Effect of External Pressure and Solvent on the Equilibrium Constant of the Diels–Alder Reaction of 9-Chloroanthracene with Tetracyanoethylene

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Abstract—The effect of external pressure and solvent on the equilibrium constant of the Diels–Alder reaction of tetracyanoethylene with 9-chloroanthracene at 25°C was studied. The molar reaction volume is strongly solvent-dependent, cm^3/mol : -11.3 ± 1.0 in *o*-xylene, -14.9 ± 1.0 in toluene, -20.6 ± 1.5 in 1,2-di-chloroethane, -22.6 ± 1.5 in ethyl acetate, and -24.2 ± 1.5 in acetonitrile.

The effect of increased external pressure on the rate and equilibrium of chemical reactions at constant temperature fits the pressure dependences of the free energies of activation and reaction [1-3]. If pressureassisted changes in solvent properties exert no rate or equilibrium effects, which can also be simulated at atmospheric pressure, then the pressure dependences of the free energies of activation or reaction at constant temperature allow the molar volumes of activation or reaction to be estimated by Eqs. (1) and (2), respectively.

$$\ln k_P / k_0 = -\Delta V^* P / RT, \tag{1}$$

$$\ln K_P/K_0 = -\Delta V P/RT.$$
(2)

Increased pressure affects such solvent properties as density, dielectric constant, and viscosity [4, 5], which may occasionally produce rate and equilibrium effects, even if the states in hand have different volumes.

Recently we showed [6], with heterolytic dipolar (2+2)-cycloaddition reactions and the Menshutkin reaction as examples, that the rate effect of external pressure is associated not only with change in the volume [Eq. (1), ΔV^*], but also with a considerable (up to 30%) additional change in the free energy of activation, which results from pressure-assisted changes in the dielectric constant of solvent. One of the reasons why relationships (1) and (2) for heterolytic reactions deviate from linearity lies in the non-linearity of the dependence of the dielectric constant (and its reciprocal) of solvent on external pressure.

It terms of the transition state theory, change in solvent viscosity may affect the transmission coefficient, and this may show up in that the experimental entropy of activation would be pressuredependent.

The problem of equilibrium between initial and transition states has been actively discussed [1-5]. There are some grounds to state that when solvent has moderate viscosity (<10 cP) and half-conversion time $(>10^{-2} \text{ s})$, the probability of such equilibrium is rather high. For faster reactions in high-viscosity media, the rate at increased pressure is already diffusion-controlled, and, therefore, not adequately described by the transition state theory, while the molar activation volume is already not the only factor controlling the rate-pressure dependence [7, 8]. Polar and especially ionic activated complexes can strongly interact with solvent; as a result, the partial molar volumes of these states decrease considerably, thus increasing the absolute molar activation volume [9]. The largest molar activation volumes in such processes are observed in nonpolar media, which is associated with increased compressibility of nonpolar solvents [1-5, 9]. However, the allowance for the pressureassisted solvent effect on the rate of heterolytic reactions results in a much weaker solvent dependence of the activation volume [6]. This may be accounted for by increased energy of interaction of the polar activated complex with more polar solvents whose compressibilies are frequently, while not always, higher that those of nonpolar media [5].

The contribution of pressure-assisted solvent effect into experimental molar volumes of reactions between polar, nonpolar, and ionic structures [Eq. (2)] can be estimated independently via the partial molar volumes of reagents and products, while the effect of electrostriction of nonpolar and polar solvents, via the partial molar volumes of polar or ionic compounds in these media. Unfortunately, because of the poor solubility of ionic compounds in nonpolar media, their partial molar volumes cannot be measured with sufficient reliability. For the highly polar Reichardt's zwitter ion (μ 12 D), no correlation between partial molar volume and solvent polarity was found [10].

