

Activation and Reaction Volumes for [4 + 2] and [3 + 2] Additions Involving Maleic Anhydride

V. D. Kiselev, G. G. Iskhakova, E. A. Kashaeva, M. S. Shikhab,
M. D. Medvedeva, and A. I. Kononov

Butlerov Research Chemical Institute, Kazan State University, Kazan, Tatarstan, Russia

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Abstract—The partial molar volumes of reactants and products of the [3+2] addition of *C*-(*p*-nitrophenyl)-*N*-phenylnitron to maleic anhydride and of the [4+2] addition of 9,10-dimethylantracene to the same dienophile were determined, and the reaction volumes were calculated. A new method was suggested for determining the reaction volume. The activation volumes of both reactions were calculated from the dependences of the reaction rates on the external pressure. The volume parameters of the reactions involving the reagents of close size are close. The ratios of the activation volumes to the reaction volumes are unity, which suggests a common concerted mechanism of the reactions. Factors that could be responsible for significant changes in the absolute values of the reaction volume parameters are discussed.

Addition of Lewis acids as catalysts accelerates cycloadditions by a factor of up to 10^6 without affecting the position of the equilibrium [1]. For exothermic reactions, the rate constants usually grow with increasing temperature, but the equilibrium constants, on the contrary, decrease. With conjugated reagents, the reactions are often slow and reversible. Apparently, neither variation of catalyst nor heating can ensure complete conversion.

For reactions accompanied by a decrease in the volume of the system, application of elevated external pressure, firstly, accelerates the process and, secondly, shifts the equilibrium toward reaction products [2–6]. From the pressure (p) dependences of the rate (k) and equilibrium (K) constants [Eqs. (1), (2)], one can calculate the activation volume (ΔV^\ddagger) and reaction volume (ΔV_0):

$$(d \ln k / dp)_{T, \varepsilon, d, \eta} = -1/RT(d \Delta G^\ddagger / dp)_{T, \varepsilon, d, \eta} = -\Delta V^\ddagger / RT, \quad (1)$$

$$(d \ln K / dp)_{T, \varepsilon, d, \eta} = -1/RT(d \Delta G / dp)_{T, \varepsilon, d, \eta} = -\Delta V_0 / RT. \quad (2)$$

Here, R is the gas constant; T , temperature; ΔG^\ddagger and ΔG , activation and reaction free energies, respectively; ε , dielectric constant; d , density; and η , viscosity of the medium.

Knowledge of the activation volume can furnish additional information on the volume of the activated complex, and the ratio $\theta = \Delta V^\ddagger / \Delta V_0$ can be considered as a criterion of the position of the transition state on the reaction coordinate [2–6]. Relationships (1)

and (2) are strictly valid for systems in which variation of the free energy with increasing pressure is due to the $p\Delta V$ contribution only. The isothermal conditions in the course of elevating pressure can be readily ensured, but it is impossible to keep constant the dielectric permittivity, density, viscosity, and other properties of solvent. In this connection, questions arise: To what extent do the experimentally determined volume parameters of a process [Eqs. (1), (2)] correspond to the true values [7–9]? If elevated pressure induces additional changes in the reaction rate and position of the equilibrium, due to changes in the properties of the medium, all the effects of the external pressure on the rate and position of the equilibrium of the reaction should be summed up. Each process, even at atmospheric pressure, is characterized by its specific activation and reaction volumes. These parameters include structural (van der Waals volumes) and solvation (contraction of the solvation shell and change in the volume of cavities) constituents. With increasing pressure, the dielectric permittivity of the medium always increases [2, 3], and this factor causes the rates of reactions with an ionic or a polar transition state to additionally increase (apart from the effect of the $p\Delta V$ factor). This may result in overestimated (in the absolute value) activation and reaction volumes. Such an analysis was made for the Menshutkin reaction and for [2+2] cycloaddition [7, 8]. It should be noted that the calculated additional contributions [7, 8] are not associated with electrostriction of the medium; this factor makes its contribution even when the reaction is performed under normal conditions.

In solvation of ionic species, the solvent undergoes electrostriction as a result of a significant energy of electrostatic interaction of charges with the medium. This is experimentally confirmed by unexpectedly low and even negative partial molar volumes of a number of salts in aqueous solutions [10]. In dissociation of an ion pair in weakly polar media to solvated ions, the observed negative activation volume is virtually exclusively due to the change in the dielectric permittivity of the medium, induced by elevated pressure [11]. The positive activation volume of a fast diffusion-controlled reverse reaction of recombination of solvated ions to an ion pair is due to an increase in the viscosity with increasing hydrostatic pressure [11]. We have shown recently that the effect of the medium on the reaction and activation volume parameters can be strong for nonpolar processes also, if the solvent interacts with one of the states [12–15].

The reaction volume can be determined from the difference between the partial molar volumes of the products and reactants at normal pressure and can be compared with a value calculated from the pressure dependence of the position of the equilibrium [Eq. (2)], whereas the only way to determine the activation volume is to calculate it from the pressure dependence of the reaction rate [Eq. (1)]. The contribution of electrostriction can be evaluated more reliably from the variation of the partial molar volumes of ionic compounds in a series of solvents. Unfortunately, for salts in nonpolar and low-polarity media such data are lacking, because the solubility in these systems is insufficient for measurements [11].

