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The Effect of Pressure on the Diels-Alder Reaction[1)]

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The effect of pressure on the Diels-Alder reaction was investigated. The observed activation volume was found to have a significant correlation with the activation free energy of the reaction. A correlation diagram between the activation volume and the activation free energy was proposed. By this diagram, the position of the transition state in the Diels-Alder reaction was discussed, and the activation volume was suggested to be a good diagnostic probe for the position of the transition state. The importance of the contribution of the volume contraction resulting from secondary orbital interaction to the apparent activation volume was pointed out.

There has been only a little concern in the literature about the position of the transition state in an organic reaction along its reaction coordinate.[2)] In this respect, investigators have used the postulates of Hammond[3)] and of Swain and Thornton,[4)] the ρ-value,[5–7)] the kinetic isotope effect,[7)] Brönsted's α-value,[2)] and some quasi-thermodynamic parameters[8)] for the examination of the relative positions of the transition states. Although the Diels-Alder reaction is exothermic, its transition state has been believed to resemble the product in a geometric sense. Moreover, the Diels-Alder selectivity-reactivity relationship[9)] has been understood unsatisfactorily. It is, therefore, of great importance to ascertain the relative position of the transition state for the Diels-Alder reaction.

The present paper will be concerned with experimental evidence for the displacement of the position of the transition state along the reaction coordinate in the Diels-Alder reaction. For this purpose, the activation volume of the reaction (Eq. (1)[10)]) was employed as a new parameter:

$$-RT(\partial \ln k/\partial P)_T = \Delta V^{\neq} \qquad (1)$$

It is well-known that the Diels-Alder reaction is a typical bimolecular, concerted, cleanly second-order reaction, and that it is almost insensitive to solvent change.[11)] In the present instance, the observed changes in the values of $\Delta V^{\neq}$ are referred to differences in the structural term, $\Delta_1 V^{\neq}$.[12)] This will make discussion rather simple, because one can eliminate the contribution of the solvation term, $\Delta_2 V^{\neq}$,[12)] in $\Delta V^{\neq}$, which occasionally introduces a puzzling effect on $\Delta V^{\neq}$.

Results and Discussion

The effects of the pressure on several Diels-Alder reactions have been investigated in order to elucidate the reaction mechanisms.[13–16)] We examined representative Diels-Alder reactions under pressures in the range from 1 to 900 kg/cm². *n*-Butyl chloride was employed as the solvent to make it possible to compare the present data with others, and because of the availability of its compressibility data.[17)] Typical rate plots at various pressures are shown in Fig. 1 for the reaction of 2,3-dimethylbutadiene with dimethyl fumarate. Since the plots of log *k* against the pressure showed a good linearity for all the reactions examined (for example, see Fig. 1), the activation volumes were calculated by Eq. (1) using the least-squares fit of the data to the following linear expression:

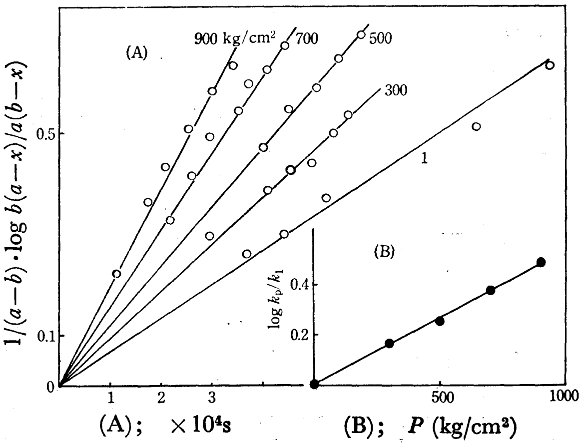


Fig. 1. (A): Rate plots under pressure for the reaction of 2,3-dimethylbutadiene with dimethyl fumarate.
(B): Plot of log k_p/k_1 against pressure for the same reaction.

$$\ln k = a + bP \qquad (2)$$

The observed values of the activation volume ($\Delta V_c^{\neq}$) were corrected by means of the following equation to give those of the molal concentration basis ($\Delta V_x^{\neq}$), taking into account the compressibility of the solvent (κ_0):[17,18)]

$$\Delta V_x^{\neq} = \Delta V_c^{\neq} - \kappa_0 RT \qquad (3)$$

The volume change of the reaction was estimated from measurements of the partial molal volumes of the reactants and the product.