Recently we showed [11, 12] that in cases where one of the states enters strong specific interactions with solvent, a strong effect of the medium of the molar reaction volume can be observed with nonpolar compounds, too. The partial molar volumes of tetracyanoethylene, a strong π -acceptor (E_A 2.88 eV [13]), cyclopentadiene, and their adduct in the Diels-Alder reaction in 11 solvents we estimated molar reaction volumes, cm³/mol, which were found to sharply decrease in going from π -donor (-21.8 in mesitylene, -24.3 in *o*-xylene, -28.6 in toluene, -32.0 in benzene, and -32.0 in chlorobenzene) to *n*-donor and inert solvents (-34.3 in cyclohexane, -35.9 in 1,4-dioxane, -36.8 in 1,2-dichloroethane, -37.2 in dichloromethane, -40.7 in acetonitrile, and -45.6 in ethyl acetate). As noted in [12], the partial molar volume of cyclopentadiene varies along this series no more than $2 \text{ cm}^3/\text{mol}$, whereas the partial molar volumes of tetracyanoethylene and the adduct are comparable vary almost equally but in different direction, which results in a large difference in the partial molar reaction volumes (in going from mesitylene to ethyl acetate, $\delta V = -23.8 \text{ cm}^3/\text{mol}$). To assess the possible pressure-assisted solvent effect on molar reaction volume, we estimated Diels-Alder reaction volumes for tetracyanoethylene in a series of solvents from the experimental dependence of the equilibrium constant on external pressure [Eq. (2)]. The Diels-Alder reaction of tetracyanoethylene with cyclopentadiene is virtually nonequilibrium; therefore, we studied the effect of external pressure on the equilibrium of the reaction between 9-chloroantharacene (I) with tetracyanoethylene (II).



When measuring equilibrium constants at increased pressure, one deals with problems of directly measur-

ing reagent absorbances at increased pressure, maintaining constant temperature, and ensuring observation time sufficient for the system to attain equilibrium. In preliminary experiments we found that the sharp temperature rise with pressure ceases within 3–5 min, while the optical density of the solution at 25°C no longer varies within 2 h in *o*-xylene and toluene and within 1 h in acetonitrile and ethyl acetate. For more precise equilibrium constants all measurements were performed with a large excess of one of the reagents.

For all the solutions we preliminarily determined optical density-pressure dependences (Table 1).

It should be noted that Tait's equation which reliably describes the dependence of solvent volume on pressure fails to predict trends in the absorbance of tetracyanoethylene and 9-chloroanthracene solutions, since increasing pressure produces bathochromic shifts of the absorption bands. Therefore, as the pressure increases, the optical density of the solutions may increase, remain invariable, or decrease, depending on whether it is measured at the descending or ascending branch of the absorption bands, or near its maximum.

The equilibrium constants were calculated by Eqs. (3) or (4), depending on whether the absorbance of diene **I** or dienophile **II** is followed, respectively.

$$K_P = c_3/(c_{01} - c_3)c_{02} = (D_{01} - D_1)/(D_1)c_{02}$$

at $c_{02} >> c_{01}$, (3)

$$K_P = c_3/(c_{02} - c_3)c_{01} = (D_{02} - D_2)/(D_2)c_{01}$$

at $c_{01} >> c_{02}$. (4)

Here D_{01} and D_1 are the initial optical density of diene I before reaction and in equilibrium, and D_{02} and D_2 , the same for dienophile II. Obviously, all optical densities should be reduced to the same pressure. Since D_{01} and D_{02} are more convenient to measure at atmospheric pressure, the equilibrium optical densities at increased pressure $(D_1 \text{ or } D_2)$ were reduced, using the preliminarily established $D_P/D_{P=1}$ – P dependence (Table 1), to P = 1. Reducing the optical densities to a pressure (P), at which K_P is determined, would give the same result, since the $(D_{01} - k_P D_1)/(k_P D_1)$ ratio for P = 1 is equal to $(D_{01}/k_P - D_1)/(D_1)$ for increased pressure P, where $k_P = D_{P=1}/D_P$. Thus estimated equilibrium constants are listed in Table 2.

The molar volumes of the Diels–Alder reactions with substituted anthracenes are always larger in absolute value than those of the reactions with cyclopentadiene and, especially, butadiene, even with the same dienophile [1-3,6]. The possible reason for this difference is, in our opinion, reduced accessibility of shielded atoms of adduct **III** for interaction with solvent. In this case, the latter adduct has more cavities inaccessible for solvent, and, therefore, its molar volume increases to a greater extent than those of the adducts with cyclopentadiene and butadiene. The variation in the equilibrium constants with increasing pressure for all the reactions (Table 2) is decribed by Eq. (5), from which follows Eq. (6):

