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Solvent effect on the volume of activation and volume of the Diels–Alder reaction

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ABSTRACT: Volumes of activation, $\Delta V^{\neq}$, and reaction, ΔV, partial molar volumes, $\bar{V}$, and enthalpies of solution, $\Delta_{\mathrm{sol}}H$, were determined for tetracyanoethylene, cyclopentadiene, 1,3-butadiene, *trans, trans*-1,4-diphenyl-1,3-butadiene and their Diels–Alder adducts at 25 °C in some solvents of π- and n-donor type. The values of the activation and reaction volumes were exceptionally small in the former type of solvents. Large solvent effects on $\Delta_{\mathrm{sol}}H_{\mathrm{TCNE}}$ (up to 26 kJ mol^{-1}), $\bar{V}_{\mathrm{TCNE}}$, ΔV and $\Delta V^{\neq}$ (up to 11 cm^{3}mol^{-1}) were observed in aromatic solvents and these values are linearly correlated with each other. Poor correlations were found for n-donor solvents, but a linear dependence between ΔV and $\delta_{\mathrm{r-n}}H$ (enthalpy of reaction) was obtained for all solvents. Copyright © 2001 John Wiley & Sons, Ltd.

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KEYWORDS: volume of activation; volume of reaction; solvent effect; tetracyanoethylene

SYMBOLS

K_{p}, equilibrium constant at pressure P; k_{p}, rate constant at pressure P; ΔG, free energy of process; $\Delta G^{\neq}$, free energy of activation; ΔV, volume of reaction; $\Delta V^{\neq}$, volume of activation; ϕ, apparent molar volume; $\bar{V}$, partial molar volume; $\bar{V}^{*}$, partial molar volume of transition state; $\Delta_{\mathrm{r-n}}H$, enthalpy of reaction; $\Delta_{\mathrm{sol}}H$, enthalpy of solution; $\Delta_{\mathrm{solv}}H$, enthalpy of solvation; $\Delta_{\mathrm{subl}}H$, enthalpy of sublimation; IP, ionization potential; T, temperature (K); R, gas constant; c_{N}, concentration of substance N at equilibrium; $c_{0,\mathrm{N}}$, initial concentration of N; D_{N}, optical density of N at equilibrium; $D_{0,\mathrm{N}}$, initial optical density of N; r, correlation coefficient; s, standard deviation; n, number of measurements; M, molar mass; d_0, density of solvent; d, density of solution.

INTRODUCTION

Information on the volume change during a reaction can be obtained from the pressure dependence of the equilibrium constant at a fixed temperature:

$$(\partial \ln K/\partial P)_T = -\frac{(\partial \Delta G/\partial P)_T}{RT} = -\Delta V/RT \qquad (1)$$

Since thermodynamic equilibrium between the initial and transition states is assumed in the transition state theory, the same conclusion is applicable to a kinetic pressure effect provided that the solvent thermal motions are fast enough:

$$(\partial \ln k/\partial P)_T = -\frac{(\partial \Delta G^{\neq}/\partial P)_T}{RT} = -\Delta V^{\neq}/RT \qquad (2)$$

Pressure affects the free energy of reaction through the $P\Delta V$ term and the various changes in the solute–solvent and solvent–solvent interactions. As an example, high pressure affects solvent properties (i.e. dielectric constant, viscosity, etc.) and for this reason additional changes of the free activation or reaction energies may occur. These effects may reflect on the validity of the volumes of activation and reaction.[1]

Another factor in the pressure effect is the intermolecular distance. Intermolecular distances decrease under pressure, leading to an increase in the potential energy. The molecules try to adjust to this new situation by taking a more crowded conformation, which occupies a smaller volume. Shifts of the conformational equilibrium of 1,2-

