

# High-Pressure Influence on the Rate of Diels–Alder Cycloaddition Reactions of Maleic Anhydride with Some Dienes

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**ABSTRACT:** The rate constants for temperature and pressure range, enthalpy, entropy, and volume of activation and reaction were measured in toluene solution for the Diels–Alder cycloaddition reaction of maleic anhydride (**1**) with a very active diene, 9,10-dimethylanthracene (**4**), and with a very inactive diene, 9-phenylanthracene (**6**), which is less reactive in the reaction with **1** by five orders of magnitude. Reaction rates under pressure up to 2600 bar were measured by using a high-pressure optical cell, adjusted to a UV-spectrophotometer. The volume of reaction was determined by two independent methods: by the difference of the partial molar volumes of the reactants and by the dependence of a specific volume of solution on the adduct concentration during the reaction. All parameters of activation and reaction were discussed. © 2013 Wiley Periodicals, Inc. *Int J Chem Kinet* 45: 613–622, 2013

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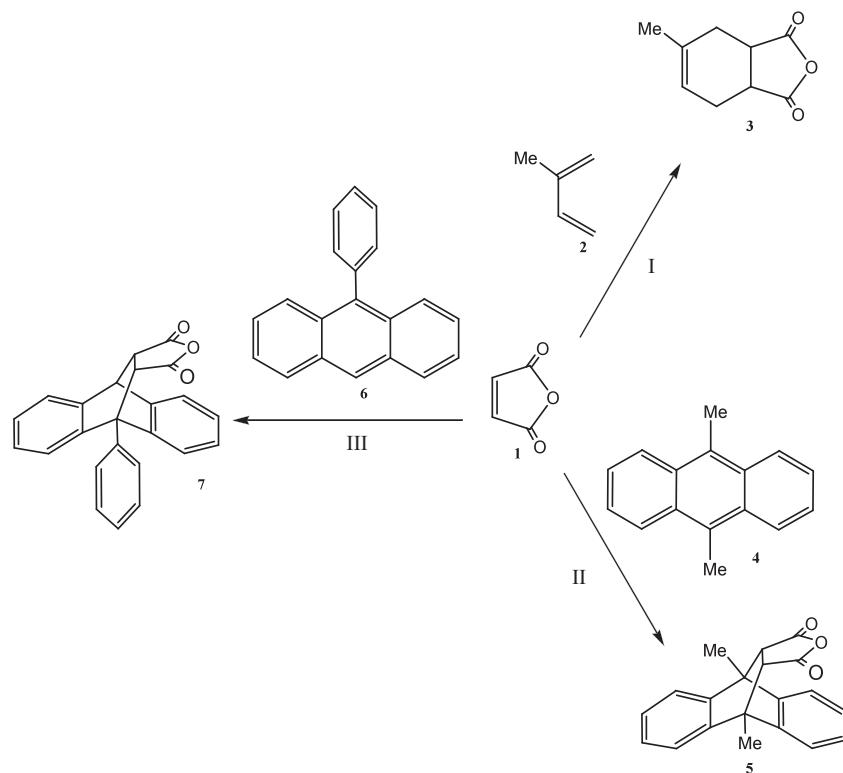
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## INTRODUCTION

The fact that values of the activation volume ( $\Delta V^\neq$ ) can get more negative than values of the reaction volume ( $\Delta V_{r-n}$ ) for the Diels–Alder cycloaddition reaction of maleic anhydride (**1**) with isoprene (**2**) (Scheme 1) was described in [1] for the first time, where the reaction was studied in nine solvents of different polarity. Solvent electrostriction in this reaction can be neglected due to the small effect of solvent polarity on the enthalpy of activation ( $\Delta H_{av}^\neq = 52 \pm 2 \text{ kJ mol}^{-1}$ ),



**Scheme 1** Diels–Alder cycloaddition reaction of maleic anhydride **1** with isoprene **2** (reaction (I)), 9,10-dimethylanthracene **4** (reaction (II)), and 9-phenylanthracene **6** (reaction (III)).

the volume of activation ( $\Delta V_{\text{av.}}^{\neq} = -38.5 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ ), and the reaction volume ( $\Delta V_{\text{r-n, av.}} = -35.5 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ ) [1]. The “abnormal” ratio of  $\Delta V^{\neq}/\Delta V_{\text{r-n}}$   $> 1$  corresponds to the higher volume compactness of the activated complex with incomplete bond formation as compared to the adduct where bond formation is entirely completed.

This means that elevated pressure should promote the retro-Diels–Alder reaction corresponding to an adduct decomposition. Currently, there are some experimental proofs of the fact that the adduct decomposition is accelerated by a pressure elevation [2–5].

In this work, the temperature and pressure influence on the rate constants of the Diels–Alder cycloaddition reaction of maleic anhydride (**1**) with 9,10-dimethylanthracene (**4**) and 9-phenylanthracene (**6**) have been studied in toluene solution (Scheme 1). The rate constant at 25°C of reaction (II) exceeds the rate of reaction (I) by three orders of magnitude, and the rate of reaction (III) by five orders of magnitude. One normally expects that for the rapid reactions the coordinate of the activated complex is placed closer to the initial state of the reaction. In the present work, we

have compared the values of activation volumes for the rapid and slow-rate reactions.

## EXPERIMENTAL

### Materials

Maleic anhydride **1** was distilled and then recrystallized from benzene (where maleic acid can be separated quantitatively as an insoluble impurity) and dried under vacuum, melting point (m.p.) 52.5–53°C, lit. 52.85°C [6]. Spectroscopically, pure dienes **4** (Alfa Aesar, Heysham, UK), m.p. 182–183°C, lit. 183–184°C [7]), and **6** (Sigma-Aldrich Chemie, Steinheim am Albuch, Germany), m.p. 156–157°C, lit. 156.5–157.5°C [8], were obtained after column chromatography with neutral alumina (eluent benzene/*n*-hexane, 1:5 v/v), and their reaction with **1** was confirmed by the complete disappearance of the initial UV-absorption of the dienes (390–405 nm) in solution with an excess of maleic anhydride. Adduct **7** was obtained by boiling a benzene solution of **1** and **6** with a large excess of maleic anhydride ( $\sim 2 \text{ mol L}^{-1}$ ) for 20 h. The crystals were washed with hexane and recrystallized from benzene, m.p.

