non-hydrogen atoms. The quantity minimized was $R = \sum w([F_o] - K[F_c])^2$ with $w = (\sigma_c^2 + 0.0025\sigma(F_o^2))^{-1}$, σ_c^2 from counting statistics. The y coordinate of S1 and the positions of the hydrogen atoms were not allowed to vary. The final R value is 0.051 for 252 variables and 2341 contributing reflections. A final difference map showed no significant resulting density. The atomic scattering factors for S, O, N, and C were those of Cromer and Mann[46] and those of Stewart et al.;[47] the CSP[44] and XRAY[48] programs were used for the calculations. The molecular structure and the atomic numbering are shown in Figure 2. The final atomic parameters are given in Table IX.

Acknowledgment. We thank Prof. C. Altona and Dr. F. A. A. M. de Leeuw for sharing unpublished data and for stimulating discussions. We thank Mr. B. Zweers for preparing compound **4** and Prof. R. J. F. Nivard for reading and critisizing the manuscript. This research was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). NMR spectra were recorded at the Dutch National 500/200 MHz hf-NMR facility at Nijmegen.

Registry No. 1, 79464-59-8; **2**, 79409-96-4; **3**, 79409-90-8; **4**, 86239-13-6; *N*-(3-phenylpropanoyl)-L-cystine methyl ester, 86259-41-8.

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Volumetric Study on the 1,3-Dipolar Cycloaddition Reaction. 2.[1] α-Benzoyl-*N*-phenylnitrone with Several Olefins

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Abstract: A high-pressure kinetic study was made of the 1,3-dipolar cycloaddition reaction of α-benzoyl-*N*-phenylnitrone (BPN) with dimethyl fumarate (DMF), dimethyl maleate (DMM), methyl acrylate (MA), and styrene (St) in toluene at 25 °C. The activation volumes ($\Delta V^{\ddagger}$) at 1 bar for DMF, DMM, MA, and St are −21.7, −19.9, −22.9, and −19.5 cm^3 mol^{-1}, respectively. The volume change (ΔV) for the reaction between BPN and DMF was determined dilatometrically: $\Delta V = -22.7$ cm^3 mol^{-1} and $\Delta V^{\ddagger}/\Delta V = 0.956$. In order to elucidate the manner in which the activation volume reflects geometrical changes of molecules reacting in the liquid phase, the experimental results are compared with theoretically calculated changes in the van der Waals volume (V_W) for the prototype 1,3-dipolar cycloaddition between HCNO and HCCH: $\Delta V_w^{\ddagger} = -4.0$ cm^3 mol^{-1}, $\Delta V_W = -8.2$ cm^3 mol^{-1}, and $\Delta V_W^{\ddagger}/\Delta V_W = 0.49$. The large gap between $\Delta V^{\ddagger}$ and $\Delta V_W^{\ddagger}$ and between ΔV and ΔV_W is explained by taking account of the size dependence of the packing coefficient for each species involved in the prototype reaction.

The primary goal of the high-pressure kinetic study on chemical reactions in solution is to account for the reaction mechanism in terms of the activation volume ($\Delta V^{\ddagger}$) obtained from the transition-state theory:[2,3]

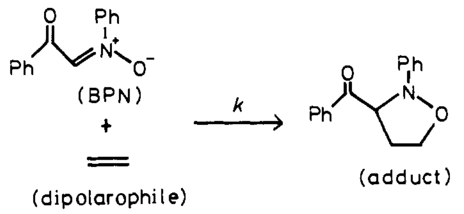
$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k}{\partial P}\right)_T + RT\left(\frac{\partial \ln \kappa}{\partial P}\right)_T \qquad (1)$$

where R, T, P, k, and κ are the gas constant, the temperature, the pressure, the rate constant (expressed in molality or mole fraction), and the transmission coefficient, respectively; the second term in eq 1 has been assumed to be negligible except for one case.[4] A large number of inorganic[5,6] and organic[7] reactions have been mechanistically studied by using this quantity together with the following additivity postulate:

$$\Delta V^{\ddagger} = \Delta_1 V^{\ddagger} + \Delta_2 V^{\ddagger} \qquad (2)$$

where $\Delta_1 V^{\ddagger}$ is the change in volume of the reacting molecules during the activation process and $\Delta_2 V^{\ddagger}$ due to solvation (electrostriction) of ionic or polar species.[2,8] However, it is not yet established how to split $\Delta V^{\ddagger}$ into the two components; determination of $\Delta_2 V^{\ddagger}$ depends on how $\Delta_1 V^{\ddagger}$ is estimated and vice versa. In this regard, a thorough study of $\Delta_1 V^{\ddagger}$ is worthwhile.