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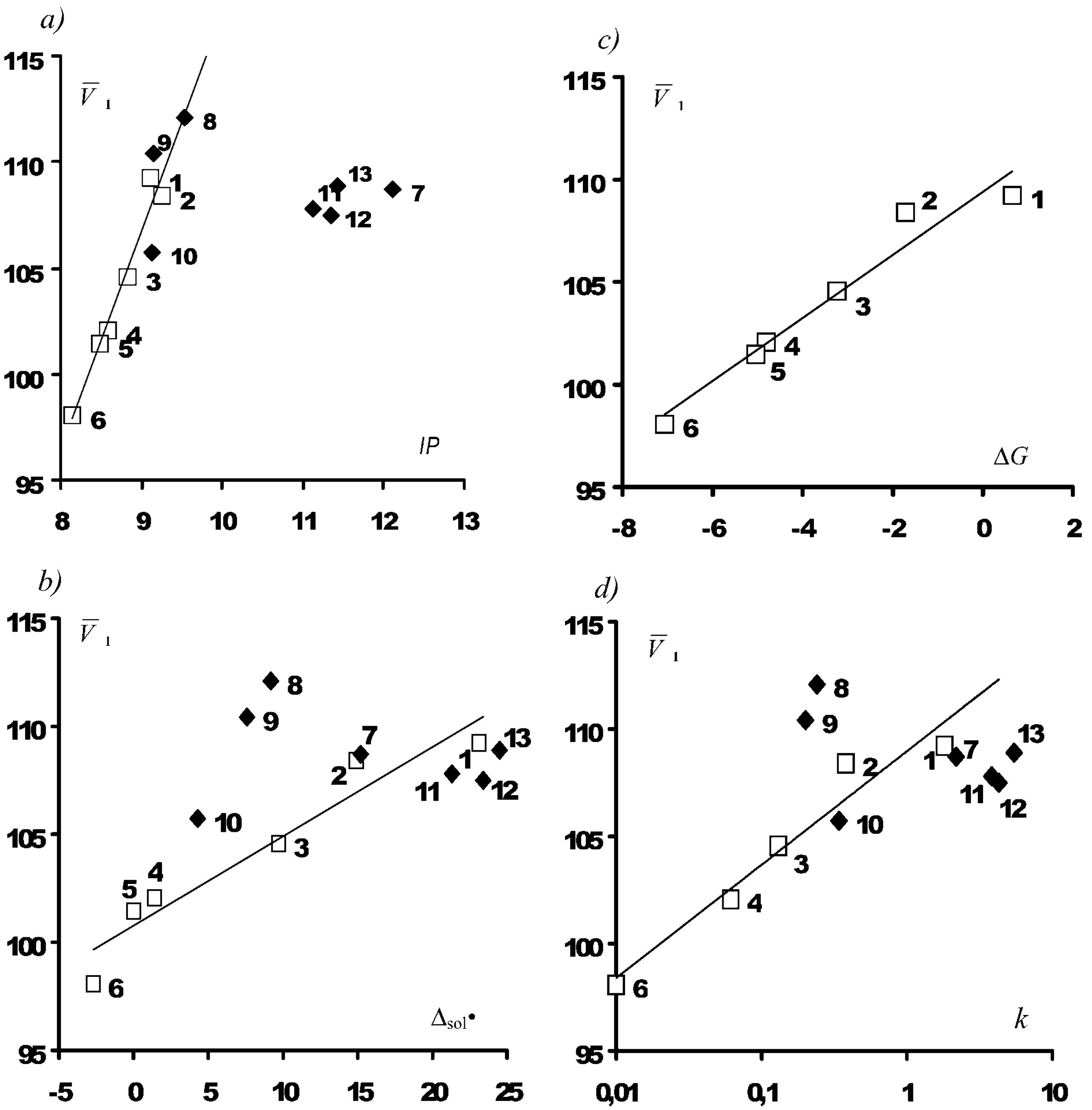


Figure 1. Correlations of the values of the partial molar volume of tetracyanoethylene ($\bar{V}_1$) with (a) the ionization potentials of the solvent, (b) the heat of solution of TCNE, (c) the free energy of the formation of the complex between TCNE and the solvent and (d) the rate constant in the Diels–Alder reaction of TCNE and anthracene using the data in Table 1. □, Aromatic solvents; ◆, non-aromatic solvents

dichloroethane from an *anti* to a *gauche* conformation ($\bar{V}_{gauche} - \bar{V}_{anti} = -3.8\ \mathrm{cm^3\ mol^{-1}}$ in hexane[2]) may be understood as a result of a combination of these two effects. In the case of fast reactions and in a medium with high viscosity the reaction rate can be controlled by diffusion and the pressure dependence of the rate constant can be complicated by this effect.[3–5]

Only when the free energy changes under pressure are caused by the contribution of the $P\Delta V$ term the values of reaction and activation volumes can be correctly determined from Eqns (1) and (2). Therefore, it is useful to compare the values of the volume parameters from pressure effects with pressure-independent measurements.

In contrast to the activation volume, the value of the reaction volume can be independently determined via the difference between the partial molar volumes of the products and of the reagents. Partial molar volumes ($\bar{V}$) of solutes at infinite dilution can be estimated by extrapolation of the apparent molar volumes (φ) obtained

Table 1. Ionization potentials of solvents (*IP*), partial molar volume of tetracyanoethylene ($\bar{V}_1$), enthalpy of solution ($\Delta_{sol}H$) and solvation ($\Delta_{solv}H$), free energy (ΔG) of complex formation of TCNE with alkylbenzenes and the rate constants (*k*) of the Diels–Alder reaction of TCNE with anthracene at 25 °C

No.	Solvent	IP^a (eV)	$\bar{V}_1$ (cm^3 mol^{-1})	$\Delta_{sol}H$ (kJ mol^{-1})	$-\Delta_{solv}H^b$ (kJ mol^{-1})	$-\Delta G^a$ (kJ mol^{-1})	k^c (1 mol^{-1} s^{-1})
1	Chlorobenzene	9.10	109.2	23.1	58.1	−0.65	1.82
2	Benzene	9.25	108.4	14.9	66.3	1.72	0.38
3	Toluene	8.82	104.6	9.7	71.5	3.24	0.13
4	*o*-Xylene	8.58	102.1	1.4	79.8	4.81	0.061
5	*p*-Xylene	8.48	101.5	0	81.2	5.04	—
6	Mesitylene	8.14	98.1	−2.7	83.9	7.07	0.010
7	Acetonitrile	12.12	108.7	15.2	66.0	—	2.18
8	Ethyl acetate	9.54	112.1	9.2	72.0	—	0.24
9	Cyclohexanone	9.14	110.4	7.6	73.6	—	0.20
10	1,4-Dioxane	9.13	105.7	4.3	76.9	—	0.34
11	1,2-Dichloroethane	11.12	107.8	21.3	59.9	—	3.82
12	Dichloromethane	11.35	107.5^d	23.4	57.8	—	4.28
13	Chloroform	11.42	108.9	24.5	56.7	—	5.47