Correlation of Activation Free Energy with Activation Volume. The apparent values of the rate constants, the activation volumes, and the volume changes in the Diels-Alder reactions are tabulated in Table 1. Although several reactions in Table 1 are known to give isomeric product mixtures, we referred to the apparent values of the activation volumes and the volume changes of the reactions because a) the difference in the activation volumes between the *endo*- and the *exo*-isomer producing processes ($\delta\Delta V^{\neq}=\Delta V_{exo}^{\neq}-\Delta V_{endo}^{\neq}$) were found to be quite small[19)] and b) in addition, the volume difference between the *endo*- and the *exo*-adducts has been reported to be negligible as well.[16a)] In the reactions where maleic anhydride was employed as a dienophile, $\delta\Delta V^{\neq}$ must be taken into account.[19)] In these cases, however, low *exo*: *endo* isomer ratios were usually found (1: 99 or less). Accordingly, the apparent values of $\Delta V^{\neq}$ could safely be

TABLE 1. VOLUME PARAMETERS FOR THE DIELS-ALDER REACTION IN *n*-BUTYL CHLORIDE

Reaction No.	Diene–Dienophile	Temp. (°C)	Rate Constant (l/mol s)	$\Delta V^{\neq}$ (cm^3/mol)	ΔV (cm^3/mol)	Ref.
	Acyclic Dienes					
1	1-Methoxybutadiene–MA[a]	35	9.34×10^{-4} [b]	−45.4	−34.9	16c
2	2,3-Dimethylbutadiene–MA[a]	30	3.54×10^{-4}	−41.3	−36.3	
3	Isoprene–MA[a]	35	1.68×10^{-4} [b]	−38.0	−36.8	16b
4	2,3-Dimethylbutadiene–dimethyl fumarate	40	6.60×10^{-6}	−32.9	−37.2	
5	2,3-Dimethylbutadiene–*n*-butyl acrylate	40	2.14×10^{-7}	−29.6	−36.4	
6	2,3-Dimethylbutadiene–methyl acrylate	40	1.84×10^{-7}	−30.2	−37.0	
	Cyclic Dienes					
7	Cyclopentadiene–dimethyl fumarate	30	1.32×10^{-3}	−32.7	−36.7	
8	Cyclohexadiene-1,3–MA[a]	35	5.24×10^{-4} [b]	−37.2[d]	−30.3[d]	16a
9	Cyclopentadiene–dimethyl acetylenedicarboxylate	35	5.64×10^{-4} [b,c]	−30.2[e]	−33.9[e]	16a
10	Cyclopentadiene–methyl acrylate	40	5.30×10^{-5}	−30.1	−35.7	
11	1,2,3,4-Tetrachlorocyclopentadiene–methyl acrylate	40	1.89×10^{-5}	−24.6	−33.2	
12	Cyclopentadiene–cyclopentadiene	40	3.97×10^{-6}	−23.7	−33.0	

a) Maleic anhydride. b) The reported values were corrected for k_2 in l/mol s for comparison. c) Calculated from data at other temperatures. d) In methylene chloride. e) In ethyl acetate.

used as a mechanistic probe of the reaction.

It can be clearly seen in Table 1 that a reaction with a larger rate constant is associated with a more negative activation volume. The activation volume of a particular reaction may be determined by several factors;[20] nevertheless, the activation free energy was shown to have a good correlation with the activation volumes. This relationship is shown in Fig. 2 for the reactions of cyclic and acyclic dienes respectively. The observed correlation of these two classes of dienes are not identical, but are separated in a rather parallel manner. In general, an acyclic diene is thought to be an equilibrating mixture of *s-cis* and *s-trans* isomers; the former will react as an effective diene with a given dienophile.[21] This means that the inherent rate for the *s-cis* isomer must be larger than the observed rate. The intervention of this *cis-trans* equilibration must be responsible for the separated trend shown in Fig. 2.