251.0–251.5°C with decomposition, lit. 249–251°C, dec. [8]. All solvents were purified and dried by known methods [9].

## Apparatus and Procedures

**Kinetic Measurements.** The rate of reactions (II) and (III) was determined by measuring the UV absorption of dienes **4** and **6** at 390–405 nm. For reaction (II), the initial concentration of diene **4** was about  $(2\text{--}4) \times 10^{-4}$  mol L<sup>-1</sup> and that of dienophile **1** about  $(1\text{--}4) \times 10^{-2}$  mol L<sup>-1</sup>. The rate constants of reaction (II) in trichloromethane–cyclohexane mixtures were measured at 40°C to ensure solubility in the full range of this mixture. For reaction (III), the initial concentration of **1** was about 2 mol L<sup>-1</sup> due to the very low reaction rate even at 60, 70, and 80°C. The water-circulated cell-holder adapter (210–2111) of the UV-spectrophotometer (Hitachi-2900) with only one-sided T-control was replaced by the homemade five-sided T-control in a water-circulated box, which allowed tracing with accuracy of  $\pm 0.1^\circ\text{C}$ . The values of the rate constants were determined with errors of  $\pm 3\%$ , enthalpy of activation of  $\pm 1$  kJ mol<sup>-1</sup>, and entropy of activation of  $\pm 4$  J mol<sup>-1</sup> K<sup>-1</sup>.

The reaction rates under elevated pressure were measured with a high-pressure system using the high-pressure pump “HP-500” and high-pressure optical cell “PCI-500” from Syn. Co. (Kyotanabe City, Japan), adjusted to a UV-spectrophotometer from SCINCO Co. (Seoul, Korea). The photodiode array of the “SCINCO” UV-spectrophotometer performs all new spectra in the selected time interval, and only a small fluctuation in the curve of the optical density was observed while monitoring the absorption on the sharp slope of the spectra of dienes **4** and **6**. Reaction (II) was measured under pressure at 25°C and reaction (III) at 60°C, both in toluene.

**Calorimetric Experiment.** The enthalpies of solution of reactants **1** and **4** were measured at 25°C with a differential calorimeter, as previously reported [10–12]. Samples were weighed into a small stainless steel cylinder, both polished sides of which were covered by thin (0.1 mm) rings of Teflon seals. The mass of the cylinders filled with diethyl ether proved to be constant after 24 h, ensuring the tightness of the container. After equalization of temperature of the inserted closed cylinder with the sample in the calorimetric cell with solution (150 cm<sup>3</sup>), these Teflon seals were cut out with a razor. The accuracy of the calorimetric measurements was verified by determining the enthalpy of dissolution of dry potassium chloride in water at 25°C. The result ( $17.4 \pm 0.2$  kJ mol<sup>-1</sup>) was in agreement with the pub-

lished value [13] of  $17.514 \pm 0.008$  kJ mol<sup>-1</sup>. The calibration was made by the introduction of a certain amount of heat. For all solutions, three to five measurements of sequentially dissolving samples of **1** and **4** were carried out. In cyclohexane, after determination of the finite base line of the thermal effect of solution of reactants **1** and **4**, an aliquot of solution was taken out and the concentration of reactants **1** and **4** was determined by UV spectrophotometric titration. The total uncertainty of the measurements did not exceed  $\pm 2\%$ . No concentration dependencies of the heat of solution were observed.

**Density Measurements.** All methods of calculation of the apparent molar volume ( $\phi_A$ ) of a solute (A) are based on the assumption that the volume of solution equals the sum of the solute volume and the unchanged volume of the solvent. In terms of molar concentration ( $c_A$ ), molal concentration ( $m_A$ ), moles per kilogram of solution ( $w_A$ ), or grams per milliliter of solution ( $T_A$ ), the following equations can be obtained:

$$1000 - (1000d - c_A M_r)/d_0 = c_A \varphi_A \quad (1)$$

$$(1000 + m_A M_r)/d = 1000/d_0 + m_A \varphi_A \quad (2)$$

$$1000/d = 1000/d_0 + W_A (\varphi_A - M_r/d_0) \quad (3)$$

$$d = d_0 + T_A (1 - \varphi_A d_0/M_r) \quad (4)$$

Here  $d_0$  and  $d$  are the densities of the solvent and solution, respectively, and  $M_r$  is the relative molar mass of the solute. Equations (1)–(4) can be transformed to a direct calculation of the value  $\phi_A$  for each concentration. In this way, Eqs. (1) and (2) can be converted to Eqs. (5) and (6) to calculate  $\phi_A$ :

$$\varphi_A = 1000(d_0 - d)/c_A d_0 + M_r/d_0 \quad (5)$$

$$\varphi_A = 1000(d_0 - d)/m_A d_0 d + M_r/d \quad (6)$$

The vibration densimeter manufactured by Anton Paar GmbH (Graz, Austria; model DSA 5000M) was used for the measurements at  $25 \pm 0.002^\circ\text{C}$ . The densimeter was calibrated with water and air following the instructions. Very small differences (only a few ppm) in the densities between the freshly prepared solutions and those after a few hours exclude by-processes. The apparent molar volume of **1**, **6**, and **7** in toluene solution was calculated from data on the density of their solutions using Eq. (6).

