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N_A = Avogadro's number
 R = response factor
 T = absolute temperature
 \bar{v}_i = partial molar volume of solute i
 V = volume
 w = weight of solution

GREEK LETTERS

β = parameter, eq 3
 ϵ_{11}^+ = lateral energy parameter
 ϵ_{1c}^+ = depth of 4-10 potential at minimum
 σ = lateral size parameter

SUBSCRIPTS

i = solute
 is = internal standard
 s = solvent

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A Study of Homogeneous Catalysis by High-Pressure Kinetics. The Mechanism of Catalysis of a Diels-Alder Reaction

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The application of high-pressure kinetics as a tool to investigate the detailed mechanism of catalysis of a reaction is demonstrated. Activation volumes have been determined for the Diels-Alder addition of 2,3-dimethylbutadiene to *n*-butyl acrylate, both uncatalyzed and catalyzed with $AlCl_3$. Also, partial molal volumes of reactants and products have been measured. From these data it is shown that the volume profile along the reaction coordinate is similar for both the catalyzed and uncatalyzed reactions. Further, both reactions proceed by a concerted one-step mechanism through a compact transition state with maximum accumulation of double bonds. Thus, the role of the Lewis acid in catalyzing the reaction is not to alter the mechanism but rather to render the dienophile more reactive by making it more electron deficient.

High-pressure kinetics has been well recognized as a powerful tool for investigating mechanisms of chemical reactions (see, *e.g.*, Gonikberg, 1963; Weale, 1967), but such studies are of primary interest to the organic chemist. Of much more direct interest to chemical engineers is the application of the same technique to ascertain the detailed mechanism by which a catalyst works. In this paper we present an example of such a study, the homogeneous $AlCl_3$ catalysis of a Diels-Alder reaction. Although the possibility of acid catalysis of this cycloaddition reaction has been evident for some time (Rubin, *et al.*, 1949; Yates and Eaton, 1960), the mechanism of the catalyzed reaction is still in doubt.

Many examples of this type of reaction have been quoted (Allen, *et al.*, 1962; Favorskaya and Auvinen, 1963; Fray and

Robinson, 1961; Inukai and Kasai, 1965; Jahn and Goetzky, 1962) in which $AlCl_3$ or other Lewis acids were useful in catalyzing Diels-Alder reactions, especially for those cases where the dienophile contained a conjugated carbonyl group. From such investigations certain aspects of the mechanism are accepted. For example, it appears that the catalysis involves complexing of the $AlCl_3$ with the carbonyl oxygen, withdrawing electrons from the conjugated system, and rendering the dienophile (the electron acceptor in the normal Diels-Alder addition) more reactive. This conclusion is supported by infrared studies of complexes between ethyl acetate and group II and group IV halides (Lappert, 1961), as well as by some of the observations made about the kinetics of the reaction (Inukai and Kojima, 1967b; Soula, *et al.*, 1966). Although the kinetics are incompletely defined, for cases where the dienophile has a conjugated carbonyl group (or nitrile) the rate

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appears to be first order with respect to diene and at least initially first order in catalyst concentration, though there is evidence that the catalyst complexes with the adduct as this product appears.

However, the detailed kinetics have not been completely elucidated, and in addition, controversy still exists about the exact mechanism of the catalyzed Diels-Alder reaction. For example, due to the very high polarity of the dienophile- AlCl_3 complex, it is tempting to propose a two-step mechanism involving a dipolar open-chain intermediate. Inukai and Kojima (1966a) assumed a one-step mechanism for the uncatalyzed reaction, which involved a transition state where both new bonds were partially formed, but they explained the differences between the catalyzed and uncatalyzed cases by proposing a two-step mechanism for the catalyzed reaction. Also, Thompson and Melillo (1970) studied the AlCl_3 -catalyzed addition of butadiene to the dienophile 2-phenyl-2-cyclohexen-1-one, and on the basis of product studies proposed a two-step, diradical intermediate mechanism.