$$\ln K_P/K_0 = a + bP, \tag{5}$$

$$\Delta V = -bRT. \tag{6}$$

For the pressure expressed in kg/cm², R =84.78 kg cm K^{-1} mol⁻¹. As seen from Table 2, the molar volume, cm³/mol, of the reaction in study is -11.3 ± 1 in *o*-xylene, -14.9 ± 1 in toluene, -20.6 ± 1.5 in 1,2-dichloroethane [6], -24.2 ± 1.5 in acetonitrile, and -22.6 ± 1.5 in ethyl acetate. Thus, the strong variation in the molar volume of the Diels-Alder reaction of tetracyanoethylene with cyclopentadiene, we deduced earlier from partial molar volumes [12], could now be revealed for the reaction of tetracyanoethylene with 9-chloroanthracene from the dependence of equilibrium constants on external pressure. We failed to determine the partial molar volume of adduct III and the molar volumes of the reactions in toluene and o-xylene because of the poor solubility and the high degree of dissociation of compound III into the initial reagents. The molar volume of the reaction in 1,2-dichloroethane has been determined in [6] from the pressure dependence of the equilibrium constant ($-20.6 \pm 1.5 \text{ cm}^3/\text{mol}$), from the difference in the activation volumes of the direct $(-28.5\pm$ 1.5 cm³/mol) and reverse (-6.5 ± 0.5 cm³/mol) reactions, and from the difference in the volumes of adduct III (255.5 \pm 1.5 cm³/mol), diene I (170.7 \pm 0.5 cm³/mol), and dienophile II (107.8 \pm 0.2 cm³/mol), from which it follows that the molar reaction volumes estimated by the three independent methods fairly agree with each other.

Since the acceptor properties of tetracyanoethylene are much reduced not only in going to the adduct, but also in going to the activation complex of the Diels–Alder reaction [14], one can expect a similar solvent effect on the molar activation volume of the reaction involving this dienophile.

EXPERIMENTAL

Tetracyanoethylene, 9-chloroanthracene, and solvents were purified as described in [6, 12, 15]. The design of the barostat with direct spectrophotometric

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Table 1. Dependence of measured optical density (*D*) on external pressure

P, kg/cm ²	D_P/D_1	P, kg/cm ²	D_P/D_1				
Solvent <i>o</i> -xylene, λ 19050 cm ⁻¹ ,							
6	$x_2 1.59 \times 10^{-3}$ N	$M, D_{P=1} 0.5$	64				
1	1	355	1.172				
200	1.090	550	1.269				
395	1.186	780	1.381				
595	1 278	1000	1 474				
800	1.270	865	1.474				
000	1.570	660	1,410				
990	1.455	460	1.319				
890	1.413	400	1.222				
/10	1.333	300	1.140				
520	1.238	150	1.072				
320	1.140	1	0.999				
$\frac{1}{D_{p}/D_{1}} = (0)$	1.001	(4.720 ± 0.0)	$(50) \times 10^{-4} P$				
	n 21 r 0.998	89 c 0 0071					
Sc	n 21, r 0.000	$\lambda 22730$ cm	n ⁻¹				
50	1.00×10^{-4} N	1 D 0.4	01				
1 ($\frac{1}{2}$ 1.90 × 10 N	$D_{P=1} 0.42$	1 2 6 2				
1	1	1000	1.262				
245	1.062	/10	1.175				
495	1.119	400	1.095				
755	1.181	270	1.053				
590	1.142	120	1.016				
410	1.104	1	0.998				
1	0.999	1010	1.281				
215	1.050	830	1.205				
380	1.095	1	0.997				
680	1.178	800	1.188				
850	1 251						
Solv	vent acetonitrile	, λ 25770	cm^{-1} ,				
C	$c_1 6.30 \times 10^{-5}$ N	$A. D_{P-1} 0.29$	95				
1	1	7760	0.888				
250	0.959	600	0.905				
530	0.919	515	0.909				
1270	0.919	410	0.919				
1270	0.041	255	0.950				
010	0.801	233	0.939				
D_{-}/D_{-}	(1.000 ± 0.001)	(1.789 ± 0)	1.001 $058) \times 10^{-4}P$				
$D_{p}/D_{1} =$	(1.000 ± 0.001) (1.000 ± 0.001) (1.000 ± 0.001)	$= (1.769 \pm 0.9)$	$0.00) \times 10^{-1}$				
0±00.01	$(+30) \times 10^{-1}$,	n 12, 7 0.9	m^{-1}				
3010	$\sim 8.02 \cdot 10^{-5}$ N	$I = \frac{1}{2} $					
1	1 8.05 × 10 $^{-1}$	$D_{P=1} 0.70$	0.055				
1	1	775	0.955				
265	0.994	1015	0.933				
440	0.981	1	1.001				
625	0.966	230	0.994				
820	0.950	425	0.985				
1030	0.937	645	0.971				
1	0.999	820	0.953				
180	0.997	1010	0.935				
360	0.984	1	1.001				
570	0.972						
$D_{P}/D_{1} =$	(1.001 ± 0.001)	$-(2.813\pm0.12)$	$526) \times 10^{-5}P$				
$-(3.703\pm0.508)\times10^{-8}P^2$; n 19. r 0.9916. s 0.002.							

