

SHORT
COMMUNICATIONS

Studying the Effect of High Pressure on the Cycloaddition Reactions of Maleic Anhydride and Substituted Anthracenes

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Received January 25, 2012

Abstract—The kinetics (rate, activation, and volume) of the high-pressure (up to 2500 bar) Diels–Alder reactions of maleic anhydride with 9-phenylanthracene and 9,10-dimethylanthracene in toluene is investigated.

Keywords: activation and reaction volume, reaction rate, high pressure.

DOI: 10.1134/S003602441301010X

INTRODUCTION

Studies of effects of pressure on reaction kinetics provide better insight into the mechanism of the formation and properties of intermediate complexes [1–5]. The abnormal ($\Delta V^{\ddagger}/\Delta V_r > 1$) ratio of activation volume ΔV^{\ddagger} to reaction volume ΔV_r found in the Diels–Alder (DA) reaction between maleic anhydride and isoprene indicates that the isopolar transition state complex has a smaller volume than that of the product [4]. Earlier, it was mistakenly thought that the rate of high-pressure reactions could be conveniently calculated using volume-independent concentration units such as molality or mole fraction [1, 2]. In practice, we must consider reducing the volume of the reaction with increasing pressure even at $\Delta V^{\ddagger} = 0$ to determine the reaction rate constant correctly:

$$\Delta V^{\ddagger} = -RT[\partial \ln(k_p/\partial P) - (n-1)\beta_T], \quad (1)$$

where k_p is the constant rate value at given pressure P , $(n-1)\beta_T$ is the correction coefficient attributed to changes in concentration due to compression, β_T is the solvent compressibility factor, and n is the order of the reaction. It should be noted that the values for the activation volume and reaction volume in the reaction of maleic anhydride and isoprene, adjusted with respect to correction coefficient $RT\beta_T$, have been found to be virtually equal. There are, however, a number of DA reactions displaying the same ratio anomaly ($\Delta V^{\ddagger}/\Delta V_r > 1$) even after taking correction effects into account. In addition, negative values of the activation volume [3, 5–7] and the solvent dependence [4, 7] were obtained in some retro-Diels–Alder reactions. We suggested in [7] that the different accessibility of the activated complex and the final adduct during the solvation process could be one reason for the observed abnormalities. In this work, we investigated the energy and volume activation parameters of

the cycloaddition reaction between maleic anhydride and substituted anthracenes in toluene.

EXPERIMENTAL

The kinetics of the reaction of maleic anhydride **1** with 9,10-dimethylanthracene **2** at 25°C and 9-phenylanthracene **3** at 60°C was studied by measuring changes in the absorption band of dienes **2** and **3** in the range of 390–405 nm. A quartz cuvette (0.4 cm) filled with a toluene solution of appropriate reagents was placed in a thermostatted (± 0.1 K) high-pressure stainless steel reactor equipped with sapphire observation windows. Distilled water was used as the compression fluid. Pressure was generated first (up to 500 bar) with a pump and then using a hydraulic multiplication (9 : 1) system (Syn. Co., Japan). Absorption spectra were recorded on a Scinco Co. (South Korea) UV–vis spectrophotometer. The working concentration of maleic anhydride **1** with 9,10-dimethylanthracene **2** in the reaction (**1** + **2**) was ~ 0.01 mol/L, and the ratio of c_1 to c_2 was about 15. The kinetics of the reaction (**1** + **3**) was studied using 1–2 mol/L solutions of **1**, due to its slower rate relative to (**1** + **2**) (~ 5 orders of magnitude). The steric hindrance from the phenyl group and the increased conjugation in the diene **3** are possible reasons for the observed lack of reactivity of **3** to **1** [8]. It should be noted that 9,10-diphenylanthracene does not react with maleic anhydride [9, 10].