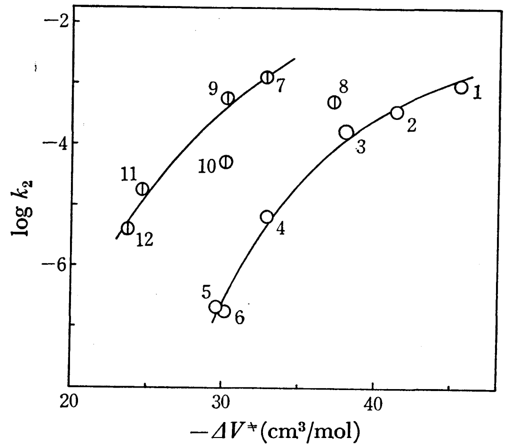
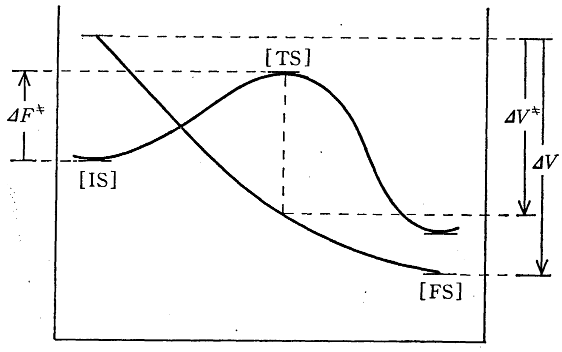


Fig. 2. Correlation of log k_2 with activation volume for the Diels-Alder reaction: numerals correspond to reaction numbers in Table 1; ○, acyclic diene; ⦶, cyclic diene.

An alternative explanation may be that the separated trend is caused by the $\Delta V^{\neq}$ term instead of the $\Delta F^{\neq}$ term. The geometry of a molecule is responsible for the magnitude of the partial molal volume of the molecule. The reaction of an acyclic diene with methyl acrylate, for example, necessarily proceeds through a monocyclic transition state, while that of a cyclic diene with the same dienophile must have a bicyclic transition state. Consequently, the differences in geometry in both the starting materials and the transition states may result in the differences in the activation volumes, which are responsible for the two separated lines in Fig. 2. However, this seems unlikely because the separated lines under consideration do not coalesce even if $\Delta F^{\neq}$ is plotted against $\Delta V^{\neq}/\Delta V$, a parameter indicating only the degree of progress for a given reaction and having no relation with the geometry of the reacting molecules and their transition states (see below).

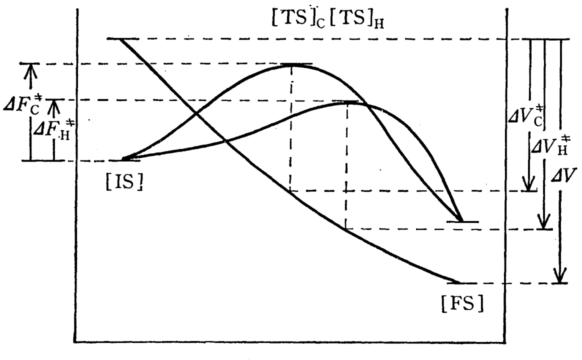
The problem of symmetry in the Diels-Alder transition state is still unsettled. However, theoretical[22] and experimental[16a,23] evidence seems to indicate that, in most of the reactions, a concerted transition state is preferred. In this discussion, we will deal with the present Diels-Alder reactions as concerted cycloaddition reactions.[24] The basic assumption is that the volume of addends in the Diels-Alder reaction decreases monotonously along the reaction coordinate except in special cases (a strong CT-complexing, large secondary orbital interaction, a highly dipolar transition state, *etc.*). In other words, the volume profile along the reaction coordinate may have no extremum, as is depicted in Fig. 3. Furthermore, the structural term, $\Delta_1 V^{\neq}$, has been considered to reflect the extent of bond formation.[25] Accordingly, the value of the activation volume ($\Delta V^{\neq}$) may safely be anticipated to be a parameter in scrutinizing the relative position of the transition state.



Reaction coordinate

Fig. 3. A schematic diagram of free energy and volume changes for the Diels-Alder reaction: [IS] denotes an initial state, [TS] a transition state, and [FS] a final state.