[a] For alkylbenzenes from Ref. 9, and for other solvents from Ref. 10.
[b] Calculated with the value of $\Delta_{subl}H$ 81.2 kJ mol^{-1} from Ref. 11.
[c] From Ref. 12.
[d] From Ref. 13.

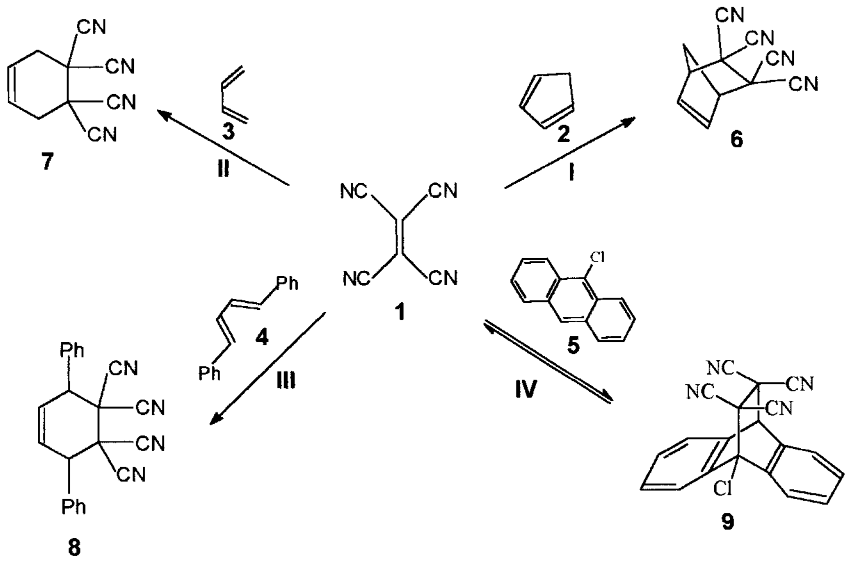
by measuring the solvent and solution densities:

$$\varphi_A = 1000(d_0 - d)/c_A d_0 + M_A/d_0 \quad (3)$$

$$\varphi_A = 1000(d_0 - d)/m_A d\, d_0 + M_A/d \quad (4)$$

$$\varphi_A = (d_0 - d)M_S(1 - x_A)/x_A d\, d_0 + M_A/d \quad (5)$$

where M_A and M_S denote the molar mass of solute and solvent, respectively, d and d_0 are the densities of solution and solvent, respectively, and c_A, m_A and x_A are the concentration scales in molarity, molality and mole fraction, respectively. For a solute the value of $\bar{V}_A$ includes the structural volume, i.e. the volume of van der Waals spheres, the voids around them and the volume change of the solvent in the process of shell formation around the solute.[6] The last contribution depends on the difference between solute–solvent and solvent–solvent interaction energies. In the case of strong ion–solvent interactions the contraction of the solvent by electrostriction can exceed the value of the structural volume of the solute and the value of the partial molar volume can be negative.[7] From this standpoint the partial molar volume is not the volume parameter of a solute only, but can be assigned to the volume change of the system as a whole, which involves the solute concentration. Nevertheless, the difference between these experimental values of partial molar volumes of the products and of the



Scheme 1

Table 2. Partial molar volumes ($\bar{V}$, cm^{3}mol^{-1}) of dienes **2** and **4** and adducts **6**, **7** and **8** and volumes of reactions **I–IV** (ΔV, cm^{3}mol^{-1}) with tetracyanoethylene in various solvents at 25 °C

		$\bar{V}$					$-\Delta V$			
No.	Solvent	**2**	**4**	**6**	**7**	**8**	**I**	**II**	**III**	**IV**
1	Benzene	83.2	199.3	159.6	161.9	280.8	32.0	34.7	26.9	—
2	Toluene	82.4	199.8	158.3	159.7	279.9	28.6	33.1	24.5	14.9
3	*o*-Xylene	82.4	199.8	160.2	160.8	280.7	24.3	29.5	21.2	11.3
4	Mesitylene	83.1	199.8	159.4	162.3	281.0	21.8	24.0	16.9	—
5	Chlorobenzene	82.4	—	159.6	—	—	32.0	—	—	—
6	Acetonitrile	82.6	200.0	150.6	157.6	275.5	40.7	39.3	33.2	24.2
7	Ethyl acetate	83.8	195.2	150.3	155.4	272.8	45.5	44.9	34.5	22.6
8	Cyclohexanone	81.4	201.7	157.5	158.6	278.1	34.3	40.0	34.0	—
9	1,4-Dioxane	81.8	200.4	151.6	156.1	279.8	35.9	37.8	26.3	—
10	Dichloromethane	83.5	—	153.8	—	—	37.2	—	—	—
11	1,2-Dichloroethane	83.6	202.7	154.7	154.4	278.8	36.7	41.6	31.7	20.6
12	Chloroform	—	199.8	—	154.2	273.8	—	42.9	34.9	—

reagents properly equals the reaction volume of the given reaction system. Similarly, the change of a heat of reaction in different solvents is determined by the difference in the heats of solution of products and of reagents. The heat of solution and the partial molar volume both reflect the changes in the intermolecular interactions.