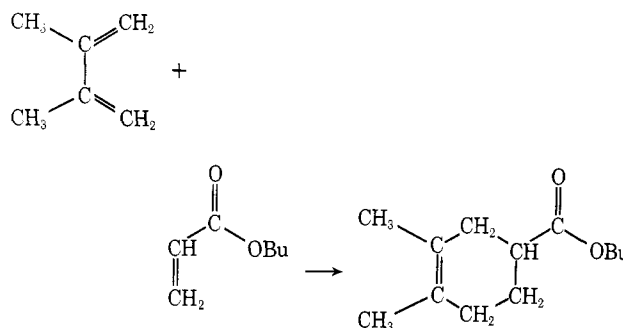
On the other hand, Inukai and Kojima (1966a, 1967a) and Kojima and Inukai (1970) found subsequent evidence which suggested the single-step mechanism for the catalyzed Diels-Alder reaction. They found that the reaction of cyclopentadiene with five dienophiles adhered more closely to the endo rule of addition when catalyzed than when uncatalyzed. This seems unlikely if there is a two-step mechanism, but for a concerted reaction this could be explained in terms of enhancement by the catalyst of the π interactions between nonbonding centers in the transition state. Subsequent isomer distribution studies of the addition of *trans*-piperylene to methyl acrylate, both with and without the presence of an AlCl_3 catalyst, substantiated this result. The catalyzed reaction resulted in a significantly greater proportion of the *cis* isomers, analogous to endo addition. Although these results may appear to defy the general concept that increased reactivity leads to lower selectivity (Leffler and Grunwald, 1963), it has been shown that such a result is not unique for the catalyzed Diels-Alder reaction, but in fact, for all Diels-Alder reactions studied the selectivity increased with the reactivity of the dienophile. All these results then seem to indicate that an AlCl_3 -complexed dienophile should be looked upon as simply a highly reactive dienophile taking part in an ordinary Diels-Alder reaction.

Recently, Williamson and Hsu (1970) studied the effect of Lewis acids on the Diels-Alder reaction between pentachlorocyclopentadiene and various dienophiles. This is an unusual Diels-Alder reaction in that it involves a reverse electron demand; that is, the dienophile, rather than the diene, is the electron donor. They found that the isomer selectivity increased for the catalyzed reactions, but that the rate of the reaction was increased only by a factor of 2-8. This could indicate that the presence of the Lewis acids still increases the secondary interactions which govern the form of the transition state (and thus the resulting isomers), but due to the reverse electron demand the dienophile is not greatly more reactive in the catalyst-complexed form and no large rate increase results.

Thus, the evidence available for the mechanism of this reaction, primarily from product structure analysis, is uncertain and ambiguous. It is the purpose of this work to present a different type of data—the results of high-pressure kinetic studies—in an attempt to resolve the mechanism. Accurate measurement of the activation volume, especially when coupled with independent determinations of the partial molal volume of reactants and products in solution, often provides

very strong mechanistic evidence. For example, by using a highly accurate high-pressure kinetic technique, several uncatalyzed Diels-Alder reactions were shown clearly to follow a single-step mechanism (Grieger and Eckert, 1970a,b). These results not only clarified earlier uncertainty about the mechanism (Benson and Berson, 1962, 1965; Walling and Peisach, 1958; Walling and Schugar, 1963) but also demonstrated the existence of secondary interactions between nonbonding centers in the transition state, as in the reactions of maleic anhydride with three dienes, where the volume of the transition state was actually smaller than that of the product. Subsequently, also by high-pressure techniques, Stewart (1971, 1972) has shown that for at least one reaction (chloroprene dimerization) both mechanisms could occur.

The reaction studied in this work is the addition of 2,3-dimethylbutadiene to *n*-butyl acrylate, which proceeds at convenient temperatures for the high-pressure technique both with and without catalyst, and which gives only a single isomer product. Normally, for a reaction in which only one bond is



formed in going to the initial transition state, (*i.e.*, a two-step Diels-Alder reaction or a Friedel-Crafts reaction) one would expect an activation volume of approximately -10 to -15 cm^3 per g-mole (Weale, 1967). Similarly, for a reaction with a transition state involving the formation of two bonds (*i.e.*, a one-step Diels-Alder reaction) one would expect an activation volume of approximately -20 to -30 cm^3 per g-mole. For example, for the Friedel-Crafts reaction between benzene and benzoyl chloride in the presence of AlCl_3 to give benzophenone, the volume change on reaction is -40 to -45 cm^3 per g-mole, and the activation volume is -13.4 cm^3 per g-mole (Coillet, *et al.*, 1965). This is consistent with the fact that the Friedel-Crafts reaction occurs by a two-step process. Thus, information about the volume of activation for the reaction chosen here, both with and without a catalyst, should indicate whether the reaction is one step or two, and even more clearly whether the addition of the catalyst alters the mechanism.

Experimental Section

Materials. Butyl acrylate was obtained commercially, dried over 4A molecular sieves, and distilled at reduced pressure under nitrogen. A middle cut of approximately 80% of the initial volume was used. Dimethylbutadiene was prepared by the hydrobromic acid method described in the literature (Organic Syntheses, 1965), and the portion used had a boiling point range of 69.5 to 70°C . AlCl_3 was sublimed under vacuum and stored in a dry nitrogen atmosphere.

