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Volumetric Study on the 1,3-Dipolar Cycloaddition Reaction of Diazodiphenylmethane with Several Olefins

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A high pressure kinetic study was made of the 1,3-dipolar cycloaddition reaction of Ph_2CN_2 with dimethyl maleate (DMM), dimethyl fumarate (DMF), methyl acrylate (MA), maleonitrile (MN), fumaronitrile (FN), and acrylonitrile (AN) in toluene at 25 °C. The activation volumes (ΔV^{*}) at 1 bar obtained for DMM, DMF, MA, MN, FN, and AN are -23.4 ± 0.5, -22.3 ± 0.2, -19.8 ± 0.4, -21.5 ± 0.6, -21.0 ± 1.1, and -23.9 ± 0.5 $cm^3 mol^{-1}$, respectively. The reaction volume (ΔV) for the reaction between Ph_2CN_2 and DMM was determined dilatometrically by taking advantage of supersaturation of the cycloadduct in solution; $\Delta V=-24.5\pm0.5$ $cm^3 mol^{-1}$ and $\Delta V^{*}/\Delta V=0.955$. The present volumetric information coupled with a kinetic analysis shows that Firestone's biradical mechanism is not the case; the concerted mechanism is supported. The experimental result is compared with that of a recent *ab initio* molecular orbital calculation with respect to the activation and reaction volumes.

One of the most fundamental thermodynamic quantities is the partial molal volume which is a function of the geometry and polarity of a molecule in solution. When this static viewpoint is taken to consider the transition state of a reaction in solution within the framework of the transition state theory,1) the activation volume (ΔV^{*}), which reflects changes in the geometry and charge distribution of reacting molecules during the activation process, can be used as a criterion for distinguishing between some conceivable reaction mechanisms. Such an example is shown in a recent report on competitive 1,2- and 1,4-cycloadditions between tetracyanoethylene and *p*-methoxystyrene.2)

In the present work, the approach mentioned above has been applied to another kind of cycloaddition, the 1,3-dipolar cycloaddition, for which two quite different mechanisms are proposed: Huisgen3) has given a concerted mechanism on the basis of such experimental results as the stereospecificity, the reactivity sequence of dipolarophiles, the small solvent effect, and the large negative activation entropy which is similar in magnitude to that for the usual 1,4-cycloaddition (Diels-Alder) reaction, while Firestone4) states that most of the experimental results are consistent with a two-step mechanism involving biradical intermediates. Recent molecular orbital calculations for the 1,3-dipolar cycloaddition between HCNO and HCCH also have led to different results on the mechanism depending on approximations used; the *ab initio* method5) indicates a relatively symmetric transition state without an intermediate but the MINDO/3 method6) a highly unsymmetric transition state with a zwitterionic intermediate.

Since the geometry of the cyclic transition state in the concerted mechanism differs significantly from that of the chainlike intermediate in the two-step mechanism, the volume profile is expected to play a decisively important role in the determination of mechanism of the 1,3-dipolar cycloaddition. As a typical 1,3-dipolar cycloaddition, the reaction of diazodiphenylmethane (Ph_2CN_2) with a series of olefins substituted by CN or $COOCH_3$ groups is chosen in the present study; the effect of temperature and solvent on the reaction rate is already clarified in a previous paper.7)

Experimental

Ph_2CN_2 and dipolarophiles, such as dimethyl maleate (DMM), dimethyl fumarate (DMF), methyl acrylate (MA), maleonitrile (MN), fumaronitrile (FN), and acrylonitrile (AN), were prepared and purified in the same way as in the previous work.7) Toluene was purified by the standard method.

The reaction rate at high pressure was determined by the batch method; it was required to prevent the compression heat from masking the pressure effect, so that the half-life period of the reaction was adjusted to 2—3 h by varying reactant concentrations. A dilute (10^{-3} to 10^{-1} mol dm^{-3}) reaction solution filled in a flexible Teflon capsule was put in a pressure bomb convenient for the quick recovery.8) The recovered solution was analyzed in the same way as in the previous work.7) The pressure was measured to ±2 kg cm^{-2} (1 kg cm^{-2}=0.9807 bar) by a Bourdon gauge (Heise) calibrated against a free piston gauge (Nagano P-3). The temperature was kept at 25.0±0.05 °C.

