Dramatic solvent effect on the volume of the Diels—Alder reaction between tetracyanoethylene and cyclopentadiene

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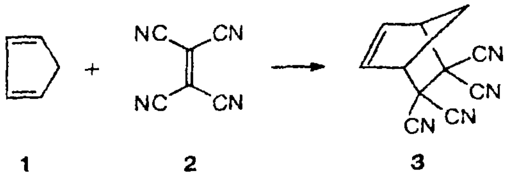
The partial molar volumes (V) and the enthalpies of dissolution ($\Delta_{dis}H$) for tetracyanoethylene, cyclopentadiene, and their Diels—Alder adduct were determined at 25 °C. Eleven solvents of the π- and n-donor type were used. The use of alkylbenzenes as solvents for tetracyanoethylene induces pronounced changes in the enthalpy of dissolution (up to 26 kJ mol^{-1}) and in the partial molar volume (up to 11 cm^3 mol^{-1}), whereas these parameters for the adduct change slightly. The V and $\Delta_{dis}H$ values for cyclopentadiene virtually do not depend on the nature of the solvent. In the case of tetracyanoethylene and the adduct in n-donor solvents, considerable variations of the V and $\Delta_{dis}H$ values are observed; they are not linear functions of the change in the partial molar volume of the adduct. Therefore, the reaction volumes in acetonitrile (−40.69) and ethyl acetate (−45.56) differ sharply from those in *o*-xylene (−24.28) and mesitylene (−21.76 cm^3 mol^{-1}).

Key words: partial molar volume, reaction volume, tetracyanoethylene, specific interactions, Diels—Alder reaction.

The use of elevated pressures provides data on the activation and reaction volumes of chemical reactions and allows more precise elucidation of the nature of the activated complex and its location on the reaction coordinate.[1—5] A recent study is devoted to the reversible Diels—Alder reaction between tetracyanoethylene and 9-chloroanthracene.[6] It was found that the reaction volumes determined by indirect methods (from the difference between the activation volumes of the forward and reverse processes and from the pressure dependence of the equilibrium constant) and by the direct method (from the difference between the partial molar volumes of the adduct and the reagents) are equal within the accuracy of determination. For polar and ionic processes, the contribution of the solvent electrostriction effect to the overall activation volume can be commensurable with and even exceed in magnitude the structural contribution.[7] A more accurate estimation of the contribution of solvent electrostriction in the solvation of a polar or ionic activation complex requires consideration of the influence of the variable properties of the medium on the reaction rate at elevated pressure.[6] An influence of the solvent on the activation volume has been established for many processes accompanied by the formation of polar or ionic states.[1—9] Testing of the process using the data on the influence of lithium perchlorate in diethyl ether on the cycloaddition rate showed that the activation complex in the Diels—Alder reaction involving tetracyanoethylene should be relatively nonpolar.[10] This means that solvent electrostriction in the solvation shell of the activated complex should be insignificant. In this work, we studied the reaction of tetracyanoethylene with cyclopentadiene in different solvents of the π- and *n*-donor type (Scheme 1).

Scheme 1



Tetracyanoethylene is a strong π-acceptor (electron affinity 2.88 eV[11]); however, its π-acceptor properties should not be manifested in full measure in the forma-

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tion of an activated complex. Therefore, it could be expected that the solvent would have a noticeable influence on the activation and reaction volumes for even this low-polarity process. These reactants were chosen not only because of the capacity of tetracyanoethylene for strong interactions with donor molecules of the solvent but also because the product formed from tetracyanoethylene and cyclopentadiene is stable against the retro-reaction and is sufficiently soluble for performing required measurements.

Results and Discussion

The partial molar volume (V) and its variation in the series of solvents provides little information on the nature of forces that determine the volume characteristics of the reaction. The variation of V for a substance dissolved in a given series of solvents is normally due to the change in the intermolecular distances in the solute—solvent system caused by the difference in the energies of interaction between the system components. However, these differences can often be due to unequal accessibilities of the sites of the dissolved substance for the approach of the solvent. When the change in the intermolecular distances is due to strong interactions, the $\Delta_{diss}H$ and V values are expected to change in parallel. In order to compare these values, the partial molar volumes and the enthalpies of dissolution were determined for a series of solvents (Table 1).

