

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

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Received February 16, 2000

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, cm³/mol: -11.3 ± 1.0 in *o*-xylene, -14.9 ± 1.0 in toluene, -20.6 ± 1.5 in 1,2-dichloroethane, -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 pressure-assisted 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.

$$\ln k_p/k_0 = -\Delta V^*P/RT, \quad (1)$$

$$\ln K_p/K_0 = -\Delta VP/RT. \quad (2)$$

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 nonlinearity 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 coef-

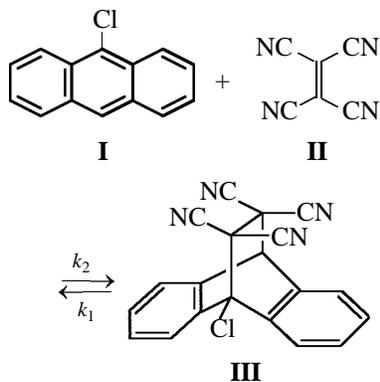
ficient, and this may show up in that the experimental entropy of activation would be pressure-dependent.

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 ($>10^{-2}$ 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 pressure-assisted 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 compressibilities are frequently, while not always, higher than 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, cm^3/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-chloroanthracene (**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.

$$K_P = c_3/(c_{01} - c_3)c_{02} = (D_{01} - D_1)/(D_1)c_{02} \quad \text{at } c_{02} \gg c_{01}, \quad (3)$$

$$K_P = c_3/(c_{02} - c_3)c_{01} = (D_{02} - D_2)/(D_2)c_{01} \quad \text{at } c_{01} \gg c_{02}. \quad (4)$$

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 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 described by Eq. (5), from which follows Eq. (6):

$$\ln K_p/K_0 = a + bP, \quad (5)$$

$$\Delta V = -bRT. \quad (6)$$

For the pressure expressed in kg/cm², $R = 84.78 \text{ kg cm K}^{-1} \text{ mol}^{-1}$. 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 ($-28.5 \pm 1.5 \text{ cm}^3/\text{mol}$) and reverse ($-6.5 \pm 0.5 \text{ cm}^3/\text{mol}$) reactions, and from the difference in the volumes of adduct **III** ($255.5 \pm 1.5 \text{ cm}^3/\text{mol}$), diene **I** ($170.7 \pm 0.5 \text{ cm}^3/\text{mol}$), and dienophile **II** ($107.8 \pm 0.2 \text{ cm}^3/\text{mol}$), 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

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

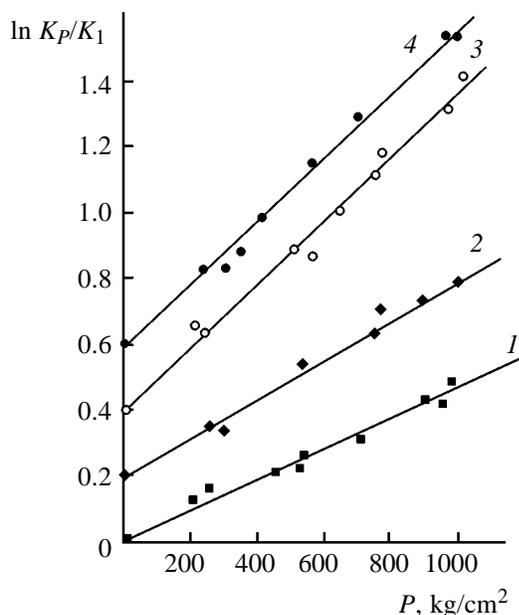
P , kg/cm ²	D_p/D_1	P , kg/cm ²	D_p/D_1
Solvent <i>o</i> -xylene, λ 19050 cm ⁻¹ , c_2 1.59×10^{-3} M, $D_{p=1}$ 0.564			
1	1	355	1.172
200	1.090	550	1.269
395	1.186	780	1.381
595	1.278	1000	1.474
800	1.370	865	1.418
990	1.453	660	1.319
890	1.413	460	1.222
710	1.333	300	1.140
520	1.238	150	1.072
320	1.140	1	0.999
1	1.001		
$D_p/D_1 = (0.999 \pm 0.003) + (4.720 \pm 0.050) \times 10^{-4} P$; n 21, r 0.9989, s 0.0071.			
Solvent toluene, λ 22730 cm ⁻¹ , c_2 1.90×10^{-4} M, $D_{p=1}$ 0.491			
1	1	1000	1.262
245	1.062	710	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		
Solvent acetonitrile, λ 25770 cm ⁻¹ , c_1 6.30×10^{-5} M, $D_{p=1}$ 0.295			
1	1	760	0.888
250	0.959	600	0.905
530	0.919	515	0.919
1270	0.841	410	0.936
1100	0.861	255	0.959
910	0.875	1	1.001
$D_p/D_1 = (1.000 \pm 0.001) - (1.789 \pm 0.058) \times 10^{-4} P$ $+ (4.350 \pm 0.458) \times 10^{-8} P^2$; n 12, r 0.9982, s 0.002.			
Solvent ethyl acetate, λ 25770 cm ⁻¹ , c_1 8.03×10^{-5} M, $D_{p=1}$ 0.708			
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		
$D_p/D_1 = (1.001 \pm 0.001) - (2.813 \pm 0.526) \times 10^{-5} P$ $- (3.703 \pm 0.508) \times 10^{-8} P^2$; n 19, r 0.9916, s 0.002.			

