

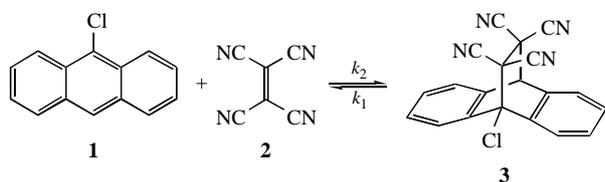
# The effect of pressure on the equilibrium in the Diels–Alder reaction between 9-chloroanthracene and tetracyanoethylene

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Equilibrium constants for the Diels–Alder reaction of 9-chloroanthracene with tetracyanoethylene have been determined in the pressure range 0–970 kg cm<sup>-2</sup> in 1,2-dichloroethane at 298 K and the value of the reaction volume (–20.6±1.5 cm<sup>3</sup> mol<sup>-1</sup>) has been compared with the difference in partial molar volume of the dienophile (107.8±0.2), diene (170.7±0.5) and adduct (255.5±1.5 cm<sup>3</sup> mol<sup>-1</sup>).

Many examples are known for reaction rates under pressure,<sup>1–6</sup> but only a few compare the reaction volumes obtained from the pressure effect on equilibrium and from the difference of the partial molar volumes of product and reactants.<sup>5</sup> The rate constants of the Diels–Alder reaction were determined at atmospheric pressure in the forward and reverse directions in different solvents, with and without catalysis.<sup>7–9</sup> The pressure effects on the rate constants of this reaction were usually studied for reactions with low rates, convenient for work in common barostats. Only two reactions were studied in the reverse direction under high pressure.<sup>10,11</sup> No information about the effect of high pressure on the equilibrium constants of the Diels–Alder reaction is available, even though such examples at atmospheric pressure are well known.<sup>7–9</sup> Diels–Alder reactions of aromatic dienes with tetracyanoethylene are too fast and are usually equilibrium processes.<sup>8</sup> Common barostats are unsuitable for equilibrium measurements of these fast reactions, but a high pressure vessel with quartz windows is convenient for direct spectrophotometric monitoring. In this work the Diels–Alder reaction of 9-chloroanthracene with tetracyanoethylene (Scheme 1) in 1,2-dichloroethane was also selected because of the opportunity of determining the partial molar volume of the adduct in solution.



Scheme 1

Monitoring of diene **1** absorbance took place at 25420 cm<sup>-1</sup>. A high pressure vessel was installed in the cell department of a spectrophotometer ('Specord UV-VIS') in the working light pathway, and the window of the comparison beam was fitted with a diaphragm. The special construction of a quartz cell of variable volume containing working solution makes it possible to compress the solution under pressure. Hexane was selected as the pressure transmitting liquid. A Bourdon gauge was connected to the hexane line to exclude the uncertainties of pressure measurements due to the resistance of the slipping plunger under high pressure. It was found that the enhancement of the diene absorbance at elevated pressure is more than that expected from Tait's equation for 1,2-dichloroethane.<sup>6</sup> This is caused by the change of solvent properties under pressure<sup>5,6</sup> and a small bathochromic shift of the diene absorbance band. Since the monitoring was carried out at the slope of the diene absorbance band, the pressure (up to 1000 kg cm<sup>-2</sup>) dependence of the absorbance is more than that predicted from Tait's equation (1):

$$D_p/D_0 = (0.995 \pm 0.003) + (3.8431 \pm 0.1482) \times 10^{-4} P - (1.4692 \pm 0.1568) \times 10^{-7} P^2 \quad (1)$$

( $r = 0.9959$ ;  $N = 17$ )

Equilibrium constants were calculated from equation (2):

$$K_{\text{eq}} = (D_0 - D_{\infty})/D_{\infty} [\text{TCNE}]_0 \quad (2)$$

where  $D_0$  and  $D_{\infty}$  are the initial and equilibrium diene absorbances, adjusted [equation (1)] to atmospheric pressure for the same extinction coefficient of diene, and  $[\text{TCNE}]_0$  is the molar concentration at atmospheric pressure, which exceeds the diene concentration ( $\sim 10^{-4}$  mol l<sup>-1</sup>) by 12–15 times.

The results of three series of measurements are collected in Table 1.

All sets of data follow the relation:

$$\ln(K_p/K_0) = (0.00352 \pm 0.00707) + (8.1405 \pm 0.0321) \times 10^{-4} P$$

( $r = 0.9974$ ;  $N = 19$ )

A polynomial equation does not improve the correlation. The value of the reaction volume (–20.6±1.5 cm<sup>3</sup> mol<sup>-1</sup>) was obtained from the equation:

$$\ln(K_p/K_0) = -\Delta V_0 P/RT$$

where  $P$  is in kg cm<sup>-2</sup>;  $R = 84.78$  cm kg mol<sup>-1</sup> K<sup>-1</sup>;  $T = 298.15$  K and  $\Delta V_0$  is in cm<sup>3</sup> mol<sup>-1</sup>.

The value of the reaction volume was independently obtained from the partial molar volumes of reagents and adduct. The densities of solutions were determined using a precise densimeter (DMA 602) and calculated using the expression:

$$V_A = 1000(d_0 - d)/C_A d_0 + M_A/d_0$$

where  $d_0$  and  $d$  are the densities of 1,2-dichloroethane and solution,  $M_A$  is the molar mass and  $C_A$  is the molarity of the solution. The triple cascade of thermostats with a reduced power of heaters provided a constant temperature during measurements with an accuracy of  $\pm(1-2) \times 10^{-3}$  K. The concentration dependence of the partial molar volume of 9-chloroanthracene (170.7±0.5) and tetracyanoethylene (107.8±0.2 cm<sup>3</sup> mol<sup>-1</sup>; 107.5±0.2 in dichloromethane<sup>12</sup>) was not observed at values less than 0.05 mol l<sup>-1</sup>. For the adduct (255.5±1.5 cm<sup>3</sup> mol<sup>-1</sup>) determinations

**Table 1** Equilibrium constants for the Diels–Alder reaction of 9-chloroanthracene and tetracyanoethylene under pressure in 1,2-dichloroethane at 298.15 K.

Series 1		Series 2		Series 3	
$P/\text{kg cm}^{-2}$	$\ln K_p/835^a$	$P/\text{kg cm}^{-2}$	$\ln K_p/800^a$	$P/\text{kg cm}^{-2}$	$\ln K_p/843^a$
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	—	—

<sup>a</sup>The experimental values of the equilibrium constants at atmospheric pressure, 1 mol<sup>-1</sup>.

were performed in 1,2-dichloroethane and in tetracyanoethylene solutions, depending on the composition of the solution. In these measurements solvent or tetracyanoethylene solution was used as a blank in the calculation.

To conclude, in this work for the first time a comparison has been made of the values of the Diels–Alder reaction volumes from pressure–equilibrium data ( $-20.6 \pm 1.5$ ) and from direct data on partial molar volumes ( $-23.0 \pm 2.0 \text{ cm}^3 \text{ mol}^{-1}$ ), and both results are in reasonable agreement.

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