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Pressure Effect on the Rate and Equilibrium Constants of the Diels-Alder Reaction 9-Chloroanthracene with Tetracyanoethylene

Vladimir D. Kiselev*, Elena A. Kashaeva, Alexander I. Konovalov

Butlerov Chemical Institute, Kazan State University. Kazan, 420008 Russia.
Fax: + 7(8432)387049; E-mail: <kiselev@butler.kazan.su>

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Abstract: *The pressure effect on the forward and backward rate constants and equilibrium constants of the Diels-Alder reaction of 9-chloroanthracene with tetracyanoethylene has been investigated in 1,2-dichloroethane up to 1000 kgcm*$^{-2}$ *at 298.15 K. The reaction volume obtained from the pressure effect on equilibrium (-20.6 ±1.5 cm*^{3}*mol*$^{-1}$ *) and as difference of activation volumes of forward (-28.5±1.5) and backward (-6.5 ± 0.5) reaction (-22.0±1.5 cm*^{3}*mol*$^{-1}$*) are in agreement with partial molar volume difference of adduct (255.5±1.5) {diene (170.7±0.5) and dienophile (107.8±0.2)} giving -23.0 ±2 cm*^{3}*mol*$^{-1}$*.*

INTRODUCTION

A lot of reaction rates under pressure have been measured,[1-6] but only a few studies on isomerisation and dissociation processes paid attention to a comparison of the reaction volumes from the pressure effects on equilibrium and from differences of the partial molar volumes of products and reactants.[5] For the Diels-Alder reaction the rate constants were determined at atmospheric pressure for numerous reagents in forward and back directions in different solvents with and without catalysis.[7-9] Only two reactions were studied in the reverse direction under high pressure.[10,11] We nowhere met information about high pressure effects on the equilibrium constants of Diels-Alder reactions, even though such examples at atmospheric pressure are well known.[7-9] The reactions of aromatic dienes with tetracyanoethylene are very fast and are usually equilibrium processes (table 1). The heat of reaction for tetracyanoethylene and 9-chloroanthracene is less exothermic than with 9-methyl- and 9,10-dimethylanthracene,

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and the determination of the equilibrium constant for reaction with the last dienes is complicated by the large equilibrium shift to the adduct direction. In reactions with 9-methoxy- and in particular with 9,10-dimethoxyanthracene, the problem is a result of a shift in the equilibrium to the reagent direction.

Table 1. Ionization potential (*IP*, e.V.), rate (k_2, l mol^{-1} s^{-1}) and equilibrium ($K_{eq.}$, l mol^{-1}) constants and enthalpy (ΔH, kJ mol^{-1}) of the Diels-Alder reaction of 9,10-substituted anthracenes with tetracyanoethylene in 1,2-dichloroethane, 298 K.[a]

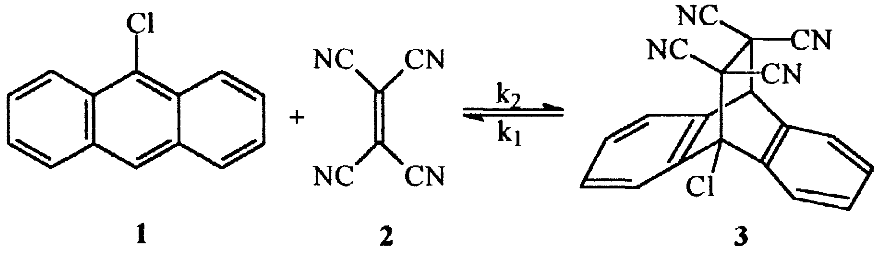
9,10- substituents in diene	*IP*	k_2	$K_{eq.}$[b]	$-\Delta H$
CH_3; CH_3	7.04	93000	-	88.3
CH_3O; CH_3O	7.09	870	15	51.5
CH_3; H	7.17	2200	-	84.5
CH_3O; H	7.17	5100	250	61.1
H; H	7.33	3.0	-	76.6
Cl; H	7.39	0.7	800	66.1
Cyclopentadiene	8.58	430 [c]	-	113

[a] Data from Ref. 8. [b] From Ref. 12. [c] In dioxane at 293 K from Ref. 13.

