

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

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**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 nonbonding 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 °).

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(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.

(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).

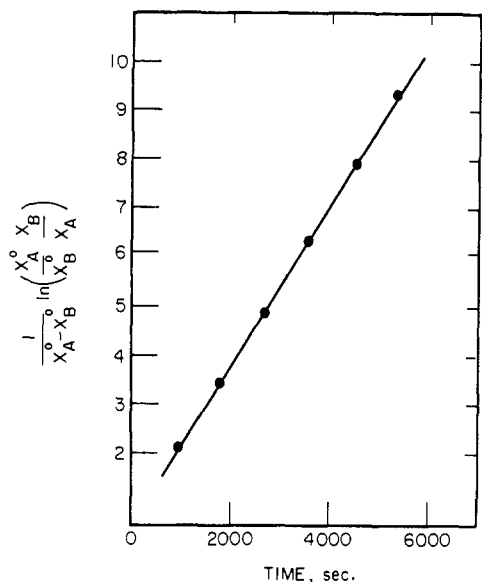


Figure 1. Plot of the integrated rate expression for a typical run—the reaction of cyclopentadiene with dimethyl acetylenedicarboxylate in ethyl acetate at 10.00° and 681 atm.

**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-dimethylacetylenedicarboxylate 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.

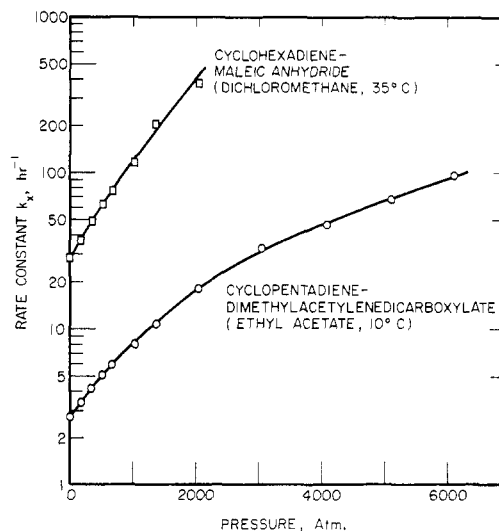


Figure 2. The effect of pressure on the rate constants of two Diels–Alder reactions.

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  $35.00^\circ$  and pressures up to about 2000 atm. For the cyclopentadiene–dimethyl acetylenedicarboxylate reaction, data were taken in ethyl acetate at  $10.00^\circ$  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	$k_x$ , hr <sup>-1</sup> <sup>a</sup>	$k_x$ , hr <sup>-1</sup> <sup>b</sup>
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  $10.00^\circ$ . <sup>b</sup> 1,3-Cyclohexadiene–maleic anhydride reaction in dichloromethane at  $35.00^\circ$ .

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

Table II. Activation Parameters and Volumetric Relationships for Several Diels–Alder Reactions

Reaction (solvent)	Activation energy, kcal/mol	Activation vol, cc/mol	—Partial molal volume at infinite dilution, cc/mol—			
			Diene	Dienophile	Transition state	Adduct
Cyclopentadiene–dimethyl acetylenedicarboxylate (ethyl acetate)	14.1	–30.2	81.4	119.9	171	167.4
1,3-Cyclohexadiene–maleic anhydride (dichloromethane)	11.4	–37.2	96.3	71.0	130	137.0
Isoprene–maleic anhydride (acetone)	14.0	–39.0	101.0	69.4	131	134.5
<i>trans</i> -1-Methoxy-1,3-butadiene–maleic anhydride ( <i>n</i> -butyl chloride)	10.7	–45.4	100.6	69.6	125	134.7

from a least-squares fit of the expression

$$\ln k_x = a + bP + cP^2$$

using only data up to 1400 atm, and from the relationship

$$\left(\frac{\partial \ln k}{\partial P}\right)_{P=0} = \frac{-\Delta v^\ddagger}{RT} = b$$

which is rigorously correct only when rate constants are based on pressure-independent concentration units.<sup>7,15</sup> The activation volumes and energies and the partial molal volumes of the reactants, products, and transition states for these two reactions are presented in Table II. Also given there for comparison are similar data for two other Diels–Alder reactions studied previously.<sup>9</sup>

