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Diels—Alder reaction volumes in the solid state and solution

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The densities of anthracene, tetracyanoethylene, maleic anhydride, *N*-phenylmaleineimide, *trans*,*trans*-1,4-diphenylbuta-1,3-diene, and their Diels—Alder adducts were measured in the solid state and in solution at 25 °C. The reaction volumes in the solid state were calculated from the difference in molar volumes. They turned out to be low, close to each other (−4 to −11 cm^3 mol^{-1}), and slightly different from the reaction volumes (−8±1 cm^3 mol^{-1}) calculated from the van der Waals radii. The reaction volumes in solutions (−15 to −32 cm^3 mol^{-1}) were found from the difference in partial molar volumes of the reactants in dioxane, acetonitrile, and 1,2-dichloroethane, The experimental Diels—Alder reaction volumes in solution are determined not only by the formation of new bonds in an adduct: a considerably higher contribution (to 75%) is made by a change in the volume of intermolecular empty spaces in solution on going from reactants to adducts.

Key words: Diels—Alder reaction, intrinsic reaction volume, pressure effect, reaction volume in solution, reaction volume in solid state, packing coefficient.

A change in the volume on going from the initial to transition or final state of a reaction corresponds to an activation volume ($\Delta V^{\neq}$) or reaction volume (ΔV). The activation or reaction volumes can be calculated from the plot of the free activation energy ($dG^{\neq}/\partial p$, Eq. (1)) or free reaction energy ($\partial G/\partial p$, Eq. (2)) *vs.* external pressure (p).

$$(d\ln k/dp)_T = -1/RT\,(dG^{\neq}/dp)_T = -\Delta V^{\neq}/RT, \qquad (1)$$

$$(d\ln K/dp)_T = -1/RT\,(dG/dp)_T = -\Delta V/RT. \qquad (2)$$

The reaction volumes determined independently from the difference in partial molar volumes of the products and reactants are usually close to the values calculated by Eqs (1) and (2).[1] The activation volumes can be determined only from the plot of the rate constant *vs.* external pressure. In common belief,[2—4] the sign and value of an activation volume provide additional information on the mechanism of the chemical reaction. In several cases, the pressure effect on the rate or equilibrium of reactions (Eqs (1) and (2)) can be caused by an energy contribution $p\Delta V^{\neq}$ or $p\Delta V$ and also by a change in the properties of the solvent due to a pressure increase. For instance, for reactions with a high-polar transition state, an elevated pressure can affect the process rate due to the contribution $p\Delta V^{\neq}$ and also due to an increase in the dielectric constant of the solvent.[1,5] Several examples are known for which an elevated pressure results in a significant increase in the viscosity of the medium, and the diffusion rate can become determining even for comparatively slow processes.[6,7] In catalytic reactions, an elevated pressure can change the concentration of active species and thus change the reaction rate.[2—4]

In the absence of similar complications under an elevated pressure, the volume parameters can reliably be determined from relations (1) and (2).

Another question arises: what is an origin for the values of activation and reaction volumes? In the first approximation, it seems evident that, when a transition state and adducts are achieved, a decrease in the volume of a system in the addition and cycloaddition reactions is caused by the formation of new bonds bringing together the initial molecules of reactants. It is known that for processes, in which one of the states has a strong charge separation volume, changes can additionally be caused by the solvent electrostriction in the solvate shell, and the value of this solvent compression can even exceed the volume change for the process itself.[2,8] Therefore, the experimentally determined volume parameters require a detailed analysis of contributions caused by different processes. However, even in the case of ideal solutions, when the molar volume of a solvent in the solvate shell of the reactants, transition state, and products is the same as that of the pure solvent, the activation and reaction volume parameters are not determined by the formation of new bonds only.