RESULTS AND DISCUSSION

The Diels-Alder reaction of 9-chloroanthracene with tetracyanoethylene (Scheme) in 1,2-dichloroethane was selected since independent determination of the rates in both directions and equilibrium under pressure and the partial molar volumes of the adduct in solution are easily observed. According to the small effect of lithium perchlorate in diethyl ether solution on the rate, this reaction belongs to a nonpolar process.[9]

It was found that the enhancement of the diene absorption at the elevated pressure exceeds one expected from Tait's equation for 1,2-dichloroethane.[6] This is caused by a change of solvent properties under pressure[5,6] and by a minor batochromic shift of the diene absorption band. Since monitoring of diene optical density was carried out on the band slope, the pressure dependence of absorption (up to 1000 kg cm^{-2}) is more than from Tait's equation: $D_p/D_o = 0.995 + 3.843\ 10^{-4} P - 1.469\ 10^{-7} P^2$ (R=0.9959; N = 17).



Scheme

The results of three series of measurements of the pressure effect on the equilibrium are collected in table 2. All sets of data follow the correlation: $\ln K_p/K_o = (0.00352 \pm 0.00707) + (8.1405 \pm 0.0321)10^{-4} P$ (R=0.9974, N=19). A polynomial equation does not improve the correlation. The value of reaction volume equals -20.6±1.5 cm^{3}mol^{-1}.

Table 2. Pressure effect on the equilibrium constants of the Diels-Alder reaction of 9-chloroanthracene with tetracyanoethylene in 1,2-dichloroethane at 298.15 K.

Set 1		Set 2		Set 3	
P, kg cm^{-2}	$\ln K_{cq.}$ /835 [a]	P, kg cm^{-2}	$\ln K_{eq.}$/800 [a]	P, kg cm^{-2}	$\ln K_{eq.}$/843 [a]
0	0	0	0	0	0
270	0.234	160	0.126	155	0.121
470	0.400	260	0.217	305	0.236
620	0.541	360	0.337	410	0.319
810	0.661	505	0.437	550	0.429
970	0.790	645	0.519	730	0.595
-	-	760	0.601	-	-

[a] In the columns $\ln K_p/K_o$ showed the experimental values of K_o, (l mol^{-1}).

The value of reaction volume was independently obtained from the partial molar volumes of the reagents and the adduct. The densities of solutions were determined using the densimeter "DMA 602". The apparent molar volume of 9-chloroanthracene (170.7±0.5) and tetracyanoethylene (107.8±0.2; 107.5±0.2 cm^3mol^{-1} in dichloromethane[14]) turned out to be independent of concentration below 0.05 mol l^{-1}. The determination of adduct volume (255.5±1.5 cm^3mol^{-1}) was performed in 1,2-dichloroethane and in tetracyanoethylene solutions with regard to the composition of these solutions.

It was thus found that the values of the Diels-Alder reaction volumes from pressure-equilibrium data (-20.6 ±1.5) and from direct data on partial molar volumes (-23.0 ±2.0 cm^3mol^{-1}) are in reasonable agreement.

The rate of adduct decomposition is complicated by the forward reaction which can easily be avoided by adding cyclopentadiene. The rate and equilibrium constants for the reaction of tetracyanoethylene with cyclopentadiene are considerably higher than with 9-chloroanthracene (table 1) and the adduct with cyclopentadiene does not decompose under these conditions. The results of the pressure effect on the rate of decomposition of adduct (**3**) are collected in table 3.

Table 3. Pressure effect on the rate constants of decomposition of adduct (**3**) at 298.15 K.