**Table I** Rate Constants ( $k_2$ ) of the Diels–Alder Cycloaddition Reaction of 9,10-Dimethylanthracene (**4**) with Maleic Anhydride (**1**), Heats of Solution of the Reactants ( $\Delta_{\text{sol}}H_4$  and  $\Delta_{\text{sol}}H_1$ ) in Pure Solvents with a Different Relative Permittivity ( $\varepsilon_r$ ) and in Binary Trichloromethane/Cyclohexane Solvent Mixtures

No.	Solvent	Data in Solvents No 1–16			Data in TCM/Cyclohexane Mixtures		
		$\varepsilon_r$	$k_2^a (\times 10^4 \text{ L mol}^{-1} \text{ s}^{-1})$	$\Delta_{\text{sol}}H_4^a (\text{kJ mol}^{-1})$	$\Delta_{\text{sol}}H_1^a (\text{kJ mol}^{-1})$	$\Delta_{\text{sol}}H_4^b (\text{kJ mol}^{-1})$	$\Delta_{\text{sol}}H_1^b (\text{kJ mol}^{-1})$
1	Acetone	20.7	92	25.2	11.3	20.0 (100)	16.1 (100)
2	<i>N,N</i> -Dimethyl formamide	36.7	111	21.4	8.1	21.3 (90)	17.4 (90)
3	Acetic acid	6.1	285	23.7	15.0	21.3 (80)	17.7 (80)
4	1,4-Dioxane	2.2	120	23.1	10.4	21.5 (70)	19.8 (70)
5	Toluene	2.4	192	21.8	16.4	22.3 (60)	20.3 (60)
6	Benzene	2.3	216	23.4	16.9	22.7 (50)	21.3 (50)
7	Nitrobenzene	34.8	250	21.3	14.2	24.1 (40)	22.5 (40)
8	Acetonitrile	37.5	244	28.9	13.1	24.5 (30)	24.0 (30)
9	Nitromethane	34.9	302	30.4	12.6	25.9 (20)	24.5 (20)
10	Chlorobenzene	5.6	452	21.4	18.3	26.3 (15)	34.3 (15)
11	Tetrachloromethane	2.2	467	23.6	24.9	27.1 (10)	43.4 (10)
12	Trichloromethane	4.8	700	20.0	16.1	29.8 (0)	46.5 (0)
13	Ethyl acetate	6.0	—	22.7	11.4	—	—
14	Anisole	4.3	—	20.9	13.8	—	—
15	Dichloromethane	9.1	—	23.1	15.9	—	—
16	Cyclohexane	2.0	636	29.8	46.4	—	—

<sup>a</sup>Data for solvents No 1–16 at 25 °C.

<sup>b</sup>In parenthesis are given the volume percentage of trichloromethane in the mixture with cyclohexane.

<sup>c</sup>At 40°C.

## RESULTS AND DISCUSSION

### Kinetic Measurements at Ambient Pressure

An analysis of the solvent influence on the enthalpy of activation of the Diels–Alder reaction and the enthalpy of solution of the reactants corroborates the conclusion that the higher energy of intermolecular interaction of reactants with the solvent molecules makes it more difficult to achieve the activated complex, as it requires desolvation, i.e., removing a part of solvent molecules from the reactants during their mutual approach [12,14]. That can explain the elevated rate constants of the Diels–Alder reaction observed in cyclohexane solution with weaker intermolecular solute–solvent interactions as compared with other solvents, including trichloromethane. But the rate of the Diels–Alder reactions is usually elevated in trichloromethane solution by the dienophile activation due to H-bond formation between the solvent and the *n*-donor groups of the dienophile [14]. Rate data in various solvents and binary trichloromethane/cyclohexane mixtures at ambient pressure are summarized in Table I, together with heats of solution of **1** and **4**.

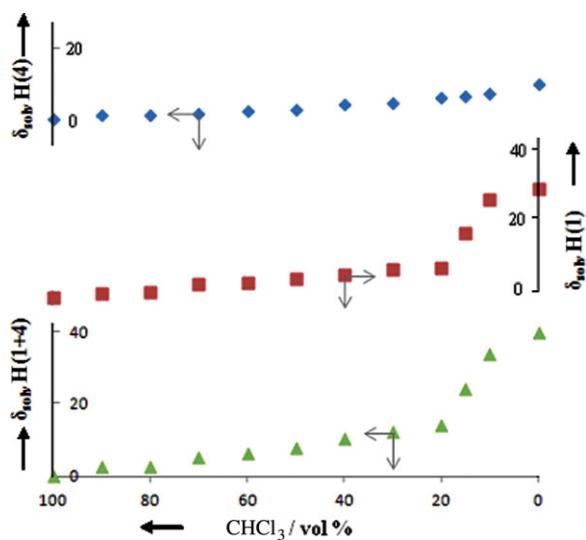
It is clear that the influence of the solvent polarity on the rate constant of this reaction is very small. Less energy of a desolvation of reactants **1** and **4** on the way

to the transition state in tetrachloromethane and cyclohexane (entries 11 and 16), compared with acetone and *N,N*-dimethyl formamide (entries 1 and 2 in Table I), is a key possible reason for the rate constant changes.

It is interesting to consider the balance of acceleration and retardation effects of reaction (II) in trichloromethane/cyclohexane solvent mixtures. Smooth changes of the heat of solvation ( $\delta_{\text{solv}}H$ , with 100% trichloromethane taken as a blank) of diene **4** can be observed in all concentration ranges (Fig. 1).

The heat values in solvation of **1** and **1 + 4** change dramatically when the trichloromethane volume is less than 20% (Fig. 1). At this mixture composition, the rate constant has the maximum value, with an optimal balance of the low energy of reactant solvation and sufficient activation of maleic anhydride by H-bond formation with trichloromethane (Fig. 2).