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For a long time it remained unclear why the volume parameters change considerably for reactions of the same type but involving the reactant molecules different in size. Among different polar processes, the volume parameters are studied in most detail for the Menshutkin reaction and solvolysis reactions.[9—12] However, in these reactions involving different in size reactant molecules, the difference in volume parameters could be caused by a change in the polarity and, hence, by a difference in the electrostriction of the solvent. The Diels—Alder reaction refers to molecular processes in which no charge separation occurs on going from reactants to products. A remarkable influence of the solvent properties on a change in the rate and volume parameters in this reaction is observed only for pronounced donor-acceptor interactions between the reactants and medium. The influence of the solvent polarity on the rate and equilibrium of the Diels—Alder reaction was not observed.[6,14] The volume parameters in the Diels—Alder reaction involving small diene molecules, such as substituted butadienes and cyclopentadiene (-35 to -45 cm^3 mol^{-1}), are much higher than those in the reactions of large diene molecules (anthracenes, tetracenes, pentacenes) with the same dienophiles (-15 to -25 cm^3 mol^{-1}). Numerous experimental data on studying the Diels—Alder reaction suggest neither the formation of only one bond (two-step mechanism), nor a considerable charge separation in the transition state and, as a consequence, electrostriction of the solvent. Therefore, more special attention was given[15] to packing of the reactant and adduct molecules in solution and to its change depending on the structure and size of the molecules. These studies require the data on the van der Waals radii[16] that make it possible to calculate a packing coefficient (η) of molecules in solution as a ratio of the intrinsic or van der Waals volume (V_W) to the experimentally observed volume (V).

$$\eta = V_W/V. \tag{3}$$

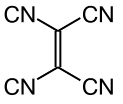
The η coefficient for gases usually does not exceed 0.002 and ranges from 0.4 to 0.7 for liquids, although for the solid state of organic compounds (0.65—0.85) it never achieves the limiting value equal to unity.[16]

The packing coefficient of a pure liquid or a dilute in solution is determined by the fraction of intermolecular empty spaces. Small organic molecules with an increased mobility in the liquid phase (or in solution) have lower η. Increased packing coefficients of organic compounds in the liquid phase and in solution are usually observed for compounds with a higher molecular weight, in the presence of heavier heteroatoms, and for more compact cyclic isomers compared to acyclic isomers.[17] Since the molecular weight of the Diels—Alder adduct is equal to the sum of weights of reactant molecules, the packing coefficient of the reaction products is usually higher than that of the reactants. The data on the influence of the packing coefficients of two reactants **A** and **B** with van der Waals volumes of 50 and 70 cm^3 mol^{-1}, respectively, and product **P** with a van der Waals volume of 110 cm^3 mol^{-1} on the observed reaction volume are presented in Table 1.

Table 1. Influence of the packing coefficient (η) of the reactants (**A**, **B**) and adduct (**P**) on the reaction volume (ΔV/cm^3 mol^{-1})

Example	**A**		**B**		**P**		ΔV
	η	V_W	η	V	η	V	
1	1	50	1	70	1	110	−10.0
2	0.7	71.4	0.7	100	0.7	157.1	−14.3
3	0.5	100	0.5	140	0.5	220	−20.0
4	0.50	100	0.55	127.3	0.60	183.3	−44.0

The intrinsic volume of this reaction determined by the difference in the van der Waals volumes of the adducts and reactant is -10 cm^3 mol^{-1}. For an unchanged packing coefficient (see Table 1, examples *2* and *3*), the observed reaction volume is more negative for a lower value of this coefficient. An increase in the packing coefficient with an increase in the size of molecules (example *4*) can result in a much more negative reaction volume than that could be expected, first of all, for addition reactions involving small in size reactant molecules. Thus, the ex-



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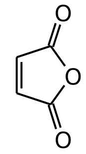

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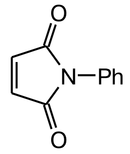

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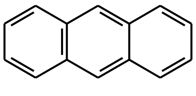

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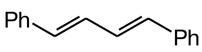

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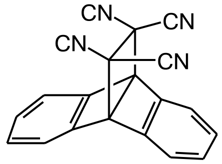