If with increasing pressure the solvent viscosity grows to such an extent that the reaction becomes diffusion-controlled, the experimental dependence of $\ln k$ on p can pass through a maximum [16]. On the contrary, there are indications that the reaction rate in n -alkanes slightly grows with increasing viscosity, i.e., under conditions far from diffusion control [17]. The latter effect is assigned to processes that occur faster in a solvent cage. Since the viscosity of a medium always grows with increasing pressure, it was suggested that this effect additionally contributes to the experimental dependence of $\ln k$ on p for a series of [4+2] and [3+2] cycloadditions [9]. However, the validity of this generalization is subject to active discussions [18, 19], because the influence of viscosity on reaction rate is weak and irregular.

Comparison of the reaction volumes determined from relationship (2) and from the difference between the partial molar volumes revealed their good agreement [2, 7]. It should be noted that, if the elevated pressure induces additional changes in the activation

free energy due to changes in the state of the activated complex (but not reactants and products), then, according to the microscopic reversibility principle, these contributions should be equal for the forward and reverse processes. Therefore, when calculating the reaction volume as the difference between the activation volumes of the forward and reverse processes, the possible additional contributions are canceled.

Additional effects can also contribute to the temperature dependences of the activation and reaction free energies [20, 21]. Since solvent properties usually vary in opposite directions with increasing pressure and temperature, the sums of contributions can differ in sign. The necessity of considering possible additional contributions is dictated by experimental data that the activation volume of the nonpolar Diels–Alder reaction can be more negative than the reaction volume [2–7, 12]. No convincing arguments have been suggested to explain the relationship $\theta = \Delta V^\ddagger/\Delta V > 1$.

For concerted Diels–Alder reactions involving such dienes as cyclopentadiene and substituted butadienes, the activation volumes usually range from -35 to $-45 \text{ cm}^3 \text{ mol}^{-1}$ [4–6]. For [3+2] cycloadditions, these parameters are approximately two times smaller in the absolute value [22–24], which could suggest a two-step mechanism of this process [25, 26]. However, this fact is insufficient for such conclusions. The stereospecificity of [3+2] additions, weak solvent effect, and large negative activation entropy—all these facts suggest a single-step concerted mechanism [27].

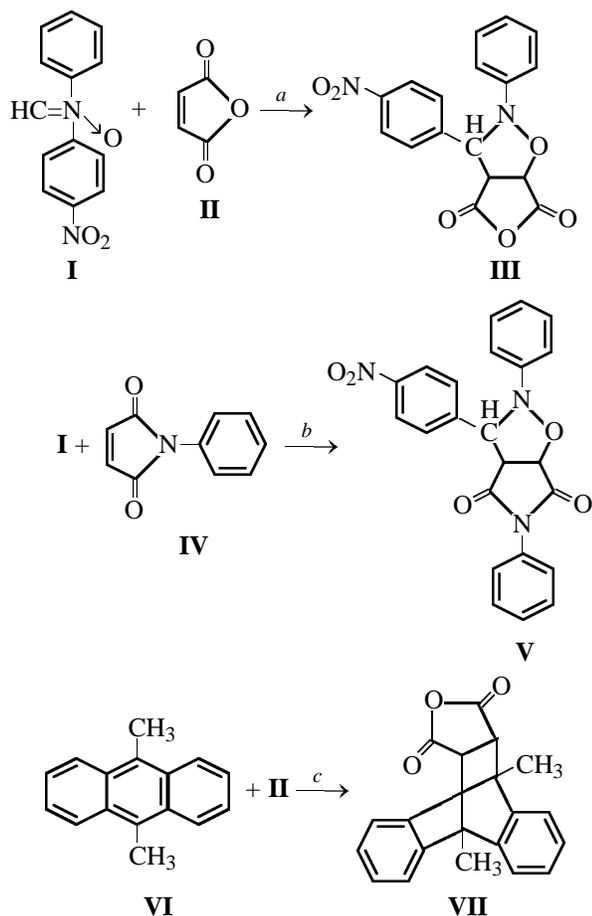
In our recent papers [7, 12, 15], we discussed the causes of significant differences in the activation and reaction volumes for a nonpolar Diels–Alder reaction. In reactions of tetracyanoethylene with dienes, in going from cyclopentadiene or substituted butadienes to substituted anthracenes, the activation and reaction volumes decrease in absolute value by $20 \text{ cm}^3 \text{ mol}^{-1}$, i.e., almost by half [12, 15]. There are no experimental grounds to suggest a two-step mechanism of the Diels–Alder reaction with substituted anthracenes [1]. Such a difference in the volume parameters may be due either to larger changes in the packing coefficients of the pertinent states in reactions involving small reactant molecules, as compared to the reactions with large molecules [22, 23], or to a relative increase in the partial molar volume of the activated complex and adduct with anthracene [12, 15]. In the latter case, the structure is sterically branched and may contain internal cavities inaccessible for solvating molecules [12, 15]. An additional contribution can be made by the difference in the size of the forming ring. With equal other effects, the volume parameters of [3+2] addi-