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-chloroanthracene at 25°C

P , kg/cm ²	D_2	D_{calc}	K_p	$\ln K_p/K_1$
<i>o</i> -Xylene D_{02} 0.600, c_{01} 2.04×10^{-2} , c_{02} 1.59×10^{-3} 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} 2.04×10^{-2} , c_{02} 1.50×10^{-3} M, v 19050 cm ⁻¹				
1	0.479	0.479	8.7	0
460	0.564	0.463	10.8	0.216
960	0.648	0.447	13.1	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
$\ln K_p/K_1 = (0.0113 \pm 0.0082) + (4.484 \pm 0.0427) \times 10^{-4}P$ n 14, r 0.9918, s 0.021. ΔV -11.3 ± 1.0 cm ³ /mol				
Toluene D_{02} 0.642, c_{01} 2.94×10^{-2} , c_{02} 2.0×10^{-4} M, v 22730 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. ΔV -14.9 ± 1.0 cm ³ /mol				

Table 2. (Contd.)

P , kg/cm ²	D_2	D_{calc}	K_p	$\ln K_p/K_1$
Acetonitrile 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
D_{01} 0.663, c_{01} 6.32×10^{-5} , c_{02} 1.10×10^{-3} M, v 25770 cm ⁻¹				
980	0.234	0.270	1323	0.935
770	0.273	0.307	1054	0.708
565	0.317	0.347	828	0.467
215	0.370	0.383	664	0.246
D_{01} 0.660, c_{01} 6.32×10^{-5} , c_{02} 1.25×10^{-3} M, v 25770 cm ⁻¹				
1	0.399	0.399	523	0
250	0.347	0.362	658	0.230
505	0.295	0.320	850	0.485
775	0.242	0.272	1140	0.779
1015	0.205	0.238	1420	0.999
645	0.271	0.300	960	0.607
$\ln K_p/K_1 = (-0.00154 \pm 0.0174) + (9.566 \pm 0.084) \times 10^{-4}P$ n 11, r 0.9958, s_0 0.003. ΔV -24.2 ± 1.5 cm ³ /mol				
Ethyl acetate D_{01} 0.688, c_{01} 8.03×10^{-5} , c_{02} 5.66×10^{-3} M, v 25770 cm ⁻¹				
1	0.415	0.415	116	0
245	0.375	0.378	145	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 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. ΔV -22.6 ± 1.5 cm ³ /mol				



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 *o*-xylene, 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 $c_{MC}/c_{II} = K_S S_0 / (1 + K_S S_0)$, from which, at known equilibrium constants (K_S) for the complexes of tetracyanoethylene with toluene (3.7 l/mol) and *o*-xylene (7.0 l/mol) [16], follows $c_{MC}/c_{II} > 0.97$. 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.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 98-03-33053a) and the Research Department of Kazan State University.

The authors are grateful to E.A. Kashaeva and M.D. Medvedev for help in certain experiments.

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