It should be noted that the determination of the heat of solution in cyclohexane is complicated by its characteristically low and slow solubility. The experimental value of the heat of solution **1** in cyclohexane (46.5 kJ mol<sup>-1</sup>) is proximate to the calculated value (45.7 kJ mol<sup>-1</sup>) derived from the heat of sublimation of **1** (68.5 kJ mol<sup>-1</sup> [6]) and the heat of solvation ( $\Delta_{\text{solv}}H_{1/c\text{-hexane}}$ ) of **1** in cyclohexane (-22.8 kJ mol<sup>-1</sup>),

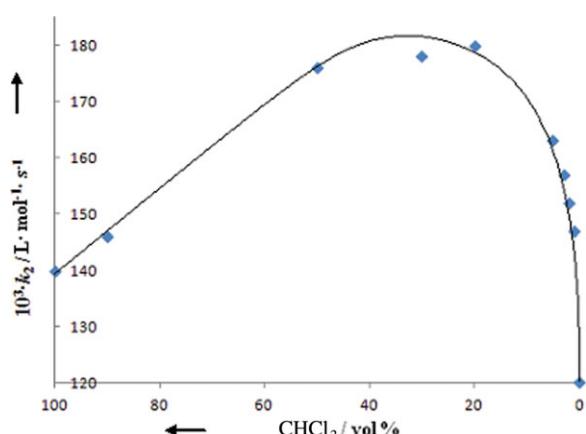


**Figure 1** Influence of the composition of trichloromethane/cyclohexane solvent mixtures on the change in solvation enthalpy of 9,10-dimethylanthracene ( $\Delta_{\text{solv}}H_4$ ; ◆), maleic anhydride ( $\Delta_{\text{solv}}H_1$ ; ■), and of both reactants ( $\Delta_{\text{solv}}H_{1+4}$ ; ▲).

predicted from the highly reliable equation (7) [15]:

$$-\Delta_{\text{solv}}H_{1/c\text{-hexane}} = 5.09 + 1.03 R_1 \quad (7)$$

Here  $R_1$  is the molar refraction of the solute. A similar calculation for the heat of solution of diene **4** in cyclohexane gives a value of  $110.6 - 82.2 = 28.4$  kJ mol<sup>-1</sup>, close to the measured one (29.8 kJ mol<sup>-1</sup>; Table I).



**Figure 2** Influence of the composition of trichloromethane/cyclohexane solvent mixtures on the rate constant of reaction (II).

A comparison of the kinetic parameters of reactions (I)–(III) at ambient pressure (Table II) indicates that the difference in the rate constants is caused by the variety in the enthalpy of activation. As for the entropy of activation, it is nearly the same for all these reactions.

Possible reasons for the substantial difference in the reactivity of dienes **4** and **6** in a reaction with **1** (five orders of magnitude) are worth considering. The reactivity of Diels–Alder reactions with the usual electronic demand (diene–donor, dienophile–acceptor) depends on the  $\pi$ -donor and  $\pi$ -acceptor properties of the diene–dienophile system and on the difference in the conjugation energy of C=C bonds [14]. The ionization potential of diene **6** (7.25 eV) is higher than that of **4** (7.11 eV) (IP) [16]. The predicted difference in the rate constants due to the variety in the values of IP [14] is only about one order of magnitude, whereas the rate constant of reaction (III) is five orders of magnitude less than that of reaction (II) (Table II). From these data, it follows that the suppression of reaction (III) is determined not only by the difference in the ionization potential and electron affinity (IP-EA). The activation energy of a concerted Diels–Alder reaction depends on the energy balance of breaking C=C and forming new C–C bonds, and the heat of reaction is a good measure of this balance [14]. The value of the heat for reaction (II) is –104 [14], and for reaction (III) this is only –81 kJ mol<sup>-1</sup> [8]. Additional rate retardation can be caused by shielding of the reaction center of diene **6**, where the phenyl group is nearly orthogonal to the anthracene plane [17].

### Kinetic Measurements at High Pressure

In spite of the amount of data in this field [18–24], there are two positions in the analysis of high-pressure effects on the reaction rate to be mentioned. For small molecules of reactants with low energies of intermolecular interaction and low boiling point (b.p.; ethylene, 1,3-butadiene, isoprene, cyclopentadiene, furan, etc.), the packing coefficients ( $\eta = V_W/V$ ), i.e., the ratio of van-der-Waals volume ( $V_W$ ) to partial molar volume (PMV) in solution ( $V$ ), are significantly smaller than those for large reactant molecules with high energies of intermolecular interaction and with high b.p. (anthracene, maleic anhydride, maleimides, their adducts, etc.) [14,25]. As follows from Table III, the larger change of the packing coefficient is found for reaction (I) than for reactions (II) and (III). As a result, the values of the activation and reaction volumes should be more negative in reaction (I) than in reactions (II) and (III).

**Table II** Rate Constants ( $k_2$ ), Enthalpy ( $\Delta H^\neq$ ), and Entropy of Activation ( $\Delta S^\neq$ ) of the Diels–Alder Cycloaddition Reactions (I)–(III), Measured in Toluene

Reaction	$T$ (°C)	$k_2$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$\Delta H^\neq$ (kJ mol <sup>-1</sup> )	$\Delta S^\neq$ <sup>a</sup> (J mol <sup>-1</sup> K <sup>-1</sup> )
<b>I</b> <sup>b</sup>	35	$3.3 \times 10^{-5}$	59.0	-149
<b>II</b>	15	$1.09 \times 10^{-2}$	40.2	-150
	25	$1.92 \times 10^{-2}$		
	40	$4.10 \times 10^{-2}$		
	25	$3.62 \times 10^{-7}$ <sup>c</sup>	68.0	-140
<b>III</b>	60	$7.11 \times 10^{-6}$		
	70	$1.50 \times 10^{-5}$		
	80	$3.00 \times 10^{-5}$		