Table 1. Solvent effect on the rate of [3+2] addition of *C,N*-diphenylnitrone to *N*-(*p*-bromophenyl)maleimide [reaction (d)] and on the rate of Diels–Alder reaction (c) of 9,10-dimethylantracene with maleic anhydride at 298.2 K

Solvent	Viscosity, cP	ϵ	1000 <i>k</i> , l mol ⁻¹ s ⁻¹	
			reaction (d)	reaction (c)
Acetone	0.306	20.7	2.41	9.2
Dimethylformamide	0.794	38.2	2.12	11.1
Chloroform	0.537	4.81	2.30	70.0
Acetonitrile	0.369	37.5	2.04	24.4
1,4-Dioxane	1.177	2.21	4.94	12.0
Benzene	0.604	2.28	8.66	21.6

tions with formation of a five-membered ring should be less negative than those of [4+2] additions with formation of a six-membered ring [28].

In this work, we determined the volume parameters of the [3+2] addition of nitrone **I** and of the [4+2] addition of 9,10-dimethylantracene **VI** to maleic



anhydride **II** (see scheme). These particular 1,3-dipole and diene were chosen because of their close partial molar volumes. Data on the solvent effect on the reaction rates are given in Table 1.

These data show that there is no correlation between the rates of both reactions and the viscosity or dielectric permittivity of the solvent. The solvent effect is weak and irregular. A noticeable difference is observed only in chloroform. Formation of a hydrogen bond between chloroform and the lone electron pair of the activating groups in dienophiles favors higher stability of the transition state of [4+2] addition [1]. In [3+2] addition, a strong hydrogen bond with the nitrone oxygen atom is additionally formed, decreasing the energy levels of both the reactants and the transition state. Data on the solvent effect on the heat of solution of maleic anhydride and on its partial molar volume are given in Table 2.

Table 2 shows that, for tetracyanoethylene, the partial molar volume and the rate of the Diels–Alder reaction appreciably decrease with increasing solvation energy in the series of alkylbenzenes. Tetracyanoethylene exhibits a strong π -acceptor power (electron affinity *EA* 2.88 eV), which results in significant changes in the volume and energy parameters depending on solvent [1, 12]. Strong intermolecular interaction of the reactants is responsible for the negative temperature coefficient in the reaction of 9,10-dimethylantracene with tetracyanoethylene [20], in contrast to the reactions with maleic anhydride (*EA* 0.97 eV) and *N*-phenylmaleimide (*EA* 0.89 eV) [1]. In the reaction of maleic anhydride with isoprene, the activation volume (-38.5 ± 1 cm³ mol⁻¹) and reaction volume (-35.5 ± 1 cm³ mol⁻¹) in a series of solvents varied in narrow ranges [29].

Reaction (a). Data on the influence of pressure on the rate of reaction (a) in toluene are summarized in Table 3.

The function $\ln(k_p/k_{p=1}) = f(p)$ (Fig. 1) is linear: $\ln(k_p/k_{p=1}) = (2.384 \pm 1.218) \times 10^{-2} + (7.220 \pm 0.059) \times 10^{-4}p$, r 0.9963, n 11. The calculated activation volume for reaction (a) in toluene is -18.2 ± 0.2 cm³ mol⁻¹.

The volume of reaction (a) in toluene at 298.2 K was determined as the difference between the partial molar volumes of adduct **III** (233.3 ± 0.9 cm³ mol⁻¹) and reactants: nitrone **I** (179.6 ± 0.5 cm³ mol⁻¹) and maleic anhydride **II** (71.1 ± 0.2 cm³ mol⁻¹); it is equal to -17.4 ± 1.6 cm³ mol⁻¹. The relatively large error (9%) in determination of the reaction volume is due to the fact that this quantity is the difference of large quantities. The low solubility of the adduct often

Table 2. Heats of solution ($\Delta_{\text{sol}}H$, kJ mol⁻¹), partial molar volumes (V , cm³ mol⁻¹), and rate constants (k , l mol⁻¹ s⁻¹) of the Diels–Alder reactions of maleic anhydride and tetracyanoethylene in a series of solvents at 25°C

Solvent	Maleic anhydride			Tetracyanoethylene ^a		
	$\Delta_{\text{sol}}H$	V	$k \times 10^3$ ^b	$\Delta_{\text{sol}}H$	V	k ^c
Benzene	16.8 ± 0.5	72.2 ± 0.3	21.6	14.9	108.4	0.38
Toluene	16.4 ± 0.4	71.1 ± 0.2	19.2	9.7	104.6	0.13
<i>o</i> -Xylene	15.1 ± 0.5	71.5 ± 0.2	–	1.4	102.1	0.061
Mesitylene	–	70.8 ± 0.5	–	–2.7	98.1	0.010
Acetonitrile	13.1 ± 0.4	70.4 ± 0.1, 69.8 ^d , 70.0 ^e	25.8	15.2	108.7	2.18
Nitromethane	12.6 ± 0.5	72.4 ^d	30.2	–	–	–
Dichloromethane	15.9 ± 0.5	71.1 ^d	–	23.4	107.5	4.28
Acetone	11.3 ± 0.4	69.4 ^d	9.2	–	–	–