Table 2. Optical densities of solutions at equilibrium reagent concentrations (D_P) at increased pressure, their values reduced from the $(D_P/D_1 - P)$ dependence to P = 1 (D_{calc}) , and equilibrium rate constants (*K*) for the Diels–Alder reaction of tetracyanoethylene with 9-chloroan-thracene at 25°C

P, kg/cm ²	<i>D</i> ₂	D _{calc}	K _P	$\ln K_P/K_1$			
o-Xylene							
D_{02} 0.600, c_{01} 2.04 × 10 ⁻² , c_{02} 1.59 × 10 ⁻⁵ M, v 19050 cm ⁻¹							
1	0.504	0.504	9.5	0			
200	0.541	0.494	10.7	0.119			
250	0.548	0.490	11.2	0.165			
450	0.578	0.485	11.8	0.217			
520	0.605	0.485	11.8	0.217			
710	0.636	0.476	13.0	0.314			
910	0.662	0.464	14.6	0.430			
$D_{02} 0.556, c_{01} 2.04 \times 10^{-2}, c_{02} 1.50 \times 10^{-3} \text{ M},$							
1	0.470	0.470	07	0			
1	0.479	0.479	ð./ 10.9	0 216			
400	0.504	0.403	10.8	0.216			
900	0.046	0.447	15.1	0.409			
D_{02} 0.566, c_{01} 2.04×10 ⁻² , c_{02} 1.55×10 ⁻³ M, v 19050 cm ⁻¹							
1	0.487	0.487	8.7	0			
530	0.586	0.468	11.3	0.258			
990	0.658	0.449	14.0	0.475			
$\ln K_P / K_1$	= (0.0113	±0.0082) + ((4.484 ± 0.04)	$(427) \times 10^{-4} P$			
n 14, r 0.9918, s 0.021.							
$\Delta V -11.3 \pm 1.0 \text{ cm}^3/\text{mol}$							
D_{02}	$0.642, c_0$	1 oluene 1 2.94 × 10 ⁻	$\frac{-2}{c_{02}}$, c_{02} 2.0	× 10 ⁻⁴ M,			
$v 22730 \text{ cm}^{-1}$							
1	0.397	0.397	20.9	0			
1000	0.385	0.307	37.1	0.574			
910	0.386	0.313	35.7	0.535			
750	0.396	0.333	31.6	0.413			
280	0.401	0.376	24.0	0.138			
1	0.398	0.398	20.9	0			
D_{02} 0.642, c_{01} 2.94×10 ⁻² , c_{02} 2.0×10 ⁻⁴ M, v 22730 cm ⁻¹							
1	0.398	0.398	20.9	0			
260	0.396	0.374	24.4	0.155			
525	0.391	0.346	29.1	0.331			
760	0.380	0.319	34.4	0.498			
$\ln K_P / K_1 = (-0.00111 \pm 0.0114) + (5.920 \pm 0.062) \times 10^{-4} P$							
n 10, r 0.9951, s 0.023.							
$\Delta V = -14.9 \pm 1.0 \text{ cm}^3/\text{mol}$							