The interpretation of the thermodynamic pressure effects in terms of molar volume changes has been proved for some reactions, e.g. the ionization of water.[6] The reaction volume derived from the pressure dependence of the ionization constant was in good agreement with that obtained from acid–base reactions. For a non-polar Diels–Alder reaction the values of the volume of reaction calculated from the difference in the activation volumes of forward and backward processes and from pressure effects on equilibrium were in good agreement with those obtained from partial molar volumes.[1] Therefore, the pressure effect can be considered as a bridge between the energetics and the volumetrics of chemical reactions. In a series of carefully selected solvents, it is reasonably expected that the solvent dependence of reaction volume is strongly correlated with the difference in the solvation energies of the reagents and of the products.

For ionic processes, the large solvent effect on the activation volumes is conditioned by the solvent electrostriction.[3,6,7] In this work the large solvent effects on activation and reaction volumes ($\Delta V^{\neq}$ and ΔV) of non-polar Diels–Alder reactions will be analyzed.

RESULTS AND DISCUSSION

Tetracyanoethylene (**1**) is known to be a good dienophile in the Diels–Alder reaction, and, owing to its strong π-acceptor tendency (lit.[8] $E_A = 2.88$ eV), its partial molar volume is expected to depend on the π-donor properties

Table 3. Enthalpy of solution ($\Delta_{sol}H$, kJ mol^{-1}) of tetracyanoethylene (**1**), dienes **2** and **4** and adducts **6**, **7** and **8** and relative change of the heat of reaction ($\delta_{r-n}H$, kJ mol^{-1}) in various solvents at 25 °C

		$\Delta_{sol}H$					$\delta_{r-n}H$		
No.	Solvent	**2**[a]	**4**	**6**	**7**	**8**	**I**	**II**	**III**
1	Benzene	0	24.1	22.9	22.9	20.3	13.6	8.3	14.0
2	Toluene	0.2	23.9	22.7	22.5	18.3	18.4	12.0	17.4
3	*o*-Xylene	0.8	24.4	23	20.7	17.3	26.4	18.2	24.2
4	Mesitylene	1.2	25.4	23	22.0	18.8	30.1	23.8	28.8
5	Acetonitrile	2.4	32.0	13.3	20.2	14.4	1.3	2.9	−0.1
6	Ethyl acetate	0.5	22.5	7.5	16.1	6.9	3.4	6.7	7.9
7	Cyclohexanone	0.5	20.5	10.3	15.2	2.7	7.8	7.4	7.3
8	1,4-Dioxane	0.1	21.4	4.1	14.8	9.1	5.3	10.7	16.1
9	1,2-Dichloroethane	0.6	24.4	16.3	21.6	13.0	0[b]	0[b]	0[b]
10	Chloroform	—	22.8	—	21.1	11.4	—	−2.6	−3.2
11	Dichloromethane	−0.2	—	16.0	—	—	−1.6	—	—
12	Chlorobenzene	0	—	22.9	—	—	5.4	—	—

[a] Data on the heat of solution of benzene from Ref. 14 (see text).

[b] 1,2-Dichloroethane was used as reference. The values of the heats of reactions **I**, **II**, **III** and **IV** in 1,2-dichloroethane are −113, −154, −97 and −66 kJ mol^{-1}, respectively, from Ref. 15.

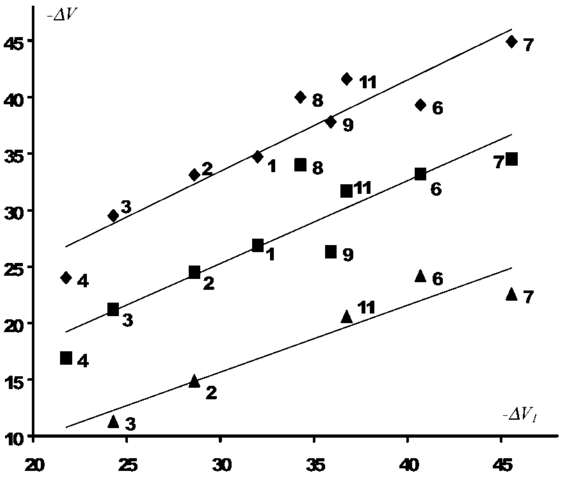


Figure 2. Correlation of solvent effect on the volumes of reactions (◆) **II**, (■) **III** and (▲) **IV** with the volume of reaction **I** from the data in Table 2. The numbers of the solvents correspond to those in Table 2