When we try to examine how $\Delta_1 V^{\ddagger}$ is correlated with structural changes of reacting molecules during the activation step, it is advantageous to select a type of reactions that has negligibly small solvent effect and therefore little contribution of $\Delta_2 V^{\ddagger}$ to $\Delta V^{\ddagger}$ in eq 2; here these nonionic reactions are called "molecular" reactions. Although the 1,3-dipolar cycloaddition is one of such molecular reactions, there has been no extensive study of the pressure effect on it. Hence, the present authors attempt to clarify volumetric aspects of the 1,3-dipolar cycloaddition in a series of studies. The first paper[1] in this series has shown that $\Delta V^{\ddagger}$ for the 1,3-dipolar cycloaddition of Ph_2CN_2 with six olefins in toluene at 25 °C and 1 bar is in the range of −20 to −24 cm^3 mol^{-1}. In the present work, the 1,3-dipole is changed to α-benzoyl-*N*-phenylnitrone in order to see how far $\Delta V^{\ddagger}$ for the 1,3-dipolar cycloaddition is affected by the nature of the 1,3-dipole. It is found here that $\Delta V^{\ddagger}$ for the 1,3-dipolar cycloaddition is little varied from one dipole to another.



How to interpret $\Delta V^{\ddagger}$ ($\Delta_1 V^{\ddagger}$) for the molecular reaction in the liquid phase at the molecular level is an open problem. A recent

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Table I. Rate Constants (k) for 1,3-Dipolar Cycloaddition Reactions of BPN with DMM, DMF, and MA in Several Solvents at 25 °C

	10^4k, M^{-1} s^{-1}		
solvent	DMF	DMM	MA
PhMe	108	11.9	66.5
PhCl	84.4	8.68	60.0
$CHCl_3$	18.4	3.72	20.0
$(CH_2Cl)_2$	44.9	3.45	40.0
MeCN	75.8	2.56	52.2

ab initio molecular orbital calculation provides useful information on changes in the molecular structure accompanying one of the simplest 1,3-dipolar cycloaddition reaction between $HC{\equiv}N^+\text{-}O^-$ and $HC{\equiv}CH$,[9] which allow us to calculate the van der Waals volumes (V_W)[10,11] for the reactants, the transition state, and the adduct.[1] In order to elucidate to what extent $\Delta V^{\ddagger}$ reflects geometrical changes of molecules reacting in the liquid phase through $\Delta V_W^{\ddagger}$, we compare the values of $\Delta V^{\ddagger}$ experimentally obtained with those of $\Delta V_W^{\ddagger}$ theoretically calculated for the prototype 1,3-dipolar cycloaddition. Although it is the best way to investigate directly the effect of pressure on the prototype 1,3-dipolar cycloaddition reaction theoretically treated, the experimental study is complicated by the oligomerization of HCNO.[12] For the comparison mentioned above, therefore, we are obliged to use the $\Delta V^{\ddagger}$ value determined for some other kinds of 1,3-dipolar cycloaddition reactions instead of the prototype reaction, after confirming that $\Delta V^{\ddagger}$ for the 1,3-dipolar cycloaddition is almost constant irrespective of any combination of 1,3-dipoles and dipolarophiles.