The Diels-Alder adduct, *n*-butyl 3,4-dimethyl-3-cyclohexene-1-carboxylate, was prepared by the slow (45-min) addition of 35.4 ml (0.312 mole) of dimethylbutadiene to a mixture of 43.6 ml (0.312 mole) of butyl acrylate with 4 g (0.03 mole) of AlCl_3 . An ice bath was used to remove heat resulting from the exothermic reaction. The mixture was al-

Table I. Rate Constants at Various Pressures for the Butyl Acrylate-Dimethylbutadiene Reaction

Catalyzed reactions		Uncatalyzed reactions			
$T = 10.00^\circ\text{C}$		$T = 50.00^\circ\text{C}$		$T = 70.00^\circ\text{C}$	
Pressure, atm	k , hr^{-1}	Pressure, atm	k , hr^{-1}	Pressure, atm	k , hr^{-1}
4.4	170.1	4.4	0.0101	4.4	0.0420
4.4	173.2	341.1	0.0132	273.1	0.0624
137.1	201.0	681.3	0.0205	545.2	0.0867
137.1	202.4	1021	0.0287	953.4	0.1161
273.1	232.3	1360	0.0432	1360	0.1734
409.2	267.9			2041	0.3612
545.2	316.1				
681.3	365.3				

lowed to stand for several hours at 45°C . The mixture was then washed with dilute HCl, followed by washing with several portions of H_2O , and dried first with Na_2SO_4 and then with 4A molecular sieves. Vacuum distillation gave approximately 30 ml (0.135 mole or 43% yield) of product. The boiling point was approximately 110°C at 8 mm. Microanalysis gave 74.5% carbon and 10.44% hydrogen (theoretical 74.3%, 10.5%). The adduct was stored in a refrigerator after a small amount of hydroquinone had been added.

The butyl acrylate- AlCl_3 complex in butyl acrylate solution used in the high-pressure runs was prepared by adding butyl acrylate to a weighed amount of AlCl_3 . Both the AlCl_3 and the solution were exposed only to a nitrogen atmosphere. The solution was stored in the refrigerator, and a new solution was prepared every 2 weeks; 1:1 molar ratios of both butyl acrylate and the adduct to AlCl_3 were prepared for use in the partial molal volume measurements. These complexes were prepared by adding small portions (0.5 g) of AlCl_3 to either the butyl acrylate or the adduct. The AlCl_3 dissolved easily in the butyl acrylate with stirring and removal of the heat from the reaction after the addition of each portion. It was necessary to stir the adduct during the addition of the AlCl_3 , and after the addition of each portion of AlCl_3 additional stirring and cooling were required.

Kinetic Runs. All kinetic measurements were made using the apparatus and procedure described previously (Grieger and Eckert, 1970a). This technique involves loading the reactants separately into each of two pistons and cylinders, separated by a thin metal diaphragm. The reactants are compressed separately and the heat of compression is permitted to dissipate before the diaphragm is burst magnetically and the contents mixed. The reaction is followed by continual sampling for analysis through fine syringe tubing and a needle valve. Such a method can yield quite accurate results for the high-pressure rates, as it avoids the common errors due to heat of compression and uncertainties in starting and stopping times of the reaction.

The high-pressure vessel containing the sample cell was immersed in an oil bath and thermostated to $\pm 0.02^\circ\text{C}$ with temperatures calibrated against NBS-calibrated thermometers. Pressures were measured by two calibrated Heise gauges, and uncertainties in pressure are estimated at ± 1 atm up to 1000 atm and ± 7 atm at higher pressures.

Samples were analyzed by vpc on a Beckman GC-5 using matched 6 ft \times $\frac{1}{8}$ in. o.d. columns packed with 20% DC-11 on Gas-Pack F and a hydrogen flame detector. For the catalyzed reaction, the analysis was based on the ratio of product peak area to that for dimethylbutadiene, as compared to ratios found for gravimetrically prepared calibration solutions. For the uncatalyzed reaction the ratio followed was that of prod-

uct peak area to butyl acrylate peak in order to avoid the possibility of error due to the evaporation in sampling of dimethylbutadiene for runs at these higher temperatures (50 and 70°C).