P, kg cm^{-2}	10^4 k_1, s^{-1}	$\ln k_p/k_o$
0	7.88±0.03	0
240	8.23±0.01	0.0435
315	8.29±0.01	0.0507
500	8.72±0.04	0.101
715	9.38±0.03	0.174
790	9.68±0.07	0.206
950	9.83±0.04	0.221

The rate constants of the adduct decomposition increase with pressure: $\ln k_p/k_o$ = (-0.014 ± 0.009) + (2.553±0.060)10^{-4} P; R=0.9886 and the activation volume equals -6.5 ± 0.5 cm^3mol^{-1}.

The determination of the forward rate constant is always complicated by the necessity to account for the adduct decomposition rate. In this work the rate constants were calculated by two methods: from the experimental curve ($\ln D_0/D_t$ - t) at the time when the optical density $D_t = D_0$ and by iteration of all the experimental data with regard to adduct decomposition rate constants. According to both methods of calculations, discrepancy was in the range ±2-7% (Table 4). Both series are given by equation: $\ln k_p/k_o$ = (-0.0095 ± 0.0255) + (0.00113 ± 0.00005) P (R = 0.9876). The quadratic equation does not improve the correlation. Thus, the activation volume of the forward reaction equals -28.5±1.5 cm^3mol^{-1}.

Table 4. Pressure effect on the rate constants of the forward Diels-Alder reaction of 9-chloroanthracene with tetracyanoethylene in 1,2-dichloroethane at 298.15 K.

Set 1			Set 2		
P, kg cm^{-2}	k_2, l mol^{-1} s^{-1}	$\ln k_p/k_o$	P, kg cm^{-2}	k_2, l mol^{-1} s^{-1}	$\ln k_p/k_o$
0	0.700	0	0	0.712	0
270	0.911	0.262	250	0.922	0.258
295	1.01	0.367	480	1.22	0.538
410	1.11	0.461	710	1.47	0.725
730	1.67	0.868	930	2.05	1.057

The results of this overall and independent study of the pressure effect on the rate and equilibrium constants of the nonpolar reaction of 9-chloroanthracene with tetracyanoethylene are the following: $\Delta V^{\#}$ (forward) = -28.5±1.5; $\Delta V^{\#}$ (retro) = -6.5±0.5 and ΔV_o = -20.6 ± 1.5 cm^3mol^{-1}. The reaction volume was found to be in good agreement from the pressure effect on the rate (-22.0±1.5), equilibrium data (-20.6±1.5) and from the difference of partial molar volumes (-23.0 ±2 cm^3mol^{-1}). When the compressibility of solutions taken into account, these values equal: $\Delta V^{\#}_{forward}$ = -26.5±1.5; $\Delta V^{\#}_{retro}$ = -6.5±0.5 and $\Delta V_{o,eq}$ = -18.6 ± 1.5 cm^3mol^{-1}.

For high polar reactions with high rate sensitivity to the solvent polarity, the relation $\delta \ln k/\delta P = -\Delta V^{\#}/RT$ can contain the contribution of the rate constant change due to the change of solvent properties under high pressure. The values of activation volumes of highly polar reactions are usually more negative in going from polar to nonpolar solvents.[6,15] The total pressure effect on the rate constants of a polar reaction can be represented as: $\Sigma\delta\ln k/\delta P = \delta\ln k_{(1)}/\delta P + \delta\ln k_{(2)}/\delta P$, where the first term is determined by the change of the rate constant due to the change of solvent properties with pressure and the second term is connected with the change of rate constant due to the $P\Delta V^{\#}$ effect. In order to evaluate these terms, let us consider two polar reactions: [2+2]-cycloaddition of butyl vinyl ether with tetracyanoethylene and the Menshutkin' reaction. Many solvent polarity scales are known,[16] but the pressure effect on dielectric constant $(\delta(1/\varepsilon)/\delta P)$[6,17,18] has been studied in a wide range of solvents and on the Reichardt' polarity scale $(\delta E_T/\delta P)$[15] only for a few solvents.

