



Pergamon

Tetrahedron 55 (1999) 1153–1162

TETRAHEDRON

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

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Received 6 August 1998; revised 5 November 1998; accepted 19 November 1998

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 ($-20.6 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$) and as difference of activation volumes of forward (-28.5 ± 1.5) and backward (-6.5 ± 0.5) reaction ($-22.0 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$) 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 $-23.0 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$.

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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-dimethylantracene,