

Effect of Elevated External Pressure on the Rate of the Diels–Alder Reaction of 9-Methylantracene with Acrylonitrile, Catalyzed by Gallium Chloride

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Abstract—External pressure was found to similarly affect the rate of a gallium chloride-catalyzed Diels–Alder reaction between 9-methylantracene with acrylonitrile and a noncatalyzed reaction of 9,10-dimethylantracene with acrylonitrile. The observation of equal activation volumes is consistent with the assumption that elevated pressure very weakly affects the bond energy in the n,ν complex of acrylonitrile with gallium chloride.

At present we have a great deal of information on the effect of Lewis acids on the rate of Diels–Alder reactions, on the formation enthalpies of n,ν complexes involving dienophiles and reaction products, and on the effect of the medium on these characteristics [1]. The reaction rate only slightly increases in the presence of boron trifluoride etherate and tin tetrachloride and increases 10^4 , 10^5 , and 10^6 times in the presence of gallium chloride and aluminum chloride and bromide, respectively [1]. With slow and, especially, equilibrium reactions, a combination of catalysis and elevated pressure is desirable, providing, at negative activation and reaction volumes, additional acceleration of the reaction and shifting the equilibrium to the reaction products [Eqs. (1) and (2)].

$$(d\ln k/dp)_T = -1/RT(d\Delta G^\ddagger/dp)_T = -\Delta V^\ddagger/RT, \quad (1)$$

$$(d\ln K/dp)_T = -1/RT(d\Delta G/dp)_T = -\Delta V_0/RT. \quad (2)$$

Here ΔG^\ddagger , ΔV^\ddagger , ΔG , and ΔV_0 are the free energies and volumes of activation and reaction, respectively.

Earlier we showed [2] that the accelerative effect of Lewis acids is proportional to the formation enthalpy of the n,ν complex [Eq. (3)].

$$\ln(k_c/k_n) = 0.19\Delta H_{MK}. \quad (3)$$

Here k_c and k_n are the rate constants of the catalytic and noncatalytic reactions and ΔH_{MA} is the formation enthalpy of the n,ν complex (kJ/mol), without inclusion of the dimerization energy of Lewis acid. The rate constant of the catalytic reaction is quite sensitive to the bond energy in the n,ν complex, which makes this parameter the most convenient model for follow-

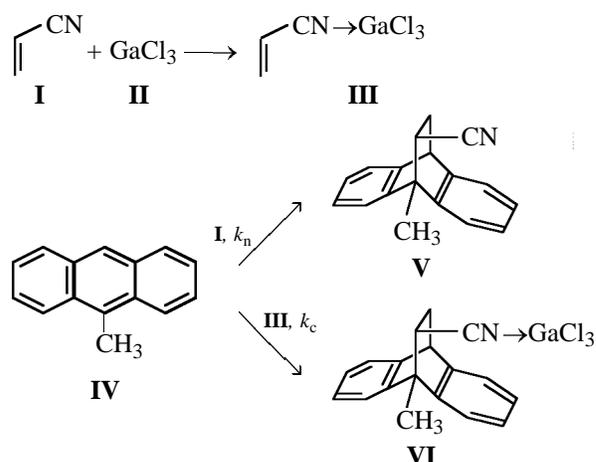
ing the possible changes in the bond energy with pressure. If the dienophile–Lewis acid bond energy and, consequently, the activity of the dienophile increase with increasing pressure, then the increase of the reaction rate is contributed not only by the $p\Delta V^\ddagger$ effect, but, like in the reaction without Lewis acid, by increased activity of the dienophile. As follows from Eqs. (1) and (3), if the bond energy of the complex increases by 1 kJ/mol at an external pressure of 1000 kg/cm², then the additional contribution into the change in the catalytic reaction rate under pressure [$\ln k_c(p)/k_c(p=0)$] is equivalent to a decrease in the activation volume of 5 cm³/mol. The activation volumes measured in modern barostats that allow directly following reaction rate under pressure are accurate to within (1–2) cm³/mol [3, 4]. The results of such measurements may form an experimental basis for analysis of the effect of elevated external pressure on the nature of bonding in the activated reaction complex. Note also the absence of techniques for calorimetric measurements under pressure. There have been only two works on the effect of external pressure on the rate of catalytic Diels–Alder reactions [5, 6]. Jenner [5] reported the activation volumes of the reactions of vinyl acetate with isoprene in acetonitrile at 34°C in the presence and in the absence of zinc chloride (–38 and –33 cm³/mol, respectively). Isaaks *et al.* [6] estimated the activation volumes of the reactions of isoprene with *N*-phenylmaleimide in diethyl ether at 30°C in the presence and in the absence of aluminum chloride at –33 and –40 cm³/mol, respectively. According to [5], the activation volume increases in going from the noncatalytic process to catalytic, whereas in [6] the reverse situation is observed. From the experimental data in [6] we could