^a Data for tetracyanoethylene were taken from [12]. ^b Rate constants of reaction with 9,10-dimethylanthracene. ^c Rate constants of reaction with anthracene [12]. ^d Data of [29] for 308.2 K. ^e Data of [24].

introduces an additional error. We suggest another method for calculating the reaction volume without using partial molar volumes of the reactants and products. The method is as follows. The volume of solution of reactants (A, B) and product (P) at time t is given by

$$V_t = V_S + (c_A^0 - c_P)V_A + (c_B^0 - c_P)V_B + c_P V_P, \quad (3)$$

$$\begin{aligned} V_t &= [V_S(c_A^0 V_A + c_B^0 V_B) + c_P(V_P - V_A - V_B)] \\ &= V_{t=0} + c_P \Delta V_0. \end{aligned} \quad (4)$$

Here, $V_{t=0}$ and V_t are the initial and current (at time t) solution volumes, respectively; V_S , solvent volume; V_A , V_B , and V_P , partial molar volumes of reactants A and B and product P, respectively; c_A^0 , c_B^0 , and c_P , initial molar concentrations of reactants and product concentration at time t , respectively; and ΔV_0 , reaction volume.

With a precision dilatometer, it is possible to calculate the reaction volume from the dependence of $V_t - V_{t=0}$ on c_P using relationship (4). When measuring the solution densities, it is more convenient to use relationships (5) and (6) taking into account that the solution weight M does not change in the reaction.

$$M/d_t = M/d_{t=0} + c_P \Delta V_0, \quad (5)$$

$$1/d_t = 1/d_{t=0} + c_P \Delta V_0 / (1000 d_{t=0}). \quad (6)$$

Here, as in the kinetic measurements, the only simplification is the assumption that variation of the solution volume in the course of the reaction does not affect the concentrations of components. However, this factor introduces only a small error (<0.1%) in

determining the reaction volume, and it can be taken into account, if necessary, in a repeated calculation. From the results of precision measurements of the density of the reaction solution in time and from the rate constant of the reaction at the same temperature, it is possible to calculate the reaction volume (ΔV_0) from the dependence of $1/d_t$ on c_P [Eq. (6)]. The volume of reaction (a) in toluene at 298.2 K, calculated by this method, is -18.2 ± 0.3 cm³ mol⁻¹. Thus, the activation volume (-18.2 ± 0.2 cm³ mol⁻¹) and the reaction volumes determined as the difference of the partial molar volumes (-17.4 ± 1.6 cm³ mol⁻¹) and by relationship (6) (-18.2 ± 0.3 cm³ mol⁻¹) are virtually equal.

Table 3. Influence of external pressure on the rate of 1,3-dipolar cycloaddition of *C*-(*p*-nitrophenyl)-*N*-phenylnitronone **I** to maleic anhydride **II** in toluene at 298.2 K

p , kg cm ⁻²	$k_p \times 10^4$, l mol ⁻¹ s ⁻¹	$\ln k_p / k_{p=1}$	r^a	n^a
1	2.32	0	0.99988	15
130	2.62	0.122	0.99992	14
230	2.94	0.237	0.99987	14
350	3.00	0.257	0.99986	26
450	3.25	0.337	0.99997	27
595	3.69	0.464	0.99999	23
680	3.92	0.525	0.99990	17
745	4.00	0.545	0.99999	23
795	4.19	0.591	0.99990	19
915	4.67	0.699	0.99992	22
985	4.80	0.727	0.99995	21

^a (r) Correlation coefficient of the kinetic dependence and (n) number of experimental points.

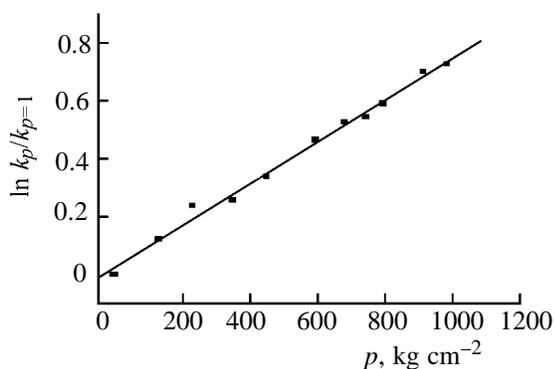


Fig. 1. Rate constant [$\ln(k_p/k_{p=1})$] of the the [3+2] addition of *C*-(*p*-nitrophenyl)-*N*-phenylnitrone to maleic anhydride in toluene at 298.2 K as a function of external pressure.