Partial Molal Volumes. The partial molal volumes of reactants and products were measured by the method of injection dilatometry (Grieger, *et al.*, 1971), wherein successive portions of solute (about 0.5 cm^3) are injected into about 50 cm^3 of solvent, and the volume change on mixing is measured quite accurately by the rise in level in a capillary. The precision of the determination depends strongly on the stability of the thermostat in which the assembly is immersed, but in general, for normal liquid solutes, values accurate to ± 0.1 cm^3 per g-mole can be achieved, and in the dilute region (0 to 0.4 M here), the variation with composition to less than this uncertainty (McCabe, *et al.*, 1970). However, the determinations made for the partial molal volumes of the AlCl_3 complexes of the butyl acrylate and especially that of the adduct were much more difficult experimentally, due to the high viscosity and reactive nature of these complexes, as well as the fact (see below) that composition variation is not negligible. As discussed below, uncertainties in these determinations are, therefore, about an order of magnitude larger.

In conjunction with the technique of injection dilatometry, it is necessary to determine exact densities of the materials used. Where literature values were unavailable these were measured with a 10- cm^3 Sprengel pycnometer by the standard technique. Such values should have a precision of about $\pm 10^{-4}$ g/cm^3 .

Results

Kinetics. The uncatalyzed reaction was run neat at 50 and 70°C at pressures up to 2000 atm; the ratio of initial molar concentrations of dimethylbutadiene to butyl acrylate was approximately three to two for all runs. The catalyzed reaction was run up to about 1000 atm at 10°C using the dienophile butyl acrylate as solvent, with the initial diene concentration at 0.23 M and the AlCl_3 at 0.023 M . Because of the volatility of the diene, as well as to facilitate sampling, the lowest pressure run was slightly above atmospheric pressure (50 psig) in each case. The catalytic effect of the AlCl_3 was so great that it was not possible to determine accurately activation volumes for the catalyzed and uncatalyzed reaction at the same temperature.

The uncatalyzed reaction is a classical second-order reaction, and the rate constants were evaluated from a least-squares fit of the linear form of the integrated rate expression. These are given in Table I.

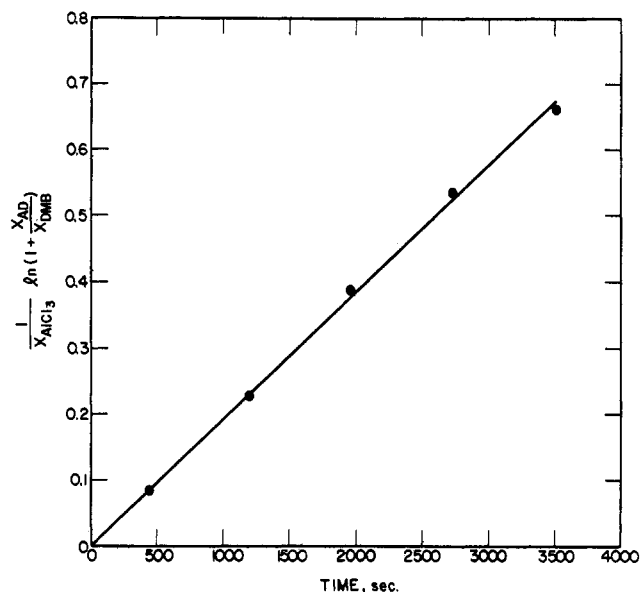


Figure 1. Typical rate plot. The catalyzed reaction of butyl acrylate and dimethylbutadiene at 10.00°C, 137.1 atm

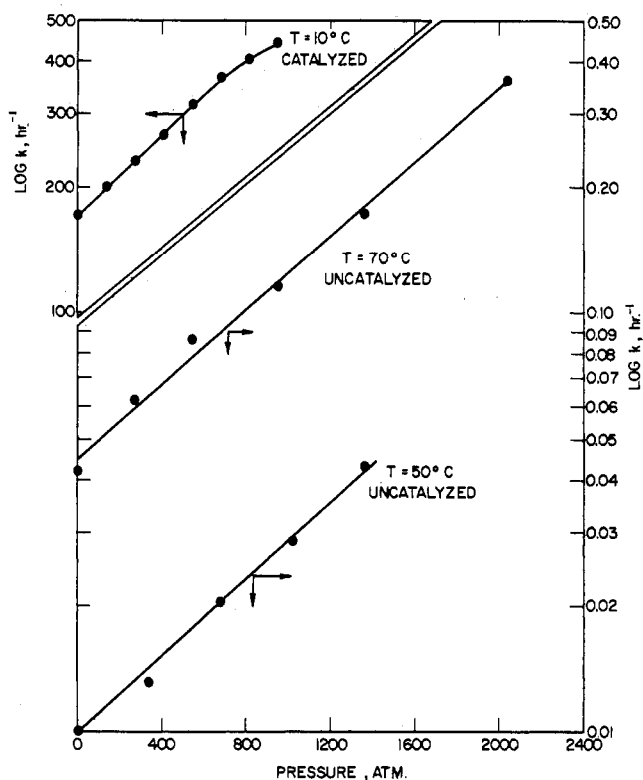


Figure 2. Effect of pressure on the rate of the butyl acrylate-dimethylbutadiene reaction

