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High-Pressure Kinetic Studies of a Transition State. The Diels–Alder Condensation of Methoxybutadiene–Maleic Anhydride

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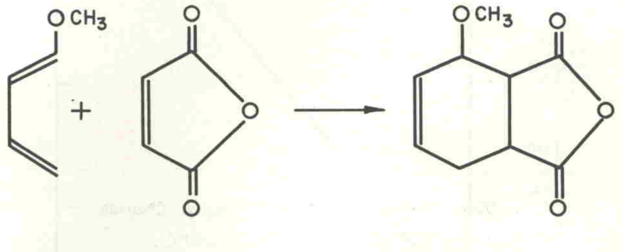
The kinetics of the Diels–Alder reaction of *trans*-1-methoxy-1,3-butadiene with maleic anhydride have been measured in five solvents and at pressures up to 20,000 psi. The results are used to show how solvent effects on the activation volume can lead to a better understanding of the structure and properties of the reaction transition state. Also, this provides a better measure of reaction polarity than the study of kinetic solvent effects alone.

A knowledge of the physical properties of the transition state provides the key for a detailed understanding of a reaction mechanism. Such information has direct engineering application in the design of chemical reaction systems—for example, in the prediction of substituent effects on reaction rates and in the prediction of kinetic solvent effects, as well as in catalysis and reactor design. Because the transition state is not isolable, its physical properties must be deduced from the effect of thermodynamic variables on the rate constant.

The temperature variation of the rate constant gives the activation energy, which can lead to calculations for the internal energy, entropy, and heat capacity of the transition state relative to the reactants. On the other hand, an equally important, if not even more valuable, approach is to measure the effect of pressure on reactions in solution. Although more difficult experimentally, if done accurately such determinations of activation volume can give information about both the atomic and electronic structure of the transition state, translatable into thermodynamic terms as partial molal volumes and activity coefficients in solution. One especially good way to study such effects is the measurement of activation volume in a variety of solvents.

In this work we report the effects of pressure and solvent on the Diels–Alder condensation of maleic anhydride (MA) with *trans*-1-methoxy-1,3-butadiene (MB) to form the cyclic adduct 3-methoxy-*cis*-4-cyclohexene-1,2-dicarboxylic anhydride (MOCDA).



MB **MA** **MOCDA**

This reaction was chosen for a number of reasons. First, the Diels–Alder reaction represents a simple, single-step molecular addition, uncomplicated by competing or reverse reactions at moderate temperatures. Although the solvent effects are not as great as for ionic reactions (Gould, 1959), they are quite significant. Moreover, previous studies (Wong and

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Table I. Experimental Rate Constants at 35.00°C (k_x for MA–MB Addition, hr^{-1})

	Pressure, psia						
Solvent	15	2500	5000	7500	10,000	15,000	20,000
Nitromethane	459	561	753	1020	1280	. . .	2940
Acetonitrile	200	245	287	378	451	647	. . .
1,2-Dichloroethane	105	139	. . .	237	285	408	557
n-Butyl chloride	32.7	43.9	55.8	75.5	95.3	148	208
Dimethyl carbonate	41.6	60.0	80.8	114	147	223	348

Eckert, 1969, 1971) have shown that for the addition of a nonpolar diene (butadiene) to MA solvent effects can be predicted well from solution theory. Also solvent effects on the activation volume of a similar reaction, isoprene with MA (Grieger and Eckert, 1970c), have substantiated the solution theory and yielded detailed information on that transition state. Finally, mechanistic studies (Grieger and Eckert, 1970b) have indicated that the transition state for this reaction could have an unusually high polarity.

The charge distribution in the transition state is a key property not only for mechanistic investigation but especially for making thermodynamic predictions of kinetic solvent effects. Most estimates of the polarity of transition states have been qualitative ones, based on the old rule of thumb that reactions for which the transition state is more polar than the reactants go faster in polar solvents, and *vice versa*. This rule was substantiated largely by studies on SN reactions (Ingold, 1953), for which electrostatic interactions with the solvent far outweigh other factors which affect the reaction rate in solution. More recently, it has been recognized that for many reactions, the effect of solvent on the reaction rate may be greatly influenced by other types of interaction, such as London forces, hydrogen bonding, and formation of charge-transfer complexes (Parker, 1967; Reichardt and Dimroth, 1968). Nevertheless, solvent effect on the reaction rate is still often used as a criterion of transition state polarity, even for a free radical reaction for which the rate constant varies by less than a factor of 3 in a wide range of solvents (Niki, *et al.*, 1969).