Experimental Section

Materials. α-Benzoyl-*N*-phenylnitrone (BPN) was prepared according to the reported procedure[13] and recrystallized several times from a benzene–cyclohexane mixture: mp 107–108 °C (cf. the literature value 109–110 °C). Dimethyl fumarate (DMF), dimethyl maleate (DMM), methyl acrylate (MA), and styrene (St) were purified in the usual manner. Such solvents as toluene, chlorobenzene, chloroform, 1,2-dichloroethane, and acetonitrile were purifed prior to use by the standard method. The adducts of BPN with DMF, DMM, MA, and St were identified by using their mp, IR, and NMR data in the literature.[14]

Kinetic Measurements. The reaction was monitored by measuring the absorption of BPN at 320 nm (the absorption coefficient $\epsilon = 1.2 \times 10^4$ mol^{-1} dm^3 cm^{-1}) with a spectrophotometer (Shimadzu UV-240) equiped with a data processor. A high-pressure optical cell was mounted on the double-beam spectrophotometer; the windows were made of synthetic sapphire, 1 cm thick, and connected with a steel plug the bore of which was 7 mm in diameter. The temperature was maintained at 25.0 ± 0.1 °C by circulating thermostated water around the high-pressure cell, and the pressure was measured to ±2 bar by a Heise Bourdon gage calibrated against a free piston gage (Nagano P-31).

All reactions studied here obeyed the second-order rate law:

$$-d[BPN]/dt = k[BPN][dipolarophile] \tag{3}$$

where [ ], t, and k denote the concentration (mol^{-1} dm^3 = M), the time, and the rate constant, respectively. The rate constant was determined from the pseudo-first-order rate treatment; [dipolarophile] was at least 100 times as large as [BPN]. The second-order rate constant determined thus was reproducible within 1% at each pressure. Although a possibility of the dimerization of nitrones was suggested elsewhere,[15] BPN was stable at 25 °C for a time (ca. 3 h) long enough for the kinetic measurements up to 2 kbar.

Table II. Numerical Values of the Parameters in Eq 4 and Activation Volumes ($\Delta V^{\ddagger}$, cm^3 mol^{-1}) at 25 °C and 1 bar

D[a]	a	10^4b	10^8c	$10^3\sigma$[b]	$\Delta V^{\ddagger}$
DMF[c]	−4.607	7.81	−8.1	13	−21.7
DMF[d]	−6.298	8.77	−8.5	2	−24.3
DMF[e]	−4.93	6.0		60	−18
DMM[c]	−6.733	7.09	−5.3	9	−19.9
MA[c]	−6.008	8.31	−7.8	9	−22.9
St[c]	−7.472	6.93	−5.1	2	−19.5

[a] Dipolarophile. [b] Standard deviation of ln k. [c] In toluene. [d] In chloroform. [e] In acetonitrile; this solvent attacked fluorine-contained rubber O rings used for sealing pressure; so the data scattered considerably.

Dilatometry. A dilatometric study on the reaction was carried out to determine the reaction volume (ΔV) in the same way as the previous work.[1]

Results

Solvent Effect. Table I summarizes rate constants for the 1,3-dipolar cycloaddition of BPN with olefins substituted by one or two $COOCH_3$ groups in nonpolar and polar solvents at 25 °C and 1 bar. The ratio of the maximum to the minimum rate constant is 3.3 for MA, 4.6 for DMM, and 5.9 for DMF, while in the case of Ph_2CN_2 it is 1.5 for MA and DMM and 1.9 for DMF in the same range of solvent polarity (the range of the dielectric constant, 2–38).[16] It is referred to elsewhere[17] that the ratio is smaller than or equal to 10 for the 1,3-dipolar cycloaddition. A few orders of magnitude larger solvent effect is observed for the 1,2 and 1,4 cycloadditions in which the transition state is zwitterionic.[18] The sufficiently small solvent effect certifies that the 1,3-dipolar cycloaddition can be classified into a molecular reaction.

Pressure Effect. Rate constants obtained at high pressure at 25 °C are expressed in the form:

$$\ln k = a + bP + cP^2 \tag{4}$$

where k (M^{-1} s^{-1}) is the rate constant, P (bar) the pressure, and a, b, and c constants. The numerical values of these constants are given in Table II. By inserting eq 4 into eq 1 where the second term is neglected and noticing the difference in the concentration scale between eq 1 and 4, we get the activation volume ($\Delta V^{\ddagger}$) at 1 bar listed in Table I as

$$\Delta V^{\ddagger} = -RT(\partial \ln k/\partial P)_T - RT\beta \tag{5}$$

$$= -RT(b + 2c) - RT\beta \tag{6}$$

Here, β is the isothermal compressibility of pure solvent; β of toluene, chloroform, and acetonitrile are from ref 19, 20, and 21, respectively.