To analyze the results for the catalyzed reaction, analysis of the kinetics is necessary. Based on evidence from the literature, as well as on data observed here, it appears that the AlCl_3 in solution can exist in any of three forms—free AlCl_3 , complexed with the dienophile (to the carbonyl group), or complexed with the reaction product (also to the carbonyl group)—and there is rapid equilibration between the three forms. However, since free AlCl_3 is an effective catalyst for diene polymerization, effectively all of the AlCl_3 must be kept complexed in order to study the Diels-Alder reaction. If the dienophile concentration is large, the equilibria are such that

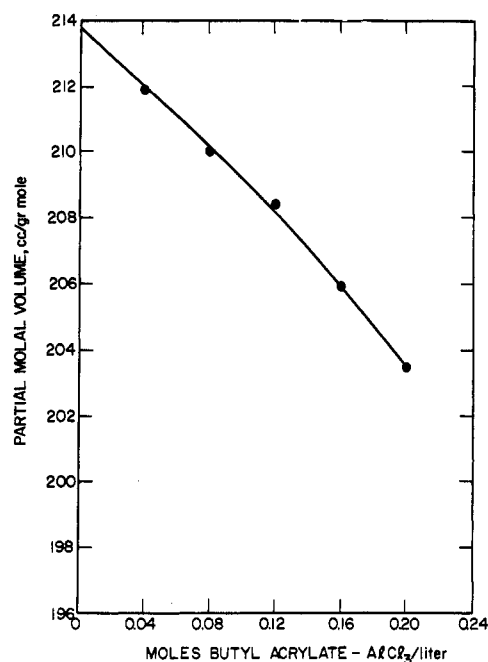


Figure 3. Variation of the partial molal volume with concentration for the complex butyl acrylate- AlCl_3 in butyl acrylate solution

essentially no free AlCl_3 exists; thus in this work the butyl acrylate concentration was always in the range of 4–7 M . Then initially all the AlCl_3 is complexed with dienophile molecules, and only those molecules which are thus complexed react to form the adduct, which upon formation is also complexed with AlCl_3 . However, an equilibrium also exists of the type butyl acrylate + adduct- $\text{AlCl}_3 \rightleftharpoons$ butyl acrylate- AlCl_3 + adduct, and this is attained very quickly with respect to the reaction rate. Therefore, at low conversions the AlCl_3 -adduct complex which appears transfers all the AlCl_3 rapidly back to complexing with the much more concentrated butyl acrylate. Actually the catalyzed reaction is second order overall, first order in diene, and first order in the AlCl_3 -butyl acrylate complex. However, because of the above transfer reaction, the concentration of this complex remains essentially constant for modest conversions, and the reaction appears to be pseudo-first order in diene only. Rate constants for the catalyzed reaction were thus obtained from least-squares fits of the linear form of the integrated first-order rate expression and are given in Table I. A typical example of such a plot is given in Figure 1. To avoid corrections for the pressure dependence of concentration units, all concentrations were expressed in mole fractions (Poling, 1971). The standard deviations for the rate plots were 3–4% for the uncatalyzed reactions and 2–3% for the catalyzed cases.

When the rate constant is expressed in pressure-independent units, such as mole fraction, the activation volume Δv^\ddagger is found rigorously from the slope of the rate plot (Figure 2) with no correction terms, by

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = -\frac{\Delta v^\ddagger}{RT} \quad (1)$$

In this work, sufficient data were taken over a relatively narrow pressure range to permit determination of the activation volume at 1 atm from a fit of the data to a straight line. The values of Δv^\ddagger thus obtained were $-25.7 \text{ cm}^3 \text{ per g-mole}$ for the catalyzed reaction and -28.7 and $-28.5 \text{ cm}^3 \text{ per g-mole}$ at 50.00 and 70.00°C, respectively, for the catalyzed case.