As is illustrated in Fig. 3, a Diels-Alder reaction characterized by a more negative activation volume may be expected to have a more product-like transition state in respect to the molal volume (and probably to the structure). From an inspection of Table 1, it seems that this interesting concept is equivalent to saying that the transition state for the more reactive Diels-Alder reaction (lower activation free energy) must have a more product-like structure in the sense of the molal volume, and *vice versa*. In Fig. 4 a schematic energy diagram of this generalization for a more reactive (H) and a less reactive (C) Diels-Alder reactions is illustrated, together with the volume parameter. It should be mentioned, however, that the activation volumes of the reactions in which maleic anhydride (MA) was used as a dienophile are more negative than anticipated (see Table 1). The reason for this will be discussed in the succeeding paragraph.



Reaction coordinate

Fig. 4. A shematic diagram of free energy and volume changes for a hot (H) and a cold (C) Diels-Alder reactions: [IS] denotes an initial state, [TS] a transition state, and [FS] a final state. Subscripts H and C correspond to the hot and cold reactions.

Volume Contraction Due to Secondary Orbital Interaction. Recent investigations of the pressure effect on the Diels-Alder reactions revealed that the activation volume of the reaction consisted not only of the structural term, $\Delta_1 V^{\neq}$, but also of the volume contraction in the transition state due to secondary orbital interaction, $\Delta_s V^{\neq}$.16,19) The value of $\Delta_s V^{\neq}$ is inevitably positive. While the importance of the secondary orbital interaction in [4+2] cycloaddition reactions seems to have been established, the degree of the interaction has scarcely been taken into consideration. When the value of $\Delta_s V^{\neq}$ is large, there is a possibility that the molal volume profile of the reaction has the minimum in Fig. 3. Hence, the value of $\Delta_s V^{\neq}$ must be estimated in order to discuss the position of the transition state.

Recently we reported that, in the reactions of cyclopentadiene with various dienophiles, the *exo*: *endo* product ratio is correlated to $\delta\Delta V^{\neq}$ (which is equal to $\Delta_s V^{\neq}$).19) This correlation enables us to estimate the values of $\Delta_s V^{\neq}$ when *exo*: *endo* ratios are given. For most of the dienophiles $\Delta_s V^{\neq}$ was estimated to be negligible (0~1.0 cm^3/mol), while in the reactions with MA the estimated value attained nearly 5 cm^3/mol;26) too large to be ignored. Hence, some of the observed $\Delta V^{\neq}$ values listed in Table 1 were corrected in order to give $\Delta V^{\neq}_{\text{corrected}}$, taking into account the provisionally assumed value of $\Delta_s V^{\neq}$, 4.0 cm^3/mol, for the reactions with MA.

In addition to the correction mentioned above, further revision was made. The use of the $\Delta V^{\neq}/\Delta V$ ratio as a parameter indicating the position of the transition state is more suitable than that of $\Delta V^{\neq}$ itself. The application of the $\Delta V^{\neq}/\Delta V$ parameter with regard to the activation free energy-activation volume relationship may cancel out any possible volume increase or decrease caused by subtle differences in the molecular structures of reagents and/or transition state species. Thus, the revised correlation of the activation free energy with $(\Delta V^{\neq}/\Delta V)_{\text{corrected}}$ is presented in Fig. 5. The correlation shown strongly supports the concept now under discussion.

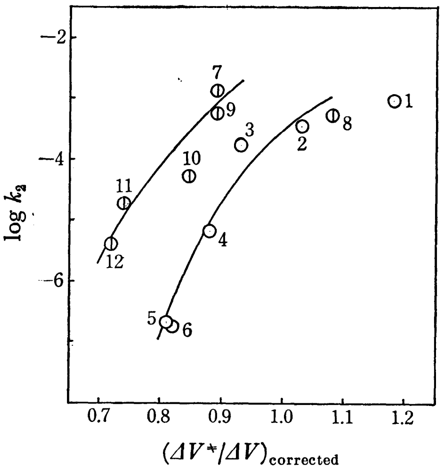


Fig. 5. Correlation of $\log k_2$ with $\Delta V^{\neq}/\Delta V$ for the Diels-Alder reaction: numerals correspond to reaction numbers in Table 1; ○, acyclic diene; ⦶, cyclic diene.

