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Kinetic Analysis of the High-pressure Diels-Alder Reactions of Tropone with Maleic Anhydride and Norbornene[1]

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The kinetics of Diels-Alder reactions of tropone with maleic anhydride and norbornene were studied at pressures up to 2000 bar. The activation volumes, obtained from the former at 378.2 K in isopropylbenzene (IPB) and *N,N*-dimethylformamide (DMF), were $\Delta V^{\neq}$(IPB)=−21.4 cm^3/mol and $\Delta V^{\neq}$(DMP)=−16.8 cm^3/mol. Those from the latter (at 408.2 K) were $\Delta V^{\neq}$(IPB)=−30.0 cm^3/mol and $\Delta V^{\neq}$(DMF)=−27.8 cm^3/mol. These $\Delta V^{\neq}$ and ΔV showed a large deviation from those of the (6+4)π process of tropone with cyclopentadiene (by le Noble) and a small deviation from those of other typical Diels-Alder reactions to support the concerted cycloaddition mechanism which has been established by the kinetic analysis at atmospheric pressure.

In the field of high pressure organic chemistry, electrocyclic reactions, *e.g.*, Diels-Alder reaction, have been intensively investigated in the last two decades, and the reaction mechanism has been interpreted in terms of the activation parameters obtained by this method.[2,3] According to general knowledge regarding the activation volume ($\Delta V^{\neq}$) and the reaction volume (ΔV), the concerted reactions show large negative values for their activation volumes; −25 to −35 cm^3/mol for Diels-Alder reactions and −18 to −24 cm^3/mol for 1,3-dipolar cycloaddition reactions.[3] $\Delta V^{\neq}/\Delta V$ is in a range between 0.5 and 1.[4] These values are in contrast to those of a two-step reaction *via* a zwitterionic intermediate in which, $\Delta V^{\neq}/\Delta V$ exceeds unity and $\Delta V^{\neq}$ might be larger than −50 cm^3/mol.

Since there should not be much difference in the nature of bond formation among various concerted cycloadditions, such reaction features may be universally recognized in the concerted reactions. However, a remarkable exception has been noticed in a cycloaddition reaction involving tropone (**1**) with cyclopentadiene (CP) in dioxane.[5] This has been the sole (6+4)π cycloaddition reaction ever studied by means of high-pressure kinetics, from which, a very small $\Delta V^{\neq}$ and ΔV (−7.5 and −4.3 cm^3/mol) with a remarkably large $\Delta V^{\neq}/\Delta V$ (1.7) was obtained.[5] Generally, when $\Delta V^{\neq}$ shows such a small negative value, $\Delta S^{\neq}$ must also be small and negative. However, as far as a kinetic analysis at atmospheric pressure shows, the $\Delta S^{\neq}$ is large and negative.[6] This result is similar to that obtained in typical concerted Diels-Alder reactions.

These small activation and reaction volumes were interpreted on the basis of an unusually small partial molar volume of **1** which might be attributable to its highly polar structure.

It is true that the chemical properties of **1**, one of the most basic nonbenzenoid aromatic compounds, have been interpreted in terms of a contribution of a delocalized limiting structure (**1a**) with a delocalized 6π structure. Thus, **1** has a large dipole moment. On the other hand, **1** is known to undergo various types of pericycloadditions, such as (2+4)π-,[7] (4+2)π-,[8] (4+6)π-,[9] (6+4)π-,[10] and (8+2)π cycloaddition[11] reactions. The concerted nature of its cycloaddition reactions has been accepted after a product analysis and kinetic investigations. Taking these into account, the above-mentioned results regarding (6+4)π cycloaddition of **1** with CP called our attention to whether the extraordinary figures which were obtained should be attributable to the characteristics of **1**, itself, as interpreted by le Noble, or to the special feature of the (6+4)π pericycloaddition of **1**. If the anomalies are due to the observed molar volume of **1** (85.6 cm^3/mol; smaller than that calculated from the parachor listings (by 20 cm^3/mol), as has been explained),[5] this might be a good reason for the large dipole moment of **1** (4.17 D[12]; 4.30 D[13]). Then, this feature should always be observed in the cycloadditions of tropones.