Table II. Partial Molal Volumes of Uncomplexed Reactants and Products

Solute	Solvent	Temp, °C	\bar{v} , cm ³ /mole ^d	v^0 , cm ³ /mole ^e	$\bar{v} - v^0$, cm ³ /mole
DMB ^a	BA ^b	10.00	111.17	111.71	-0.54
AD ^c	BA	10.00	219.81	220.64	-0.83
BA	Mix ^f	10.00	140.83	140.89	-0.06
DMB	Mix	10.00	111.64	111.71	-0.07
AD	Mix	10.00	218.84	220.64	-1.80
BA	Mix	30.00	144.28	144.19	+0.09
DMB	Mix	30.00	114.36	114.53	-0.17
AD	Mix	30.00	220.03	222.32	-2.29

^a 2,3-Dimethylbutadiene. ^b *n*-Butyl acrylate. ^c Diels-Alder adduct of BA and DMB, *n*-butyl 3,4-dimethyl-3-cyclohexene-1-carboxylate. ^d Partial molal volume. ^e Molar volume. ^f Mixture of BA (37.1 mole %), DMB (56.2 mole %), and AD (6.7 mole %).

Table III. Partial Molal Volumes of AlCl₃ Complexes at 10.00°C

Injection	$\bar{v}_{AD-AlCl_3}$ in adduct, cm ³ /mole	$\bar{v}_{BA-AlCl_3}$ in butyl acrylate, cm ³ /mole
1	291	213
2	298	212
3	305	218
4	273	217
5	305	213
Average	294	215
Molar volume of pure complex	294	214

The uncertainty in these values is estimated as ± 1 cm³ per g-mole.

Partial Molal Volumes. The activation volume is a difference in partial molal volumes, $\Delta v^\ddagger = \bar{v}_{\text{transition state}} - (\Sigma \bar{v})_{\text{reactants}}$, and for a detailed study of the mechanism, it is preferable to evaluate absolute values of the partial molal volumes of individual species. This determination was made for both the reactants and for the products in two different solvents. The first of these, butyl acrylate, was the solvent used in the catalyzed reactions. The second was a mixture of butyl acrylate (37.1 mole %), dimethylbutadiene (56.2 mole %), and their Diels-Alder adduct (6.7 mole %). This mixture approximated the composition of the reaction mixture for the uncatalyzed reaction. Partial molal volumes for all reactants and products except the AlCl₃ complexes are given in Table II.

The partial molal volume of the butyl acrylate-AlCl₃ complex in butyl acrylate was first obtained by injecting a 1:1 (molar ratio) butyl acrylate-AlCl₃ complex into butyl acrylate. The partial molal volume variation over this concentration range can be seen in Figure 3.

The value of the partial molal volume of the adduct-AlCl₃ complex in butyl acrylate could not be measured by injecting the complex into butyl acrylate, since the transfer reaction shown above would take place immediately, presumably exhibiting an additional volume change. Thus the value actually observed, the volume change resulting from injecting adduct-AlCl₃ complex into butyl acrylate, would consist of two inseparable contributions, (1) the volume of solution and (2) the volume change of the equilibration reaction.

However, from Figure 3 it can be seen that the partial molal volume of the butyl acrylate-AlCl₃ complex at infinite dilution is very close to its molar volume of 214 cm³ per g-mole. Therefore, it was assumed that the value of the adduct-AlCl₃ complex in butyl acrylate was also close to its molar volume of 294

Table IV. Densities of Pure Materials

Compound	Densities, g/cm ³		
	10.00°C	50.00°C	70.00°C
Butyl acrylate	0.9095	0.8690	0.8475
Dimethylbutadiene	0.7356	0.6963	0.6762
Adduct	0.9528	0.9228	0.9073
BA-AlCl ₃ complex	1.2220		
AD-AlCl ₃ complex	1.1686		

cm³ per g-mole at infinite dilution. Consequently, the molar volumes were used in place of the partial molal volumes for the AlCl₃ complexes. To substantiate the validity of this procedure, the partial molal volume of the adduct-AlCl₃ complex in solution in adduct was determined. Since the adduct complex was very viscous at 10°C, a solution of adduct-AlCl₃ complex (33 mole %) in adduct (67 mole %) was injected into pure adduct. The contribution to the volume change on injection due to the pure adduct was subtracted from the total volume change, and the partial molal volume of the adduct complex in adduct was calculated. A similar measurement for butyl acrylate was made by injecting a solution of butyl acrylate-AlCl₃ complex (33 mole %) in butyl acrylate (67 mole %) into butyl acrylate. The results of these two measurements are given in Table III. Though the uncertainty in this type of measurement is larger for both measurements, the average of the partial molal volumes was within experimental error of the molar volumes.

The densities of pure species used in this work, given in Table IV, were taken from reported values in the literature when available (Beilstein, 1968; Faraday's Encyclopedia, 1957; Walling and Schugar, 1963); the rest were determined by pycnometry.