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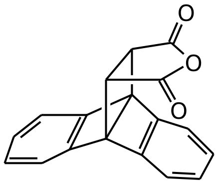

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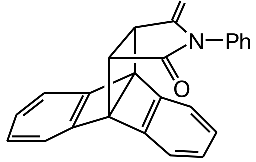

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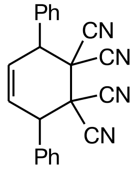

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perimentally observed reaction volume in solution in the latter case (see Table 1, *4*) can be caused by both a change in the volume due to the formation of new bonds (-10 cm^3 mol^{-1}, 23% of the whole effect) and a decrease in the volume of empty spaces in solution upon the transformation of the reactants into the product (-34 cm^3 mol^{-1}, 77% of the total effect). To use in practice high pressures in chemical processes, it is important to know the activation and reaction volumes. At the same time, when using the volume parameters to elucidate the reaction mechanism, one should know the nature of contributions forming the observed volume parameters. In this work, to check the influence of packing on the volume parameters, we determined the molar volumes in the solid state and in solution for tetracyanoethylene (**1**), maleic anhydride (**2**), and *N*-phenylmaleineimide (**3**) as dienophiles, anthracene (**4**) and *trans,trans*-1,4-diphenylbuta-1,3-diene (**5**) as dienes, and the products of Diels—Alder reaction **6—9**.

These data made it possible to compare the reaction volumes in the solid state with those calculated from the difference in the van der Waals volumes and also to compare them with the reaction volumes in solution (Tables 2 and 3).

In the most cases, the densities of solid reactants were found to achieve a limiting value already upon compression to 3—5 kbar and remain unchanged upon repeated compression even to 10—12 kbar. The limiting compacting of the sterically branched reaction products is achieved under a higher pressure. Therefore, the obtained results were compared with the data of picnometric and X-ray diffraction (XRD) measurements (see Table 2). The mo-

Table 2. Weighed samples (*a*) of the solid specimens and their volumes (*v*) and densities (ρ) obtained after compression in a barostat cylinder at 25 °C according to the data of XRD and picnometric measurements

Compound	*a*/g	*v*/cm^3	ρ/g cm^{-3}		
			I[a]	II[b]	XRD
1	1.5738	1.1989	1.313		1.313,[19] 1.316,[20] 1.312,[21] 1.32[22]
	1.4971	1.1397	1.314		
2	1.9310	1.2876	1.500		1.499[23]
	2.1114	1.4091	1.498		
3	1.7020	1.2148	1.401		
	1.7613	1.2500	1.409		
4	1.5098	1.2019	1.256	1.264	1.245,[24] 1.248,[25] 1.248,[26,27]
	1.6069	1.2799	1.256		1.251[28,29]
	1.7211	1.3670	1.259		
5	1.3867	1.1991	1.152		1.149[30]
	1.2892	1.1113	1.150		
6	1.5753	1.2118	1.300	1.309,	1.323[c] [31]
	1.7216	1.3263	1.298	1.301	
7	1.6888	1.2158	1.389	1.387	1.379,[32] 1.381[33]
	1.4669	1.0614	1.382		
8	2.1175	1.5882	1.333	1.363, 1.361, 1.365	
9	1.7463	1.392	1.254	1.252	
	1.6782	1.3452	1.247		
Anthraquinone[d]	1.7065	1.1859	1.439		1.447,[34] 1.428,[35] 1.446,[36]
	1.4215	0.9892	1.437		1.444,[37,38] 1.445[39]
			1.438[17]		
9,10-Dihydroanthracene[e]	1.4986	1.2207	1.227		1.207,[40] 1.214[41]
	0.4118	0.3367	1.223		
			0.8976[17,18]		
Potassium chloride (powder)	2.4327	1.2254	1.985		1.9868[17] (Sylvite)
	2.5758	1.2976	1.985		

Note. [a] The results of this work were obtained upon powder compression in a barostat unit.