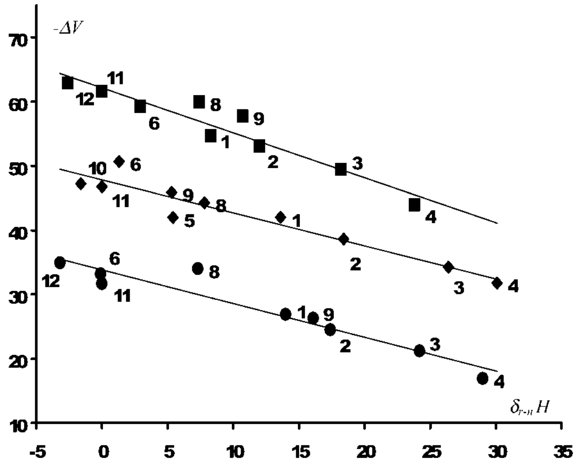


Figure 3. Correlation of solvent effect on the volumes of reactions (◆) **I**, (■) **II** and (●) **III** with the solvent effect on the heats of these reactions from the data in Tables 2 and 3. The numbers of the solvents correspond to those in Table 2. The ordinate values of reactions **I** and **II** are shifted up by 10 and 20 cm^3 mol^{-1}, respectively

of the solvent. Table 1 lists some effects of specific interactions of acceptor **1** with the solvent. The results for π-donor solvents (Nos 1–6, Table 1) demonstrate strong correlations between $\bar{V}_1$ and other magnitudes, as shown in Fig. 1. From these correlations one can conclude that π,π-complex formation plays a major role in the stabilization of **1** and this stabilization results in an approximately proportional decrease in the partial molar volume. On the other hand, however, poor correlations were found for n-donor solvents despite the large differences in $\Delta_{sol}H$. The increase in the solute–solvent interaction energy does not result in a regular decrease in $\bar{V}_1$, probably because the n-π interaction does not restrict the thermal motions of the solvent molecules as much as the π–π interaction, does.

From the results in Table 1 we can propose that the volume of reaction, ΔV, and the heat of reaction, $\Delta_{r-n}H$, for the Diels–Alder reaction of TCNE will change systematically in π-donor solvents. In order to examine this possibility, the partial molar volumes and the enthalpies of solution of cyclopentadiene (**2**), 1,3-butadiene (**3**) and *trans, trans*-1,4-diphenyl-1,3-butadiene (**4**) and those of their adducts with TCNE (Scheme 1) were determined. For reactions **I–III** the results are given in Tables 2 and 3.

The tetracyanoethanoic part in an adduct no longer has π-acceptor properties and this is reflected in the constancy of the values of $\bar{V}$ (**6–8**) (Table 2) and $\Delta_{sol}H$ (**6–8**) in aromatic solvents (Table 3). The heats of solution of the adducts are more endothermic in the aromatic solvents than in the others. This may be one of the reasons for their very low solubility in aromatic solvents. As expected, the reaction volumes tend to be less negative in the aromatic solvents than in the others, as a result of the smaller partial molar volume of TCNE, caused by π–π interactions. From the enthalpy cycle

Table 4. Experimental dependences of the optical densities (D_1 or D_5) and the equilibrium constants (K) on pressure (1–1000 kg cm^{-2}) and volume (cm^3 mol^{-1}) of reaction **IV** in various solvents at 25 °C

Solvent	Experimental relations
Toluene	$D_p/D_1 = 0.992 \pm 0.004 + (2.632 \pm 0.0132) \times 10^{-4}P$; $n = 21$; $r = 0.9937$; $s = 0.0070$; $v = 22730$ cm^{-1}; absorption of complex (**1**–solvent) $\ln K_p/K_1 = (-0.00111 \pm 0.0114) + (5.920 \pm 0.062) \times 10^{-4}P$; $n = 10$, $r = 0.9951$, $s = 0.023$; $\Delta V = -14.9 \pm 1.0$
o-Xylene	$D_p/D_1 = (0.999 \pm 0.003) + (4.720 \pm 0.050) \times 10^{-4} P$; $n = 21$; $r = 0.9989$; $s = 0.0071$; $v = 19050$ cm^{-1}; absorption of complex (**1**–solvent) $\ln K_p/K_1 = (0.0113 \pm 0.0082) + (4.484 \pm 0.0427) \times 10^{-4}P$; $n = 14$; $r = 0.9918$; $s = 0.021$; $\Delta V = -11.3 \pm 1.0$
Ethyl acetate	$D_p/D_1 = (1.001 \pm 0.001) -(2.813 \pm 0.526) \times 10^{-5}P -(3.703 \pm 0.508) \times 10^{-8}P^2$; $n = 19$; $r = 0.9916$; $s = 0.002$; $v = 25770$ cm^{-1}; absorption of diene **5**. $\ln K_p/K_1 = (-0.00953 \pm 0.0108) + (8.952 \pm 0.060) \times 10^{-4}P$; $n = 10$; $r = 0.9980$; $s = 0.003$; $\Delta V = -22.6 \pm 1.5$
Acetonitrile	$D_p/D_1 = (1.000 \pm 0.001) -(1.789 \pm 0.058) \times 10^{-4}P + (4.350 \pm 0.458) \times 10^{-8}P^2$; $n = 12$; $r = 0.9982$; $s = 0.002$; $v = 25770$ cm^{-1}; absorption of diene **5**. $\ln K_p/K_1 = (-0.00154 \pm 0.0174) + (9.566 \pm 0.084) \times 10^{-4}P$; $n = 11$; $r = 0.9958$; $s = 0.003$; $\Delta V = -24.2 \pm 1.5$

