Table II. Activation Parameters and Partial Molal Volumes for the MA–MB Reaction

Solvent	Activation energy, E_a, kcal/mole	Activation volume, $\Delta v^{\ddagger}$, cc/mole	Partial molal volumes, cc/mole			
			$\bar{v}_{MA}{}^a$	$\bar{v}_{MB}{}^a$	$\bar{v}_{MOCDA}{}^a$	$\bar{v}^{\ddagger}$
Nitromethane	9.2	−43.0	72.4	100.4	144.6	130
Acetonitrile	10.5	−32.0	69.8	99.6	137.0	137
1,2-Dichloroethane	9.6	−43.7	72.2	100.8	142.6	129
n-Butyl chloride	10.7	−45.4	69.6	100.6	134.7	125
Dimethyl carbonate	. . .	−53.6	70.9	101.0	139.7	118

^{a} Measured by high-precision injection dilatometry (Grieger, *et al.*, 1971).

rate constants were also determined at 10.00°C and at 1 atm to allow calculation of activation energies. Each rate constant was calculated from a least-squares fit of a straight line to a plot of the integrated second-order rate expression for unequal reactant concentrations. A typical rate plot is shown in Figure 1. Because use of pressure-independent concentration units allows straightforward calculation of activation volumes (Hamann, 1963), all rate constants are based on mole fractions. The results are presented in Table I.

Activation volumes (at zero pressure) can most readily be determined from a least-squares fit of a quadratic expression (Golinkin, *et al.*, 1966) of the form

$$\ln k_x = a + bP + cP^2 \tag{1}$$

and from the thermodynamic relationship

$$\left(\frac{\partial \ln k_x}{\partial P}\right)_{T,P=0} = -\frac{\Delta v^{\ddagger}}{RT} = b \tag{2}$$

A typical plot for the pressure variation of the rate constant is shown in Figure 2.

The volume of activation is rigorously the difference in partial molal volume between the transition state and the reactants.

$$\Delta v^{\ddagger} = \bar{v}^{\ddagger} - \bar{v}_{MA} - \bar{v}_{MB} \tag{3}$$

In Table II are reported the values of the activation volume, found from eq 2, and the partial molal volumes of all species in solution. These have been used to calculate from eq 3 the partial molal volume of the transition state in each solvent,
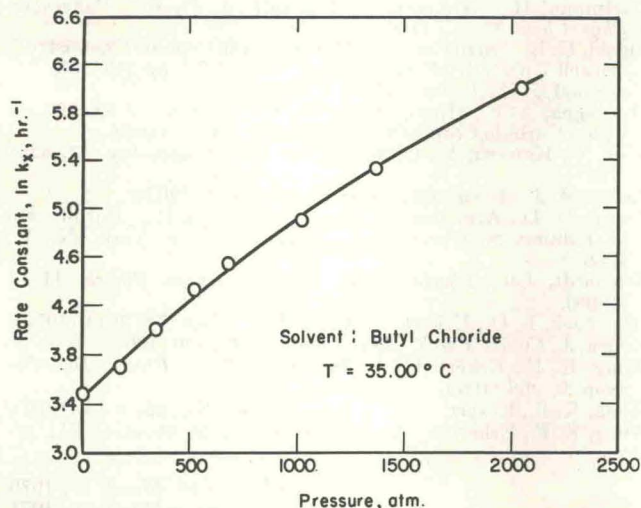
also given in Table II. Also, activation energies in four solvents are given in Table II.

Discussion

The Kirkwood (1934) model provides a simple expression for the Gibbs energy (work at constant T and P) required to place an ideal dipole μ at the center of a spherical cavity of radius r within a continuum of dielectric constant ϵ, as

$$\Delta g = -\frac{\mu^2}{r^3}\left(\frac{\epsilon - 1}{2\epsilon + 1}\right) \tag{4}$$