For the dilatometric determination of the reaction volume, a pycnometer of the Lipkin-Davison type with a capacity of 4.7 cm^3 was employed, by which the relative volume change was measured to $\pm5\times10^{-5}$. The temperature was controlled to ±0.01 °C.

Results

The rates of the reactions studied obeyed the second-order rate law,

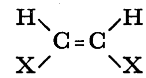
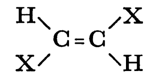
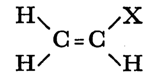
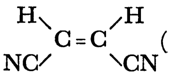
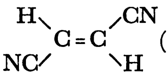
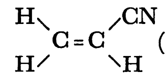
$$-d[Ph_2CN_2]/dt = k[Ph_2CN_2][\text{dipolarophile}], \tag{1}$$

where [ ], *t*, and *k* denote the concentration, the time, and the rate constant, respectively. The rate constants were determined from the second-order plots, *i.e.*, log $[Ph_2CN_2]/[\text{dipolarophile}]$ *vs.* *t* at each pressure; they are summarized in the middle columns of Table 1. According to the transition state theory, the pressure (P) effect on the rate constant allows us to determine the activation volume by

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{*}}{RT} + \kappa, \tag{2}$$

where R, T, and κ are the gas constant, the temperature, and the isothermal compressibility of toluene,9) respectively. A plot of the logarithmic values of k

Table 1. Rate constants ($10^4\,k$/mol^{-1} dm^3 s^{-1}) and activation volumes (ΔV^*/cm^3 mol^{-1}) for the 1,3-dipolar cycloaddition of Ph_2CN_2 in toluene at 25 °C

Dipolarophile[a]	P/kg cm^{-2}				ΔV^*
	1	500	1000	1500	
 (DMM)	2.77±0.03	4.40±0.0	6.62±0.2	10.4±0.3	−23.4±0.5
 (DMF)	53.3±0.3	81.5±1.3	127±2	186±3	−22.3±0.2
 (MA)	19.8±0.2	28.2±0.7	42.0±0.8	59.5±0.8	−19.8±0.4
 (MN)	25.0±0.1	39.0±0.3	56.0±0.5	82.0±1.2	−21.5±0.6
 (FN)	9.97±0.05	16.7±0.2	22.1±0.2	32.3±0.7	−21.0±1.1
 (AN)	9.72±0.06	15.2±0.3	22.9±0.2	34.0±1.0	−23.9±0.5

a) X=$COOCH_3$.

in Table 1 against pressure gives a straight line in each system. Applying Eq. 2 to such a linear relation, we can obtain the activation volume. The ΔV^* values thus obtained are listed in the last column of Table 1.

The values of ΔV^* in Table 1 are in the range of −20 to −24 cm^3 mol^{-1}, which are comparable with a value of −20 cm^3 mol^{-1} for another kind of 1,3-dipolar cycloaddition between a nitrile oxide and HCN in diisopropyl ether at 40 °C[10] but considerably larger than a value of −32 cm^3 mol^{-1} for the same kind of 1,3-dipolar cycloaddition between Ph_2CN_2 and a bicyclic olefin in toluene at 24.5 °C.[11] The small difference in ΔV^* between DMM and DMF might be ascribed to the steric hindrance by the bulky groups of $COOCH_3$, as already noticed in reactions of other kinds.[12,13] A similar trend is found previously for the activation entropy (ΔS^*).[7] The meaning of the obtained activation volumes will be discussed later in relation to the reaction mechanism.