However, this parameter should not be used if the solvation term ($\Delta_2 V^{\neq}$) is too large to be ignored. The reaction of methoxybutadiene with MA is typical; the activation volume of this reaction is abnormally negative and is dependent on the solvent (−32~−52 cm^3/mol).16c) This contribution of the solvation term can be estimated from the solvent dependence of $\Delta V^{\neq}/\Delta V$. The values of $\Delta V^{\neq}/\Delta V$ and $(\Delta V^{\neq}/\Delta V)_{\text{corrected}}$ are presented in Table 2 for the reactions of methoxybutadiene[16c)] and isoprene[16b)] with MA. The $\Delta V^{\neq}/\Delta V$ is solvent-dependent for the reaction of MA–methoxybutadiene, as expected, while that for the reaction of MA–isoprene is solvent-independent within the limits of experimental error. Actually, $(\Delta V^{\neq}/\Delta V)_{\text{corrected}}$ is anomalous for the former reaction, as is shown in Fig. 5 (point number 1). This anomaly is undoubtedly due to the highly dipolar transition state of the reaction.[16c)] The other anomaly shown in Fig. 5 is the deviation of the reaction of cyclohexadiene-1,3 with MA (point number 8), which shows a rather larger $(\Delta V^{\neq}/\Delta V)_{\text{corrected}}$ value than expected. The reason for this is not yet fully understood. Possibly both the specificity of the solvent, dichloromethane (Table 2), and the geometric peculiarity of the reaction (a six-membered diene→bicyclo[2.2.2]-transition state) may be responsible for the observed anomaly.

Table 2. Solvent dependence of $\Delta V^{\neq}/\Delta V$ and $(\Delta V^{\neq}/\Delta V)_{\text{corrected}}$[a)]

Solvent	Methoxybutadiene–MA	Isoprene–MA
Acetonitrile	0.99 (0.86)[a)]	1.09 (0.97)[a)]
Nitromethane	1.52 (1.38)	1.06 (0.93)
1,2-Dichloroethane	1.44 (1.30)	1.04 (0.93)
n-Butyl chloride	1.30 (1.18)	1.03 (0.92)[c)]
Dimethyl carbonate	1.68 (1.55)	1.07 (0.96)[c)]
Acetone	—	1.09 (0.98)
Dichloromethane	—	1.20 (1.07)
Zeroelectrostriction	1.18 (1.00)[b)]	1.08 (0.97)

a) $(\Delta V^{\neq}/\Delta V)_{\text{corrected}}$ is given in parenthese. b) Estimated value from $\Delta V^{\neq}=-32$ cm³/mol and $\Delta V=-28$ cm³/mol. c) Calculated using ΔV in ethyl acetate.

In the reaction of isoprene with MA as well as in the other reactions under consideration, the solvation term may thus be thought to be negligible. Ideally, the value of $\Delta V^{\neq}/\Delta V$ at zeroelectrostriction should be referred to. However, the values of $\Delta V^{\neq}$ and ΔV at zeroelectrostriction are not so reliable.

The proposed reaction characteristics for the Diels-Alder reactions (Fig. 4) may allow us to scrutinize the selectivity-reactivity relationship of the reactions. The details will be reported elsewhere.[27)]

Experimental

The NMR spectra were recorded on a JEOL PS-100 spectrometer, using TMS as the internal standard. The chemical shifts were expressed in δ-values. The analytical determination by glc was performed on a JEOL JGC-20K. The preparative glc was performed on a JEOL JGC-1100. The following stainless steel columns were used: A, 2m PEG 20M (5%); B, 1m Apiezon Grease L (5%); C, 1m PEG 20M (1%); D, 3m TCEP (7%); E, 2m Silicone QF-1 (7%).