Discussion

The activation volumes measured for both the uncatalyzed and catalyzed reactions suggest that two bonds are being formed in the transition state, and thus correspond to a concerted, single-step four-center cycloaddition mechanism. Such a mechanism implies that the transition state has a compact form and that both bonds are either partially or wholly formed. Although both bonds need not be formed to the same extent (in fact, it is unreasonable to assume that they would be for unsymmetrical molecules), an open-chain diradical structure is definitely ruled out. Also, the compact form of the transition state allows secondary interactions to play an important role in determining what isomer might or might not appear as the product of the reaction where more than one product is possible.

Table V. Partial Molal Volumes for the Butyl Acrylate-Dimethylbutadiene Reaction at 10.00°C

	Catalyzed	Uncatalyzed
$(\Sigma \bar{v})_{\text{reactants}}, \text{cm}^3/\text{mole}$	325	252.4
$\Delta v^\ddagger, \text{cm}^3/\text{mole}$	-25.7	-28.6
$\bar{v}_{\text{transition state}}, \text{cm}^3/\text{mole}$	299	224
$\bar{v}_{\text{product}}, \text{cm}^3/\text{mole}$	294	220

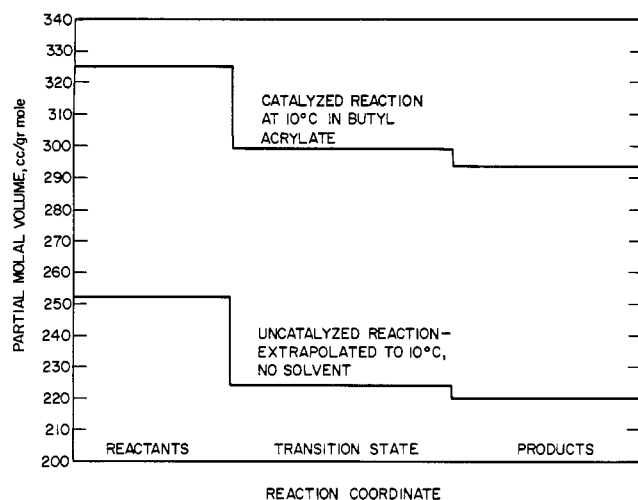


Figure 4. Partial molal volume profile along the reaction coordinate for the butyl acrylate-dimethylbutadiene addition

For purposes of comparison, the activation volume of the uncatalyzed reaction was extrapolated to 10°C. The two values measured at 50 and 70°C were identical well within experimental uncertainty, so the activation volume was assumed to be temperature-invariant, or an average value of -28.6 cm^3 per g-mole was assumed at 10°C. This corresponds to assuming that the volume of the transition state is essentially linear over the range 10–70°C and parallel to the sum of the reactant volumes (which are themselves linear and virtually parallel). The only reasonable alternative on physical grounds would be to assume that the magnitude of the activation volume decreases with decreasing temperature, which could only strengthen the conclusions drawn below by making the values of Δv^\ddagger for the catalyzed and uncatalyzed cases even closer to each other.

The values of the partial molal volumes of the reactants, transition states, and products for both the catalyzed and uncatalyzed reactions are compared in Table V and their relative values along the reaction coordinate are illustrated in Figure 4. The volume profiles along the reaction path are essentially identical for the catalyzed and uncatalyzed reactions, except that the partial molal volumes for the catalyzed reaction are shifted upwards by approximately 73 cm^3 per g-mole due to the presence of the AlCl_3 . Not only does this suggest that both reactions proceed by the same mechanism, but it also substantiates some of the details of the catalyzed reaction which have up until now been assumed—such as the assumption that a molecule such as butyl acrylate complexes with AlCl_3 (Lappert, 1961). Figure 4 indicates that the product of the reaction, the adduct, is complexed with AlCl_3 for a brief time before the AlCl_3 transfers back to another butyl acrylate molecule to act again as a catalyst for Diels-Alder cycloaddition.

In comparing these conclusions with previous work, they are completely consistent with previous high-pressure studies