P, kg/cm ²	<i>D</i> ₂	D _{calc}	K _P	$\ln K_P/K_1$			
D_{01} 0.663, c_{01} 6.32×10 ⁻⁵ , c_{02} 1.10×10 ⁻³ M, v 25770 cm ⁻¹							
1	0.422	0.422	519	0			
$ \begin{array}{ccccccccccccc} D_{01} & 0.663, \ c_{01} & 6.32 \times 10^{-5}, \ c_{02} & 1.10 \times 10^{-3} \ \mathrm{M}, \\ & \mathrm{v} & 25770 \ \mathrm{cm}^{-1} \end{array} $							
980 770 565 215	0.234 0.273 0.317 0.370	0.270 0.307 0.347 0.383	1323 1054 828 664	0.935 0.708 0.467 0.246			
$ \begin{array}{cccccccc} D_{01} & 0.660, \ c_{01} & 6.32 \times 10^{-5}, \ c_{02} & 1.25 \times 10^{-3} \ \mathrm{M}, \\ & \mathrm{v} & 25770 \ \mathrm{cm}^{-1} \end{array} $							
1 250 505 775 1015 645	0.399 0.347 0.295 0.242 0.205 0.271	0.399 0.362 0.320 0.272 0.238 0.300	523 658 850 1140 1420 960	0 0.230 0.485 0.779 0.999 0.607			
$\ln K_P / K_1 = (-0.00154 \pm 0.0174) + (9.566 \pm 0.084) \times 10^{-4} P;$ <i>n</i> 11, <i>r</i> 0.9958, <i>s</i> ₀ 0.003. $\Delta V - 24.2 \pm 1.5 \text{ cm}^3 / \text{mol}$							
Ethyl acetate							
D_{01} 0.688, c_{01} 8.03×10 ⁻⁵ , c_{02} 5.66×10 ⁻³ M,							
1	0 415	0.415	1	0			
1 245	0.415	0.415	110	0 223			
350	0.364	0.369	153	0.277			
410	0.345	0.351	170	0.382			
700	0.296	0.308	218	0.631			
1000	0.249	0.266	280	0.881			
D_{01} 0.688, c_{01} 8.03×10 ⁻⁵ , c_{02} 5.66×10 ⁻³ M,							
$v 25770 \text{ cm}^{-1}$							
1	0.415	0.415	116	0			
300	0.375	0.379	144	0.216			
620	0.313	0.323	200	0.545			
990	0.249	0.266	280	0.881			
$\ln K_P / K_1 = (-0.00953 \pm 0.0108) + (8.952 \pm 0.060) \times 10^{-4} P;$							
$n \ 10, \ r \ 0.9980, \ s_0 \ 0.003.$							
$\Delta V = -22.6 \pm 1.5 \text{ cm}^3/\text{mol}$							

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Effect of external pressure on the equilibrium constant of the Diels–Alder reaction of tetracyanoethylene with 9-chloroanthracene in (1) o-xylene, (2) toluene, (3) acetonitrile, and (4) ethyl acetate at 25°C. The $\ln K_P/K_1$ values for the reactions in toluene, acetonitrile, and ethyl acetate were increased by 0.2, 0.4, 0.6 unit scale.

detection (Specord UV-Vis) and its operation have been described in [6, 15]. The reaction equilibria in ethyl acetate and acetonitrile were followed by the absorbance of diene I, and those in toluene and oxylene, by the absorbance of the molecular π,π complex (MC) of the solvent (S) with tetracyanoethylene (II). The fraction of complexed tetracyanoethylene was determined by the equation $c_{\rm MC}/c_{\rm II} = K_{\rm S}S_0/(1 + C_{\rm II})$ $K_{\rm S}S_0$), from which, at known equilibrium constants $(K_{\rm s})$ for the complexes of tetracyanoethylene with toluene (3.7 l/mol) and o-xylene (7.0 l/mol) [16], follows $c_{\rm MC}/c_{\rm II} > 0.97$. It is clear that the considerable increase in D_{MC} [1.5-fold in o-xylene (Table 1)] at increasing pressure is associated not with change in the concentration of the molecular complex but, first of all, with shift of its absorption band.

The ratios of the optical densities at any pressure in the range studied for solutions of tetracyanoethylene in toluene and *o*-xylene and of 9-chloroanthracene in acetonitrile and ethyl acetate of various concentrations strictly corresponds to the ratios of these concentrations, which substantiates the use of Eqs. (3) and (4) for calculating equilibrium constants. All repeated series of measurements with freshly prepared solutions for each solvent gave the same plot (see figure). Measurements in benzene and mesitylene were not performed, since in the former solvent the absorption bands of the reagents appreciably overlap, while in the second, a very low equilibrium constant is observed.

The concentration of the reagent taken in excess was considered to be independent of pressure.

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