Since the extent of charge separation in a 1,3-dipole decreases upon adduct formation, the reaction volume could be expected to regularly change in going from less polar to more polar solvents [2–6]. It is commonly believed [2, 3] that the electrostriction of low-polarity solvents with a lower cohesion energy density and usually with a higher isothermal compressibility coefficient causes a stronger decrease in the partial molar volumes, compared to polar media. This assumption was put forward to explain the more negative activation volume in low-polarity solvents for a series of reactions with a highly polar transition state [30]. Here, at least two effects are superimposed. First, more polar solvents certainly interact with a charge more strongly, forming a stronger and more compact solvation packing. On the other hand, polar solvents containing heteroatoms are usually “packed” themselves more tightly than nonpolar solvents [23]. As already noted, the experimental values of the activa-

Table 4. Kinetic data for Diels–Alder reaction (c) of 9,10-dimethylantracene **VI** with maleic anhydride **II** in acetonitrile at 298.2 K and various pressures

p , kg/cm ²	$k_p \times 10^2$, l mol ⁻¹ s ⁻¹	$\ln k_p/k_{p=1}$	r	n
1	2.58	0	0.99983	24
300	3.32	0.252	0.99962	18
400	3.54	0.316	0.99986	22
495	4.09	0.461	0.99981	17
525	3.96	0.428	0.99990	20
650	4.41	0.536	0.99993	21
700	4.87	0.635	0.99988	18
730	4.89	0.639	0.99994	30
885	5.60	0.775	0.99980	22
900	6.00	0.844	0.99981	21
980	6.00	0.844	0.99998	30

tion volumes of ionic reactions can include additional contributions originating from variation of the solvent properties with increasing pressure, whereas the partial molar volumes of polar and some ionic compounds can be determined under normal pressure. However, the available direct experimental data on variation of the partial molar volumes of polar compounds in a series of solvents [31] do not confirm the suggested decrease in the partial molar volumes in low-polarity solvents. The low solubility of the majority of salts in nonpolar media excludes direct measurement of their partial molar volumes [11]. For lithium perchlorate, the partial molar volume in a series of solvents does not correlate with the enthalpy of its solvation, cohesion energy, and compressibility coefficient of the solvent [32]. Thus, the factors affecting the partial molar volumes in solvents are numerous and remain to be fully elucidated.

The volume of reaction (a) in acetonitrile at 298.2 K was determined as the difference between the partial molar volume of the adduct (224.8 ± 0.6 cm³ mol⁻¹) and those of the nitrone ($175. \pm 0.7$ cm³ mol⁻¹) plus maleic anhydride (70.4 ± 0.4 cm³ mol⁻¹). It should be noted that, in acetonitrile, the partial molar volumes of all the reaction participants are noticeably smaller than in toluene (233.3, 179.6, and 71.1, respectively), but the reaction volume in acetonitrile (-20.9 ± 1.3 cm³ mol⁻¹) differs from that in toluene insignificantly. The volume of reaction (a) in DMSO was determined from the results of kinetic and densimetric measurements at 298.2 K [Eq. (6)] to be -19.2 ± 0.1 cm³ mol⁻¹. The molar volume of 1,3-dipole **I** in DMSO is 186.8 ± 0.1 cm³ mol⁻¹.

Reaction (b). Adduct **V** is poorly soluble in toluene, which prevented kinetic measurements at elevated pressure and determination of the reaction volume as the difference between the partial molar volumes of the product and reactants. On the other hand, at normal pressure adduct **V** does not precipitate from solution containing **I** and **IV** until its concentration of 5×10^{-3} M is attained. From relationship (6), we calculated the reaction volume in toluene (-17.4 ± 0.5 cm³ mol⁻¹) and DMSO (-19.9 ± 0.1 cm³ mol⁻¹).

Reaction (c). To compare the volume parameters of [3+2] and [4+2] cycloadditions, we studied reaction (c) (see scheme) of maleic anhydride with 9,10-dimethylantracene **VI**.

The effect of pressure on the reaction rate (Table 4) is described by a linear dependence $\ln(k_p/k_{p=1}) = (-1.717 \pm 1.938) \times 10^{-2} + (9.015 \pm 0.088) \times 10^{-4} p$, r 0.9947, n 11 (Fig. 2). From this dependence, the activation volume of reaction (c) can be determined as -22.7 ± 0.2 cm³ mol⁻¹.

Table 5. Volume characteristics ($\text{cm}^3 \text{mol}^{-1}$) of reaction (a) of nitrone **I** with maleic anhydride **II**, reaction (b) of nitrone **I** with *N*-phenylmaleimide **IV**, and reaction (c) of 9,10-dimethylanthracene **VI** with maleic anhydride **II** in solvents at 298.2 K

Reaction	Solvent	Partial molar volumes of compounds			$-\Delta V_0$	$-\Delta V^\ddagger$
(a)	Toluene	179.6±0.5 (I)	71.1±0.2 (II)	233.3±0.9 (III)	19.4±1.6 ^a	18.2±0.2
	CH ₃ CN	175.3±0.7 (I)	70.4±0.4 (II)	224.8±0.6 (III)	20.9±1.3 ^a	
	DMSO	186.8±0.5 (I)			19.2±0.1 ^b	
(c)	CH ₃ CN	187.2±1.1 (VI)	70.4±0.4 (II)	232.2±1.3 (VII)	25.4±2.5 ^a	22.7±0.2

^a Calculated as the difference between the partial molar volumes of the product and reactants. ^b Calculated by Eq. (6). For reaction (a) in toluene, this calculation gives $\Delta V_0 -18.2 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$; for reaction (b) in toluene, $-17.4 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$, and in DMSO, $-19.9 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$; and for reaction (c) in acetonitrile, $-23.6 \pm 0.16 \text{ cm}^3 \text{ mol}^{-1}$.