The reaction volume (ΔV) has to be measured in some manner in order to establish the volume profile. However, since the 1,3-dipolar cycloaddition reactions of the dipolarophiles other than DMM are accompanied by a rapid consecutive reaction,[7] only the Ph_2CN_2–DMM system can be studied here. There is another problem: the cycloadduct (4,5-bis(methoxycarbonyl)-3,3-diphenyl-4,5-dihydro-3H-pyrazole) between Ph_2CN_2 and DMM has so low a solubility in toluene that we cannot determine its partial molal volume by the usual density measurement. Very fortunately, however, it turned out that when we employed the dilatometric method the solution could be highly supersaturated with respect to the product. If we assume that the volume change accompanying the 1,3-dipolar cycloaddition is independent of the concentration in the dilute solution, the following equation holds under the condition of $[Ph_2CN_2]=[DMM]$:

$$\frac{1}{A-x}-\frac{1}{A}=kt, \tag{3}$$

$$x=(m_t/m_\infty)A, \tag{4}$$

where A is the initial concentration of Ph_2CN_2, m_t, and m_∞ ($=\Delta V$) are the volume changes at t and $t=\infty$, respectively, and x is the amount of the consumed Ph_2CN_2. From Eqs. 3 and 4, we get

$$m_t=\frac{m_\infty}{1+1/kAt}. \tag{5}$$

Figure 1 shows the plot of m_t against $1/(1+1/kAt)$, and the linearity before the precipitation point indicates adequacy of the assumption utilized for deriving

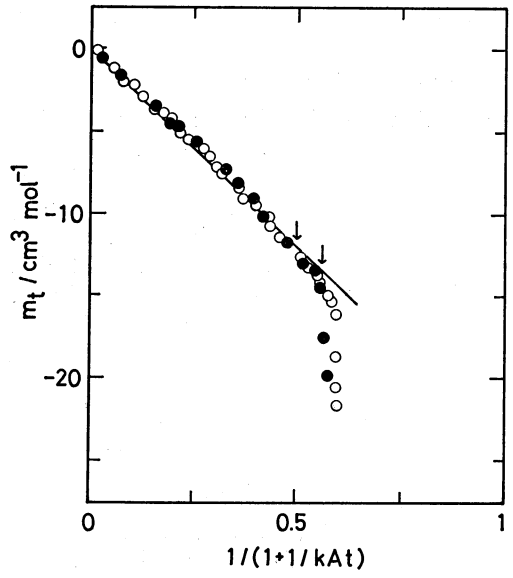
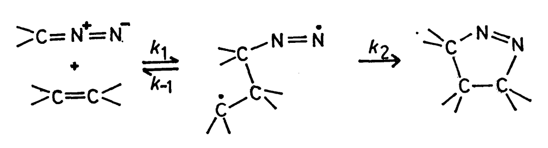


Fig. 1. Plot of Eq. 5.
●: A=0.168 mol dm^{-3}, ○: A=0.191 mol dm^{-3}. The arrows indicate the precipitation point at about 6 h; the left-hand one for A=0.168 mol dm^{-3}.

Eqs. 3 and 4. Applying the least-squares method to the linear portion of the plot, we obtained -24.5 ± 0.5 cm^3 mol^{-1} as ΔV for the 1,3-dipolar cycloaddition between Ph_2CN_2 and DMM. Probably, we can take this value as a representative one because ΔV^* does not differ so much from one dipolarophile to another as seen in Table 1.

Discussion

Biradical vs. *Concerted Mechanisms.* It is important to transform Firestone's idea on the reaction mechanism into a kinetic expression, before it is tested by the present volumetric investigation. His reaction scheme is given by



(6)

From the above scheme and the qualitative energy profile illustrated by him,[4] we get the following expression for the observed rate constant (k):

$$k = \frac{k_1 k_2}{k_{-1}+k_2} \tag{7}$$

$$= Kk_2, \tag{8}$$

where

$$K = k_1/k_{-1}, \tag{9}$$

$$k_1 \ll k_2 \ll k_{-1}. \tag{10}$$

From Eqs. 2 and 8, we have

$$\Delta V^* = \Delta V(K) + \Delta V^*(k_2), \tag{11}$$

where $\Delta V(K)$ and $\Delta V^*(k_2)$ are the reaction and the activation volumes correspoding to K and k_2, respectively. The cyclization step (k_2) of an extended biradical intermediate[14] would be diffusion controlled, the rate constant of which is inversely proportional to the bulk shear viscosity (η) of the solvent in the simplest approximation.[15] This approximation leads to