Table 5. Effect of pressure (1–1000 kg cm^{-2}) on the rate constant (k, l mol^{-1} s^{-1}) and volume of activation (cm^3 mol^{-1}) of reaction **III** in various solvents at 25 °C

Solvent	Experimental relations
Benzene	$\ln k = (-4.940 \pm 0.015) + (1.298 \pm 0.014) \times 10^{-3}P$; $n = 8$; $r = 0.9970$; $s = 0.0237$; $\Delta V^{\neq} = -32.7 \pm 0.4$
Toluene	$\ln k = (-5.972 \pm 0.021) + (1.175 \pm 0.014) \times 10^{-3}P$; $n = 7$; $r = 0.9970$; $s = 0.0345$; $\Delta V^{\neq} = -29.6 \pm 0.4$
o-Xylene	$\ln k = (-6.818 \pm 0.018) + (1.067 \pm 0.010) \times 10^{-3}P$; $n = 10$; $r = 0.9962$; $s = 0.0314$; $\Delta V^{\neq} = -26.9 \pm 0.3$
Mesitylene	$\ln k = (-8.476 \pm 0.037) + (9.180 \pm 0.235) \times 10^{-4}P$; $n = 6$; $r = 0.9903$; $s = 0.0453$; $\Delta V^{\neq} = -23.2 \pm 0.6$
1,2-Dichloroethane	$\ln k = (-2.344 \pm 0.018) + (1.260 \pm 0.011) \times 10^{-3}P$; $n = 10$; $r = 0.9972$; $s = 0.0303$; $\Delta V^{\neq} = -31.7 \pm 0.3$
Acetonitrile	$\ln k = (-2.522 \pm 0.020) + (1.312 \pm 0.013) \times 10^{-3}P$; $n = 8$; $r = 0.9971$; $s = 0.0297$; $\Delta V^{\neq} = -33.1 \pm 0.3$
Cyclohexanone	$\ln k = (-4.260 \pm 0.026) + (1.346 \pm 0.018) \times 10^{-3}P$; $n = 9$; $r = 0.9938$; $s = 0.0510$; $\Delta V^{\neq} = -34.1 \pm 0.5$

Table 6. Volume of activation of the forward ($\Delta V^{\neq}{}_{f}$) and backward ($\Delta V^{\neq}{}_{b}$) Diels–Alder reaction **III**, partial molar volume of the transition state ($\bar{V}$*) and the ratio ($\Delta V^{\neq}{}_{f}/\Delta V_{III}$) in various solvents at 25 °C (cm^3 mol^{-1})

No.	Solvent	$\bar{V}^*$	$\Delta V^{\neq}{}_{f}$	$\Delta V^{\neq}{}_{b}$	$\Delta V^{\neq}{}_{f}/\Delta V_{\mathbf{III}}$
1	Acetonitrile	275.6	−33.1	1.4	1.00
2	Cyclohexanone	278.0	−34.1	−0.1	1.00
3	1,2-Dichloroethane	278.8	−31.7	0.0	1.00
4	Benzene	275.0	−32.7	−5.8	1.21
5	Toluene	274.8	−29.6	−5.1	1.21
6	*o*-Xylene	275.0	−26.9	−5.7	1.27
7	Mesitylene	274.7	−23.2	−6.3	1.37

[Eqn. (6)] the relative reaction enthalpy, $\delta_{r-n}H$, with respect to 1,2-dichloroethane (S$_0$) was calculated:

$$\begin{aligned}\delta_{r-n}H &= \Delta_{r-n}H(S_i) - \Delta_{r-n}H(S_0)\\ &= \Delta_{sol}H_{\mathbf{6}}(S_i) - \Delta_{sol}H_{\mathbf{6}}(S_0)\\ &\quad - \Delta_{sol}H_{(\mathbf{1+2})}(S_i) + \Delta_{sol}H_{(\mathbf{1+2})}(S_0)\end{aligned} \tag{6}$$

For reactions **I**–**III** all the data are summarized in Table 3.

For reaction **IV**, which is reversible at room temperature, the values of the reaction volume can be obtained only from the pressure effect on the equilibrium constants (Table 4). It is obvious that the change in partial molar volume of tetracyanoethylene in aromatic solvents makes an essential contribution to the change in reaction volume. When the volumes of reactions **II, III** and **IV** are compared with the volume of reaction **I** (Fig. 2), nearly the same solvent effect on the reaction volumes is observed. It is interesting to note (Table 2, Fig. 2) that for the same process of breaking and forming bonds of non-polar Diels–Alder reactions **I**–**IV**, the values of the reaction volume differ sharply, depending on the adduct structure. In solution the voids in the crowded structure of adducts **8** and especially **9** are more or less inaccessible to solvent molecules. For this reason, the values of the partial molar volumes of these adducts are larger than those of the adducts with a structure completely accessible for solvation. The volume of reaction **IV** differs from that of reactions **I** and **II** by 20 cm^3 mol^{-1} and from that of reaction **III** by 10 cm^3 mol^{-1}. The crowding in the transition state of the non-polar Diels–Alder reaction is less than that in the adduct and, because of this, the value of the $\Delta V^{\neq}/\Delta V$ ratio can be >1.