To verify this point, we carried out Diels-Alder reactions of **1** with two kind of dienophiles: i) polar-, electron-deficient maleic anhydride (**2**) and ii) nonpolar-, a strained and rigid bicyclic compound, norbornene (**3**). Each is known to give a single product.[8,14] Particularly, the selection of the hydrocarbon, **3**, should provide reliable data for comparisons with the le Noble's experiment.

Experimental

Materials. Tropone (**1**) was prepared using Nozoe's procedure,[15] purified by silica-gel chromatography, and distilled using a Kugelrohr tube *in vacuo*.. The purity was over 99.0%. Maleic anhydride (**2**) was sublimed *in vacuo* to show a mp of 53.5—54.0 °C. Norbornene (**3**) was used without further purification (a commercial Extra-Pure brand of Tokyo Kasei Co.). The adducts, **4** and **5**, were purified by repeated recrystallizations from acetone and pentane, respectively. They showed pertinent melting points, elemental analyses, and IR, NMR, and mass spectra. Isopropylbenzene (IPB) was distilled over Na and *N,N*-

dimethylformamide (DMF) was dried on CaH_2 and distilled *in vacuo*. Both solvents were gas-liquid chromatographically pure.

Kinetic Measurements. All kinetic runs, including the atmospheric runs, were carried out in a pressure vessel with an outlet valve for sampling. The temperature was controlled within 0.5 K and the pressure was measured using a Heise-Bourdon gauge. The initial concentrations of the reactants were *ca.* 0.007 mol/kg for **1** and 0.14 for **2** or **3**. The progress of the reactions was gas-liquid chromatographically monitored with a JEOL JGC-20KFP model gas chromatograph (column: 10%-Silicone XE 60 on Chromosorb W-DMCS) connected to a digital integrator, by observing the change of **1** (in the reaction with **2**) or **5** (in the reaction with **3**). Reliable data were collected after at least 1 h when thermal and pressure equilibrums were achieved. An analysis was performed as a *pseudo*-first-order reaction for **1**. Each reaction was repeated at least three times and second-order rate constants (k) were obtained from the observed rate constants (calculated by least-squares method).

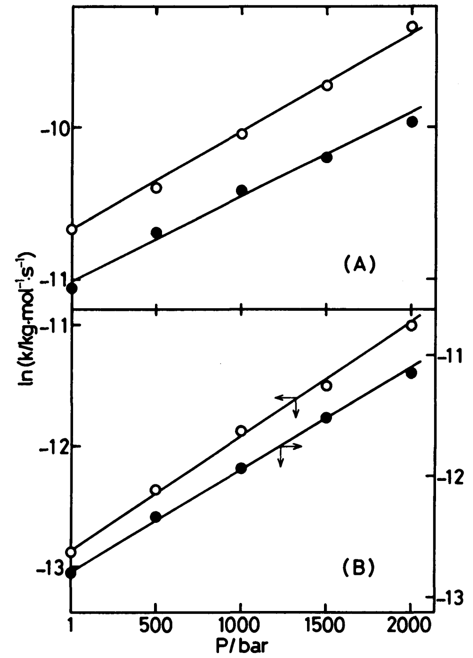

Fig. 1. Pressure Dependence of ln k
(A): **1**+**2** at 378.2 K, (B): **1**+**3** at 408.2 K.
○: in IPB, ●: in DMF

Measurements of the Partial Molar Volumes. The partial molar volume of each substrate (V_i) was determined by an extrapolation of the apparent molar volume (ϕ_i) to infinite dilution (obtained by a measurement of the density with Ostwald's pycnometer at 333.15±0.01 K). For each substrate, ϕ_i was almost constant for the same solvent.

$$\Phi_i = [(1000+M_i m_i)/d_{mi} - 1000/d]/m_i \qquad (1)$$

where the subscript i represents the solute and M the molecular weight. d_{mi} and d are the densities of the solution and a pure solvent, respectively, and m_i is the molality. V_4 in IPB could not be obtained due to the insolubility of **4**.