Table 6. Influence of the packing coefficient $\eta = V_{\text{W}}/V$ on the volume ($\text{cm}^3 \text{mol}^{-1}$) of the Diels–Alder reaction of maleic anhydride **II** with isoprene **VIII** to form 2-methylcyclohexene-4,5-dicarboxylic anhydride **IX** and with 9,10-dimethylanthracene **VI** to form adduct **VII**

Parameter	Reaction of maleic anhydride with isoprene				Reaction of maleic anhydride with 9,10-dimethylanthracene			
	V_{II}	V_{VIII}	V_{IX}	ΔV	V_{II}	V_{VI}	V_{VII}	ΔV
η	0.69	0.53	0.68		0.69	0.69	0.73	
V	70	100	135	-35	70	187	232	-25
V_{H}	21.6	47.1	47.0	-26	21.6	57.2	62.3	-16.5
V_{W}^{a}	48.4	52.9	92.3	-9.0	48.4	129.8	169.8	-8.5

^a Calculated by the MOLVOL program.

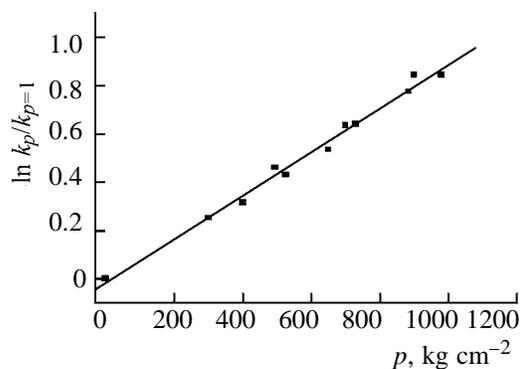
The volume of reaction (c) in acetonitrile, calculated from the partial molar volumes of adduct **VII** ($232.2 \pm 1.3 \text{ cm}^3 \text{ mol}^{-1}$), maleic anhydride ($70.4 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$), and diene **VI** ($187.2 \pm 1.1 \text{ cm}^3 \text{ mol}^{-1}$), is $-25.4 \pm 2.5 \text{ cm}^3 \text{ mol}^{-1}$. Again, the large relative error (10%), as in reaction (a), is due to the fact that the reaction volume is the difference of large quantities. From the dependence of the reaction mixture density on the conversion [Eq. (6)], the volume of this reaction in acetonitrile can be determined as $-23.63 \pm 0.16 \text{ cm}^3 \text{ mol}^{-1}$. The repeated measurement gave $-23.50 \pm 0.15 \text{ cm}^3 \text{ mol}^{-1}$.

The volume parameters obtained are listed in Table 5. In [3+2] cycloaddition (a) in toluene, the ratio of the activation volume ($-18.2 \text{ cm}^3 \text{ mol}^{-1}$) to the reaction volume ($-18.2 \text{ cm}^3 \text{ mol}^{-1}$) is unity. For Diels–Alder reaction (c) in acetone, this ratio is also close to unity: $(-22.7 \text{ cm}^3 \text{ mol}^{-1})/(-23.6 \text{ cm}^3 \text{ mol}^{-1}) = 0.96$.

The volume parameter of reactions (a) and (c) differ by only $4\text{--}5 \text{ cm}^3 \text{ mol}^{-1}$. It should be noted that, although in the activated complex, as compared to the product, the bonds are formed only partially, the partial molar volumes of the activated complex and product are virtually equal in both reactions.

The known volume effects in 1,3-dipolar additions involving diphenyldiazomethane [22–24] and *C*-benzoyl-*N*-phenylnitron [24] are close to the values given in Table 5.

The contributions of changes in the van der Waals volumes to the total activation and reaction volumes are considered in [22, 23, 28, 33]. According to different estimates, these contributions are much less than 50%. The coefficient of molecular packing in solution

**Fig. 2.** Rate constant [$\ln(k_p/k_{p=1})$] of the [4+2] addition of 9,10-dimethylanthracene to maleic anhydride in acetonitrile at 298.2 K as a function of external pressure.

η is defined as the ratio of the own (van der Waals) volume (V_W) to the total partial molar volume (V): $\eta = V_W/V$. An important consequence following from the dependence of η on the molecular size is that a sharp growth of η (from 0 to 0.65) should be expected only in the range of partial molar volumes of up to 150–200 cm³ mol⁻¹ [22, 23, 28]. The partial molar volumes of 9,10-dimethylantracene and *C*-(*p*-nitrophenyl)-*N*-phenylnitronone appeared to be fairly close (Table 5) and considerably larger than the partial molar volumes of cyclopentadiene (81 cm³ mol⁻¹) and butadiene (82 cm³ mol⁻¹) [12]. Based on data from [22, 23, 28, 33], we can estimate the contribution to the volume (ΔV_0) of the Diels–Alder reaction of maleic anhydride with isoprene and 9,10-dimethylantracene (Table 6), made by the change in the volume of intermolecular cavities ($\Delta V_{0,H}$): $\Delta V_0 = \Delta V_{0,H} + \Delta V_{0,W}$.