For tetracyanoethylene (**2**), the partial molar volume (V) sharply decreases on going from benzene to mesitylene. The $\Delta_{diss}H$ value decreases proportionally (Table 2). The variation of these values is in good agreement with the variation of the free energy of formation of the π,π-complexes from tetracyanoethylene and alkylbenzenes.[13] It is of interest that V of acceptor (**2**) in *o*-xylene is equal and that in mesitylene is smaller than the molar volume of the acceptor in the crystalline state[14] (102 cm^3 mol^{-1}). The $\Delta_{diss}H$ value for tetracyanoethylene in mesitylene is negative, while those in chlorobenzene, dichloromethane, and 1,2-dichloroethane $\Delta_{diss}H$ read the highest positive values. Evidently, some solvents (Nos. *5*, *10*, and *11*) can be considered to be especially inert with respect to acceptor (**2**). Comparison of the variations of the partial molar volume and the heat of dissolution of **1** shows (Fig. 1) that all the values for oxygen-containing n-donor solvents (No. *7*—*9*) are arranged above the straight line drawn for the series of alkylbenzenes, while chlorine-containing solvents are distinguished by low V values. Unlike the π,π-complexes formed by tetracyanoethylene and alkylbenzenes, in which molecules are arranged, according to X-ray diffraction analysis, in parallel planes,[15] in the case of n,π-complexes involving the lone electron pairs of the solvent heteroatoms (No. *6*—*9*, Table 1), no clear-cut proportionality between the variations of the thermal and volume effects was observed.

In pure cyclopentadiene, packing is more dense (V = 80.8 cm^3 mol^{-1}) than in solutions (see Table 1); however, the differences between V values are insignificant. The nonplanar cyclopentadiene molecule is packed more compactly in the solvation shells of nonplanar cyclohexanone (81.36 cm^3 mol^{-1}) and 1,4-dioxane (81.81 cm^3 mol^{-1}).

The tetracyanoethane fragment in the adduct does not exhibit π-acceptor properties; accordingly, the partial molar volume and the heat of dissolution of the adduct virtually do not change over the series of aromatic solvents (see Tables 1 and 2). The enthalpies of dissolution of the adduct in solvents (No. *1*—*5*, Table 2) assume much greater positive values. This is apparently the main reason for the virtually quantitative crystallization of most of the Diels—Alder adducts formed from diverse dienes and tetracyanoethylene in aromatic solvents. The points corresponding to oxygen-containing solvents (No. *7*—*9*) are located above the straight line containing the points for all the other solvents (Fig. 2).

Table 1. Partial molar volumes (V/cm^3 mol^{-1}) of cyclopentadiene (**1**), tetracyanoethylene (**2**), and their adduct (**3**) and the volume of the Diels—Alder reaction for the series of solvents at 25 °C

No.	Solvent	V_1	V_2	V_3	$-\Delta_r V$
1	Benzene	83.24±0.10	108.40±0.26	159.64±0.28	32.00
2	Toluene	82.39±0.05	104.56±0.37	158.34±0.20	28.61
3	*o*-Xylene	82.40±0.05	102.06±0.32	160.18±0.20	24.28
4	Mesitylene	83.05±0.10	98.07±0.10	159.36±0.50	21.76
5	Chlorobenzene	82.39±0.19	109.23±0.14	159.63±0.46	31.99
6	Acetonitrile	82.59±0.05	108.70±0.20	150.60±0.30	40.69
7	Ethyl acetate	83.77±0.07	112.09±0.25	150.30±0.25	45.56
8	Cyclohexanone	81.36±0.22	110.42±0.35	157.50±0.42	34.28
9	1,4-Dioxane	81.81±0.18	105.72±0.16	151.62±0.19	35.91
10	Dichloromethane	83.50±0.50	107.50±0.20*	153.76±0.10	37.24
11	1,2-Dichloroethane	83.64±0.13	107.81±0.20	154.70±0.10	36.75

* According to Ref. 12. The averaged values and the errors over three to five measurements are given.