estimate the errors in the determination of the activation volumes of the noncatalytic ($\pm 3.7 \text{ cm}^3/\text{mol}$) and catalytic ($\pm 8.5 \text{ cm}^3/\text{mol}$) processes. The large measurement errors allow no definite conclusions as to the trends in activation volumes. But, what is more important, the choice of solvent in [5, 6] is quite poor. Acetonitrile and diethyl ether are in themselves strong n -donors. The formation enthalpies of the n, ν complex of these n donors with antimony pentachloride are -59.0 and -80.3 kJ/mol , respectively [7]. In [5, 6], the n, ν complexes with the solvents are stronger than with dienophiles [1, 8]. We recently showed [9] that addition of as little as 0.5 vol % of dibutyl ether to 1,2-dichloroethane almost completely suppresses the Diels–Alder reaction between 9,10-dimethylantracene with maleic anhydride, catalyzed by aluminum chloride. The reason for this effect is that all catalyst is bound in complex with ether as a stronger n donor. Clearly, most Lewis acids in [5, 6] were bound with n -donor solvents. Moreover, great uncertainties in calculating reaction rate constants might be associated with the possible redistribution of Lewis acid between an n -donor solvent and an n -donor dienophile, produced by increasing external pressure. According to [6], the reaction with isoprene in the presence of aluminum chloride in diethyl ether is accelerated 30 times, while the rate enhancement in a solvent inert toward aluminum chloride (dichloromethane, 1,2-dichloroethane, benzene) is more than 7×10^5 times [1, 10]. These data are consistent the fact that the distribution of aluminum chloride between diethyl ether and maleimide [6] results in that the fraction of active dienophile gets smaller than 0.01%. Data on the effect of π - and n -donor solvents on the properties of π and ν acceptors are presented in Table 1.

As seen from Table 1, gallium chloride, unlike tetracyanoethylene, much stronger interacts with n -donor compared with π -donor solvents. It is also seen that gallium chloride very weakly interacts with benzene, toluene, and 1,2-dichloroethane. At 23°C , a temperature optimal for kinetic measurements, benzene crystallizes already at 650 bar, whereas toluene does not crystallize even at 1500 bar [11].

Acrylonitrile (**I**) in toluene forms with gallium chloride (**II**) a strong n, ν complex **III** which reacts with 9,10-dimethylantracene in a time insufficient for the reaction rate to be measured under elevated pressure. The Diels–Alder reaction with 9-methylantracene (**IV**) proved to be more suitable for measurements.

For each solution we measured the rate of the catalytic reaction at atmospheric and elevated pressures, not changing the solution in a closed variable-



volume quartz cell placed in a high-pressure optical bomb. Under such conditions, the error in the ratio of the rate constants at elevated and atmospheric pressures [$k_c(p)/k_c(p = 0)$] should be minimal.

The reaction rate constants were calculated by Eq. (4).

$$\ln c_{\text{IV}}^0/c_{\text{IV}} = \ln(D_{\text{IV}}^0/D_{\text{IV}}) = k_c c_{\text{III}} t. \quad (4)$$

Here c_{IV}^0 and c_{IV} are the initial and current concentrations of diene **IV**, D_{IV}^0 and D_{IV} are the initial and current optical densities of diene **IV**, and k_c is the second-order rate constant of the catalytic reaction. The $k_c(p) c_{\text{III}}/k_c(p = 0) c_{\text{III}}$ ratio involved no possible errors in the concentration of active dienophile (c_{III}), since the concentration of active nucleophile in each of the seven measurement series was constant. The resulting data are listed in Table 2.

Comparison of the k_c values for different measurement series at atmospheric pressure (Table 2) shows that the mean error is about 11%. This result is explained by that the weighted and true concentrations of active gallium chloride in solution differ from each other, whereas the $k_c(p) c_{\text{III}}/k_c(p = 0) c_{\text{III}}$ ratios within each measurement series are free of this error. The figure represents the pressure dependence of [$\ln(k_c(p)/k_c(p = 0))$]. All experimental series fit Eq. (5).

$$\ln [k_c(p)/k_c(p = 0)] = (5.1 \pm 56.4) \times 10^{-4} (6.737 \pm 0.023) \times 10^{-4} p; \quad (5)$$

$$R \ 0.9984, \ N \ 17, \ S \ 1.59 \times 10^{-2}.$$

Quadratic regression does not improve the correlation. For a pressure measured in kg/cm^2 the R constant [Eq. (1)] is equal $84.78 \text{ cm}^3(\text{kg/cm}^2)\text{K}^{-1} \text{ mol}^{-1}$. The activation volume estimated from these data is $-16.9 \pm 1.0 \text{ cm}^3/\text{mol}$.

