the solution, d and d_0 are the densities of the solution and solvent, and M_A is the molar weight of the solute.

It is more reliable to determine the partial molar volume (V_A) from the concentration dependence. For this purpose, Eq. (11) was transformed into (12).

$$(1000 + m_A M_A)/d = V_A m_A + 1000/d_0 \quad (12)$$

The angular coefficient of the dependence of $(1000 + m_A M_A)/d$ on m_A is equal to V_A .

The order of operation of a DMA-602 precision densimeter has been described previously.³ The temperature of the resonating tube was maintained with deviations of $\pm 2 \cdot 10^{-3} \text{ °C}$.

The data on the change in the density of solutions of the reactants with the conversion at least 50% were used for the kinetic method of calculation of the reaction volumes (Eq. (7)). The experimental plots are presented in Figs 2, 5, and 7. In several cases, it was more convenient to determine the reaction volumes from the data on a change in the density of the reaction mixture at the completion of the process. Here only the data on the concentration of the reactant taken in deficiency are additionally needed. The change in the density of a solution of the reactants was determined in an interval of 20–30 min and extrapolated to the moment of preparation of the solution. Then this solution of the reactants was left in the tube of a densimeter until the reaction was completely ceased. In parallel, the initial solution of the reactants in a sealed vessel was stored to the completion of the reaction ($\geq 99\%$, UV monitoring), and then its density was determined. A good correspondence of the reaction volumes indicates the absence of side processes. The kinetic method (Eq. (7)) makes it possible to determine the reaction volume with a considerably smaller error.

The equilibrium constant of the reaction between diene **1** and tetracyanoethylene ($K = 2140 \text{ L mol}^{-1}$) was calculated from the data on the absorption of diene **1** before the reaction and after equilibration in 1,2-dichloroethane at 25 °C. The initial concentration of diene **1** was equal to $(3.5–5.5) \cdot 10^{-4} \text{ mol L}^{-1}$, and that of tetracyanoethylene was $(2–10) \cdot 10^{-3} \text{ mol L}^{-1}$. The change in the absorption of diene **1** at 390–400 nm was 70–80%. The enthalpy of the reaction between these reactants in 1,2-dichloroethane at 25 °C was calculated from the data on the thermal effect of the reaction ($-27.2 \pm 0.7 \text{ kJ mol}^{-1}$) for the mixing of a weighed sample of crystals of diene **1** with a solution of tetracyanoethylene (0.021 mol L⁻¹) in 1,2-dichloroethane

(153 mL) in the calorimeter cell and the heat of dissolution ($30.6 \pm 0.5 \text{ kJ mol}^{-1}$) of crystalline diene **1** in 1,2-dichloroethane.

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