The heat of solution and the partial molar volume both depend on the solute–solvent interactions. When the volumes of reactions **I**–**III** are compared with the changes in the heat of these reactions (Fig. 3), there is a clear tendency for a more negative volume of reaction with a larger exothermic heat of reaction in the solvents under consideration.

The volumes of activation were determined here only for the relatively sluggish reaction **III** (Table 5). It is interesting that the effect of aromatic solvents on the values of activation volume is related to that on the reaction rate: $\Delta V^{\neq} = -46.1 - 2.75\ln k_2$, $r = 0.996$. The values of the partial molar volume of the transition state ($\bar{V}^*$) (Table 6) were calculated from the experimental values of the activation volume of the forward reaction **III** ($\Delta V^{\neq}{}_{f}$) (from Table 5) and the partial molar volumes of reagents **1**–**4** (from Table 2). The values of the activation volume of the backward reaction **III** ($\Delta V^{\neq}{}_{b}$) were calculated from the difference between $\bar{V}^*$ and $\bar{V}_{\mathbf{8}}$. From the data in Table 6 it can be seen that the activation volumes of the backward reaction in non-aromatic solvents (Nos 1–3) are close to zero, and appreciably negative (−5 to −6 cm^{3}mol^{-1}) in aromatic solvents (Nos 4–7). To a first approximation, the ratio $\Delta V^{\neq}/\Delta V$ reflects the progress of the transition state along the reaction coordinate. In this work the ratio of the volumes of activation and reaction (Table 6) is very close to unity in non-aromatic solvents and appreciably longer in aromatic solvents. This means that in aromatic solvents the transition state is more accessible for solvation, compared with the branched structure of the adduct **8**.

The changes of partial molar volume of tetracyanoethylene in aromatic solvents correlate strongly with the volume of activation of the forward reaction **III** [Eqn. (7)] and with the volumes of reactions **I** [Eqn. (8)], **II** [Eqn. (9)] and **III** [Eqn. (10)]:

$$\Delta V^{\neq}{}_{\mathbf{III}} = (-0.89 \pm 0.01)\bar{V}_{\mathbf{1}} + 64.4;\ r = 0.997;\ n = 7 \tag{7}$$

$$\Delta V_{\mathbf{I}} = (-1.03 \pm 0.05)\overline{V}_{\mathbf{1}} + 79.7; r = 0.985; n = 4 \quad (8)$$

$$\Delta V_{\mathbf{II}} = (-1.06 \pm 0.07)\overline{V}_{\mathbf{1}} + 79.6; r = 0.971; n = 4 \quad (9)$$

$$\Delta V_{\mathbf{III}} = (-0.99 \pm 0.04)\overline{V}_{\mathbf{1}} + 80.1; r = 0.990; n = 4 \quad (10)$$

From the values of the slopes, it can be definitely concluded that the π-acceptor properties of tetracyanoethylene are entirely lost in adducts **6–8** and that they are still partly retained in the transition state of reaction **III** (within 10%).

From these results, a strong solvent effect would be expected on the activation and reaction volumes not only of ionic and polar reactions, as is well known from the literature,[3,7] but also of non-polar processes, where one of the states of the process under consideration interacts with solvent specifically.

CONCLUSION

The strong dependence of the heat of solution, the partial molar volume of TCNE, the volume of activation and the volume and the heat of reaction in aromatic solvents unequivocally demonstrated that π–π interactions play a vital role in the Diels–Alder reaction of TCNE. This is the first example of large systematic solvent effects on ΔV, $\Delta V^{\neq}$ and $\delta_{\mathrm{r-n}}H$ of non-polar Diels–Alder reactions. In contrast to π-donor aromatic solvents, n–π and n–n interactions between n-donor solvents and the reagents are possible. Moreover, relatively strong n–n interactions with the transition state and the reaction product can occur. This is the reason for the very sharp difference in the solubilities of adducts **6–9** in π- and n-donor solvents. The partial molar volumes should be larger for the branched structure in comparison with the less branched, more solvated structure. This difference may be the reason for the change in the volumes of activation and reaction: $\Delta V_{\mathbf{I}} \approx \Delta V_{\mathbf{II}} < \Delta V_{\mathbf{III}} < \Delta V_{\mathbf{IV}}$. From the same standpoint, the structure of the transition state of non-polar Diels-Alder reactions is less branched than that of the adduct and because of this the value of the $\Delta V^{\neq}/\Delta V$ ratio can be >1.