Table 1. Partial molar volumes (\bar{V} , cm³/mol) and solution enthalpies ($\Delta_{\text{sol}}H$, kJ/mol) of gallium chloride and tetracyanoethylene (TCE) in some solvents

| Solvent | \bar{V}_{GaCl_3} | $\Delta_{\text{sol}}H_{\text{GaCl}_3}$ | \bar{V}_{TTCSE} | $\Delta_{\text{sol}}H_{\text{TTCSE}}$ |
|--------------------|---------------------------|--|--------------------------|---------------------------------------|
| Benzene | 74.8±0.1 | 9.6±0.6 | 108.4±0.3 | 14.9±0.4 |
| Toluene | 68.7±0.1 | 2.5±0.6 | 104.4±0.4 | 9.7±0.5 |
| <i>o</i> -Xylene | 67.1±0.1 | -0.8±0.4 | 102.2±0.3 | 1.4±0.1 |
| Mesitylene | 64.8±0.4 | -7.1±0.6 | 98.1±0.2 | -2.7±0.4 |
| 1,2-Dichloroethane | 73.4±0.4 | 5.1±0.6 | 107.8±0.2 | 21.3±0.3 |
| Ethyl acetate | 60.7±0.3 | -65.7±2.1 | 112.8±0.1 | 9.2±0.5 |
| Acetonitrile | 61.9±0.3 | -71.1±2.0 | 109.8±0.1 | 15.2±0.2 |
| 1,4-Dioxane | 61.5±0.5 | -74.0±2.0 | 106.1±0.2 | 4.3±0.2 |

Table 2. Initial concentrations of acrylonitrile (c_{I}), its n, v complex with gallium chloride (c_{III}), and first- ($k_c c_{\text{III}}$) and second-order (k_c) rate constants of the catalyzed Diels–Alder reaction of 9-methylanthracene (**IV**) with n, v complex **III** under external pressure (p) and correlation coefficients (R) of kinetic dependences in toluene at 23°C

| c_{I} M | $c_{\text{III}} \times 10^2$, M | p , kg/cm ² | $(k_c c_{\text{III}}) \times 10^4$, s ⁻¹ | R | $k_c \times 10^3$, l mol ⁻¹ s ⁻¹ | $\ln [k_c(p)/k_c(p=0)]$ |
|---------------------|-------------------------------------|-----------------------------|---|--------|--|-------------------------|
| 0.59 | 6.33 | 0 | 4.47 | 0.9997 | 7.06 | 0 |
| | | 490 | 6.22 | 0.9998 | 9.83 | 0.330 |
| | | 1010 | 8.80 | 0.9997 | 13.9 | 0.676 |
| 0.44 | 6.35 | 0 | 4.62 | 0.9995 | 7.28 | 0 |
| | | 995 | 9.23 | 0.9996 | 14.5 | 0.692 |
| 0.18 | 2.26 | 0 | 2.24 | 0.9999 | 9.91 | 0 |
| | | 380 | 2.81 | 0.9993 | 12.4 | 0.228 |
| | | 860 | 3.92 | 0.9998 | 17.3 | 0.560 |
| 0.36 | 6.87 | 0 | 6.77 | 0.9995 | 9.85 | 0 |
| | | 920 | 12.4 | 0.9999 | 18.0 | 0.602 |
| 0.30 | 2.83 | 0 | 2.23 | 0.9998 | 7.88 | 0 |
| | | 565 | 3.28 | 0.9990 | 11.6 | 0.385 |
| 0.55 | 3.66 | 0 | 2.94 | 0.9990 | 8.03 | 0 |
| | | 405 | 4.00 | 0.9993 | 10.9 | 0.307 |
| | | 895 | 5.89 | 0.9998 | 16.1 | 0.593 |
| 0.43 | 1.76 | 0 | 1.47 | 0.9997 | 8.35 | 0 |
| | | 810 | 2.61 | 0.9995 | 14.8 | 0.573 |