RESULTS AND DISCUSSION

Our data on the rate constants of reactions (**1** + **2**) and (**1** + **3**) at different pressures are given in the table. As was shown earlier [3, 6, 7], the packing factor values $\eta = V_w/V$ (where V_w is the Van der Waals volume and

Dependence of rate constants k_2 (L/(mol s)) on pressure P (bar) for Diels–Alder reactions (1 + 2) at 25°C and (1 + 3) at 60°C in toluene

Reaction (1 + 2)			Reaction (1 + 3)		
P	$k_2 \times 10^3$	$\ln(k_p/k_{p=1})$	P	$k_2 \times 10^6$	$\ln(k_p/k_{p=1})$
1	17.4 ± 0.4	0	1	6.6 ± 0.2	0
273	23.3 ± 0.2	0.292	661	11.2 ± 0.1	0.529
503	28.7 ± 0.4	0.500	975	16.0 ± 0.2	0.885
645	31.0 ± 0.15	0.578	1406	23.3 ± 0.1	1.261
1085	51.8 ± 0.3	1.091	1673	29.2 ± 0.2	1.487
1592	73.7 ± 1.1	1.443	2061	36.6 ± 0.7	1.713
2147	131.6 ± 0.2	2.023	2342	46.4 ± 0.4	1.950
2602	180.7 ± 1.2	2.340	—	—	—

V is the partial molar volume) for low-boiling compounds with weak intermolecular interactions (e.g., ethylene, isoprene or furan) are considerably lower than for high-boiling molecules that have strong intermolecular forces (e.g., anthracene and maleic anhydride). As a result, the activation and reaction volumes are typically smaller for the latter. The angle coefficients for reactions (1 + 2) (9.044×10^{-4} , $R = 0.9972$, $N = 7$) and (1 + 3) (8.439×10^{-4} , $R = 0.9985$, $N = 8$) were estimated in turn from the dependences of the rate constant $\ln(k_p/k_{p=1})$ under external pressure at constant temperature (Fig. 1). Calculated experimental activation volumes were found to be -21.8 ± 0.7 and $-22.8 \pm 0.8 \text{ cm}^3/\text{mol}$, respectively. Adjusted with respect to toluene compressibility factors of 91.9×10^{-6} and $116.1 \times 10^{-6} \text{ bar}^{-1}$ at 25 and 60°C [11], respectively, the activation volume values were $-19.6 \pm 0.7 \text{ cm}^3/\text{mol}$ for the (1 + 2) reaction and $-19.7 \pm 0.8 \text{ cm}^3/\text{mol}$ for the (1 + 3) reaction.

The reaction volume ΔV_r is usually determined as the difference in the partial molar volume of the products and initial reagents [1–7] with an absolute uncertainty of $\pm 1\text{--}2 \text{ cm}^3/\text{mol}$. Due to the low solubility in toluene, we were unfortunately not able to measure the partial molar volume of adduct in the (1 + 2) reaction and were thus forced to use another procedure. The total volume of product (Add) and reagents 1 and 2 at any given moment (t) can be described by the equations

$$V_t = V_s + (c_1^0 - c_{\text{Add}, t})V_1 + (c_2^0 - c_{\text{Add}, t})V_2 + c_{\text{Add}, t}V_{\text{Add}}, \quad (2)$$

$$V_t = [V_s + (c_1^0 V_1 + c_2^0 V_2)] + c_{\text{Add}, t}(V_{\text{Add}} - V_1 - V_2) = V_{t=0} + c_{\text{Add}, t}\Delta V_r, \quad (3)$$

where $V_{t=0}$ and V_t are the solution volumes at the beginning of the reaction and over period of time t ; V_s is the volume of solvent; V_1 , V_2 , and V_{Add} are the partial molar volumes of reagents 1 and 2 and adduct, respectively;

c_1^0 and c_2^0 are the initial reagent concentrations; $c_{\text{Add}, t}$ is the concentration of product at given moment t ; and ΔV_r is the volume of the reaction. Since the total mass (M) of the system remains unchanged, we can follow the course of a reaction by measuring the density of the reaction mixture instead of the volume:

$$M/d_t = M/d_{t=0} + c_{\text{Add}, t}\Delta V_r, \quad (4)$$

$$1/d_t = 1/d_{t=0} + c_{\text{Add}, t}\Delta V_r/(1000d_{t=0}). \quad (5)$$

This was done for the (1 + 2) reaction at $25 \pm 0.002^\circ\text{C}$ using a high-precision DSA 5000M density meter. The linear dependency between the density of the reaction mixture and the concentration of the final adduct $c_{\text{Add}, t}$ continued up to the moment of product precipitation (reagent conversion of $\sim 80\%$) (Fig. 2):