The contribution from the change in the van der Waals volume ($\Delta V_{0,W}$), –8 to –10 cm³ mol⁻¹, agrees with data of [22, 23]. The major contribution to the experimental reaction volume (ΔV_0) can be made by the change in the volume of intermolecular cavities ($\Delta V_{0,H}$), which, within this concept, should approach the limiting value, from –15 to –20 cm³ mol⁻¹, at further increase in the partial molar volumes of the reactants.

Thus, replacement of low-polarity toluene (ϵ 2.4) by acetonitrile (ϵ 36.6) and DMSO (ϵ 47.2) results in irregular changes in the partial molar volumes of the 1,3-dipole, dipolarophile, and their adduct. The activation and reaction volumes in the reactions of nitronone **I** with maleic anhydride **II** and *N*-phenylmaleimide **IV** vary in the above solvents insignificantly (from –17.4 to –20.9 cm³ mol⁻¹), in agreement with published data [22–24]. Comparison of [3+2] and [4+2] cycloadditions in which the 4 π -reagents have large and comparable partial molar volumes shows that the activation and reaction volumes of these processes differ insignificantly and their ratio is close to unity. This fact additionally supports the single-step concerted mechanism of these reactions.

It should be noted in conclusion that the real volume parameters of activation and reaction, determining the effect of external pressure on the rate and equilibrium of reactions in solution, are not governed solely by the change in the structural volume ($\Delta V_{0,W}$). The packing coefficient η does not reach the limiting value of unity even in solids. This follows from the fact that an increase in the density and hence in the packing coefficient of a substance in its passing from a solution or liquid state to the solid state is relatively low (~10%). Furthermore, packing of large spherical

molecules like fullerene C₆₀ can become more compact in solution than in crystals [34].

EXPERIMENTAL

Substituted nitronones were prepared and purified as described in [35]. 9,10-Dimethylantracene (Aldrich) was additionally purified by passing through a column packed with alumina (eluent hexane–benzene, 3 : 1). The optical purity of diene **VI** was evaluated by the final absorption (24 600–25 300 cm⁻¹) of its solution in the presence of excess maleic anhydride. Maleic anhydride after distillation was additionally purified by crystallization from benzene in which maleic acid is virtually insoluble. *N*-Phenylmaleimide (Aldrich) was used without additional purification. Adducts **III** and **VII** were prepared by published procedures [27, 36].

The progress of reaction (a) in toluene and of reaction (c) in acetonitrile at 298.2 K under normal and elevated pressures was monitored by the variation of the absorption of nitronone **I** in the range 23 820–23 900 cm⁻¹ and that of diene **VI** in the range 24 600–24 880 cm⁻¹, respectively (Specord UV-Vis). The initial concentration of reactants in reaction (a) was as follows: diene (5–7) × 10⁻⁴ and maleic anhydride 0.13–0.15 M. The procedure of kinetic measurements at elevated pressure is described in detail elsewhere [7, 12].

The apparent molar volumes of the reactants and adducts in solution were calculated from the densities of solutions of known concentrations and solvent density, as described in [7, 12]. The high accuracy of density measurements ($\pm 2 \times 10^{-6}$ g cm⁻³, $\pm 2 \times 10^{-3}$ K, DMA-602 densimeter) allowed experiments with dilute solutions. The apparent molar volumes did not change in the concentration range 0.005–0.10 mol kg⁻¹ and were used as partial volumes. Calculations were performed using relationship (7) obtained in [32]:

$$y = (1000 + Mm)/d = 1000/d_0 + m\varphi, \quad (7)$$

where M is the molar weight of the solute; m , molal concentration; d_0 and d , densities of the solvent and solution, respectively; and φ , apparent molar volume. The experimental data are listed in Table 7.

Determination of the reaction volume from kinetic data. Using data on variation of the reaction mixture density in time and knowing the reaction rate constant, we can calculate the reaction volume without using data on partial molar volumes. Relationship (6) is deduced above. Although the relative error in determination of the partial molar volumes (<0.5%) is

Table 7. Solute concentrations (m , mol kg⁻¹), solution densities (d , g cm⁻³), functions y [cm³ g⁻¹, Eq. (7)], and calculated apparent molar volumes (φ , cm³ mol⁻¹) at 298.2 K