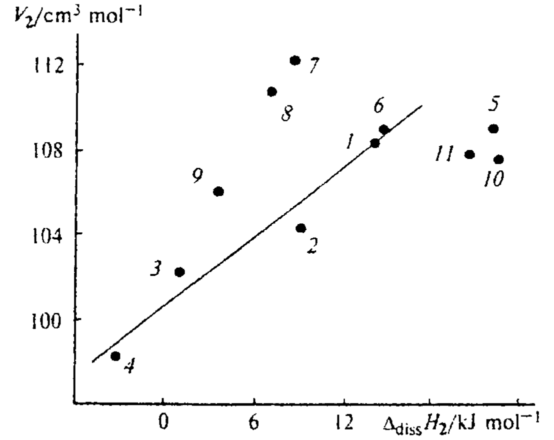

Fig. 1. Comparison of the effects of the medium on the enthalpy of dissolution ($\Delta_{diss}H_2$) and on the partial molar volume (V_2) of tetracyanoethylene. *1—11* are the numbers of solvents, see Table 1.

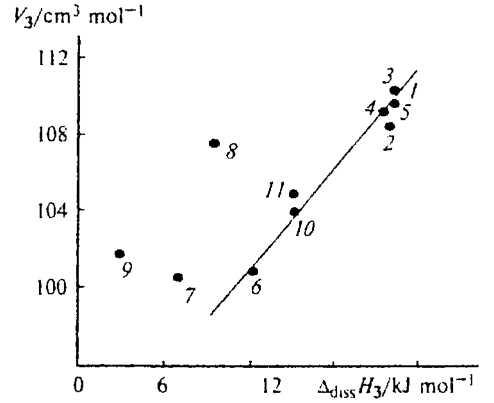

Fig. 2. Comparison of the effects of the medium on the enthalpy of dissolution ($\Delta_{diss}H_3$) and on the partial molar volume (V_3) of the adduct of the reaction. *1—11* are the numbers of solvents, see Table 1.

Table 2. Enthalpies of dissolution $\Delta_{diss}H$ (kJ mol^{-1}) and the change in the enthalpy of the Diels—Alder reaction of cyclopentadiene with tetracyanoethylene in a series of solvents at 25 °C

No.	Solvent	$\Delta_{diss}H_1$[a]	$\Delta_{diss}H_2$	$\Delta_{diss}H_3$	δ_rH
1	Benzene	0	14.9	22.9	13.6
2	Toluene	0.2	9.7	22.7	18.4
3	*o*-Xylene	0.8	1.4	23[b]	26.4
4	Mesitylene	1.2	−2.7	23[b]	30.1
5	Chlorobenzene	0.0	23.1	22.9	5.4
6	Acetonitrile	2.4	15.2	13.3	1.3
7	Ethyl acetate	0.5	9.2	7.5	3.4
8	Cyclohexanone	0.5	7.6	10.3	7.8
9	1,4-Dioxane	0.1	4.3	4.1	5.3
10	Dichloromethane	−0.2	23.4	16.0	−1.6
11	1,2-Dichloroethane	0.6	21.3	16.3	(0)

[a] The data of Ref. 16 on the heats of dissolution in benzene are given (see the text).

[b] Large experimental error (±2 kJ mol^{-1}) is due to the low solubility of the adduct in these media.

