

# Solvent Effect on the Volume of the Diels–Alder Reaction between Tetracyanoethylene and *trans,trans*-1,4-Diphenyl-1,3-butadiene

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**Abstract**—From the partial molar volumes of tetracyanoethylene, *trans,trans*-1,4-diphenyl-1,3-butadiene, and their Diels–Alder adduct, the volumes of the reaction in a series of solvents at 25°C (cm<sup>3</sup> mol<sup>-1</sup>) were calculated: in dioxane, -26.4; in chloroform, -34.9; in ethyl acetate, -34.5; in acetonitrile, -4.4; in cyclohexanone, -34.0; in 1,2-dichloroethane, -31.8; in benzene, -26.9; in toluene, -24.5; in *o*-xylene, -21.1; and in mesitylene, -16.9. The solvent effects on the activation and reaction volumes and on the partial molar volumes of the reactants, activated complex, and adduct were discussed.

Studies of how the elevated pressure affects the rates and equilibria of chemical and biochemical processes furnish additional information on their mechanisms [1–3]. The activation volume is an important additional activation parameter allowing calculation of the partial molar volume of the activated complex. The foundations for using the activation volume as an additional characteristic of the activated complex were laid in [4, 5]. By now, apparatus have been developed for studying reactions at elevated pressure with direct monitoring by various methods, including NMR, IR, and UV spectroscopy [1–3]. Barostats with direct monitoring are especially convenient for determining the volume characteristics of fast and/or reversible reactions.

The activation volume is the difference between the partial molar volumes of the activated complex and reactants in the given solvent; it can be calculated from the pressure dependence of the rate constant:

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

The reaction volume can be determined from the pressure dependence of the equilibrium constant:

$$(\partial \ln K / \partial P)_T = -(\partial \Delta G / \partial P)_T / RT = -\Delta V_r / RT. \quad (2)$$

Precision measurements of the density of dilute solutions allow determination of the apparent molar volumes and calculation of the partial molar volumes of the reactants and reaction products at infinite dilution. Therefore, in contrast to the activation volume,

the reaction volume can be also determined directly, as the difference between the molar volumes of the products and reactants, and compared with the value obtained from the pressure dependence of the equilibrium constant [Eq. (2)]. For the reversible Diels–Alder reaction of tetracyanoethylene with 9-chloroanthracene in 1,2-dichloroethane, determinations of the reaction volume by independent measurements of the activation volumes of the direct and reverse reactions, by examination of the pressure dependence of the equilibrium constants, and by direct measurements of the apparent molar volumes gave similar results [6].

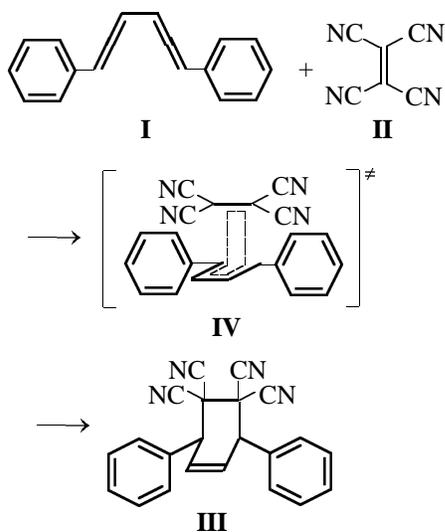
It is known that for reactions with significant charge separation in the activated complex the activation volume strongly depends on the solvent polarity [1–3]. We suggested that the solvent effect on the volume characteristics should be significant for any reactions in which one of the states is capable of strong specific interaction with the solvent [7, 8]. It was shown recently that for such a strong  $\pi$  acceptor as tetracyanoethylene the volumes of the reversible reaction with 9-chloroanthracene [9] and irreversible reaction with cyclopentadiene [10] and the activation volume in the irreversible reaction with *trans,trans*-1,4-diphenyl-1,3-butadiene [11] in aromatic solvents depend on the  $\pi$ -donor power of the solvent. With the majority of dienes tetracyanoethylene reacts very fast or reversibly, so that measurements at elevated pressure in common barostats without direct monitoring of the concentration variation are inefficient. The reaction with *trans,trans*-1,4-diphenyl-1,3-butadiene

Partial molar volumes of *trans,trans*-1,4-diphenyl-1,3-butadiene ( $\bar{V}_I$ ), tetracyanoethylene ( $\bar{V}_{II}$ ), adduct ( $\bar{V}_{III}$ ), and activated complex ( $\bar{V}_{IV}$ ), reaction volume ( $\Delta V_r$ ), and activation volumes of the direct ( $\Delta V_1^\ddagger$ ) and reverse ( $\Delta V_{-1}^\ddagger$ ) reactions in a series of solvents at 25°C, cm<sup>3</sup> mol<sup>-1</sup>