$$\Delta V^*(k_2) = RT(\partial \ln \eta/\partial P)_T, \tag{12}$$

which is 14.5 cm^3 mol^{-1} for toluene-d_8 at 25 °C; *cf.* 10.3 and 7.3 cm^3 mol^{-1} as activation volumes for the molecular and internal rotations, respectively.[16] By using $\Delta V^* = -23.4$ cm^3 mol^{-1} and $\Delta V^*(k_2) = 14.5$ cm^3 mol^{-1} in Eq. 11, we obtain -37.9 cm^3 mol^{-1} as a value of $\Delta V(K)$ for the Ph_2CN_2–DMM system, which is "smaller" than the reaction volume. This contradicts the stepwise bond formation in Firestone's mechanism; it is impossible that the bond formation due to the biradical cyclization is accompanied by as large a "positive" volume change as 13.4 cm^3 mol^{-1} ($=\Delta V - \Delta V(K)$). The value of -37.9 cm^3 mol^{-1} is also too small for the single-bond formation because no dramatic solvation can be expected for such a nonpolar intermediate; in fact, there is little solvent effect on this reaction.[7] Thus, Firestone's two-step mechanism is not supported by the present volumetric investigation.

The difference in the partial molal volume between the transition state and the cycloadduct is only 1.1 cm^3 mol^{-1} in the Ph_2CN_2–DMM system; $\Delta V^*/\Delta V = 0.955$. This indicates that the transition state resembles the product in regard to the geometry and suggests that the two bonds between the 1,3-dipole and dipolarophile develop to a large extent in the transition state. Such a resemblance is exhibited also by the usual 1,4-cycloaddition[17] which is considered to proceed *via* the concerted mechanism; *e.g.*, in the reaction between cyclopentadiene and DMF in 1-chlorobutane at 30 °C, $\Delta V^* = -32.7$ cm^3 mol^{-1} and $\Delta V = -36.7$ cm^3 mol^{-1} with $\Delta V^*/\Delta V = 0.891$.[18] The volumetric analogy between the two typical cycloadditions and the above-mentioned failure of Firestone's mechanism lead us to accept the concerted mechanism for the 1,3-dipolar cycloaddition.

Volume Profile. Figure 2 illustrates the volume profile of the 1,3-dipolar cycloaddition reaction between Ph_2CN_2 and DMM. The main features of the profile would not vary with the dipolarophile because of the similar values of ΔV^* in Table 1. It is interesting to compare the volume profile established experimentally for the 1,3-dipolar cycloaddition in solution with the theoretical one for the 1,3-dipolar cycloaddition between HCNO and HCCH in the gas phase.[5] When the van der Waals radii[19] of the relevant atoms are combined with the geometry determined by the *ab initio* method (double ζ basis set SCF), van der Waals volumes (V_{W}) of HCNO, HCCH, the transition state, and the product (isoxazole) are computed as 24.1, 23.1, 43.2, and 39.0 cm^3 mol^{-1}, respectively.[20] From these values we get changes in V_{W} accompanying the activation and reaction; $\Delta V^*_{\mathrm{W}} = -4.0$ cm^3 mol^{-1} and $\Delta V_{\mathrm{W}} = -8.2$ cm^3 mol^{-1} with $\Delta V^*_{\mathrm{W}}/\Delta V_{\mathrm{W}} = 0.49$. The theoretically predicted volumes for the transition state and the product are smaller than the volume of the reactants as a whole, but it seems that the predicted transition state is expanded relative to the product more than the one observed. If we bear it in mind that the packing fraction $\phi = V_{\mathrm{W}}/V$ for most neutral