**Physical Properties of the Transition State.** A detailed and accurate study of the effect of pressure on the kinetics of a reaction in solution yields important information about the properties of the transition state. Such data can be vital to the interpretation of reaction mechanisms, yet they are not available from any other type of experimental determinations. Because the transition state by its very nature cannot be isolated for study, the physical properties must be found from transition state theory and thermodynamic relationships. Often, the temperature dependence of the rate constant is used to estimate the relative internal energy, entropy, and even heat capacity of the transition state. However, these properties all represent a geometric effect, produced by a change in translational, rotational, and vibrational degrees of freedom, and an electronic effect, due to shifts in electronic energy levels. Thus it is difficult to use the effect of temperature on reaction rate to interpret mechanism.

On the other hand, the effect of pressure on the rate constant permits access to information which is much more useful in interpreting the mechanism of the reaction. Directly, it gives the activation volume, or rigorously the difference in partial molal volume between transition state and reactants. In conjunction with this, it is relatively easy to make accurate determinations of partial molal volumes of reactants and products for calculation of and comparison with the partial molal volume of the transition state. Moreover, a study of solvent effects on these properties yields especially useful data on the physical properties of the transition state; the volume can be separated into a geometric effect and a solvent effect. The former

(15) As is shown in ref 7, the internal consistency of high-pressure kinetic data can be verified if the activation volume from a quadratic fit of the lower pressure points agrees with the extrapolated value obtained from the higher pressure data by the Benson and Berson treatment. Such agreement is found for the cyclopentadiene–dimethyl acetylenedicarboxylate reaction.

represents the volume associated with the geometry of the atomic nuclei in the transition configuration, whereas the latter represents the solvent–transition state intermolecular interactions, such as electrostriction or hydrogen bonding, and has been used to yield estimates of the dipole moment.<sup>9,16</sup>

The most important consideration in using high-pressure kinetics in this manner is the precision of the data themselves. Typically, solvent effects on the volume of a transition state are 5–15 cc/mol. Unfortunately, it has not been infrequent that experimental uncertainties or ambiguities of interpretation led to errors of comparable magnitude. Consequentially, the value of high-pressure kinetics as a tool for mechanistic interpretation has not always been apparent.

The solvent effects on the partial molal volumes of the transition states for the Diels–Alder reactions of maleic anhydride with isoprene and with *trans*-1-methoxy-1,3-butadiene have been reported elsewhere.<sup>17</sup> Estimates of the dipole moments for the transition states are 4 D for the isoprene reaction<sup>9a</sup> and 8 D for the *trans*-1-methoxy-1,3-butadiene reaction.<sup>9b</sup> The dipole moment for the transition state of the isoprene reaction is about the same as for the adduct (4.46 D),<sup>18</sup> but the dipole moment for the transition state of the *trans*-1-methoxy-1,3-butadiene reaction is significantly higher than that of the adduct (5.25 D).<sup>18</sup> The relatively large dipole moment for this transition state has been attributed to increased charge transfer from the diene to the dienophile, facilitated by the attachment of the electron-releasing methoxy group to an atom participating in bond formation.<sup>9b</sup> The large dipole moment of the transition state is manifested in a large solvent effect on the activation volume. However, the reactions reported in this work should resemble the isoprene–maleic anhydride reaction and exhibit little solvent dependence of the activation volumes. Therefore, it is reasonable to use activation volumes measured in only one solvent as a criterion of mechanism in these two cases.

Another physical property of the transition state which can be evaluated from accurate high-pressure kinetic data is the compressibility of the transition state. It has been argued that the partially formed bonds in the transition state have abnormally low force constants,

(16) H. Heydtmann, A. P. Schmidt, and H. Hartmann, *Ber. Bunsenges. Phys. Chem.*, **70**, 444 (1966).