Values of $\Delta V^{\ddagger}$ in Table II are in the range of −18 to −24 cm^3 mol^{-1}, which can be compared with the range of −20 to −24 cm^3 mol^{-1} obtained for the 1,3-dipolar cycloaddition of Ph_2CN_2 with several olefins including DMF, DMM, and MA in toluene at 25 °C.[1] Therefore, it can be concluded that $\Delta V^{\ddagger}$ for the 1,3-dipolar cycloadditions studied so far are in the range of −18 to −24 cm^3 mol^{-1} irrespective of 1,3-dipoles, dipolarophiles, and solvents, being about 10 cm^3 mol^{-1} less negative than those for the usual 1,4-cycloaddition reactions. The meaning of $\Delta V^{\ddagger}$ will be discussed later in relation to the reaction mechanism.

Reaction Volume. The reaction volume (ΔV) has been determined dilatometrically for the 1,3-dipolar cycloaddition of BPN with DMF in toluene which provides a typical value of $\Delta V^{\ddagger}$ as shown in Table II. The rate equation (eq 3) for this second-order

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reaction takes the following integrated form:

$$k\alpha t = \ln \frac{r - z}{r(1 - z)} \quad (7)$$

$$\alpha = [\mathrm{DMF}]_0 - [\mathrm{BPN}]_0 \quad (>0) \quad (8)$$

$$z = -([\mathrm{BPN}] - [\mathrm{BPN}]_0)/[\mathrm{BPN}]_0 \quad (9)$$

$$r = [\mathrm{DMF}]_0/[\mathrm{BPN}]_0 \quad (>1) \quad (10)$$

where $[\ ]_0$ and z denote the initial concentration and the degree of reaction, respectively. When the partial molal volumes of the reactants and the product are assumed to be independent of the concentration in dilute solution, we have the following useful relation:

$$\Delta V_t = z\Delta V, \quad (11)$$

where ΔV_t and ΔV designate the changes in volume due to the reaction at time t and $t = \infty$, respectively. The time-dependent value of z in eq 11 can be obtained from eq 7 by using k in Table I and α and r known from initial concentrations of the reactants through eq 8 and 10, respectively. The dilatometrically determined values of ΔV_t are plotted against z in Figure 1. The linearity of this plot indicates the validity of the used assumption. The slope affords -22.7 ± 0.5 cm^3 mol^{-1} as ΔV. This value agrees with the less accurate[22] one that can be obtained indirectly from the partial molal volumes ($\bar{V}$) of the reactants and the product; $\Delta V = -25 \pm 3$ cm^3 mol^{-1}, $\bar{V}$ of BPN, DMF, and the adduct being 182, 129, and 286 cm^3 mol^{-1}, respectively. The dilatometrically determined value of ΔV is comparable with $\Delta V = -19 \pm 3$ cm^3 mol^{-1} for the 1,3-dipolar cycloaddition of α-phenyl-N-methylnitrone with ethyl acrylate; this value has been calculated on the basis of the density data for solutions of the reactants and the adduct in benzene at 25 °C.[23] Furthermore, the present value of ΔV is close to $\Delta V = -24.5$ cm^3 mol^{-1} determined dilatometrically for the 1,3-dipolar cycloaddition of $\mathrm{Ph_2CN_2}$ with DMM in toluene at 25 °C.[1] Thus, these different 1,3-dipoles and dipolarophiles provide similar values of ΔV as well as of $\Delta V^{\ddagger}$.

Discussion

Observed $\Delta V^{\ddagger}$ (ΔV) and Calculated $\Delta V_W^{\ddagger}$ (ΔV_W). As shown in Table III, the prominent volumetric feature of the 1,3-dipolar cycloaddition differs little from BPN to $\mathrm{Ph_2CN_2}$ studied previously, although the former is attacked at the nonlinear group CNO and the latter at the linear group CNN. Actually, there exists an empirical rule that a category of reactions have similar activation (reaction) volumes[7] as found here. This rule encourages us to compare the values of $\Delta V^{\ddagger}$ and ΔV experimentally obtained for the 1,3-dipolar cycloaddition with those of $\Delta V_W^{\ddagger}$ and ΔV_W theoretically calculated for the prototype 1,3-dipolar cycloaddition between HCNO and HCCH for the purpose mentioned in the introduction.