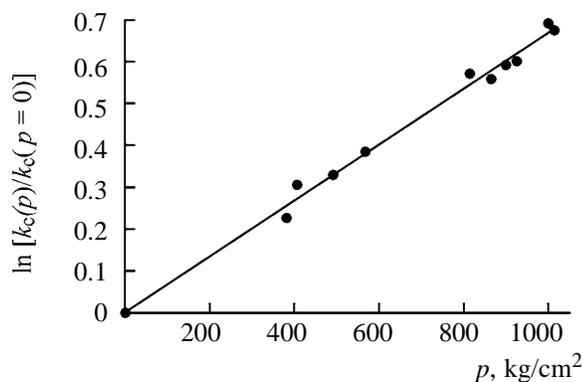
Because of its quite a low rate [k_n 1.10 × 10⁻⁷ l mol⁻¹ s⁻¹, $\tau_{0.5}$ 3500 h at 23°C [1]], the noncatalytic reaction was very difficult to directly follow by spectrophotometry. A noncatalytic Diels–Alder reaction between acrylonitrile and a more active diene, 9,10-dimethylanthracene [k_n 2.5 × 10⁻⁶ l mol⁻¹ s⁻¹ at 30°C] in acetonitrile we studied earlier [12] at an external pressure of up to 4000 kg/cm². In these measurements we made use of a multiplied-pressure barostat and followed the optical density of the reaction mixture. As a result, the following linear regression was obtained.

$$\ln[k_n(p)]/k_n(p=0) = (2.99 \pm 4.20) \times 10^{-2} + (7.002 \pm 0.055) \times 10^{-4} p; \quad (6)$$

$$R \ 0.9953, \ N \ 13, \ S \ 8.49 \times 10^{-2}.$$

According to the estimates in [12], the activation volume [Eq. (1)] of this noncatalytic reaction is -18.0 ± 1.0 cm³/mol.

The activation volumes of the noncatalytic (-18.0 ± 1.0 cm³/mol) and catalytic (-16.9 ± 1.0 cm³/mol) reactions are equal to each other within error. This result suggests that increasing pressure produces no additional increase of the bond energy and, consequently, of the activity of the dienophile in the n, v



Effect of external hydrostatic pressure on the rate of the gallium-catalyzed Diels–Alder reaction between 9-methylanthracene (**IV**) and n,ν complex **III** in toluene at 23°C.

complex with gallium chloride. These data can be considered as experimental evidence for the assumption in [3, 4] that the character of bonds in the transition state either does not vary or only slightly varies (at least to a pressure of up to 1000 kg/cm²). In the reaction studied in the present work, the concentration of the n,ν complex of gallium chloride with acrylonitrile does not increase with pressure, even though the rate constant increases. Because of the high equilibrium constant of this n,ν complex, the binding degree is close to 100% even at atmospheric pressure. With weak n,ν complexes, a different pressure effect on the catalytic reaction rate would be expected. The binding degree for such complexes at atmospheric pressure may be much lower than 100%. In such catalytic systems, the concentration of the dienophile in complex with Lewis acid will increase with pressure because of the increasing equilibrium constant. As a result, the apparent activation volume of the catalytic reaction may prove to be much more negative compared with noncatalytic.

EXPERIMENTAL

9-Methylanthracene (**IV**) was purified by column chromatography on Al₂O₃, eluent benzene–hexane (1:5), mp 79–80°C (79–80°C [13]). Acrylonitrile was twice distilled, dried over 4 Å molecular sieves, and additionally distilled before use. Gallium chloride was obtained as described in [14] and distilled in a vacuum under argon, mp 77–78°C (77.1°C [14]). Toluene was distilled, refluxed over sodium in the presence of traces of 9-methylanthracene (**IV**) until a stable coloration appeared, and distilled before use.

The reaction progress was followed by the absor-

bance of diene **IV** in the range 395–401 nm, where dienophile **I**, complex **III**, and adducts **V** and **VI** are optically transparent. The reaction was performed at a much lower concentration of diene **IV** (10⁻³–10⁻⁴ M) compared with the concentration of complex **III**. The contribution of the noncatalytic reaction into the overall reaction rate was lower than 0.01% and was neglected in calculations.

A high-pressure optical cell with quartz windows was placed into the cell compartment of a Specord UV-Vis spectrophotometer. Preliminary experiments showed that the concentration of the n,ν complex with gallium chloride gradually decreased on contact with mercury, and, therefore, we could not use a high-pressure cell with a mercury seal. Such problems are absent when one works with a variable-volume quartz cell with cylindrical quartz joints. In each of the seven measurement series, the reagent concentrations in the cell were used in rate measurements at atmospheric and elevated pressures (Table 2), lowering, if required, the working wavelength by 0.1–0.2 nm. Preliminarily, for a solution containing no diene **IV**, we found that such change in the wavelength decreases the photocurrent by no more than 1% in the pressure range studied. Under such conditions, we should no longer know the true concentration of gallium chloride in the solution, but the constancy of this concentration throughout one measurement series is guaranteed. Therefore, in calculating $\ln[k_c(p)/k_c(p=0)]$ values within each series we took the concentration ratio for gallium chloride was taken to be equal to one. The operation of the barostat was described in detail in [15].

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