Materials. 2,3-Dimethylbutadiene,[28)] cyclopentadiene,[29)] and 1,2,3,4-tetrachlorocyclopentadiene-1,3[30)] were prepared by the reported procedures. The other dienophiles and solvents were commercial materials and were purified when necessary. The following Diels-Alder adducts were prepared by the usual methods: 4-carbomethoxy-2,3-dimethylcyclohexene-1, bp 114—115 °C/27 mmHg; 4-carbobutoxy-2,3-dimethylcyclohexene-1, bp 118—118.5 °C/5 mmHg; *trans*-4,5-dicarbomethoxy-2,3-dimethylcyclohexene-1, bp 131—132 °C/5 mmHg; 1,2-dimethylcyclohex-1-ene-4,5-dicarboxylic anhydride, mp 78—79 °C; *trans*-2,3-dicarbomethoxy-5-norbornene, bp 104—105 °C/4 mmHg. The *exo* and *endo* isomers of 2-carbomethoxy-5-norbornene were prepared by the reaction of cyclopentadiene with methyl acrylate and were separated by glc (column D); NMR spectrum, the *exo* isomer, 3.63 (CO_2CH_3); the *endo* isomer, 3.57 (CO_2CH_3). The *exo* and the *endo* isomers of 2-carbomethoxy-1,4,5,6-tetrachloro-5-norbornene were prepared by the reaction of 1,2,3,4-tetrachlorocyclopentadiene-1,3 with methyl acrylate and were separated by glc (column E); NMR spectrum, the *exo* isomer, 3.83 (CO_2CH_3); the *endo* isomer, 3.78 (CO_2CH_3). 2-Carbomethoxy-1,4,5,6,7,7-hexachloro-5-norbornene was prepared by the reaction of hexachlorocyclopentadiene with methyl acrylate; bp 140—145 °C/7 mmHg. The glc and NMR indicated the presence of a single product. NMR spectrum; 3.65 (CH), 2.60—2.76 (CH_2), 3.82 (CO_2CH_3).

High-Pressure Apparatus. The basic design of the pressure apparatus is essentially identical with that described by Whalley.[31)] The high-pressure vessel was immersed in a thermostatted-bath, and the temperature was controlled within ±0.03 °C. The high-pressure hydroaulic liquid used was Silicon Oil KF-96 (200 cs, Shin-etsu Chem. Ind.).

Kinetics and Analysis. Stock solutions of a diene and a dienophile in *n*-butyl chloride were prepared and stored in a freezer. Aliquots were taken from the stock solutions and mixed for each kinetic run. The kinetic solution was transferred into a reaction vessel (20 cm³ glass syringe) and pressurized. Reactions were carried out at five fixed pressures (1, 300, 500, 700, 900 kg/cm²). Analysis was done by glc by means of a comparison of the peak areas or heights on a chromatogram. The initial concentrations of the dienes and the dienophiles, the column specifications and the internal standards for quantitative glc analyses are shown in Table 3.

Table 3. Data for kinetic measurement

Reaction No.[a)]	Initial concentration (×10 M) Diene	Initial concentration (×10 M) Dienophile	Glc column[b)]	Glc internal standard
2	1.28∼2.88	1.36	B	*p*-bromo-*t*-butylbenzene
4	1.13	1.58∼1.91	A	dimethyl benzylmalonate
5	4.89∼5.31	8.82∼11.0	A	ethyl phenylacetate
6	8.91∼11.6	21.3∼31.3	A	methyl phenylacetate
7	0.506	0.203∼0.502	C	diethyl adipate
10	0.503	4.82∼7.48	B	2,4-dichlorotoluene
11	2.33	2.20	C	2-carbomethoxy-1,4,5,6,7,7-hexachloro-5-norbornene
12	14.8∼16.6	—	A	*p*-chlorotoluene

a) Reaction number cited corresponds to that in Table 1.
b) See Experimental part.

Each reaction studied was cleanly second-order and gave only a single product or a mixture of *exo-endo* isomeric products. Although a small amount of a by-product (cyclopentadiene dimer) appeared in the reaction of cyclopentadiene with methyl acrylate (reaction No. 10), the use of an excess of dienophile depressed the formation of this dimer. The second-order rate constants were calculated by the usual second-order rate expression.[32]

Partial Molal Volume. The technique employed for the determination of the partial molal volumes of liquid samples was the dilatometric method of Hyne and his coworkers.[33] For solid samples, the pycnometric method[34] was employed and calculations were made for the apparent partial molal volumes.

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