This has often been used to represent the partial molal Gibbs energy of a dipolar solute at infinite dilution, where non-electrostatic effects are assumed negligible. Then the pressure derivative of eq 4 gives the electrostatic contribution to the partial molal volume

$$\bar{v} = \bar{v}_0 - \frac{\mu^2}{r^3}\frac{\partial}{\partial P}\left(\frac{\epsilon - 1}{2\epsilon + 1}\right) \tag{5}$$

where $\bar{v}_0$ is the volume of the solute in a solvent in which

Figure 2. Effect of pressure on the rate constant of the methoxybutadiene–maleic anhydride reaction in n-butyl chloride
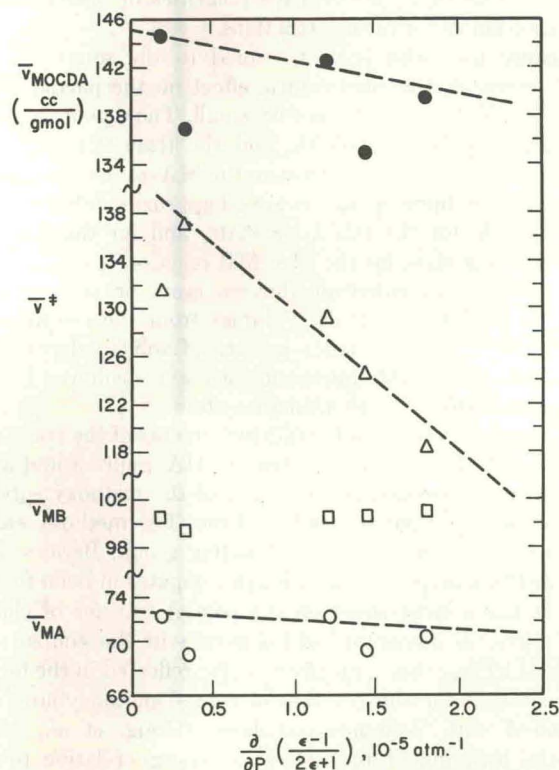
Figure 3. Solvent effects on the partial molal volumes at infinite dilution for reactants, transition state, and product of the methoxybutadiene–maleic anhydride reaction

Table III. Dipole Moments for MA, MOCDA, and the Transition State

	Estimated from Figure 3	Lit. value[a]
MA	3 D	3.94 D
Transition state	8 D	...
MOCDA	5 D	5.25 D

[a] Wong and Eckert, 1970.

there is no electrostriction. Nonelectrostatic interactions which affect partial molal volumes, such as hydrogen bonding and formation of charge-transfer complexes, are expected to cause negative deviations in volume from the electrostatic model.

Plots of the partial molal volumes of MA, MB, MOCDA, and the transition state for the reaction vs. the pressure derivatives of the dielectric constant factors for the solvents are shown in Figure 3. Pressure derivatives of dielectric constants were calculated from reported data (Greiger and Eckert, 1970c; Hartmann, et al., 1968; Schornack and Eckert, 1970).

Dipole moments can be estimated from eq 5, using the slopes of the lines in Figure 3. The values used for r^3 are calculated from the molar volumes of the solutes, using a model of close-packed spheres. In drawing the lines it was assumed that deviations from eq 5 due to specific solvent–solute interactions would always be negative, thus in effect neglecting the low points. Such an application of the Kirkwood theory gives only a semiquantitative evaluation of the dipole moment, with a probable uncertainty of 10 to 25%. Even this, however, is of sufficient accuracy to be quite useful in comparing the relative polarities of reactants and transition states for various reactions.

Because the slope is proportional to the square of the dipole moment, the electrostatic effect on the partial molal volume of MB ($\mu \approx 1$ D) is very small. The dipole moments estimated for MA, MOCDA, and the transition state are shown in Table III. In contrast to the MA–isoprene reaction, for which the dipole moments are all approximately the same size for MA, for the transition state, and for the product, the transition state for the MA–MB reaction is significantly more polar than either of the reactants or the product. Deviations of partial molal volumes from the electrostatic model, which show a similar pattern of solvent dependence for MA and MOCDA, apparently are overshadowed by the electrostatic effect for the transition state.