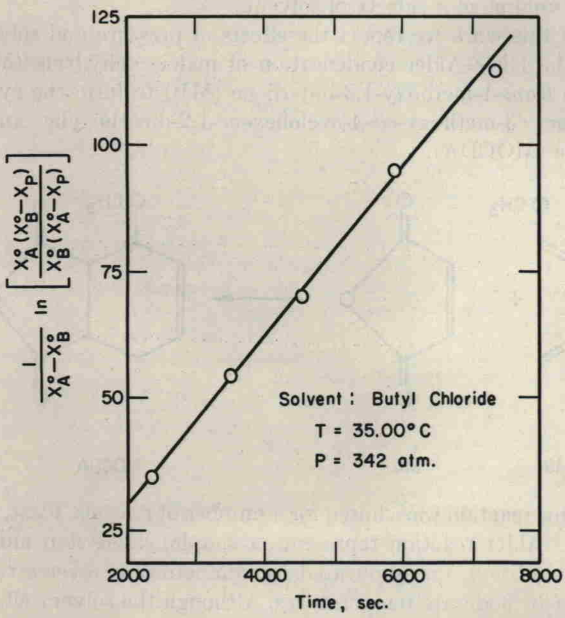

Figure 1. Typical rate plot for the methoxybutadiene–maleic anhydride reaction

Here we use the solvent effect on the activation volume in conjunction with partial molal volume measurements on the reactants to evaluate the volume in solution of the transition state. In terms of an electrostatic model for dipole interactions, this leads to an estimate of the absolute value of the dipole moment of the transition state.

Experimental Section

Reagent grade MA was recrystallized twice from ethyl ether and vacuum sublimed (mp 53°C). 1,1,3-Trimethoxybutane was dehydrogenated (Montagna and Hirsh, 1960) to make MB, which was washed, dried, and distilled to give 99% purity by gpc. The MB was all-trans by nmr. The product MOCDA was made by the reaction of MA with MB (mp 97–98°C). The solvents nitromethane, 1,2-dichloroethane, dimethyl carbonate, *n*-butyl chloride, and acetonitrile were purified, dried, and distilled by the methods of Perrin, *et al.* (1966). The hygroscopic acetonitrile contained no more than 0.01% water by Karl Fischer titration.

Kinetic measurements were made using the newly developed technique and equipment for high-pressure rate measurements reported previously (Grieger and Eckert, 1970a). This method employs *in situ* mixing of equilibrated reactants at high pressure, coupled with continual sampling for analysis; the resulting rate constants are more accurate than those determined by previous techniques because intrinsic errors due to heat of compression and uncertainty in reaction time are avoided.

For this study master solutions of MA and MB were prepared and stored in the dark at −15°C. All the high-pressure rate constants in a particular solvent were measured using similar initial concentrations of reactants, approximately 0.05 *M*. Copolymerization was inhibited by the addition of a trace of hydroquinone, which has been shown to have no effect on the rate of the Diels–Alder reaction (Stepek, 1964).

Analysis was done by gpc, using the ratio of peak areas for MA and MOCDA measured on a Beckman GC-5 chromatograph, equipped with dual 6 ft × $^1/_8$ in. columns with silicone DC-11 on a Teflon Gas-Pak F support and with dual flame ionization detectors. This method is independent of both sample volume and solvent losses due to evaporation in sampling. Moreover, it is more sensitive to the extent of reaction than analysis with an inert reference material. The calibration factor was determined by using several solutions of known concentration of MA and MOCDA. The standard deviation of the calibration factor was 1.6%. Reaction within the chromatograph was shown to be insignificant by simultaneous injection of MA and MB solutions.

Results

Reaction rates were determined in five solvents at 35.00°C and at pressures up to 20,000 psi. In four of the solvents,