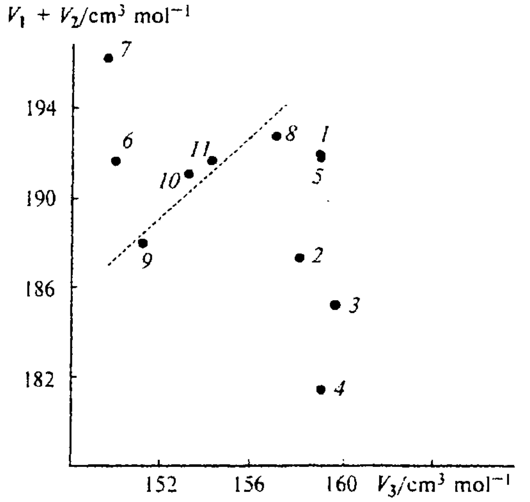

Fig. 3. The relationship between the variation of the partial molar volume of the adduct (V_3) and the reagents (V_1 + V_2) in a series of solvents. *1—11* are the numbers of solvents, see Table 1.

It follows from the data presented in Fig. 3 that the change in the partial molar volume of the reactants (**1** + **2**) is not proportional to the change in the partial molar volume of the adduct (**3**).

Only for some of the solvents (No. *8—11*), does this proportionality hold with a slope close to unity (see Fig. 3). This means that the volume of the reaction (−36±1 cm^3 mol^{-1}) is virtually independent of the nature of these solvents. On passing from benzene to mesitylene, the reaction volume ($\Delta_rV = V_3 - V_2 - V_1$) increases monotonically from −32 to −21.8 cm^3 mol^{-1}. The highest negative values for the reaction volume are observed for acetonitrile (−41.77) and ethyl acetate (−45.65 cm^3 mol^{-1}). The sharp change in the reaction volumes observed on going from benzene, toluene, *o*-xylene, and mesitylene to acetonitrile and, especially, to ethyl acetate is due to the fact that the effects of this groups of solvents on the partial molar volumes of the reactants (**1** and **2**) and the adduct (**3**) are opposite to those of the group of "normal" solvents (No. *8—11*, Fig. 3).

The change in the enthalpy of the reaction in this series of solvents with respect to an arbitrarily chosen standard medium can be calculated using the enthalpy cycle. This can be done using the equation

$$\delta_rH = \Delta_rH(s_i) - \Delta_rH(s_0) = \Delta_{diss}H_3(s_i) - \Delta_{diss}H_3(s_0) - \\ - \Delta_{diss}H_{1+2}(s_i) + \Delta_{diss}H_{1+2}(s_0),$$

where $\Delta_rH(s_0)$ is the enthalpy of the reaction in the reference solvent; $\Delta_{diss}H_3(s_i)$ and $\Delta_{diss}H_{1+2}(s_i)$ are the enthalpies of dissolution of the adduct and the reactants in another solvent. The changes in the enthalpy of the reaction in different media with respect to that in 1,2-dichloroethane are presented in Table 2. The obtained data make it possible for the first time to compare

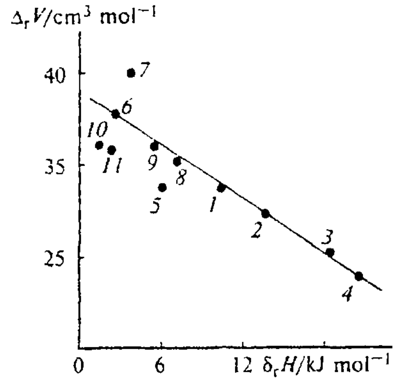

Fig. 4. The relationship between the change in the enthalpy of the Diels—Alder reaction between tetracyanoethylene and cyclopentadiene for the series of solvents ($\delta_r H$) and the volume of this reaction ($\Delta_r V$). *1—11* are the numbers of solvents, see Table 2.

the variations of the volume and the enthalpy of reaction (Fig. 4).

It can be seen in Fig. 4 that, as the process becomes more exothermic in the given series of solvents, the reaction volume decreases. Note that the data available on the volumes[2—4] and the enthalpies[17] of (4+2)-cycloaddition reactions for compounds of other structures do not obey the dependence presented in Fig. 4, which seems to be merely due to the difference in the solvation of the components.