The large difference in the dipole moments of the transition states for the Diels–Alder reactions of MA–isoprene and MA–MB may be explained by the effect of the methoxy substituent at the 1 position of the butadiene. The methoxy entity is a relatively strong electron-donating group. Because it is attached to a carbon atom which participates in bond formation, it has a large effect on the partial transfer of charge from diene to dienophile which occurs in the course of a Diels–Alder reaction. This effect is also reflected in the higher rate constant for the reaction of trans-1-methoxybutadiene compared with 2-methoxybutadiene (Craig, et al., 1961) and the lowering of the activation energy relative to the isoprene reaction.

In conclusion, it has been shown that the concurrent determination of pressure and solvent effects on the rate of a chemical reaction can yield important information about the structure and properties of the transition state. For example, although the solvent effects on the rate constant of this reaction at atmospheric pressure are somewhat larger than for the isoprene–MA reaction, no quantitative estimate of the relative polarity of the two transition states can be made from solvent effects alone. However, accurate measurement of the solvent effect on the partial molal volume of the transition state not only allows estimation of its dipole moment, but also gives some indication of solvent–transition state interactions.

Nomenclature

a, b, c = empirical constants
E_a = activation energy, kcal/g mole
g = molar Gibbs energy, cal/g mole
k_x = rate constant based on mole fraction, hr^{-1}
P = pressure, psia
r = radius of spherical cavity, cm
R = gas constant
T = temperature
$\Delta v^{\ddagger}$ = activation volume, cc/g mole
$\bar{v}$ = partial molal volume, cc/g mole
$\bar{v}_0$ = volume in nonelectrostricted solvent, cc/g mole
ϵ = dielectric constant
μ = dipole moment, D

SUBSCRIPTS

MA = maleic anhydride
MB = trans-1-methoxy-1,3-butadiene
MOCDA = 3-methoxy-cis-4-cyclohexene-1,2-dicarboxylic anhydride

Literature Cited

Craig, D., Shipman, J. J., Fowler, R. B., J. Amer. Chem. Soc. 83, 2885 (1961).
Golinkin, H. S., Laidlaw, W. G., Hyne, J. B., Can. J. Chem. 44, 2193 (1966).
Gould, E. S., "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 537.
Grieger, R. A., Eckert, C. A., A.I.Ch.E. J. 16, 766 (1970a).
Grieger, R. A., Eckert, C. A., J. Amer. Chem. Soc. 92, 7149 (1970b).
Grieger, R. A., Eckert, C. A., Trans. Faraday Soc. 66, 2579 (1970c).
Grieger, R. A., Chaudoir, C., Eckert, C. A., IND. ENG. CHEM., FUNDAM. 10, 24 (1971).
Hamann, S. D., in "High Pressure Physics and Chemistry," R. S. Bradley, Ed., Academic Press, New York, N. Y., Vol. II, 1963, p 165.
Hartmann, H., Neumann, A., Schmidt, A. P., Ber. Bunsenges. Phys. Chem. 72, 877 (1968).
Ingold, C. K., "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 345–355.
Kirkwood, J. G., J. Chem. Phys. 2, 351 (1934).
Montagna, A. E., Hirsh, D. H., U. S. Patent No. 2,905,722 (to Union Carbide Corp.) Chem. Abstr. 54, 2168e (1960).
Niki, N., Kamiya, Y., Ohta, N., Bull. Chem. Soc. Jap. 42, 3224 (1969).
Parker, A. J., Advan. Phys. Org. Chem. 5, 173 (1967).
Perrin, D. D., Armarego, W. L. F., Perrin, D. R., "Purification of Laboratory Chemicals," Pergamon, New York, N. Y., 1966.
Reichardt, Ch., Dimroth, K., Fortschr. Chem. Forsch. 11, 1 (1968).
Schornack, L. G., Eckert, C. A., J. Phys. Chem. 74, 3014 (1970).
Stepek, J., Collect. Czech. Chem. Commun. 29, 390 (1964).
Wong, K. F., Eckert, C. A., Ind. Eng. Chem., Process Des. Develop. 8, 568 (1969).
Wong, K. F., Eckert, C. A., Trans. Faraday Soc. 66, 2313 (1970).
Wong, K. F., Eckert, C. A., J. Chem. Eng. Data 16, 56 (1971).