Table 5. Rate constant (ln*k*) of the reaction of butyl vinyl ether with tetracyanoethylene in some solvents, total pressure effect ($\Sigma\delta\ln k/\delta P$), the contribution of the effect of solvent dielectric constant change under pressure on the rate constants ($\delta\ln k_{(1)}/\delta P$), the values of total apparent activation volume ($\Sigma\Delta V^{\#}$), solvent contribution ($\Delta V^{\#}_{(1)}$) and refined activation volume ($\Delta V^{\#}_{(2)}$). Inaccuracy ±4 cm^3 mol^{-1}.

Solvent	$-\ln k^a$	$1/\varepsilon^b$	$10^6\delta(1/\varepsilon)/\delta P^b$	$\Sigma\delta\ln k/\delta P$	$\delta\ln k_{(1)}/\delta P$	$\Sigma\Delta V^{\#}$	$\Delta V^{\#}_{(1)}$	$\Delta V^{\#}_{(2)}$
Carbon tetrachloride	8.99	0.446	-38	0.00196	0.00060	-49	-15	-34
Benzene	7.00	0.439	-34	0.00160	0.00054	-40	-13	-27
Dichloromethane	2.81	0.110	-17	0.00157	0.00028	-39	-7	-32
Acetone	2.43	0.047	-9.0	0.00143	0.00014	-36	-4	-32
Acetonitrile	0.79	0.027	-4.1[c]	0.00119	0.00007	-30	-2	-28

[a] From Ref. 19 at 303 K. [b] From Ref. 18 . [c] For propionitrile.

The values of $(\delta(1/\varepsilon)/\delta P)$ in the work[6] overestimated by 2.303 times when compared with the original data.[18] For highly polar reactions, the dependence of the rate constants in the row of solvents can be represented by the equation: $\ln k_{(1)} = a + b(1/\varepsilon)$ with the pressure derivative: $\delta\ln k_{(1)}/\delta P = b\,\delta(1/\varepsilon)/\delta P$. All required data on the reaction of butyl vinyl ether with tetracyanoethylene are collected in Table 5. For this reaction, experimental data follow the dependence: $\ln k = -1.02 - 15.8\ (1/\varepsilon)$, R= 0.972. It is clear from these data that the change of dielectric constant under pressure is more important for the rate constant in nonpolar solvents where the refined activation volume decreases about 30 %.

Table 6. Rate constant ($\ln k$) of the reaction of triethylamine with methyl iodide and butyl iodide and of pyridine with ethyl iodide in some solvents, pressure coefficient of dielectric constant ($\delta(1/\varepsilon)/\delta P$), the values of total apparent activation volume ($\Sigma\Delta V^{\#}$), solvent contribution ($\Delta V^{\#}_{(1)}$) and refined activation volume ($\Delta V^{\#}_{(2)}$). Inaccuracy ±4 $\mathrm{cm^3\ mol^{-1}}$.

Reaction	Solvent	$-\ln k$[a]	Slope, (b)	$10^6\ \delta(1/\varepsilon)/\delta P$[b]	$-\Sigma\Delta V^{\#}$[a]	$-\Delta V^{\#}_{(1)}$	$-\Delta V^{\#}_{(2)}$
Et_3N + MeI	Hexane	11.08	12.5	-61	45.4	19	26
	Benzene	5.34		-34	40.1	12	28
	Acetone	3.08		-9.0	38.3	3	35
Et_3N + BuI	Benzene	12.91	12.5	-34	52.5	12	41
	Acetone	10.09		-9.0	51.2	3	48
	Nitrobenzene	9.07		-2.6	41.6	1	41
Py + EtI	Benzene	12.26	10	-34	36.7	10	27
	Acetone	-		-9.0	30.4	3	27
	Nitrobenzene	8.81		-2.6	27.7	1	27

[a] From Ref. 20 . [b] From Ref. 18.

