

# Mechanistic Evidence for the Diels–Alder Reaction from High-Pressure Kinetics<sup>1</sup>

R. A. Grieger and C. A. Eckert<sup>2</sup>

Contribution from the Department of Chemical Engineering, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801.

Received March 30, 1970

**Abstract:** New activation volume data are reported for the Diels–Alder reactions of 1,3-cyclohexadiene with maleic anhydride and of cyclopentadiene with dimethyl acetylenedicarboxylate. Comparison of these data with results for the solvent effects on the volumes of the transition states for two similar Diels–Alder reactions gives much basic information about the physical properties of the transition state, as well as permitting mechanistic interpretation. These Diels–Alder reactions are shown clearly to follow a concerted, one-step mechanism. In three reactions of maleic anhydride the transition state is smaller than the adduct, due to secondary interactions between non-bonding atoms in the transition state.

The effect of pressure on the rate of a chemical reaction in solution can yield information vital for the interpretation of the mechanism of that reaction as well as for the physical properties of the reaction transition state. In this work such data for several Diels–Alder reactions are used as an example of the investigation of transition-state properties, and new evidence is presented and discussed for the mechanism of that reaction. Although the one-step and two-step mechanisms are otherwise kinetically indistinguishable, comparison of the activation volume in solution with the partial molal volumes of reactants and products yields strong evidence not otherwise obtainable for the concerted mechanism.

Several authors have previously reported activation volumes for Diels–Alder reactions,<sup>3</sup> but considerable controversy has arisen concerning the accuracy and interpretation of these data.<sup>3c</sup> In particular, three different values of the activation volume have been calculated from the high-pressure kinetic data for the dimerization of isoprene,<sup>3b,4,5</sup> and these data have thus been interpreted to support either a two-step diradical mechanism<sup>3b</sup> or a concerted multicenter mechanism.<sup>4</sup> This situation has naturally led to skepticism regarding any mechanistic interpretation of these data. Moreover, it has cast some doubt on the value of using high-pressure kinetics as a tool for mechanistic interpretation.

New high-pressure kinetic data for Diels–Alder reactions have been measured, using an improved technique involving *in situ* mixing to avoid errors in rate constants from the heat of compression.<sup>6</sup> Consideration has also been given to the method used for deriving activation volumes from high-pressure kinetic data,<sup>7</sup> use of partial molal volumes for reactants and products,<sup>8</sup> and the solvent effect on the activation volume.<sup>9</sup> In this work, new high-pressure kinetic data

are reported for the Diels–Alder reactions of 1,3-cyclohexadiene with maleic anhydride and of cyclopentadiene with dimethyl acetylenedicarboxylate. Comparison of the activation volumes for these reactions with those recently measured for the reactions of maleic anhydride with isoprene<sup>9a</sup> and with *trans*-1-methoxy-1,3-butadiene<sup>9b</sup> leads to a detailed picture of the reaction mechanism for the Diels–Alder reaction. As previously reported,<sup>10</sup> the transition states for the reaction of maleic anhydride with isoprene, *trans*-1-methoxy-1,3-butadiene, and 1,3-cyclohexadiene are *smaller* than the corresponding adducts.<sup>11</sup> To attempt to explain this result partial molal volume measurements have been carried out to determine whether such an effect could be attributable to either an endo–exo transition or to a  $\pi$ -complex formation. These data suggest that this unique result is due to secondary attractive forces at nonbonding atoms, as proposed by Hoffmann and Woodward.<sup>12</sup>

## Experimental Section

**Solvents.** Reagent grade dichloromethane (Matheson Coleman and Bell) was purified by repeated treatment with concentrated sulfuric acid, washed successively with water, 5% aqueous sodium carbonate, and water, dried successively with anhydrous magnesium sulfate and Linde 4A Molecular Sieves, and distilled. Nitromethane was purified in a similar manner. Spectrophotometric grade ethyl acetate was dried over Linde 4A Molecular Sieves and distilled.

**Reagents.** Cyclopentadiene was distilled from the dimer through a 4-ft column packed with nickel helices. A small fraction was collected in a receiving flask immersed in Dry Ice–acetone (bp 41°). 1,3-Cyclohexadiene and dimethyl acetylenedicarboxylate (Aldrich) were 97% pure (GPC) and were used as received. Maleic anhydride was recrystallized twice from ethyl ether and sublimed under vacuum (mp 53°).

**Tetracyanoethylene.** Tetracyanoethylene was recrystallized several times from chlorobenzene and sublimed under vacuum (mp 198–200°).