[b] The results of this work were obtained by the picnometric method.

[c] The crystal cell had the composition [8 $(C_{20}H_{10}N_4)\cdot(C_6N_4)\cdot 2\,(CH_2Cl_2)$].

[d] $V_W = 115.6$, $\eta_{cr} = 0.798$.

[e] $V_W = 113.5$, $\eta_{cr} = 0.772$.

Table 3. Molar van der Waals volumes (V_W) of compounds **1—9**, molar volumes in the solid state (V_{cr}) and in dioxane (V_1), acetonitrile (V_2), and 1,2-dichloroethane (V_3), packing coefficients (η), intrinsic reaction volumes (ΔV_W), and reaction volumes in the solid state (ΔV_{cr}) and in dioxane (ΔV_1), acetonitrile (ΔV_2), and 1,2-dichloroethane (ΔV_3) at 25 °C

Compound	V_W (η_W)	V_{cr} (η_{cr})	V_1 (η_1)	V_2 (η_2)	V_3 (η_3)	ΔV_W	ΔV_{cr}	ΔV_1	ΔV_2	ΔV_3
1	68.1	97.5	105.7	108.7	107.8	—	—	—	—	—
	(1)	(0.698)	(0.644)	(0.626)	(0.632)					
2	48.4	65.4	71.3	70.4	72.0	—	—	—	—	—
	(1)	(0.740)	(0.679)	(0.688)	(0.672)					
3	96.4	123.2	137.1	133.3	138.1	—	—	—	—	—
	(1)	(0.782)	(0.700)	(0.723)	(0.698)					
4	109.7	141.6	159.5	158.2	161.9	—	—	—	—	—
	(1)	(0.775)	(0.688)	(0.693)	(0.678)					
5	135.6	179.4	200.4	200.0	202.7	—	—	—	—	—
	(1)	(0.756)	(0.677)	(0.678)	(0.669)					
6	171.0	235.5	249.5	251.1	255.2	−6.8	−3.6	−15.7	−15.8	−14.5
	(1)	(0.726)	(0.685)	(0.681)	(0.670)		±2	±1	±1	±1
7	149.7	200.2	205.9	201.8	207.4	−8.4	−6.8	−24.9	−26.8	−26.6
	(1)	(0.748)	(0.727)	(0.742)	(0.722)		±2	±1	±1	±1
8	197.8	256.0	276.9	272.6	279.8	−8.3	−8.8	−19.7	−18.9	−20.2
	(1)	(0.773)	(0.714)	(0.726)	(0.707)		±2	±1	±1	±1
9	195.6	267.5	279.8	275.5	278.8	−8.1	−11.5	−26.3	−33.2	−31.7
	(1)	(0.731)	(0.699)	(0.710)	(0.702)		±2	±1	±1	±1

lar volumes of the reactants and adducts in the solid state and in solutions are presented in Table 3. The comparison of these values shows that the experimental reaction volumes in the solid state are rather close to the van der Waals reaction volumes and considerably lower than the reaction volume in solution. Among the reactions of dienophiles **1—3** with common diene **4** in the solutions under study, the smallest change in the packing coefficient is observed on going from reactants **1** and **4** to adduct **6**. For the formation of adducts **8** and especially **7**, the packing coefficient increases remarkably. The absolute values of the reaction volumes increase in the same direction as the packing coefficients do (see Table 3).