Results and Discussion

Activation Volume. The rate constants for reactions of **1** with **2** and **3** at various pressures in IPB and in DMF are listed in Table 1. There are good linear correlations between ln k and the pressure in the range of 1 to 2000 bar, exhibited in Fig. 1 (correlation coefficient r: 0.998 and 0.992 for the reactions of **1** with **2** in IPB and in DMF, respectively; 0.997 and 0.999 for **1** with **3** in IPB and DMF, respectively). From Eq. 2 (derived from transition-state theory), $\Delta V^{\neq}$ was obtained and is listed in Table 2, together with the V_i for each compound and the volume profile ($\Delta V^{\neq}/\Delta V$).

$$\Delta V^{\neq} = -RT(\partial \ln k/\partial p)_T \qquad (2)$$

The values of $\Delta V^{\neq}$ in Table 2 are large negative figures and (especially for the reaction with **3**) are typical values for Diels-Alder reactions.[2] Therefore, as far as the activation volume is concerned, the

Table 1. Rate constants for the Diels-Alder reaction of **1** with **2** ($10^5\,k$/kg mol^{-1} s^{-1}) and **3** ($10^6\,k$/kg mol^{-1} s^{-1}) under various pressures

Dienophiles	Temperature/K	Pressure/bar	Solvents	
			IPB	DMP
2	378.2	1	2.32±0.02	1.56±0.09
		500	3.03±0.11	2.31±0.02
		1000	4.29±0.29	3.02±0.06
		1500	5.99±0.26	3.69±0.31
		2000	9.02±0.21	4.71±0.25
3	408.2	1	2.55±0.05	2.78±0.05
		500	4.32±0.18	4.40±0.09
		1000	7.07±0.07	6.61±0.02
		1500	9.97±0.09	9.96±0.16
		2000	15.4±0.2	14.3±0.1

TABLE 2. PARTIAL MOLAR VOLUMES (V_i), ACTIVATION VOLUMES ($\Delta V^{\neq}$), AND REACTION VOLUMES (ΔV) FOR THE REACTION OF **1** WITH **2** AND **3** (in cm³/mol)

Reactants	Solvent	V_1	V_2 or V_3	V_4 or V_5	ΔV	$\Delta V^{\neq}$	$\Delta V^{\neq}/\Delta V$
1+**2**	IPB	99.8	75.0	—	—	−21.4	—
	DMF	97.0	72.6	144.1	−25.5	−16.8	0.66
1+**3**	IPB	99.8	106.8	173.1	−33.5	−30.0	0.90
	DMF	97.0	106.0	170.9	−32.1	−27.8	0.87

V_i and ΔV are obtained at 333.15 K, and $\Delta V^{\neq}$ at 378.2 K for **1** and **2**, and at 408.2 K for **1** and **3**.

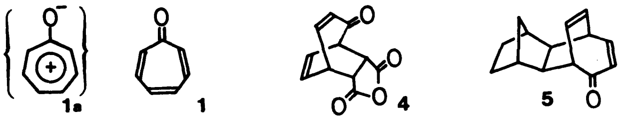

Chart 1

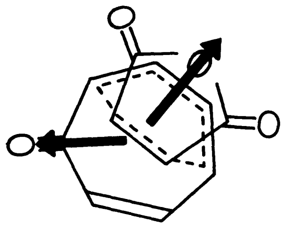

Fig. 2. Schematic Model of Dipoles in the Transition States.

Diels-Alder reaction of **1** clearly falls into a category of the concerted reaction. If one trusts the present results, the electrostriction of **1** must not be as large as has been suggested.

Nevertheless, the negative values for the activation volumes of reaction of **1** with **2** were slightly small. In this case, should the difference in the size of molecule be negligible, it is important that both reactants are equally polar molecules (dipole moments: 4.17 D for **1**[12] and 3.95 D for **2**[16]). In the initial state, **1** and **2** contract due to their high polarity. The polarity should decrease during the transition state, but should not cause a reduction in the volume if one considers a geometry in which the dipole moments of the two components are oriented at large angles with each other (θ=130 to 140°, Fig. 2) in the transition state. In other words, the contracted volumes of the two components are responsible for the small $\Delta V^{\neq}$ in the reaction of **1** with **2**. This conclusion is supported by the observed difference in the activation volumes in the two solvents. The value $\Delta V^{\neq}(\mathrm{IPB})-\Delta V^{\neq}(\mathrm{DMF})=-4.6\,\mathrm{cm^3/mol}$ is quite similar to the difference between the sums of the volumes of the reactants in the two solvents ($\Sigma[V_i(\mathrm{IPB})-V_i(\mathrm{DMF})]=5.2\,\mathrm{cm^3/mol}$). Therefore, the volumes of the transition state are almost same in the two solvents. As the solvent effect on the partial molar volume (V_i) is parallel to the polarity of the reactant and the solvent,[17] the transition state is, therefore, less polar than the initial state.