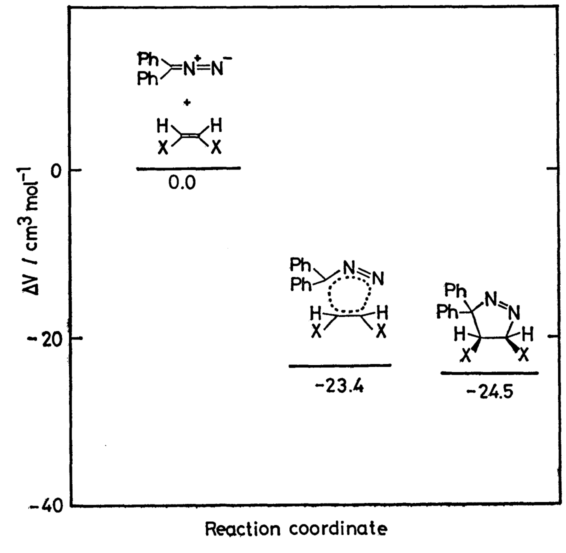


Fig. 2. The volume profile of the 1,3-dipolar cycloaddition between Ph_2CN_2 and DMM in toluene at 25 °C at 1 bar.
X=$COOCH_3$.

molecules are in the range of 0.5 to 0.6, a quantitative agreement between theory and experiment can be obtained; for example, one may take 0.5 and 0.6, respectively, for the reactants and the transition state to get $\Delta V^{*}=-22.4\ \mathrm{cm^3\ mol^{-1}}$.[22] It is important to clarify how the activation and reaction volumes in the condensed phase are related to the theoretically calculated van der Waals volumes from the point of view of liquid theory in a further study.

Conclusion

The activation volumes for the 1,3-dipolar cycloaddition reactions of Ph_2CN_2 with olefins in toluene at 25 °C at 1 bar are in the range of -20 to $-24\ \mathrm{cm^3\ mol^{-1}}$, and they are about $10\ \mathrm{cm^3\ mol^{-1}}$ less negative than those for the usual 1,4-cycloaddition reactions. The partial molal volume of the transition state is close to that of the cycloadduct rather than to the sum of the partial molal volumes of the reactants. These observations are in favor of the concerted mechanism proposed by Huisgen without the volumetric information as obtained here. On the other hand, the product-oriented idea on the mechanism by Firestone that the 1,3-dipolar cycloaddition reaction proceeds *via* an extended-biradical intermediate does not succeed in explaining the pressure dependence of the rate constant. Although the *ab initio* molecular orbital calculation for the chemical reaction has so far been compared with the kinetic experiment with respect to energy, its comparison with respect to volume would serve as a tool for interpreting the experimentally obtained volumes of activation and reaction at the molecular level.

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14) Firestone assumes that an extended form which plays an important role in his explanation of most important experimental results has the same energy as the cyclic one but is much more difficult to cyclize. Thus, an entropy factor related to the chance of intramolecular encounter of the radical ends is implicitly considered in his mechanism, which leads to the diffusion control.

15) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

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17) The previous work[2] discloses an unusual 1,4-cycloaddition in which the transition state has the zwitterionic character to some extent and $\Delta V^{*}/\Delta V>1$.

18) K. Seguchi, A. Sera, and K. Maruyama, *Bull. Chem. Soc. Jpn.*, **47**, 2242 (1974).

19) A. I. Kitaigorodsky, "Molecular Crystals and Molecules," Academic Press, New York (1973), Chap. 1; van der Waals radii for C, N, O, and H atoms are 180, 158, 153, and 117 pm, respectively.

20) Since overlapping of the van der Waals spheres of the atoms makes the calculation rather complicated, the spheres are divided into a large number of specimens with a dimension of about 5 pm in order to compute V_{W} by the numerical integration with an error of 0.1%. The molar volume (V) of isoxazole is $64.06\ \mathrm{cm^3\ mol^{-1}}$ from its density,[21] and the ratio of V_{W}/V is 0.609 which is comparable with the corresponding quantities for many other nonpolar molecules.[19]

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22) It would be reasonable to take a larger packing fraction for the larger molecule in view of an analytical solution[23] of the Percus-Yevick equation for hard-sphere liquids,

$$\left(\frac{\partial\phi}{\partial V_{\mathrm{W}}}\right)_{P,T}=\frac{P}{Nk_{\mathrm{B}}T}\frac{(1-\phi)^3}{1+5\phi+9\phi^2-3\phi^3}>0,$$

where P, N, k_{B}, and T are the pressure, the molecular number, the Boltzmann constant, and the temperature, respectively. Actually, such a trend is found when we calculate the ϕ values for normal alkane liquids using their molar volumes[24] and V_{W} obtained by the method employed here.

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