(17) Solvent effects on the isoprene reaction have been studied in nine solvents—dimethyl carbonate, *n*-butyl chloride, 1,2-dichloroethane, acetonitrile, nitromethane, isopropyl ether, ethyl acetate, dichloromethane, and acetone—with activation volumes ranging from –39.8 to –32.5 cc/mol. The methoxybutadiene addition was investigated in the first five solvents listed, and the range of activation volumes was –53.0 to –32.0 cc/mol.

(18) K. F. Wong and C. A. Eckert, *J. Chem. Eng. Data*, in press.

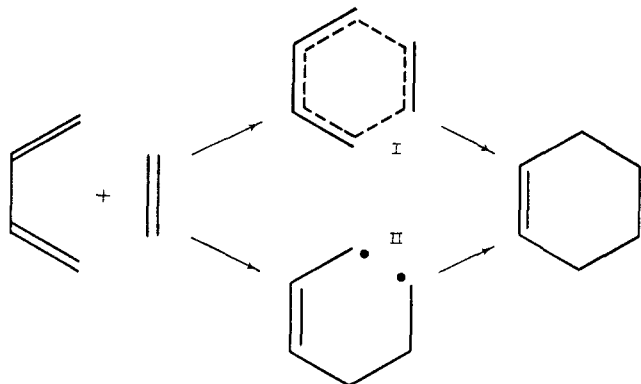


Figure 3. Alternate mechanisms proposed for the Diels-Alder reaction.

which is manifested in a high compressibility of the transition state.<sup>19</sup> Benson and Berson have calculated that even for extremely low values of the force constant, there will be a negligible effect on the compressibility of the transition state.<sup>20</sup> A least-squares fit of Tait equation parameters to high-pressure data for the isoprene-maleic anhydride and the cyclopentadiene-dimethyl acetylenedicarboxylate reactions shows that the transition states have relatively *low* compressibilities, consistent with the compressibility of a normal molecule with a compact, cyclic structure.<sup>7</sup>

**Mechanism of the Diels-Alder Reaction.** The particular Diels-Alder reactions for which high-pressure kinetic studies have been carried out were each chosen for specific reasons. First of all, no attempt was made to investigate the isoprene dimerization reaction, because the advantages of the *in situ* mixing technique would be lost on a self-addition reaction. Rather, the first reaction studied in detail was the addition of isoprene to maleic anhydride, which is easy to run and for which many data on solvent effects were available. The methoxybutadiene addition to maleic anhydride was studied first as an example of the addition of a polar diene, and secondly as an example of a much more highly polar transition state. The condensation of cyclohexadiene with maleic anhydride provided an example of a Diels-Alder reaction for which the diene was locked in a cisoid configuration, to view the effect on the activation volume and energy. Finally, as is discussed below, the cyclopentadiene-dimethyl acetylenedicarboxylate reaction gives specific evidence about the existence of secondary interactions in the transition state.

Although the Diels-Alder reaction appears to be a relatively simple one, there has long been disagreement among many investigators about the mechanism of the reaction. The two mechanisms proposed are a single-step, concerted multicenter mechanism, in which both new bonds are partially formed in the transition state (I), or a two-step ring closure, involving the formation of a diradical intermediate (II), as shown in Figure 3.

Evidence cited in support of the two-step mechanism includes the relatively small activation volume for the dimerization of isoprene,<sup>3b</sup> the stereospecific rearrangement of  $\alpha$ -1-hydroxy-*endo*-dicyclopentadiene,<sup>21</sup> which

indicates opening of only one bond, and formation of 1,2 and 1,4 adducts from the reaction of butadiene with 1-cyanovinyl acetate, in which both adducts are presumably formed from a common diradical transition state.<sup>22</sup>

The concerted mechanism is supported by the stereospecificity of the reaction, even for a system chosen to favor diradical formation,<sup>23</sup> the secondary isotope effect for the reverse Diels-Alder reaction,<sup>24</sup> and consideration of Hammett reactivity coefficients for more than thirty sets of Diels-Alder reactions.<sup>25</sup>