<sup>a</sup>Calculated for 25°C.<sup>b</sup>Data in acetonitrile from [1].<sup>c</sup>Calculated by extrapolation.**Table III** Partial Molar Volumes (V), Van-der-Waals Volumes ( $V_W$ ), Volumes of Intermolecular Holes ( $V_H$ ) in Solution, Packing Coefficients ( $\eta$ ) of Compounds **1–7** and the Volume Changes ( $\Delta V$ , cm<sup>3</sup> mol<sup>-1</sup>) in the Diels–Alder Cycloaddition Reactions of Maleic Anhydride with Isoprene (**I**), 9,10-Dimethylanthracene (**II**), and 9-Phenylanthracene (**III**), Measured in Acetonitrile at 25°C

Parameter	Reactants 1–7							Reaction Volume		
	1	2	3	4	5	6	7	$\Delta V_I$	$\Delta V_{II}$	$\Delta V_{III}$
$V$	70 <sup>a</sup>	100 <sup>a</sup>	135 <sup>a</sup>	187 <sup>a</sup>	232 <sup>a</sup>	219.5 <sup>b</sup>	263.3 <sup>b</sup>	-35	-25	-27.3 <sup>b</sup>
$V_W$ <sup>c</sup>	43.9	49.0	88.4	122.0	162.1	144.0	184.2	-4.5	-3.8	-3.7
$V_H$ <sup>d</sup>	26.1	51.0	46.6	65.0	69.9	75.5	79.1	-30.5	-21.2	-22.5
$\eta$ <sup>e</sup>	0.63	0.49	0.65	0.65	0.70	0.66	0.70	-	-	-

<sup>a</sup>Values of V in acetonitrile of reactants **1–3** taken from [1] and **4, 5** from [25].<sup>b</sup>In toluene at 25°C, this work.<sup>c</sup>Calculated by Marvin Sketch software.<sup>d</sup>Calculated by the difference of V and  $V_W$ .<sup>e</sup>Calculated from ratio  $\eta = V_W/V$ .

It should be noted that in all Diels–Alder reactions, the value of the van-der-Waals reaction volume is about  $-(4\text{--}5)$  cm<sup>3</sup> mol<sup>-1</sup>. It is appropriate to mention that the volume of the Diels–Alder reaction of maleic anhydride with anthracene in the solid state ( $\Delta V_{r-n, \text{solid}} = 200.2 - 141.6 - 65.4 = -6.8$  cm<sup>3</sup> mol<sup>-1</sup>) is nearly the same as  $\Delta V_W = (141.4 - 101.4 - 43.9 = -3.9$  cm<sup>3</sup> mol<sup>-1</sup>), and the large negative value of the reaction volume in acetonitrile ( $\Delta V_{r-n} = 201.8 - 158.2 - 70.4 = -26.8$  cm<sup>3</sup> mol<sup>-1</sup>) is generated mainly by the change of intermolecular holes in solution [25]. Since the total compression of the intermolecular holes of 2 mol of reagents in solution is higher than that of 1 mol of activated complex, the dependence  $\ln(k_p)$  versus  $P$  should show a convex curve, and the limiting value of the volume of activation in solution under very high pressure will approach to  $\Delta V_w$ . According to Table III, the convex curvature for reaction (I) should be larger than that for reactions (II) and (III).

Another problem is related to the account for the volume concentration change of solutions under pres-

sure. It was suggested to use the pressure-independent concentration scales (mole fraction, molality, etc.) [26]. However, the increased pressure leads to the compression and an increase in the number of molecules per unit of volume in the liquid and the gas phase, where the difference is only in the size of an effect.\* Consequently, the rate of the second-order reaction in solution under pressure should be increased even when the value of  $\Delta V^\neq$  is zero. This additional increase in the reaction rate should be related with the increased concentration of reagents for the correct determination of the rate constants, because  $(\partial \ln k_2 / \partial P)_T = 0$ , when  $\Delta V^\neq = 0$ . Using the initial values of the concentration as prepared at ambient temperature and pressure, the calculated value of the rate constant under pressure is overestimated and the calculation of

\*Unsuitability of the mole fraction and weight concentration scales is particularly clearly seen when trying to describe the rate of the second-order reaction in the gas phase ( $r = k_2 x_A x_B$ ) between the same reagents located, e.g., in the volume of 1 cm<sup>3</sup> and m<sup>3</sup>.

**Table IV** Volumes of Activation for Reaction (I), Calculated Using the Mole Fraction Concentration Scale ( $\Delta V^\neq_{\text{exp}}$ ), Compressibility Coefficients ( $\beta_T$ ) for the Solvents, Correction Factors ( $\beta_T \cdot RT$ ), Corrected Volumes of Activation ( $\Delta V^\neq_{\text{corr}}$ ), and Volumes of Reaction (I) ( $\Delta V_{r-n}$ )

No.	Solvent	$\Delta V^\neq_{\text{exp}}^a$ ( $\text{cm}^3 \text{ mol}^{-1}$ )	$\beta_T^b$ ( $\times 10^6 \text{ bar}^{-1}$ )	$\beta_T \cdot RT^c$ ( $\text{cm}^3 \text{ mol}^{-1}$ )	$\Delta V^\neq_{\text{corr}}^d$ ( $\text{cm}^3 \text{ mol}^{-1}$ )	$\Delta V_{r-n}^e$ ( $\text{cm}^3 \text{ mol}^{-1}$ )	$\Delta V^\neq_{\text{corr}}/$ $\Delta V_{r-n}$
1	Ethyl acetate	-37.4	117	2.8	-34.6	-36.8	0.94
2	Dichloromethane	-39.8	103	2.5	-37.3	-33.4	1.11
3	Nitromethane	-32.5	72.5	1.8	-30.7	-30.7	1.0
4	Dimethyl carbonate	-39.3	97	2.3	-37.0	n.d. <sup>e</sup>	—
5	Acetonitrile	-37.5	113	2.7	-34.8	-34.5	1.0
6	Diisopropyl ether	-38.5	183	4.4	-34.1	-38.3	0.89
7	1-Chlorobutane	-38.0	119	2.9	-35.1	n.d. <sup>e</sup>	—
8	Acetone	-39.0	129	3.1	-35.9	-35.9	1.0
9	1,2-Dichloroethane	-37.0	80	1.9	-35.1	-35.5	0.99

<sup>a</sup>Experimental values of activation volume at 35°C [1].