No.	Solvent	$\bar{V}_I$	$\bar{V}_{II}$	$\bar{V}_{III}$	$\bar{V}_{IV}$	$\Delta V_r$	$\Delta V_1^\ddagger$	$\Delta V_{-1}^\ddagger$
1	1,4-Dioxane	200.4±0.2	105.7±0.2	279.8±0.1	—	-26.3±0.5	—	—
2	Ethyl acetate	195.2±0.3	112.1±0.1	272.8±0.3	—	-34.5±0.6	—	—
3	Acetonitrile	200.0±0.3	110.0±0.1	275.5±0.1	276.9±0.7	-34.5±0.5	-33.1±0.3	1.4±0.8
4	Cyclohexanone	201.7±0.3	110.4±0.4	278.1±0.3	278.0±1.2	-34.0±0.9	-34.1±0.5	-0.1±1.4
5	1,2-Dichloroethane	202.7±0.4	107.8±0.2	278.8±0.2	278.8±0.9	-31.7±0.8	-31.7±0.3	0.0±1.1
6	Dichloromethane	—	107.8±0.2 <sup>a</sup>	—	—	—	—	—
7	Chloroform	199.8±0.1	108.9±0.1	273.8±0.1	—	-34.9±0.3	—	—
8	Chlorobenzene	—	109.2±0.1	—	—	—	—	—
9	Benzene	199.3±0.3	108.4±0.3	280.8±0.2	275.0±1.0	-26.9±0.6	-32.7±0.4	-5.8±1.0
10	Toluene	199.8±0.2	104.6±0.4	279.9±0.3	274.8±1.0	-24.5±0.9	-29.6±0.4	-5.1±1.3
11	<i>o</i> -Xylene	199.8±0.1	102.1±0.3	280.7±0.4	275.0±0.7	-21.2±0.8	-26.9±0.3	-5.7±1.1
12	Mesitylene	199.8±0.1	98.1±0.1	281.0±0.2	274.7±0.8	-16.9±0.4	-23.2±0.6	-6.3±1.0

<sup>a</sup> According to [12].

(see scheme) appeared to be convenient for determination of the activation and reaction volumes.



Comparison of the activation and reaction volumes in a series of solvents gives insight into the structure of the transition state. In this work we determined the partial molar volumes of reactants **I** and **II** and adduct **III** in ten  $\pi$ - and  $n$ -donor solvents and calculated the reaction volumes (see table).

The decisive effect of the specific interactions of aromatic solvents with tetracyanoethylene on the free energy of formation of  $\pi, \pi$  complexes, activation free energy in the Diels–Alder reaction, enthalpy of solution, and partial molar volume was discussed in [7, 8]. The partial molar volumes of diene **I** and adduct **III** ( $\bar{V}_I$ ,  $\bar{V}_{III}$ , see table) vary insignificantly in the exam-

ined solvent series, except ethyl acetate in which the packing of these compounds is closer than in the other examined solvents. The partial volumes of diene **I** and dienophile **II** in chloroform suggest lack of strong hydrogen bonding of chloroform with these reactants.

Variation of the reaction and activation volumes in aromatic solvents correlates with variation of the partial molar volume of tetracyanoethylene (see figure). For the activation volume, the correlation for aromatic and nonaromatic solvents is common (curve 1):

$$\Delta V^\ddagger = -0.8593\bar{V}_{II} + 60.83; R 0.9952, N 7. \quad (3)$$

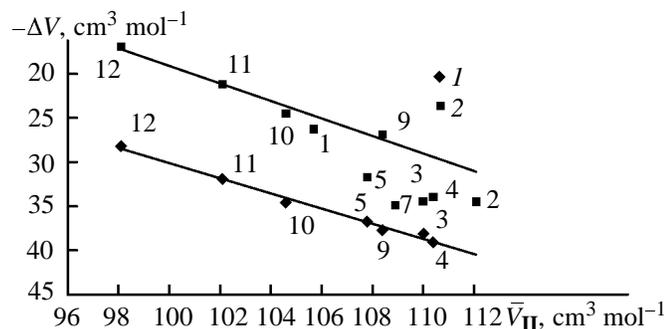
The correlation with the reaction volume for aromatic solvents (nos. 9–12, curve 2)

$$\Delta V_r = -0.9918\bar{V}_{II} + 80.08; R 0.9904, N 4. \quad (4)$$

does not include data for nonaromatic solvents.

In the group of solvents nos. 1–5 and 7, the packing features of diene **I** and adduct **III** noticeably differ from those in aromatic solvents (nos. 9–12), which results in more negative reaction volumes in the nonaromatic solvents (curve 2). Dioxane with respect to the capability for complexation with tetracyanoethylene occupies an intermediate position between benzene and toluene.