Reaction Volume and Volume Profile. An analysis of ΔV and $\Delta V^{\neq}/\Delta V$ led to the same conclusion as above. The volume changes and the volume profiles for the reaction of **1** with **3** were the same as those for ordinary Diels-Alder reactions. We also obtained small values for ΔV and $\Delta V^{\neq}/\Delta V$ during the reaction of **1** with **2**. The former can be attributable to the polarity of the reactants and the latter represents a smaller polar transition state than for the product, **4**, as discussed above. Since the dipole moments of **1** and **2** are almost the same, we can assume that the volume reduction of **1** due to polarity is just as large as that of **2**. In this respect, the value of the previously reported partial molar volume of **1** in dioxane[5,18] is too small unless there are some unusual solvent-solute interactions.

Solvent Effect. The reaction rates of **1** with **2** or **3** in solvents having different polarities were slightly different from ordinary Diels-Alder reactions due to an increase in the dielectric constant (36.7 (DMF) from 2.4 (IPB)). The rates changed by only a factor of 1.1 (for the reaction with **3**) and 0.67 (with **2**) at atmospheric pressure. This means: i) the change of polarization is small during the rate-determination step in both reactions, and ii) in the reaction with **2**, the polarity of solvent decreases the rate; *i.e.*, the transition state should be less polar than the initial state. The former (i) seems to conflict with the above discussion concerning volumes, but it does not. Because that depends on the total dipole moment during the transition state. This means that the conclusion regarding the solvent effect is in accord with that for the activation volume.

*Activation Energy and Entropy of the Reaction of **1** with **2**.* For a further determination of the transition state of the cycloaddition of **1** with **2**, atmospheric reactions were examined in IPB and DMF (the rate constants are summarized in Table 3). Arrhenius plots gave good linear correlations (*r*: 0.997 in IPB and 0.998 in DMF). The activation energy (E_a), activation entropy ($\Delta S^{\neq}$) and activation free energy ($\Delta G^{\neq}$) at 378.2 K are shown in Table 4. The remarkably large negative $\Delta S^{\neq}$ undoubtedly in-

TABLE 3. THE RATE CONSTANTS OF THE DIELS-ALDER REACTION OF **1** WITH **2** AT ATMOSPHERIC PRESSURE ($10^6\,k$/kg mol^{-1} s^{-1})

Solvent	Temperature/K			
	378.2	388.2	398.2	408.2
IPB	2.32±0.02	3.66±0.08	5.50±0.18	7.36±0.15
DMF	1.56±0.09	2.51±0.01	3.96±0.16	5.54±0.12

TABLE 4. THE ACTIVATION PARANETERS FOR THE DIELS-ALDER REACTION OF **1** WITH **2** AT 378.2 K

Solvent	E_a/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta G^{\neq}$/kJ mol^{-1}
IPB	49.7±3.3	−229±9	133±7
DMF	54.8±2.5	−219±7	134±5

dicates a concerted character regarding the reaction. This is parallel to kinetic studies of other Diels-Alder reactions,[19] including those of troponoids.[14,20] In addition, the E_a values, larger in DMF than in IPB, support the proposal that the initial state is more stabilized than the transition state in DMF, *i.e.*, the transition state is less polar than the initial state.

In conclusion, from the reactions with **2** and **3**, it was clarified that in the Diels-Alder reaction of **1**, the activation and reaction volumes are affected by the polarities of the initial state and the transition state. However, they are not negatively small as reported for the reaction of **1** with CP. We will report on studies regarding the (6+4)π cycloaddition of **1** with dienes in order to understand the thermal reactions of tropones.

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$$q_p = \partial[(\varepsilon-1)/(2\varepsilon-1)]/\partial p.$$

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