$$1/d_t = (1.157610 \pm 1.18 \times 10^{-6}) - (2.318 \times 10^{-2} \pm 1.437 \times 10^{-4})c_{\text{Add}, t}, \quad (6)$$

$$R = 0.9986, \quad N = 76.$$

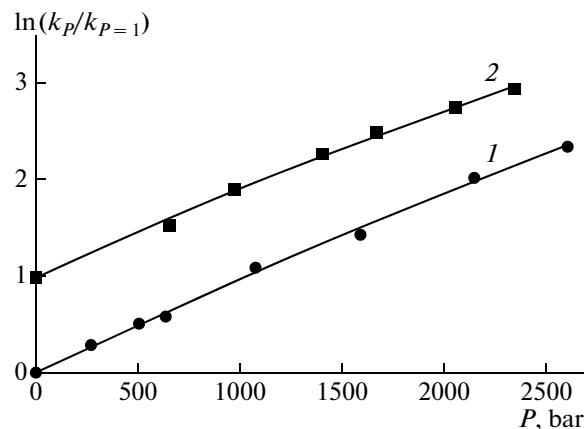


Fig. 1. Dependence of the rate constant on pressure for reactions of maleic anhydride (1) with 9,10-dimethylanthracene at 25°C and (2) with 9-phenylanthracene at 60°C. The graph 2 is shifted up by one unit for convenience.

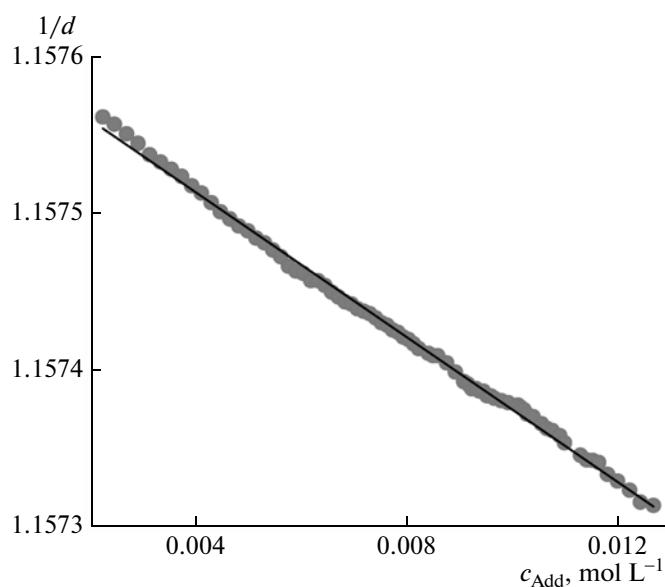


Fig. 2. Adduct concentration c_{Add} dependency of specific volume $1/d$ in the reaction between maleic anhydride and 9,10-dimethylanthracene at 25°C.

We estimated the reaction volume value for the reaction **(1 + 2)** to be $-20 \pm 0.2 \text{ cm}^3/\text{mol}$, while no data was obtained for the reaction **(1 + 3)** owing to its lower reaction rate.

CONCLUSIONS

It was shown that the activation volumes of reactions **(1 + 2)** and **(1 + 3)** were very close (-19.6 ± 0.7 and $-19.7 \pm 0.8 \text{ cm}^3/\text{mol}$, respectively), despite the considerable difference between their constant rates. Notably, the activation ($-19.6 \pm 0.7 \text{ cm}^3/\text{mol}$) and

reaction ($-20 \pm 0.2 \text{ cm}^3/\text{mol}$) volumes of the **(1 + 2)** DA reactions were virtually equal, which agrees well with the data derived earlier from the DA reaction between maleic anhydride and isoprene.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 12-03-00029), and by the federal target program Scientists and Science Teachers of an Innovative Russia, 2009–2013 (project nos. P2345, 14.740.11.0377, and OK-1/2010).

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