Values of $\Delta V_W^{\ddagger}$ and ΔV_W for the prototype 1,3-dipolar cycloaddition, which are obtained in a manner described elsewhere,[1] are given in Table IV together with those for the prototype 1,4 cycloaddition between $\mathrm{H_2C{=}CHCH{=}CH_2}$ and $\mathrm{H_2C{=}CH_2}$; van der Waals volumes of the species involved in the latter reaction are computed by the numerical integration method[1] by using the structural parameters provided by a quantum mechanical calculation.[24] The negative sign of $\Delta V_W^{\ddagger}$ and ΔV_W is mainly due to the concerted formation of the two new bonds between the reactant molecules in both prototype cycloaddition reactions; the volume contraction accompanying the bond formation overwhelms the volume expansion caused by the elongation of the bonds in the reactant moieties. In both cycloaddition reactions, the intermolecular bonds formed partially at the transition state are 210–220 pm, which amounts to 60–70% of the sum of the van der Waals radii of the pertinent atoms, and are shortened further by 70–90 pm in the adduct. Although $\Delta V_W^{\ddagger}$ has been calculated by using a cylindrical model for the bond to be formed or broken and assuming constancy of the cross section, the present analysis on the basis of the van der Waals sphere model discloses that the cross section varies simultaneously with the length. The present result in Table IV is in contrast to Hamann's conclusion[8b,25] that the bond-formation process has $\Delta V_W^{\ddagger}$ considerably larger in magnitude than that for the reverse process.

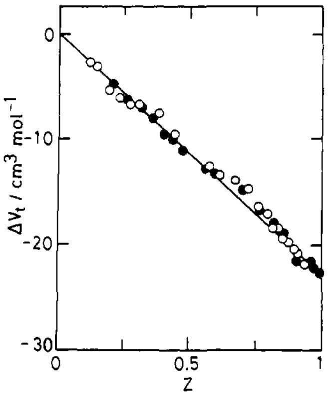

Figure 1. Plot of eq 11 at 25 °C: (○) [BPN] = 0.0538 M and [FDM] = 0.0562 M; (●) [BPN] = 0.0684 M and [FDM] = 0.0352 M.

Table III. Values of $\Delta V^{\ddagger}$, ΔV, and $\Delta V^{\ddagger}/\Delta V$ for 1,3-Dipolar Cycloadditions in Toluene at 25 °C and 1 bar

system	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	ΔV, cm^3 mol^{-1}	$\Delta V^{\ddagger}/\Delta V$
BPN + DMF	−21.7	−22.7	0.956
$\mathrm{Ph_2CN_2}$ + DMM[a]	−23.4	−24.5	0.955

[a] From ref 1.

Table IV. Values of $\Delta V_W^{\ddagger}$, ΔV_W, and $\Delta V_W^{\ddagger}/\Delta V_W$ for the Prototype 1,3-Dipolar Cycloaddition and 1,4 Cycloaddition

system	$\Delta V_W^{\ddagger}$, cm^3 mol^{-1}	ΔV_W, cm^3 mol^{-1}	$\Delta V_W^{\ddagger}/\Delta V_W$
1,3[a]	−4.0	−8.2	0.49
1,4[b]	−5.2	−9.2	0.57

[a] 1,3-Dipolar cycloaddition between HCNO and HCCH. [b] 1,4 cycloaddition between $\mathrm{H_2C{=}CHCH{=}CH_2}$ and $\mathrm{H_2C{=}CH_2}$.

Comparison of the experimental results in Table III and the theoretical ones in Table IV can be summarized as follows: (1) $\Delta V_W^{\ddagger}$ and ΔV_W are negative as are $\Delta V^{\ddagger}$ and ΔV but far smaller in magnitude than $\Delta V^{\ddagger}$ and ΔV, respectively, (2) $|\Delta V_W^{\ddagger}|$ and $|\Delta V_W|$ for the 1,3-dipolar cycloaddition are smaller by 1 cm^3 mol^{-1} than the corresponding values for the 1,4 cycloaddition, while the experimentally obtained difference in $\Delta V^{\ddagger}$ between the former and the latter reactions is about 10 cm^3 mol^{-1}, and (3) $\Delta V_W^{\ddagger}/\Delta V_W$ are approximately one half, while $\Delta V^{\ddagger}/\Delta V$ are close to unity. The first and second points summarized above tell us that the sign of activation and reaction volumes for the molecular reactions in the liquid phase is actually determined by changes in the geometry (size and shape) of reacting molecules but to their magnitude not directly; the former relation is convenient but insufficient for the use of $\Delta V^{\ddagger}$ and ΔV as a reliable probe in mechanistic studies, so a further analysis of the latter relation is required.