(9) (a) R. A. Grieger and C. A. Eckert, *Trans. Faraday Soc.*, **66**, 2579 (1970); (b) R. A. Grieger and C. A. Eckert, *Ind. Eng. Chem., Fundam.*, in press.

(10) A preliminary report has appeared: R. A. Grieger and C. A. Eckert, *J. Amer. Chem. Soc.*, **92**, 2918 (1970).

(11) It was stated in the preliminary report, ref 10, that this is the first example reported of a bimolecular reaction for which the transition state is smaller than the product. This is incorrect without qualification; it is the first reported example of such a phenomenon without the participation of extra solvent molecules in the transition state. For example, the additions of water, methanol, and ammonia to mesityl oxide have been shown to exhibit such behavior due to solvent participation in the transition states (J. J. Scott and K. R. Brower, *J. Amer. Chem. Soc.*, **89**, 2682 (1967).

(12) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4388 (1965).

(1) Presented at the Joint CIC/ACS Conference, Toronto, Ontario, May 28, 1970.

(2) To whom correspondence should be addressed.

(3) (a) B. Raistrick, R. H. Sapiro, and D. M. Newitt, *J. Chem. Soc.*, 1761 (1939); (b) C. Walling and J. Peisach, *J. Amer. Chem. Soc.*, **80**, 5819 (1958); (c) C. Walling and H. J. Schugar, *ibid.*, **85**, 607 (1963).

(4) S. W. Benson and J. A. Berson, *ibid.*, **84**, 152 (1962).

(5) H. S. Golinkin, W. G. Laidlaw, and J. B. Hyne, *Can. J. Chem.*, **44**, 2193 (1966).

(6) R. A. Grieger and C. A. Eckert, *AIChE J.*, **16**, 766 (1970).

(7) C. A. Eckert, R. A. Grieger, S. P. Sawin, and C. K. Hsieh, to be published.

(8) R. A. Grieger, C. Chaudoir, and C. A. Eckert, *Ind. Eng. Chem., Fundam.*, in press.

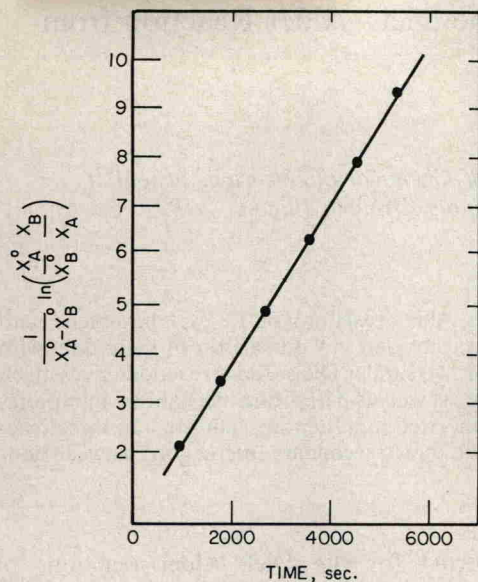


Figure 1. Plot of the integrated rate expression for a typical run—the reaction of cyclopentadiene with dimethyl acetylenedicarboxylate in ethyl acetate at 10.00° and 681 atm.

**Durene.** Reagent grade durene was used without further purification.

**Diels–Alder Adducts.** The Diels–Alder adduct of cyclopentadiene and dimethyl acetylenedicarboxylate, and the endo adducts of cyclopentadiene and 1,3-cyclohexadiene with maleic anhydride were prepared by dropwise addition of the diene to a solution of the dienophile in ethyl acetate at 0°. *endo*-5-Norbornene-2,3-dicarboxylic anhydride (mp 165–167°) and *endo*-bicyclo[2.2.2]-5-octene-1,2-dicarboxylic anhydride (mp 147–149°) were purified by repeated recrystallization from a mixed solvent of ethyl acetate and petroleum ether. 2,5-Norbornadiene-2,3-dimethyldicarboxylate was distilled twice under vacuum (bp 136°, 10 mm). *exo*-5-Norbornene-2,3-dicarboxylic anhydride (mp 139–141°) was prepared from the endo adduct by the method of Craig<sup>13</sup> and purified by repeated recrystallization from petroleum ether–ethyl acetate.

**Kinetic Runs.** All kinetic measurements were made using a newly developed high-pressure apparatus and technique<sup>6</sup> which employs *in situ* mixing and continual sampling to avoid errors due to heat of compression and due to uncertainties in the starting and stopping time of the reaction. Basically it consists of two piston and cylinders, each containing one reactant in solution, separated by a thin aluminum-foil diaphragm. After the heat of compression<sup>14</sup> is dissipated, the foil is burst and the solutions are mixed magnetically. Samples are withdrawn periodically through fine syringe tubing and a needle valve.