It is noteworthy that none of the evidence for either the diradical or concerted mechanism has been accepted as completely unambiguous. The measurement of activation volumes should allow a clear-cut decision to be made between the two-step and one-step mechanisms. Using the decomposition of benzoyl peroxide as a model, Walling and Peisach<sup>3b</sup> estimated that the activation volume for isoprene dimerization with a concerted mechanism should be about  $-35$  cc/mol, compared to  $-45$  cc/mol volume change for the reaction. By reevaluating the experimental data Golinkin, *et al.*,<sup>5</sup> and Walling and Tanner<sup>19</sup> have independently revised the calculation of the activation volume for this reaction to  $-30$  cc/mol, as compared with the original calculation of about  $-25$  cc/mol. The correction which should be added to this value because of the use of pressure-dependent concentration units is about  $-5$  cc/mol. The result of  $-35$  cc/mol agrees well with Walling's estimate for a concerted mechanism.

The large (negative) activation volumes reported here for all four Diels-Alder reactions investigated can be interpreted in terms only of a concerted mechanism. Especially comparison of the partial molal volumes of the transition states with those for the adducts substantiates such a conclusion. The solvent studies on the volumes of two of the transition states<sup>9</sup> demonstrate that the result is not due to solvent effects. Thus, although one cannot say whether partial formation of one bond is farther advanced than the other, certainly both bonds are partially formed in the transition state.

Hammond has proposed that for exothermic reactions, such as the Diels-Alder reaction, the transition state should resemble the reactants more than the product.<sup>26</sup> Ingold has stated that the Hammond proposal should refer only to the electronic states and not to the geometric arrangements of the atoms.<sup>27</sup> Recent measurements<sup>28</sup> of the relative activity coefficients of the reactants, adduct, and transition state for the 1,3-butadiene-maleic anhydride addition indicate that the behavior of the activity coefficient of the transition state in various solvents closely parallels that of maleic anhydride, but is quite different from that of the adduct. This result suggests that the electronic state of the transition state resembles the electronic state of the reactants. On the other hand, the activation volume data show that the distances between atoms participating in bond formation are quite close

(21) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(22) J. C. Little, *J. Amer. Chem. Soc.*, **87**, 4021 (1965).

(23) J. B. Lambert and J. D. Roberts, *Tetrahedron Lett.*, 1457 (1965).

(24) S. Seltzer, *J. Amer. Chem. Soc.*, **87**, 1534 (1965).

(25) M. Charton, *J. Org. Chem.*, **31**, 3745 (1966).

(26) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(27) C. Ingold, *Chem. Soc. Spec. Publ.*, No. 16, 119 (1962).

(28) K. F. Wong and C. A. Eckert, *Trans. Faraday Soc.*, **66**, 2313 (1970).

(19) C. Walling and D. T. Tanner, *J. Amer. Chem. Soc.*, **85**, 612 (1963).

(20) S. W. Benson and J. A. Berson, *ibid.*, **86**, 259 (1964).

to the interatomic distances in the adduct. These results support Ingold's contention.

**Secondary Interactions in the Transition State.** For the three reactions studied with the strongly electron-withdrawing maleic anhydride as dienophile, the transition state was actually *smaller* than the volume of the corresponding adduct, even when solvent effects on the partial molal volumes of reactants and transition states are taken into consideration.