Size Dependence of Packing Coefficient η. A nonpolar molecule in liquid or solution has some free volume available for its dynamic motions, so the molal and partial molal volumes[26,27] exceed the

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(25) His calculation is based on a simple cylindrical model combined with less trustworthy quantum mechanical information. Although quantities calculated by him are designated by $\Delta_1 V^{\ddagger}$, they correspond just to $\Delta V_W^{\ddagger}$ treated here.

(26) For the case of a nonpolar solute in an inert solvent, the partial molal volume is often equal to the molal volume in its pure liquid state within a few percent according to the data in ref 27.

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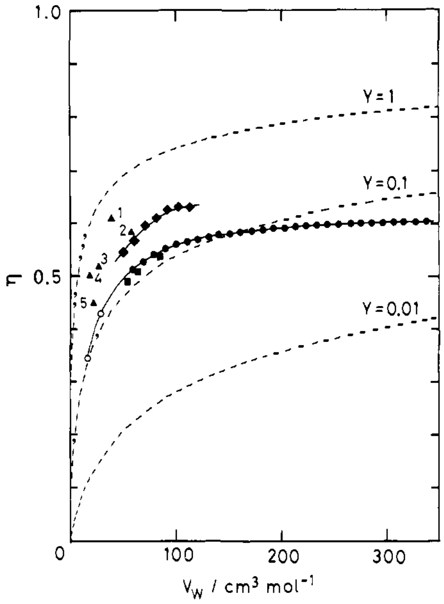

Figure 2. Dependence of the packing coefficient η on the van der Waals volume V_W for a few types of organic liquids at 25 °C: (●) *n*-alkanes in the pure state (28 alkanes from *n*-pentene to *n*-dotriacontane);[28] (○) methane and ethane in CCl_4;[30] (■) *n*-1-alkenes in the pure state (*n*-pentene, *n*-hexene, and *n*-octene);[28] (◆) cycloalkanes in the pure state (cyclopentane,[28] cyclohexane,[28] cycloheptane,[29b] cyclooctane (20 °C),[29b] cyclononane (15.2 °C),[29b] cyclodecane (20 °C),[29b] cycloundecane (20 °C)[29b]); (▲) micellaneous compounds in the pure state (1, isoxazole;[29a] 2, cyclohexene;[29a] 3, CH_3NO_2;[28] 4, HN_3 (20 °C);[29a] 5, CH_3CN[28]); (- - -), due to eq 13 for $Y = 1$, 0.1, and 0.01 cm^{-3} mol. Correction of η due to the thermal expansion between 15 and 25 °C is about 0.01 at most.

van der Waals volume V_W to some extent. A physical term connecting V with V_W is called the packing coefficient η defined as

$$\eta = V_W/V \quad (<1) \tag{12}$$

the numerical value of which is very characteristic of the condensed phase. If the widely employed, fundamental assumption that the second term in eq 1 is negligible is valid, all the points summarized above are to be explained by taking account of the packing coefficient for each species.

We have calculated the packing coefficient for organic liquids of interest by using the values of V_W[1,10] and V.[28-30] Figure 2 shows how η varies with the molecular size and shape. For the case of linear-hydrocarbon liquids η initially rises sharply with an increase in the molecular size, say up to V_W = 100 cm^3 mol^{-1} and η = 0.56 for nonane, and increases only by 0.05 between 100 and 300 cm^3 mol^{-1}. This trend found empirically can be approximately simulated by the analytical solution[31] of the Percus–Yevick compressibility equation for hard-sphere fluids expressed by