EXPERIMENTAL

Tetracyanoethylene (Merck) was sublimed *in vacuo* (50 Pa) at 110 °C as white crystals, m.p. 200–201 °C. Cyclopentadiene, after cracking of the dimer, was dried with $CaCl_2$ and distilled before the measurements. *trans, trans*-1,4-Diphenyl-1,3-butadiene was recrystallized from ethanol, m.p. 150–151 °C. 9-Chloroanthracene was purified on an alumina column, eluted with *n*-hexane–benzene (5:1), m.p. 100–101 °C. The adducts **6–8** were obtained as described[16] with a yield of about 90% and dried *in vacuo*, m.p. adduct **6** 211–213 °C (lit.[16] 206–209 °C), adduct **7** 202–203 °C (lit.[16] 197–199 °C) and adduct **8** 211–212 °C (lit.[16] 211–212 °C). The adduct **9** was prepared as described previously.[1] All the solvents were purified by known methods,[17] stored over molecular sieves 4A and distilled before the measurements. The water content was ≤0.002% (w/w) in aromatic solvents and ≤0.02% (w/w) in all the other solvents.

The heats of solution were measured at 25 °C using a differential calorimeter with a volume of solvent in each vessel of 180 cm^3, as reported previously.[18] The accuracy was within 2%. The heat of solution of cyclopentadiene was very low in the usual range of concentrations [$(1–5)\times10^{-3}$ mol l^{-1}]. When the concentration increased to 0.1 mol l^{-1}, the heat effect of the diene (**2**) dimerization was overlapping. For this reason, the heat of solution of benzene[14] was used as an alternative to that of cyclopentadiene. The same changes in the heat of solution applied to 1,3-butadiene.

Apparent molar volumes were determined at $25 \pm 1 \times 10^{-3}$ °C by means of a Paar digital vibrating-tube densimeter (DMA 602) with accuracy ≤0.5%. The apparent molar volumes of compounds **1**, **2**, **4** and **6–8** for each of the solutions were invariable in the concentration range 0.01–0.05 mol l^{-1}. No changes in the densities of solutions were observed within a few hours. The molar volume of 1,3-butadiene was assumed to be 82.2 $cm^3 mol^{-1}$ in all the solvents under consideration.

Pressure effects on the equilibrium constants were determined only for reaction **IV** of tetracyanoethylene with 9-chloroanthracene in some solvents (Table 4). The adducts **6–8** are very stable to decomposition under these conditions. The values of the equilibrium constants were determined from the equations

$$K = c_{\mathbf{9}}/(c_{0,\mathbf{5}} - c_{\mathbf{9}})c_{0,\mathbf{1}} = (D_{0,\mathbf{5}} - D_{\mathbf{5}})/D_{\mathbf{5}}c_{0,\mathbf{1}} \quad (11)$$

$$K = c_{\mathbf{9}}/(c_{0,\mathbf{1}} - c_{\mathbf{9}})c_{0,\mathbf{5}} = (D_{0,\mathbf{1}} - D_{\mathbf{1}})/D_{\mathbf{1}}c_{0,\mathbf{5}} \quad (12)$$

This depends on the monitoring of the absorption of diene **5** [in non-aromatic solvents when $c_{0,\mathbf{1}} >> c_{0,\mathbf{5}}$, Eqn. (11)] or of dienophile **1** [in aromatic solvents when $c_{0,\mathbf{5}} >> c_{0,\mathbf{1}}$, Eqn. (12)]. In Eqns (11) and (12), $D_{0,\mathbf{5}}$ and $D_{\mathbf{5}}$ are the optical densities of diene **5** corresponding to the concentrations $c_{0,\mathbf{5}}$ before the reaction and $c_{\mathbf{5}}$ at equilibrium. $D_{0,\mathbf{1}}$, $D_{\mathbf{1}}$, $c_{0,\mathbf{1}}$ and $c_{\mathbf{1}}$ are the corresponding characteristics for dienophile **1**. It is clear that all the values of D should be recalculated to the same pressure. The optical densities as a function of pressure were determined for all solutions of reactants **1** and **5** (Table 4). The Tait equation can never be used because of a minor bathochromic shift of the absorption bands under pressure. Optical densities can increase or decrease with the pressure, depending on whether monitoring is performed on the descending or ascending side of the absorption bands. It was checked that the ratio of the optical densities of solutions with different concentrations at each value of pressure equals the ratio of these concentrations. The change in optical density of tetracyanoethylene (reaction **IV**) in *o*-xylene and in toluene solutions under pressure is not related to the increase in the fraction of the molecular complex (MC) **1**–solvent. From the values of the equilibrium constants of the molecular complex of **1** with toluene (3.7 $\mathrm{l\,mol^{-1}}$) or with *o*-xylene (7.0 $\mathrm{l\,mol^{-1}}$, Ref. 9) the ratio $c_{\mathrm{MC}}/c_{0,\mathbf{1}}$ is >0.97.

All the sets of measurements ($\ln K$–P, Table 4) for each of solvents were fitted by a single linear dependence. The reagent concentration taken in excess was considered here as independent of pressure.

For reaction **III**, the measurements of the rate constants under pressure were performed in non-aromatic solvents following the change in the optical density of diene **4** and in aromatic solvents following the change in absorption of the molecular complex between tetracyanoethylene and solvent (Table 5). The procedure for measurements was the same as reported previously.[1] All experimental details for the results (Tables 4 and 5) are available as Supplementary Material at the epoc website at http://www.wiley.com/epoc.

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