m , mol kg ⁻¹	d , g cm ⁻³	1000 y , cm ³ g ⁻¹	m , mol kg ⁻¹	d , g cm ⁻³	1000 y , cm ³ g ⁻¹
Maleic anhydride in toluene			C-(<i>p</i> -Nitrophenyl)- <i>N</i> -phenylnitrone in DMSO		
0	0.862294	1159.70	0	1.095073	913.18
0.0599	0.864177	1163.96	0	1.095080	913.17
0.0846	0.864911	1165.78	0.02261	1.096054	917.35
0.1172	0.865989	1169.01	0.03383	1.096464	919.48
φ 71.11 ± 0.11, r 0.99994, n 4			0.04348	1.096835	921.31
Maleic anhydride in acetonitrile			0.06104	1.097558	924.56
	0.777078	1286.87	φ 186.83 ± 0.14, r 0.99999, n 6		
	0.777073	1286.88	9,10-Dimethylantracene in acetonitrile		
0.1090	0.780708	1294.57	0	0.777055	1286.91
0.2077	0.783978	1301.51	0.01289	0.777654	1289.34
φ 70.37 ± 0.07, r 0.99999, n 5			0.00999	0.777288	1288.74
C-(<i>p</i> -Nitrophenyl)- <i>N</i> -phenylnitrone in toluene			φ 187.21 ± 1.13, r 0.99989, n 3		
0	0.861984	1160.11	Adduct VII in acetonitrile		
0	0.861988	1160.11	0	0.777056	1286.91
0.00626	0.862471	1161.22	0.00547	0.777592	1288.17
0.00797	0.862602	1161.52	0.00686	0.777722	1288.50
0.01076	0.862799	1162.04	0.00618	0.777623	1288.40
0.01160	0.862846	1162.21	0.00438	0.777456	1287.97
φ 179.56 ± 0.51, r 0.99988, n 6			φ 232.2 ± 1.30, r 0.9989, n 5		
C-(<i>p</i> -Nitrophenyl)- <i>N</i> -phenylnitrone in acetonitrile			Adduct III in toluene		
0	0.776521	1287.79	0	0.861987	1160.11
0.01501	0.777731	1290.46	0.00638	0.862764	1161.59
0.01891	0.778101	1291.06	0.00777	0.862936	1161.91
0.02282	0.778396	1291.78	0.00853	0.862990	1162.11
0.02961	0.778925	1292.99	0.00999	0.863170	1162.42
φ 175.30 ± 0.71, r 0.99986, n 5			φ 233.32 ± 0.90, r 0.99985, n 5		
			Adduct III in acetonitrile		
			0	0.776496	1287.84
			0.00849	0.777600	1289.72
			0.01059	0.777873	1290.19
			0.01305	0.778173	1290.74
			0.01669	0.778631	1291.60
			φ 224.81 ± 0.61, r 0.99988, n 5		

smaller than in calculation with Eq. (6) (1–3%), in the former case we deal with the difference between large quantities, which results in a large (reaching 10%) error in the reaction volume, $\pm(1.5\text{--}2.5)$ cm³ mol⁻¹. The direct method for calculating the reaction volume [Eq. (6)] is considerably more accurate: the error is $\pm(0.15\text{--}0.5)$ cm³ mol⁻¹. Another advantage of the suggested calculation procedure is that Eq. (6) is applicable in cases when a supersaturated solution of a poorly soluble adduct is formed (which is observed frequently); in such cases, the direct method for determination of partial molar volumes [Eq. (7)] is unsuitable. The optimal reaction half-time in a tube of a precision densimeter is 0.5–3 h. At temperature

deviations ($\pm 3 \times 10^{-3}$ K), the measured values of density were corrected using the coefficient of thermal expansion of the solvent. The experimental dependence for reaction (a) in DMSO is shown as example in Fig. 3. The rate constant of reaction (a) is 2.38×10^{-4} l mol⁻¹ s⁻¹ at 298.2 K and concentrations of nitrone **I** and maleic anhydride of 0.02542 and 0.4350 M, respectively.

Simple transformations of experimental data (using, e.g., Origin 4.0 software) allow us to obtain the dependence of the specific volume ($1/d_t$) on the concentration of adduct **III**. The calculated volume of reaction (a) in DMSO, determined at 25% conversion

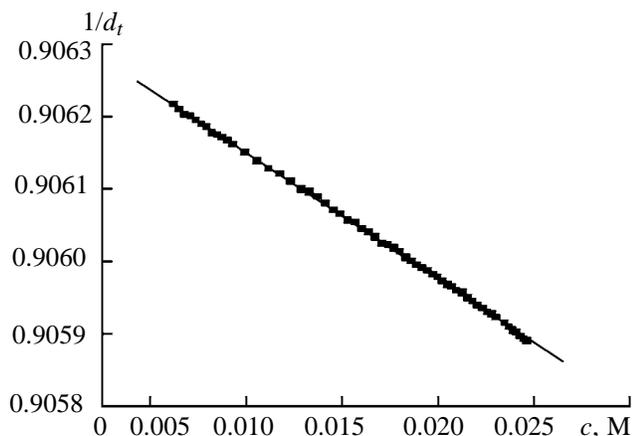


Fig. 3. Reciprocal density $1/d_t$ of solution of a mixture of *C*-(*p*-nitrophenyl)-*N*-phenyltrione (c_0 0.02542 M) with maleic anhydride (c_0 0.4350 M) in DMSO as a function of concentration c of the forming product. T 298.2 K.

(60 min), is $-19.02 \pm 0.18 \text{ cm}^3 \text{ mol}^{-1}$ (r 0.9993, n 8); at 50% conversion (112 min), $-18.95 \pm 0.08 \text{ cm}^3 \text{ mol}^{-1}$ (r 0.9997, n 32); and at 78% conversion (240 min), $-19.21 \pm 0.05 \text{ cm}^3 \text{ mol}^{-1}$ (r 0.9998, n 58).

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