It seems useful to compare the volume parameters of the reactions of anthracene and *trans,trans*-1,4-diphenylbuta-1,3-diene with the common dienophile tetracyanoethylene in solutions. In all solvents studied, a stronger increase in the packing coefficient is observed for the formation of adduct **9** compared to the formation of adduct **6**, resulting in more than twofold difference in reaction volumes. The reliability of the calculated van der Waals volumes of all compounds is confirmed by rather close values of intrinsic volumes of all reactions ($\Delta V_W = -8\pm1$ cm^3 mol^{-1}). A comparison of the data obtained suggests that the fraction of the intrinsic volume of the reactions under study (see Table 3) is lower than the halved experimental value in solution. In other words, the most part (to 75%) of the change in the volume of the system during the reaction considered is caused by a change in the packing of the reacting molecules in solution and determined not only by bond formation in the transition state of the reaction. The nature of packing of compounds in solution remains unclear yet. For instance, specific features of the packing of compounds **7**, **8**, and **9** in acetonitrile result in the substantially lowered values of partial molar volumes (see Table 3). However, the initial reactants also have lowered partial molar volumes in this medium. As a result, only an insignificant difference in reaction volumes is observed.

Experimental

Reagents from Aldrich were used. Tetracyanoethylene was purified by sublimation *in vacuo* (m.p. 199—200 °C).[17] Maleic anhydride (m.p. 53—54 °C),[17] *N*-phenylmaleineimide (m.p. 89—90 °C),[17] and *trans,trans*-1,4-diphenylbuta-1,3-diene (m.p. 152—153 °C)[17] were purified by crystallization from a hexane—benzene (5 : 1) mixture. Scintillation anthracene (m.p. 217—218 °C)[17] was used without additional purification. Compounds **6** (m.p. 253—256 °C, decomp.), **7** (m.p. 260—261 °C), **8** (m.p. 225—226 °C), and **9** (m.p. 211—212 °C) were synthesized in ~100% yield according to a described procedure.[14] Compounds **1—9** and their solutions were stable under the conditions of measurements. These reagents were chosen for the study, because for them possible differences in a change in the volume parameters of the reaction could be excluded due to regio- and stereoisomerism of the adducts.

Densities and partial molar volumes of compounds **1—9** in 1,4-dioxane, acetonitrile, and 1,2-dichloroethane were measured on a DMA-602 precision densimeter at $25\pm(1-2)\cdot10^{-3}$ °C. The procedure of measurements was described earlier.[1]

The results of three different methods of measuring the density of compounds **1—9** in the solid state are presented in Table 2. The most exact X-ray diffraction method for determining the density of crystals is not always accessible because of problems of single crystal formation, including the occlusion of solvent molecules. In the picnometric method, all errors of intermediate measurements are included in the determined density of crystals and, therefore, rather large weighed samples of compounds are needed. In addition, the solubility of some compounds even in alkanes can be rather high. We placed at least 1.5 g of a powdered substance into a 10-mL picnometer, added freshly distilled cyclohexane (5—6 mL), and the picnometer was stored in an ultrasonic bath until the powder was wetted completely. An additional mechanical stirring of the suspension did not change the results.

The method for determining the density of solid organic compounds proposed in this work is based on the determination of the limiting volume of a sample after compression to several kilobars. A weighed sample was compressed in a barostat cylinder. Since the strength of crystals of organic compounds is low, their initial size had no effect on the final results. Already under a pressure of ~1 kbar, the heights of pellets of all initial reactants approached to their limiting values. Under an additional compression to 4—6 kbar, the height of each pellet decreased reversibly, and well reproduced results were obtained after the pressure was discharged. The constant height of a pellet (cross section surface area of pellets was 1.557 cm^2) along with compressing rods and steel joints was checked by a micrometer after pressure discharge. In some cases, we succeeded to take the intact, undestroyed compressed pellets from the barostat cylinder and compare the calculated sizes. The divergence was at most ±0.5%. It was much more difficult to compress compounds **6—9** to a limiting volume even under a pressure of 10—12 kbar, probably, because of their branched structure. Therefore, the densities of these substances were additionally compared to the data of picnometric or XRD measurements (see Table 2). To verify the proposed method, we additionally determined the densities of 9,10-dihydroanthracene, 9,10-anthraquinone, and potassium chloride. The comparison of these results (see Table 2) shows that the method of specimen compression in a barostat gives reliable results, while the reference literature[17,18] can contain errors.

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