The high-pressure vessel was immersed in an oil bath controlled to  $\pm 0.02^\circ$ , and temperatures could be read to  $0.01^\circ$  on thermometers with calibration traceable to the National Bureau of Standards. Pressure measurements were made on calibrated Heise Bourdon tube gauges, with an uncertainty of  $\pm 1$  atm up to 1000 atm, and  $\pm 7$  atm at higher pressures.

Master solutions of diene and dienophile (*ca.* 0.2 M) were prepared in a drybox and stored in the dark at  $-15^\circ$ . They were loaded separately into each half of the reaction cell and the amounts determined by weighing. Rates of reaction were determined by following the relative concentrations of dienophile and adduct, by sampling and gpc measurement of the ratio of their peak areas, using a Beckman GC-5 with a flame ionization detector and a recorder with a disc integrator. Complete solubility of the adduct at even the highest pressures was assured by calculation from the partial molal volumes as well as by an independent experiment.<sup>9a</sup>

(13) D. Craig, *J. Amer. Chem. Soc.*, **73**, 4889 (1951).

(14) In order to check the extent of the heat of compression experiments were carried out with a thermocouple inside the reaction cell. For pumping rates comparable to those used in ref 3a and 3b, a temperature rise of  $15^\circ$  was found at 1000 atm and of  $36^\circ$  at 3000 atm. The effect of initial temperature rise on the accuracy of the results can be expressed in terms of the reaction activation energy, and some typical results are given in ref 6.

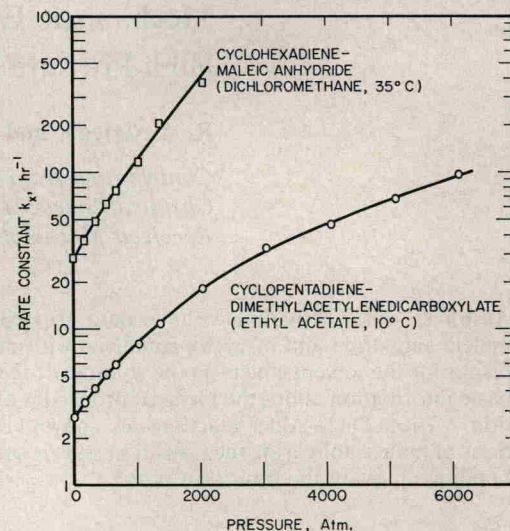


Figure 2. The effect of pressure on the rate constants of two Diels–Alder reactions.

The factor to convert peak area ratios to concentration ratios was determined by repeated injection of samples of calibration solutions of dienophile and adduct. The standard deviation of concentrations determined by this method was 1.0–1.5%.

Five to seven samples were taken for each kinetic run, which lasted 2–5 hr. Values of rate constants were obtained from a least-squares fit of a straight line to the integrated rate expression from a second-order reaction with unequal reactant concentrations. A typical rate plot is shown in Figure 1.

**Partial Molal Volumes.** A high-precision injection dilatometer<sup>8</sup> was used to measure partial molal volumes at the relatively low concentrations used in this work. This apparatus was also used to measure the volume change accompanying formation of a  $\pi$  complex in dilute solution. The accuracy of this technique was such that the uncertainty in the partial molal volume at infinite dilution of a liquid solute was  $\pm 0.1$  cc/mol.

## Results

Rate constants were determined for the 1,3-cyclohexadiene–maleic anhydride reaction in dichloromethane at 35.00° and pressures up to about 2000 atm. For the cyclopentadiene–dimethyl acetylenedicarboxylate reaction, data were taken in ethyl acetate at 10.00° and at pressures up to 6000 atm. For both reactions additional rate constants were determined at atmospheric pressure to permit calculation of the energy of activation. The rate constants are reported in Table I,

Table I. Experimental Rate Constants

Pressure, atm	$k_x, \text{hr}^{-1}{}^a$	$k_x, \text{hr}^{-1}{}^b$
1	2.72	29.0
171	3.38	36.6
341	4.18	47.9
511	5.09	61.1
681	5.94	75.4
1022	8.10	122
1362	10.8	192
2042	18.1	263
3063	33.0	
4084	46.3	
5104	67.2	
6125	95.7	

<sup>a</sup> Cyclopentadiene–dimethyl acetylenedicarboxylate reaction in ethyl acetate at 10.00°. <sup>b</sup> 1,3-Cyclohexadiene–maleic anhydride reaction in dichloromethane at 35.00°.

and shown as a function of pressure in Figure 2. Activation volumes at zero pressure were determined