<sup>b</sup>Values of compressibility coefficients at 25°C [30].

<sup>c</sup>Correction factor calculated for 25°C. For 35°C, it should be increased approximately on 10%.

<sup>d</sup>Calculated by Eq. (8).

<sup>e</sup>No data because of very low solubility of adduct **3** [1].

the correct value of  $\Delta V^\neq_{\text{corr}}$  requires the adjustment:  $(n - 1) \cdot RT \cdot \beta_T$  (Eq. (8)).

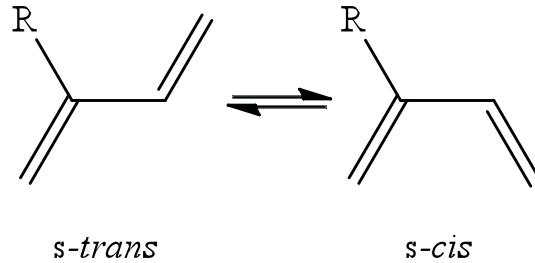
$$\Delta V^\neq_{\text{corr}} = -RT \partial \ln(k_P)/\partial P + (n - 1) \times RT \times \beta_T \quad (8)$$

Here  $k_P$  is the rate constant under pressure, calculated without correction of the value of concentration (molarity, molality, or mole fraction) under pressure  $P$ , and  $(n - 1) \cdot RT \cdot \beta_T$  is the correction term, where  $n$  is the reaction order and  $\beta_T = \partial \ln(d)/\partial P$  is the solvent compressibility coefficient (positive value). Therefore, the apparent value of the activation volume of the Diels–Alder reaction will be more negative than corrected by Eq. (8). It should be noted that an equation similar to (8) was proposed more than 90 years before by Williams [27] and repeatedly mentioned by Eyring in 1938 [28].

The experimental and corrected values of activation volume for reaction (I) are collected in Table IV.

With the corrected values of the volume of activation of reaction (I), the “normal” ratio,  $\Delta V^\neq_{\text{corr}}/\Delta V_{r-n} \leq 1$ , can be obtained, except for the data in dichloromethane (Table IV). All substituted butadienes are in equilibrium between the *s-trans* and the *s-cis*-isomer (see Scheme 2) [1,29].

Because this equilibrium shifts to the *s-trans*-isomer, and it is the *s-cis*-isomer that can react only in Diels–Alder reactions, the apparent rate constant ( $k_{\text{app}}$ ) of reaction (I) is equal to  $K_{\text{eq}} \cdot k_{s-cis}$ . Commonly, the *cis*-isomer is 1–2% more compact as compared with the *trans*-isomer [18,19]. Therefore, the additional pressure effect on  $K_{\text{eq}}$  is included in the value of



**Scheme 2**

the apparent volume of activation and should be about  $-(1-2) \text{ cm}^3 \text{ mol}^{-1}$ . Very large variations of the ratio  $\Delta V^\neq/\Delta V_{r-n}$  (from 1.0 to 1.69) were observed in the reaction of **1** with *trans*-1-methoxybutadiene in different solvents [29]. There is a direct experimental validation of the acceleration of some retro-Diels–Alder reactions under elevated pressure [2–5].

The response to the pressure effects on the rate constants of reactions (II) and (III) is presented in Table V.

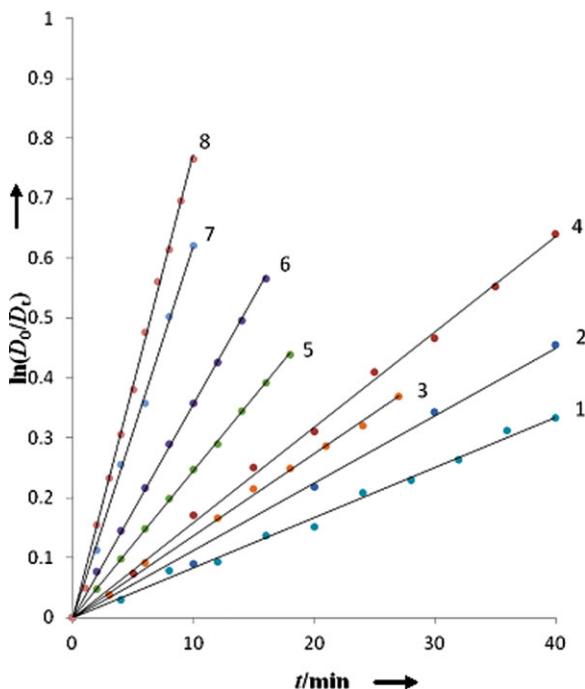
All kinetic runs under pressure (Fig. 3) were analyzed as straight lines at a conversion of  $\geq 50\%$  with a correlation coefficient of  $R \geq 0.999$ .

From the dependence  $\ln(k_P/k_{P=1}) = bP + cP^2$  (Fig. 4), the value  $b$  was determined for reaction (II) as  $9.91 \times 10^{-4}$ ,  $R = 0.9982$ ,  $N = 8$ , and for reaction (III) as  $9.75 \times 10^{-4}$ ,  $R = 0.9985$ ;  $N = 7$ . The experimental values of the volume of activation of reaction (II) at 25°C are equal to  $-23.9 \pm 1.0$ , and reaction (III) at 60°C equals to  $-26.3 \pm 1.2 \text{ cm}^3 \text{ mol}^{-1}$ .