$$YV = (1 + \eta + \eta^2)/(1 - \eta)^3 \tag{13}$$

$$Y = P/RT \tag{14}$$

where P, T, and R the pressure, the temperature, and the gas constant; when we make T equal to 298 K (25 °C), Y = 0.1 cm^{-3} mol corresponds to P = 2.48 kbar, which is comparable with the internal pressure for these organic liquids. In addition, the following trends are noticed in Figure 2: (1) the tendency that smaller molecules have a smaller packing coefficient is shown also by the *n*-alkenes and cyclic compounds, (2) the packing coefficient is only slightly decreased by the introduction of a double bond to *n*-alkanes, (3) the cyclic compounds have a definitely larger packing coefficient than does an *n*-alkane of the corresponding size, and (4) heteroatoms seem to increase the packing coefficient. All of these trends are of great importance to bridge $\Delta V^{\ddagger}$ (ΔV) observed and $\Delta V_W^{\ddagger}$ (ΔV_W) calculated for the concerted cycloaddition reactions, as clarified below.

Table V. Values of $\Delta V^{\ddagger}$ (cm^3 mol^{-1}) and ΔV (cm^3 mol^{-1}) Predicted for the Prototype 1,3-Dipolar Cycloaddition and 1,4 Cycloaddition Reaction on the Basis of the Suitable Packing Coefficients η for the Relevant Species

species	V_W	η	V	$\Delta V^{\ddagger}$	ΔV	$\Delta V^{\ddagger}/\Delta V$
		1,3-Dipolar Cycloaddition				
HCNO	24.1	≅0.50[b]	48	−31	−38	0.82
HCCH	23.1	0.43[c]	54[c]			
TS[a]	43.2	≅0.61	71			
isoxazole	39.0	0.61[d]	64[d]			
		1,4 Cycloaddition				
$H_2C{=}CHCH{=}CH_2$	43.1	≅0.48[e]	90	−41	−48	0.85
$H_2C{=}CH_2$	25.3	0.42[c]	60[c]			
TS[a]	63.5	≅0.58	109			
cyclohexene	59.2	0.58[d]	102[d]			

[a] Transition state, η of which is assumed to be equal to that of the product. [b] Taken from η of a structurally similar molecule HN_3 in the pure state.[29] [c] For the solution in CCl_4.[30a] [d] In the pure state.[29] [e] Estimated from Figure 2.

Role of η in Determining $\Delta V^{\ddagger}$ (ΔV). If the packing coefficient is known in some manner for each species involved in the prototype cycloadditions, we can predict $\Delta V^{\ddagger}$ and ΔV for the reactions by using eq 12. Such a prediction is shown in Table V. $\Delta V^{\ddagger}$ and ΔV for the prototype 1,3-dipolar cycloaddition are predicted to be −31 and −38 cm^3 mol^{-1}, respectively, which are compared with the experimental values in Table III. The predicted values are more negative than the obserbed, and the difference is partly due to the uncertainty of η estimated (e.g., for HCNO and the transition state) and partly due to the strong dependence of η on size for small molecules (see Figure 2); the reactants used in the experiment are actually much larger in size than both HCNO and HCCH. Thus the size dependence of the packing coefficient plays an important role in determining the magnitude of $\Delta V^{\ddagger}$ for the addition reaction. If η is constant, for example, $\Delta V^{\ddagger}$ amounts only to $\Delta V_W^{\ddagger}/\eta$, which is $1.7\Delta V_W^{\ddagger}$ for η = 0.6 and $2.5\Delta V_W^{\ddagger}$ for η = 0.4, and $\Delta V_W/\Delta V_W$ equals $\Delta V^{\ddagger}/\Delta V$ in disagreement with the present result.

The difference in $\Delta V^{\ddagger}$ between the 1,3-dipolar cycloaddition and the 1,4 cycloaddition is reproduced successfully in Table V; the difference is due to the fact that the heteroatoms increase the packing coefficient rather than due to the small difference in $\Delta V_W^{\ddagger}$. The calculated values of $\Delta V^{\ddagger}$ and ΔV have a difference of 7 cm^3 mol^{-1}, which is considerably larger than the observed (about 1 cm^3 mol^{-1}). However, if a more plausible value of η, which would be larger than that assumed in Table V because of the larger size, is taken for the transition state, the difference gets closer to the observed one. The ratios of $\Delta V^{\ddagger}$ to ΔV are also in reasonable agreement with those observed in spite of the approximations utilized in estimating V_W[32] and η in Table V.