It should be noted that the reaction and activation volumes appreciably change (by 17 and 11 cm<sup>3</sup> mol<sup>-1</sup>, respectively) in going from inert solvents to mesitylene, which is the strongest  $\pi$  donor among the solvents examined. The slope of 0.86 of relationship (3) suggests that in the activated complex the  $\pi$ -acceptor



Comparison of the solvent effects on the (1) activation volume and (2) reaction volume, plotted vs. the partial molar volume of tetracyanoethylene ( $\bar{V}_{\text{II}}$ ). The point nos. correspond to the solvent nos. in the table. The points corresponding to the activation volumes are shifted along the ordinate by  $5 \text{ cm}^3 \text{ mol}^{-1}$ .

power of tetracyanoethylene is preserved to only 14%, and in going to the adduct [Eq. (4)] its  $\pi$ -acceptor power is fully lost.

The data obtained allow calculation of the partial molar volume of the activated complex ( $V_{\text{IV}}^\ddagger$ ) and the activation volume of the reverse reaction ( $\Delta V_{-1}^\ddagger$ ) from the relationships  $\bar{V}_{\text{IV}}^\ddagger = (\bar{V}_{\text{I}} + \bar{V}_{\text{II}} + \Delta V_{-1}^\ddagger)$  and  $\Delta V_{-1}^\ddagger = \Delta V_{-1}^\ddagger - \Delta V_{\text{r}} = \bar{V}_{\text{IV}}^\ddagger - \bar{V}_{\text{III}}$ . The results (see table) show that the partial molar volumes of the activated complex and adduct in nonaromatic solvents (nos. 3–5) are constant and equal to each other. In the aromatic solvents (nos. 9–12), the partial molar volumes of the activated complex and adduct are also constant, but the molar volume of the transition state is smaller by  $5\text{--}6 \text{ cm}^3 \text{ mol}^{-1}$  than that of the adduct. Therefore, the activation volume of the retro reaction is close to zero in the first group of solvents and negative in aromatic solvents. The negative activation volume for the adduct decomposition was noted in numerous papers [6, 13]. The more compact structure of the activated complex as compared to the adduct of the Diels–Alder reaction was tentatively attributed to secondary interactions of the unsaturated fragments [13]. Another explanation is associated with the possible increase in the fraction of voids inaccessible for the solvent in the adduct, as compared to the structure of the activated complex which is more accessible for solvation [6].

Our experimental data (see table and figure) suggest that, with respect to the volume parameters, the activated complex is considerably closer to the adduct than to the reactants.

## EXPERIMENTAL

*trans,trans*-1,4-Diphenyl-1,3-butadiene was purified by recrystallization from alcohol; mp  $150\text{--}151^\circ\text{C}$

( $149\text{--}150^\circ\text{C}$  [14]). Tetracyanoethylene (Merck) was sublimed in a vacuum ( $\sim 50 \text{ Pa}$ ) at  $110^\circ\text{C}$ . The melting point of the white crystalline substance was  $200\text{--}201^\circ\text{C}$  ( $201\text{--}202^\circ\text{C}$  [15]). Adduct **III** was prepared from equimolar solutions of **I** and **II** in 1,2-dichloroethane with subsequent recrystallization from benzene, mp  $211\text{--}212^\circ\text{C}$  ( $211\text{--}212^\circ\text{C}$  [16]). All the solvents were purified by common procedures [17].

The apparent molar volumes ( $\varphi$ ) were calculated from the relationship  $\varphi = (1/d - 1/d_0) \times 1000/m + M/d$ , where  $d$  and  $d_0$  are the densities of the solution and solvent,  $m$  is the molal concentration, and  $M$  is the molecular weight of the solute. In all the solutions the apparent molar volumes ( $\varphi$ ) of **I–III** in the concentration range  $0.01\text{--}0.04 \text{ mol kg}^{-1}$  were independent of the concentration and therefore could be considered as partial molar volumes ( $\bar{V}$ ). The densities of solutions and solvents were determined from the vibration frequency of the vibrating tube of a DMA-602 densimeter at  $25 \pm 0.001^\circ\text{C}$ . The temperature was maintained with a three-step cascade of thermostats containing 20 l of water each, kept at 21.0, 24.3, and  $25^\circ\text{C}$ . In the last thermostat, the heater power was decreased to 16 W. The densimeter was arranged in a glove box with a constant temperature ( $25 \pm 0.2^\circ\text{C}$ ). The measurement procedure is described elsewhere [6, 10]. For each solution, 4–5 measurements were performed. In the check measurements of the apparent molar volumes of **I–III** performed after a 3-month period in freshly purified dioxane, the results given in the table were fully reproduced.

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