For the Menshutkin' reaction it was shown that the solvent effect is very similar for different pairs of reagents.[15,21-24] The value of the slope $\{b$, in $\ln k_{(1)} = a + b(1/\varepsilon)\}$ equals about 12.5 for the reaction of triethylamine with methyl iodide and butyl iodide and about 10 for the reaction of pyridine with ethyl iodide (Table 6). From the data of Tables 5 and 6, one can see that the refined values of activation volume decrease in nonpolar solvents by about 30 % compared to the total pressure effect.

From this standpoint, the value of activation volume of the nonpolar [4+2]-cycloaddition reaction of tetracyanoethylene with 9-chloroanthracene (Table 4) is nearly the same as the value of refined activation volume in the [2+2]-cycloaddition reaction with butyl vinyl ether. For the polar reactions (Table 5,6), the refined activation volumes are insensitive to the solvents under consideration. The change of partial molar volumes of highly polar compounds in the row of solvents can be a measure of solvent electrostriction. The Menshutkin products have very low solubility in aprotic solvents for such measurements,[25] and for highly polar Reichardt' dye (μ = 12 *D*), the change of partial molar volume does not correlate with solvent polarity.[26]

EXPERIMENTAL

Materials and methods. Tetracyanoethylene (Merck) was sublimed (~ 50 Pa, 380 K) as white crystals, m.p. 473-474 K. 9-Chloroanthracene was synthesized by a literature method[27] and purified on an aluminum oxide column, eluted with n-hexane-benzene (5:1): m.p. 373-374 K (lit.,[27] 374-375 K). Adduct (**3**) was obtained from equimolar solutions of reagents in benzene, from which it crystallized in near quantitative yield. M.p. (decomp.) of the white crystals 433-436 K with formation of a deep green fusion. Found (%): C 70.80; H 2.78. $C_{20}H_{10}N_4$ requires C 70.49; H 2.66. Cyclopentadiene, after cracking of dicyclopentadiene (420-430 K), was dried and redistilled before use.

A high pressure thermostated vessel was installed in the cell department of a spectrophotometer "Specord UV-VIS" in the working light pathway, and compare light pathway was supplied with diaphragm. The special construction of a quartz cell of variable volume has the ability to compress the solution under pressure. *n*-Hexane was chosen as the pressure transmitting liquid. A Bourdon gauge was connected in the *n*-hexane line to exclude uncertainties of pressure measurements due to resistance of slipping plunger under high pressure.

Rate and equilibrium measurements were performed following the change in diene (**1**) optical density at 25420 cm^{-1}. All other reagents and adducts are optically transparent. For the rate of forward reaction and equilibrium measurements, the diene (**1**) concentration (1-1.5) 10^{-4}

was less than the dienophile one in 12-15 times. The concentration of the adduct in the decomposition reaction was (1-1.5) 10^{-4} and cyclopentadiene ~ 1 10^{-3} mol l^{-1}. The rate constants of the retro reaction were calculated from the equation: $\ln D_{\infty} - \ln(\log T_t/T_{\infty}) = k_1 t$, where T_t and T_{∞} are transmission values at the time of measurement and when reaction was finished, respectively. The first 4-5 minutes were needed for temperature relaxation. Rate constants of the forward reaction were calculated by differentiation of polynomial function $\delta(\ln D_o/D_t)/\delta t$ at t, when optical density $D = D_o$ and by iteration of the equation: $\{1/(k_1 + k_2[\mathrm{TCNE}])\}\ln\{D_{start}(k_1 + k_2[\mathrm{TCNE}]) - k_1D_o\}/\{D_t(k_1 + k_2[\mathrm{TCNE}]) - k_1D_o\} = t$, where k_2 and k_1 are the rate constants of the forward and back reactions, D_{start} is diene optical density at the start time of measurements, D_o - initial and D_t - current diene optical density.

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