

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.^{7,15} 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.⁹

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.^{9,16}

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.¹⁷ Estimates of the dipole moments for the transition states are 4 D for the isoprene reaction^{9a} and 8 D for the *trans*-1-methoxy-1,3-butadiene reaction.^{9b} The dipole moment for the transition state of the isoprene reaction is about the same as for the adduct (4.46 D),¹⁸ 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).¹⁸ 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.^{9b} 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.

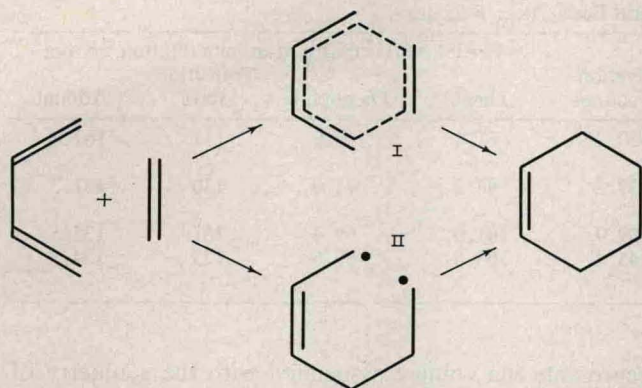


Figure 3. Alternate mechanisms proposed for the Diels-Alder reaction.

which is manifested in a high compressibility of the transition state.¹⁹ 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.²⁰ 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.⁷

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,^{3b} the stereospecific rearrangement of α -1-hydroxy-*endo*-dicyclopentadiene,²¹ which

(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).

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.²²

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

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^{3b} 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.*,⁵ and Walling and Tanner¹⁹ 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 states⁹ 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.²⁶ Ingold has stated that the Hammond proposal should refer only to the electronic states and not to the geometric arrangements of the atoms.²⁷ Recent measurements²⁸ 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).