One might attempt to explain this by assuming that the diene and maleic anhydride, which are coplanar in the transition state, undergo a volume increase as new bonds are formed and the anhydride entity assumes its final position. A somewhat similar difference in position is found between *endo*- and *exo*-5-norbornene-2,3-dicarboxylic anhydride. The partial molal volumes for these compounds were measured with an injection dilatometer in two solvents of very different polarity. The results, given in Table III, show clearly that the

**Table III.** Partial Molal Volumes of *endo*- and *exo*-5-Norbornene-2,3-dicarboxylic Anhydride at Infinite Dilution

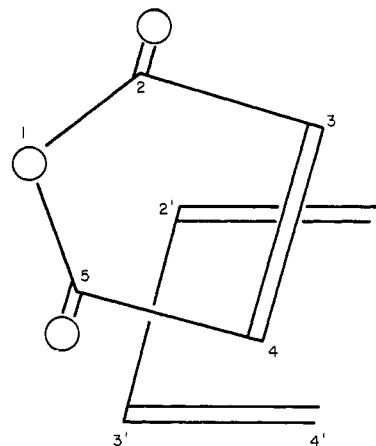
Adduct	Solvent, cc/mol	
	Nitromethane	Dichloromethane
endo	126.9 ± 0.4	123.7 ± 0.4
exo	127.4 ± 0.4	124.1 ± 0.4

volume difference between the two forms is far too small for this type of transition to account for the unusually small volumes of the maleic anhydride transition states.

Another possible explanation for these results is the possibility of secondary interactions in the transition complex. According to Hoffmann and Woodward,<sup>12</sup> the general rule for preferential formation of *endo* adducts can be explained by secondary  $\pi$ -electron interactions at nonbonding atoms. This concept may also explain the abnormally small volumes of the transition states for the maleic anhydride reactions. For example, for the maleic anhydride transition states as shown in Figure 4, bonds are being formed between carbon atoms 3 and 1' and between 4 and 4', while secondary interactions occur between 2 and 2' and between 5 and 3'. For the reaction of the acetylenic dienophile, in which the positions of nonbonding atoms do not allow secondary interactions to occur, the transition state is somewhat *larger* than the product, as expected. El'yanov, *et al.*,<sup>29</sup> have found that the volume of the transition state for the *ortho-cis* addition of *trans*-piperylene to methyl acrylate, which corresponds to *endo* addition, is smaller than the transition state for *ortho-trans* addition. This result can also be explained in terms of secondary  $\pi$  interactions in the *endo* transition state.

Investigations were carried out to ascertain whether the volume changes associated with  $\pi$ -complex for-

(29) B. S. El'yanov, S. K. Shakhova, S. V. Vitt, and M. G. Gonikberg *Izv. Akad. Nauk SSSR, Ser. Khim.*, 565 (1969).



**Figure 4.** Schematic for the transition state for diene addition to maleic anhydride.

mation in solution are of a sufficient magnitude to account for the anomalously small volume of the maleic anhydride transition states—probably about 10–20 cc/mol smaller than expected. X-Ray diffraction studies of  $\pi$  molecular complexes in the solid state typically show a 10% decrease in intermolecular distance from the sum of the van der Waals radii.<sup>30</sup> Using the injection dilatometer, a measurement of the volume change accompanying formation of a  $\pi$  complex in dilute solution (0.05 *M*) was made for the tetracyanoethylene–durene complex in dichloromethane. An equilibrium constant, based on mole fraction, was determined for this system by Merrifield and Phillips.<sup>31</sup> The partial molal volumes for this system are shown in Table IV. As has been found for solid-state complexes,

**Table IV.** Partial Molal Volumes of Tetracyanoethylene, Durene, and Their  $\pi$ -Molecular Complex in Dilute Solution in Dichloromethane

Compd	Partial molal volume, cc/mol
Tetracyanoethylene	113.0 ± 0.5
Durene	159.1 ± 0.4
$\pi$ complex	248 ± 5

the volume decrease for complex formation in solution is also about 10%. A somewhat smaller volume decrease accompanying  $\pi$ -electron interactions between nonbonding atoms would explain the anomalously small volumes of the transition states for the maleic anhydride reactions.

**Acknowledgment.** The financial support of the U. S. Army Research Office (Durham) and the National Science Foundation is gratefully acknowledged.

(30) D. S. Brown, S. C. Wallwork, and A. Wilson, *Acta Crystallogr.*, 17, 168 (1964).

(31) R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 80, 2778 (1958).