Concluding Remarks

The 1,3-dipolar cycloaddition reactions in the liquid phase have $\Delta V^{\ddagger}$ in the range of −18 to −24 cm^3 mol^{-1}, which is about 10 cm^3 mol^{-1} less negative than $\Delta V^{\ddagger}$ for the usual 1,4 cycloaddition reactions. The reverse process of the 1,3-dipolar cycloaddition has an activation volume of about 1 cm^3 mol^{-1}. The changes in the van der Waals volume for the prototype 1,3-dipolar cycloaddition between HCNO and HCCH, which have been computed

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by applying the van der Waals sphere model for atoms to the available quantum mechanical information on the structural changes, are found to be much smaller in magnitude than the observed activation and reaction volumes. The present work discloses that the most important factor controlling the large gap between $\Delta V^{\ddagger}$ (ΔV) and $\Delta V_W^{\ddagger}$ (ΔV_W) is the size dependence of the packing coefficient η. $\Delta V^{\ddagger}$ and ΔV predicted for the prototype 1,3-dipolar cycloaddition on the basis of V_W and η are in reasonable agreement with those observed for the 1,3-dipolar cycloaddition reactions of complicated molecules. Thus, no serious problems have been brought about in the present volumetric study even if we have calculated $\Delta V^{\ddagger}$ values by neglecting the pressure dependence of the transmission coefficient in the transition-state theory (see eq 1).

Registry No. BPN, 5492-70-6; DMM, 624-48-6; DMF, 624-49-7; MA, 96-33-3; HCNO, 51060-05-0; HCCH, 74-86-2; $H_2C{=}CHCH{=}CH_2$, 106-99-0; $H_2C{=}CH_2$, 74-85-1.

Reactions with Aromatic Compounds of Recoiling Bromine Atoms Formed from the ^{76,77}Kr → ^{76,77}Br Transformations. Liquid-Phase Reactions[1a]

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Abstract: Bromine atoms produced via the ^{76}Kr(EC)^{76}Br and ^{77}Kr(β^+/EC)^{77}Br transformations were reacted with simple benzenoid compounds in the liquid phase. For both ^{76}Kr and ^{77}Kr, bromodeprotonation resulted in a reactivity constant $\rho^+ \simeq -0.6$, with higher yields for ^{76}Br. Whereas bromodeprotonation was hypothesized to occur via formation of a product-determining σ-complex by radical bromine species, ipso substitution was described in terms of a two-step addition–elimination mechanism in which bond breakage is product determining. While radical bromine species are probably involved in substituent displacements from monosubstituted arenes, polysubstituted aromatic compounds activated to nucleophilic attack were shown to involve an additional nucleophilic reaction pathway.

The use of solution chemistry to study the mechanisms of aromatic substitution is complicated by the occurrence of several side processes, such as disproportionation of the substrate,[2-4] halogen exchange with the catalyst,[5,6] internal halogen transfer[3,5,7] catalyzed arylation, or polymerization by the Scholl reaction,[8] solvation effects,[9,10] and ion pairing.[11-13] These problems not only make elucidation of substitution mechanisms difficult, but may also constrain mechanistic information to a particular set of reactions or experimental conditions.

A useful technique that avoids these problems is the study of nucleogenic decay in organic substrates.[14] Electrophilic, homolytic, and nucleophilic processes may be studied in an environment consisting solely of the aromatic substrate and carrier-free quantities of the parent nuclide. Because of the efficiency of radioanalytical techniques, only picomolar concentrations of parent isotope are required, which makes double-substitution pathways improbable and minimizes radiolytic degradation of the substrate compounds. Finally, due to the variety of charge states and kinetic energies imparted to the daughter atom of different decay systems, different reaction pathways can be studied that may shed light on the general problem of aromatic hydrogen substitution mechanisms.

In addition to the commonly studied aromatic hydrogen substitution reactions, mechanisms of ipso attack and aromatic substituent displacement are of interest because the particular reaction pathways that are followed are a function of several parameters, such as the nature of the attacking species, the mobility of the displaced atom or group, the nature of the acceptor for the displaced group, substituent-induced activation or deactivation of the respective aromatic nucleus, and solvation effects on the reactant or product species. This plethora of chemical variables allows for electrophilic,[15,16] free-radical,[17,18] as well as

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