The value of the correction term ( $RT\beta_T$ ) was calculated, using the compressibility coefficient of toluene at

**Table V** Pressure (Pbar) Influence on the Rate Constants ( $k_2$ ) of the Diels–Alder Cycloaddition Reaction of Maleic Anhydride (**1**) with 9,10-Dimethylanthracene (**4**) (Reaction (II)), Measured at 25°C and with 9-Phenylanthracene (**6**), (Reaction (III)), Measured at 60°C in Toluene

Reaction (II)			Reaction (III)		
P (bar)	$\cdot k_2 (\times 10^3 \text{ L mol}^{-1} \text{ s}^{-1})$	$\ln(k_p/k_{p=1})$	P (bar)	$k_2 (\times 10^6 \text{ L mol}^{-1} \text{ s}^{-1})$	$\ln(k_p/k_{p=1})$
1	$19.2 \pm 0.4$	0	1	$6.6 \pm 0.2$	0
273	$25.6 \pm 0.2$	0.292	661	$11.2 \pm 0.1$	0.529
503	$31.6 \pm 0.4$	0.500	975	$16.0 \pm 0.2$	0.885
645	$34.1 \pm 0.15$	0.578	1406	$23.3 \pm 0.1$	1.261
1085	$57.0 \pm 0.3$	1.091	1673	$29.2 \pm 0.2$	1.487
1592	$81.1 \pm 1.1$	1.443	2061	$36.6 \pm 0.7$	1.713
2147	$145 \pm 0.2$	2.023	2342	$46.4 \pm 0.4$	1.950
2602	$199 \pm 1.2$	2.340	—	—	—



**Figure 3** Kinetic runs of reaction (II), measured in toluene at 25°C under pressure: 1, –1; 2, –273; 3, –502; 4, –643; 5, –1085; 6, –1591; 7, –2147; 8, –2602 bar.

25°C ( $92 \times 10^{-6}$ ) and at 60°C ( $116 \times 10^{-6}$  bar $^{-1}$ ) [30]. The corrected value of the volume of activation of reaction (II) is  $-21.7 \pm 1.0$  at 25°C, and that of reaction (III) at 60°C is  $-23.2 \pm 1.2$  cm $^3$  mol $^{-1}$ .

The difference of PMVs is the commonly used method for the determination of the value of  $\Delta V_{r-n}$  with an accuracy of about  $\pm(1-2)$  cm $^3$  mol $^{-1}$  [18–23]. The solubility of adduct **5** of reaction (II) in toluene was insufficient for PMV determination. Here we used a more convenient method. The total volume of a solution with reactants (A, B) and adduct (Add) can be

written as Eqs. (9) and (10):

$$V_{(t)} = V_s + (c_A^0 - c_{\text{Add},t}) V_A + (c_B^0 - c_{\text{Add},t}) V_B + c_{\text{Add},t} V_{\text{Add}} \quad (9)$$

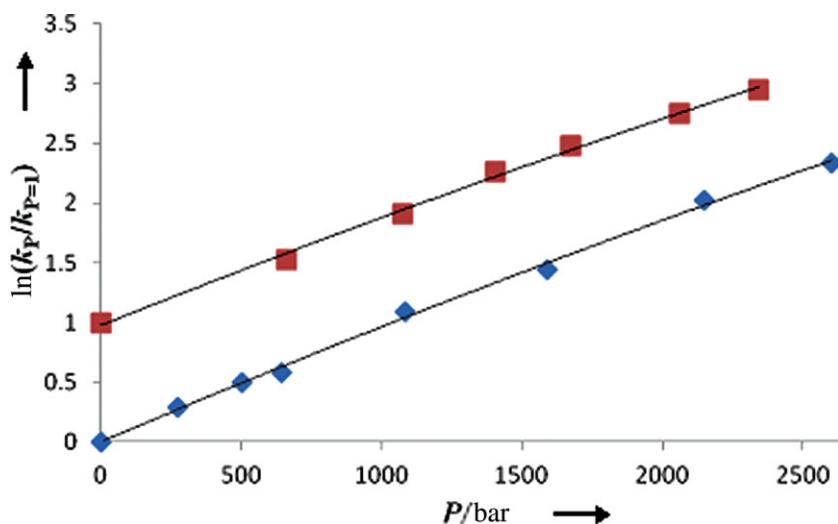
$$\begin{aligned} V_{(t)} &= [V_s + (c_A^0 V_A + c_B^0 V_B)] \\ &+ c_{\text{Add},t} (V_{\text{Add}} - V_A - V_B) \\ &= V_{(t=0)} + c_{\text{Add},t} \Delta V_{r-n} \end{aligned} \quad (10)$$

$$1/d(t) = 1/d_{(t=0)} + c_{\text{Add},t} \Delta V_{r-n} / 1000 d_{(t=0)} \quad (11)$$

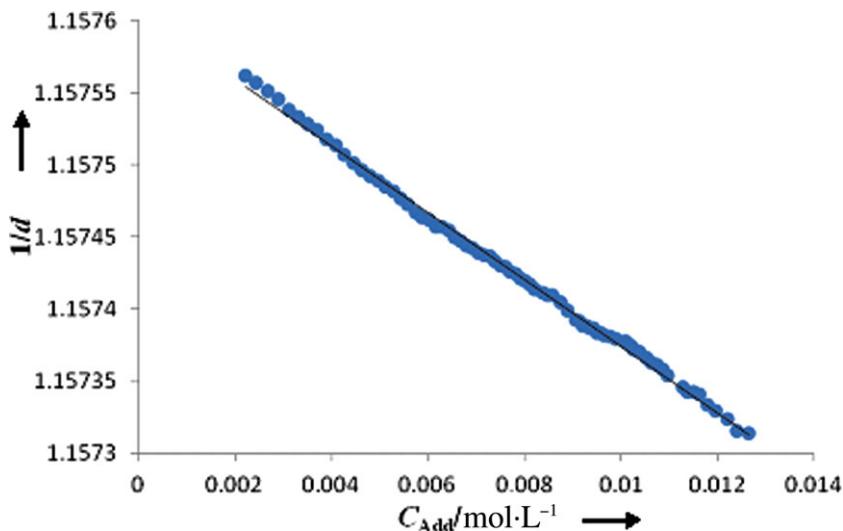
Equation (11), rewritten from Eq. (10), is more convenient for the density measurements of reaction mixtures. Here,  $V_{(t=0)}$  and  $V_{(t)}$  are the solution volumes at the start of and during the reaction, respectively;  $V_s$  is the volume of solvent;  $V_A$ ,  $V_B$ , and  $V_{\text{Add}}$  are PMVs of compounds (A), (B) and (Add), respectively;  $c_A^0$ ,  $c_B^0$ , and  $c_{\text{Add},t}$  are the initial molar concentrations of [A] and [B] and the current concentration of [Add], respectively; and  $\Delta V_{r-n}$  is the reaction volume. A linear dependence  $1/d_{(t)}$  versus  $c_{\text{Add},t}$  [Fig. 5, Eq. (12)] has been obtained for up to 80% of conversion, followed by a sharp bend due to the beginning of the adduct crystallization from the oversaturated solution in the densimeter tube:

$$\begin{aligned} 1/d_{(t)} &= (1.15836 \pm 2.8 \times 10^{-7}) \\ &- (2.188 \times 10^{-2} \pm 7.1 \times 10^{-5}) c_{\text{Add},t}; \\ R &= 0.9997; N = 43 \end{aligned} \quad (12)$$

From relation (12), the volume of reaction (II),  $\Delta V_{\text{II}}$ , is  $-18.9 \pm 0.2$  cm $^3$  mol $^{-1}$ . Repeated measurements ( $R = 0.9995$ ;  $N = 55$ ) gave  $-18.6 \pm 0.2$  cm $^3$  mol $^{-1}$ . When the same reaction mixture ( $c_1 > c_4$ ) in



**Figure 4** Pressure ( $P$ ) influence on the rate constants [ $\ln(k_p/k_{p=1})$ ] of reaction (II) ( $\blacklozenge$ ), measured at 25°C and reaction (III) ( $\blacksquare$ ), measured at 60°C in toluene. For clarity, data points for reaction (III) have been shifted upward by unity on the ordinate axis.



**Figure 5** Dependence of the specific volume ( $d^{-1}/(\text{cm}^3 \text{ g}^{-1})$ ) of the solution of diene **4** ( $c^0_4 = 0.00806 \text{ mol L}^{-1}$ ) and dienophile **1** ( $c^0_1 = 0.03092 \text{ mol L}^{-1}$ ) on the adduct **5** concentration, according to Eq. (11).

toluene was placed in the cell of the densimeter (DSA 5000M) and in the quartz cell of the UV spectrophotometer (Hitachi 2900), the values of  $c_{\text{Add}(t)}$  were calculated independently by relation (13):

$$c_{\text{Add}(t)} = c^0_4 (D^0_4 - D_4) / D^0_4 \quad (13)$$

Here,  $D^0_4$  and  $D_4$  are the UV absorptions of diene **4** at the start of and during reaction (II). The same value of  $\Delta V_{\text{II}}$  was obtained from Eqs. (13) and (12), but with Eq. (13) the calculation was performed without the data for  $k_{\text{II}}$  and  $c^0_1$ .

The volume of the very slow reaction (III) in toluene at 25°C ( $k_{\text{III}} = 3.3 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1}$ ) was not determined by this method. But because of the sufficient solubility of adduct **7**, the volume of reaction (III) was calculated by the difference of PMVs (Eq. (6)). The mean values of three measurements are as follows:  $V_1 = 71.1 \pm 0.3$ ;  $V_6 = 219.5 \pm 0.8$ ; and  $V_7 = 263.3 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ , whence the value  $\Delta V_{\text{III}}$ , is equal to  $-27.3 \pm 1.6 \text{ cm}^3 \text{ mol}^{-1}$ . From these results, it follows that the corrected values of activation volume of reaction (II) at 25°C ( $-21.7 \pm 1.0$ ) and that of reaction (III) at 60°C ( $-23.2 \pm 1.2 \text{ cm}^3 \text{ mol}^{-1}$ ) are very close in spite of the huge difference in reactivity. For reactions (II)

and (III) in toluene solution, a diverse ratio  $\Delta V_{\text{corr}}^{\neq} / \Delta V_{\text{r-n}}$  was obtained: 1.15 and 0.85, respectively. With a solvent change for reaction (II) from acetonitrile to toluene, the ratio  $\Delta V_{\text{corr}}^{\neq} / \Delta V_{\text{r-n}}$  transforms from a “normal” ( $-20.0/-23.6 = 0.85$  [24]) to an “abnormal” value ( $-21.7/-18.9 = 1.15$ ).

## SUMMARY

It was noted that the solvent influence on the changes of PMV and the enthalpy of solution is usually very different, in contrast to the changes in entropy [12,18,19]. A comparison of the kinetic parameters of reactions (II) and (III) makes it clear that the difference in the rate constants is caused by the variety in the enthalpy of activation, with nearly the same values of activation entropy and activation volume. It was concluded that the apparent volume of activation, obtained with the pressure-independent concentrations, should be corrected for second-order reactions on the value  $RT\beta_T$ .

It is necessary to note that the solvent influence on the values of PMVs for different planar structures of dienes and dienophiles (except tetracyanoethylene as a strong  $\pi$ -acceptor) with the surface accessible for solvation is usually small [31]. On the contrary, large differences of the partial molar volumes of the branched molecular structure of adducts were observed [12,21–23,32]. The results obtained in this work are in agreement with the suggestion [12] that the abnormal volume ratio  $\Delta V_{\text{corr}}^{\neq} / \Delta V_{\text{r-n}} > 1$  for the forward isopolar Diels–Alder reactions can be caused by the differing abilities of solvent molecules to penetrate into the large branched molecules of the activated complex and adduct.

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