The obtained data lead to the following conclusions. First, sharp changes in the reaction volume induced by replacement of the solvent should be expected not only for polar and ionic processes but also for low-polarity reactions in which reactants or products can experience strong intermolecular interactions with the solvent. Second, the proportional dependences of the reaction enthalpy as well as the reaction volume can be due to the difference in the energy of solvation.

The volume of the reaction under study becomes more and more negative as the process becomes more exothermic in a series of solvents. The change of the volume of the reaction between low-polarity reactants reaches 24 cm^3 mol^{-1} in the series of solvents studied (see Table 1). The major contribution to this effect is made by the change in the volume of tetracyanoethylene in this series of solvents. The change in the activation enthalpy in a series of solvents for the Diels—Alder reaction between tetracyanoethylene and dienes possessing strong or weak π-donor properties is virtually the same.[18] This means that the π-acceptor properties of tetracyanoethylene are no longer manifested in the formation of the activated complex. In the case of dienes with strong electron-donating properties, which form an "early" transition state, the fact that the transition state does not depend on the nature of the solvent is due to the formation of a strong complex between the reactants,[18] whereas for dienes with weak electron-donating properties, this is due to the more extensive rearrangement of the reacting bonds and displacement of the activated complex along the reaction coordinate toward the adduct.[17] Thus, a similar effect of the solvent on the activation volume should be expected for reactions involving tetracyanoethylene.

Experimental

Tetracyanoethylene **2** (Merck) was sublimed *in vacuo* (~50 Pa, 380 K) as snow-white crystals, m.p. 473—474 K. Cyclopentadiene (**1**) obtained by cracking of dicyclopentadiene (420—430 K) was dried with $CaCl_2$ and distilled prior to the measurements. Adduct **3** was prepared from equimolar (0.1 mol L^{-1}) solutions of the reactants in benzene; at 283 K, it was isolated from the solution in 90% yield. After drying *in vacuo*, m.p. 481—483 (*cf.* Ref. 19: 478—481 K). The solvents were purified by known procedures[20] and distilled prior to the measurements. Preliminarily distilled acetonitrile and ethyl acetate were refluxed over P_2O_5, which was replaced three times during the process, distilled over freshly calcined potassium carbonate, and stored over calcined 3A molecular sieves. The content of water (according to Fisher) was ≤0.02%.

The enthalpies of dissolution were determined at 298 K using a differential calorimeter (the cell volume was 180 cm^3). The procedure of the measurements was described previously.[21] The standard check of the operation of the calorimeter against the heat of dissolution of KCl in water gave a value of 17.4±0.2 kJ mol^{-1} (more precisely[22] 17.57±0.05 kJ mol^{-1}). The enthalpies of dissolution were averaged over two or three successive measurements. The heats of dissolution of cyclopentadiene were not determined because their molar values are low. Therefore, the heats of dissolution of benzene in the same series of solvents were used for comparison.[16]

The partial molar volumes (V) were calculated from the ratio

$$V = (1/d - 1/d_0)1000/m + M/d,$$

where d and d_0 are the densities of the solution and the solvent, m is the molality, M is the molar weight of the dissolved substance. The molar volumes of compounds **1**—**3** in all the studied solutions did not vary to within the experimental error at concentrations lower than 0.05 mol L^{-1}. The densities of solutions and solvents were determined from the oscillation frequency of the vibrating tube of a DMA 602 densimeter at 25±0.001 °C. The temperature was maintained constant using a system of three thermostats each containing 20 L of water (21.0, 24.3, and 25 °C); the power of the heater in the last thermostat was decreased to 16 W. The densimeter was arranged in a box with a constant air temperature (25±0.2 °C). Instead of syringes, specially manufactured glass dispensers were used to supply the solution. The outlet tube of the dispenser was connected to the input needle in the stopper of the measuring tube through a ground joint. The design of the dispensers allows injection of solutions or solvents in the measuring tube at a low rate, needed for complete wetting of the tube surface; the dispenser itself remained closed during all repeated measurements. For each solution, the measurements were repeated four of five times. The solution density was measured after the density of the solvent had been measured and the measuring tube had been then washed and dried.

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