of uncatalyzed Diels-Alder reactions carried out by this improved technique (Grieger and Eckert, 1970b), but contradict the conclusions of Walling and Schugar (1963), who determined the activation volume for the butyl acrylate-dimethylbutadiene addition, uncatalyzed, in bromobenzene. The latter authors reported the volume of activation to be -22.6 cm^3 per g-mole at 80°C and the volume change on reaction (based on pure component molar volumes, not partial molal volumes) as -42 cm^3 per g-mole. From this, Walling and Schugar concluded that the reaction proceeded by a two-step mechanism, since approximately half of the total volume change occurred in going from the reactants to the transition state. At 10°C, however, the volume change on reaction (again based on pure-component densities) is only -32 cm^3 per g-mole, while, according to this work, the activation volume appears to be temperature independent. Thus, one must examine not only the percent of the total volume change that the activation volume represents, but also the magnitude of the activation volume itself. In fact the values of activation volumes obtained by Walling and coworkers have been questioned, and it has been suggested that they are generally too low, due primarily to temperature errors resulting from the heat of compression of the reaction mixture (Benson and Berson, 1962, 1965; Grieger and Eckert, 1970b). As a check on this conclusion, the technique used here was used to determine the rate constant of the same reaction in the same solvent, bromobenzene, at 80°C and 1 atm, where there can be no error due to compression, and it was found to be $3.26 \times 10^{-6} \text{ l./mole-sec}$, in good agreement with Walling and Schugar's value of $3.47 \times 10^{-6} \text{ l./mole-sec}$.

The results of Thompson and Melillo (1970) are not completely consistent with this conclusion. Although about 95% of their products can be accounted for by a one-step mechanism (see Poling, 1971), a small amount appears to come from a two-step process. In view of the findings of Stewart (1971, 1972), it seems probable that both mechanisms occur for the reaction of Thompson and Melillo as well. Thus it is evident that one should not generalize either their results or the conclusions presented here to include all catalyzed Diels-Alder reactions.

Conclusions

From high-pressure kinetic studies strong evidence has been found supporting a single-step, concerted mechanism for both the catalyzed and uncatalyzed reaction of butyl acrylate with dimethylbutadiene.

A Lewis acid affects both the rate and selectivity of a Diels-Alder reaction, but the rate effect was demonstrated in this work. Although the mechanism was the same whether a Lewis acid was present or not, the rate constant for the catalyzed case was larger than that of the uncatalyzed reaction by a factor of approximately 10^5 . This tremendous increase is attributed to the fact that a dienophile complexed with AlCl_3 is simply much more electron deficient, and thus more reactive, than when in its uncomplexed form. Williamson and Hsu (1970) demonstrated that this rate effect could be separated from the second effect a Lewis acid might have on a Diels-Alder reaction. This selectivity effect with respect to the isomer distribution of the products has been discussed by several authors (Inukai and Kojima, 1966b, 1967a; Thompson and Melillo, 1970; Williamson and Hsu, 1970). This selectivity apparently results from either increased or decreased secondary interactions in the transition state due to the presence of the Lewis acid. It would be interesting to study the effect of pressure on the isomer distribution of a Diels-Alder

reaction, both with and without a Lewis acid catalyst. If all isomers are formed from a common transition state, the reaction should yield the same product distribution at all pressures, whereas if two or more transition states are involved, the distribution would be pressure dependent. For example, if the system studied by Thompson and Melillo (1970) proceeds through multiple transition states, the product distribution should vary with pressure, as it does for chloroprene (Stewart, 1971, 1972). Moreover, if any two or more of the products appear in the same ratio, regardless of variations in pressure or solvent, they probably proceed through the same transition state.

Finally, and perhaps most important, the application of high-pressure kinetics has been demonstrated as an experimental tool to study the detailed role of the catalyst in a homogeneously catalyzed liquid-phase reaction. Used in conjunction with other types of data, a high-pressure kinetics experiment is clearly capable in many cases of yielding new and valuable information about mechanisms of catalysis.

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Adsorption Equilibria at High Pressures in the Helium-Nitrogen-Activated Carbon System

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Adsorption equilibria in the helium-nitrogen-activated carbon system were measured volumetrically at 100 and 150°K, at pressures up to 100 atm, for gas-phase compositions of 0.000327 and 0.001059 mole fraction of nitrogen. The corresponding pure component isotherms were also determined. A general method for the prediction of multicomponent adsorption equilibria is proposed. This method is based on the calculation of constituent fugacities in pure and mixed equilibrium gas phases at constant temperature and adsorbate volume, and the assumption of an ideal mixed adsorbate. Deviations from an ideal mixed adsorbate can be described in terms of activity coefficients. The method predicts the total volumes adsorbed and the adsorbate composition within experimental error for the system studied, except at the highest coverages, where the assumption of an ideal mixed adsorbate apparently becomes invalid.

The growing application of new adsorption processes for the separation and purification of gas mixtures requires useful methods for predicting and correlating mixed adsorption equilibria. These methods should strike a balance between

complexity and ease of engineering application. In addition, such methods should be based on fundamental principles whenever possible, so that some physical interpretations of the adsorption process are possible.

In the past 50 years, numerous methods have been proposed for the prediction of mixed gas adsorption equilibria. The earliest of these approaches was based on extensions of the

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