2% cross-linked catalysts and 5–60% with more highly cross-linked catalysts, depending on catalyst activity, particle size, stirring rate, and reaction time.

A plot of $\ln a^*/(a^* - x)$ vs. time was made, and the pseudo-first-order rate constants were evaluated from the slope of the best hand-drawn straight line. Here a^* is the concentration of phenylacetonitrile at the first data point, and x is the concentration of phenylacetonitrile at subsequent data points. Up to 30% conversion no deviations from pseudo-first-order kinetics were observed. In a few kinetic experiments, some of the catalyst splashed and stuck on the upper wall of the flask out of contact with the reaction mixture. Such runs were discarded.

(B) Reverse Addition Method. A 100-mL three-necked flask was charged with 0.1–0.6 g of the catalyst, 45 mL of 50% w/w NaOH (19.086 M), and 2 mL (1.52–1.53 g) of *n*-pentadecane (internal standard for GC), placed in a thermostat at 80 ± 0.2 °C, and stirred mechanically. After 50 min 2 mL of phenylacetonitrile was added. After 10 min the stirring speed was increased, and 25 mL of preheated 1-bromobutane at 80.0 ± 0.2 °C was quickly added at the zero time. Small samples (0.1 mL) of the organic phase were withdrawn, quenched in toluene containing anhydrous calcium chloride, and analyzed by GLC. The initial rates of disappearance of phenylacetonitrile were evaluated from plots of $\ln a^*/(a^* - x)$ vs. time. Duplicate runs were carried out with seven different catalysts, and the rate constants differed by an average of 2.7%.

Particle Size Measurement. After the last sample was drawn in a kinetic run, the stirrer was stopped, and beads were removed immediately with a pipet. The beads were placed in a covered flat-bottom glass container and viewed under a microscope equipped with a calibrated movable stage. The diameters of 20 particles selected in a single area of the viewer were measured. Average diameters are used in the tables and figures. Thus the particle sizes were determined at room temperature, the particles being swollen by the reaction mixture. Every recovered catalyst consisted entirely of whole, unbroken beads.

Control Experiments. Reactions were carried out with 0.6 g of 2% cross-linked polystyrene beads containing no functional groups and with no polymer at all. Less than 0.1% butylation of phenylacetonitrile occurred in 60 min in both cases.

Experiment A, Table IV. A 2% cross-linked 60/100-mesh benzyltrimethylammonium chloride catalyst was recovered after 60 min of reaction, washed with water, methanol, tetrahydrofuran (THF), acetone, and anhydrous methanol, and dried under vacuum at 60 °C. One portion of it was used for another kinetic run. The other portion was swelled in THF, treated with 3 N HCl for 3 h, washed with water, acetone, methanol, THF, acetone, and anhydrous methanol, dried under vacuum at 60 °C, and analyzed for chloride ion. From a separate reaction mixture the recovered catalyst was converted to the chloride form by treatment with 3 N HCl in THF, washed and dried as above, and used for a new kinetic experiment.

Experiment B, Table IV. A 2% cross-linked, 100/200-mesh benzyltrimethylammonium ion catalyst was recovered after 45 min of reaction, washed with water until the washings were neutral, and dried in air on a fritted filter overnight.

Distribution of Phenylacetonitrile, 1-Bromobutane, Monobutyl Product, and *n*-Pentadecane in a Reaction Mixture. Two 2% cross-linked 60/100-mesh benzyltrimethylammonium chloride catalysts (1.27 and 2.99 mequiv of Cl^-/g) in reverse addition experiments were filtered separately as quickly as possible from reaction mixtures after 30 min and washed with water to remove the NaOH on the surface of the beads. Each catalyst was then swelled in 50 mL of THF and filtered. The beads were washed twice with 20 mL portions of THF. The THF solutions were dried over anhydrous sodium sulfate and analyzed by GLC with hexadecane as an internal standard. The various amounts (in mole percent) were as follows: phenylacetonitrile, 73.9, 75.1; 1-bromobutane, 5.5, 4.9; monobutyl product, 20.7, 20.0. The starting mixture contained 7.0 mol % of phenylacetonitrile and 93.0 mol % of 1-bromobutane.

Swelling of Catalyst. (A) Dry catalyst (1.0 mL) was placed in a graduated centrifuge tube, and 25 mL of 1-bromobutane was added. The catalyst floated.

(B) Dry catalyst (1.0 mL) was heated to 80 °C, and 3 mL of phenylacetonitrile at 80 °C was added, stirred, and allowed to stand. The catalyst sunk. The catalyst volume increased to 3.0 mL in 5 min and did not change after 12 h. Experiment B was repeated at 70 and 60 °C. The swollen volumes after 5 min were 2.8 and 2.4 mL, and they remained constant for 12 h.

Acknowledgment. We thank Jeanne Lee for analyses of the ion-exchange capacities of the catalysts and Prof. E. J. Eisenbraun for the loan of the vibromixer and the ultrasonic mixer.

Registry No. Phenylacetonitrile, 140-29-4; 1-bromobutane, 109-65-9; sodium hydroxide, 1310-73-2.

Effect of Pressure on the 1,3-Dipolar Cycloaddition Reaction of Diphenyldiazomethane to Carbon–Carbon Multiple Bonds

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The volume profiles for the 1,3-dipolar cycloaddition reactions of diphenyldiazomethane to dimethyl acetylenedicarboxylate, diethyl maleate, diethyl fumarate, and maleic anhydride were measured in various solvents. Generally, the volumes of activation amount to ca. −20 cm^3/mol and the volumes of reaction to ca. −28 cm^3/mol. Cohesive energy densities and probably small electrostatic interactions contribute to the solvent effects in the above quantities.

1,3-Dipolar cycloaddition reactions have attracted much interest during the past 2 decades; their synthetic potential is far from being exhausted. According to mechanistic studies,[1] they belong to the concerted processes which once were called, half in jest, "no mechanism reactions",[2] because no intermediate occurs which allows interference. The electronic prototype of the 1,3-dipolar cycloaddition is the (hypothetical) combination of the allyl anion with ethylene; the π electronic description, $[_\pi 4_s + _\pi 2_s]$, is shared

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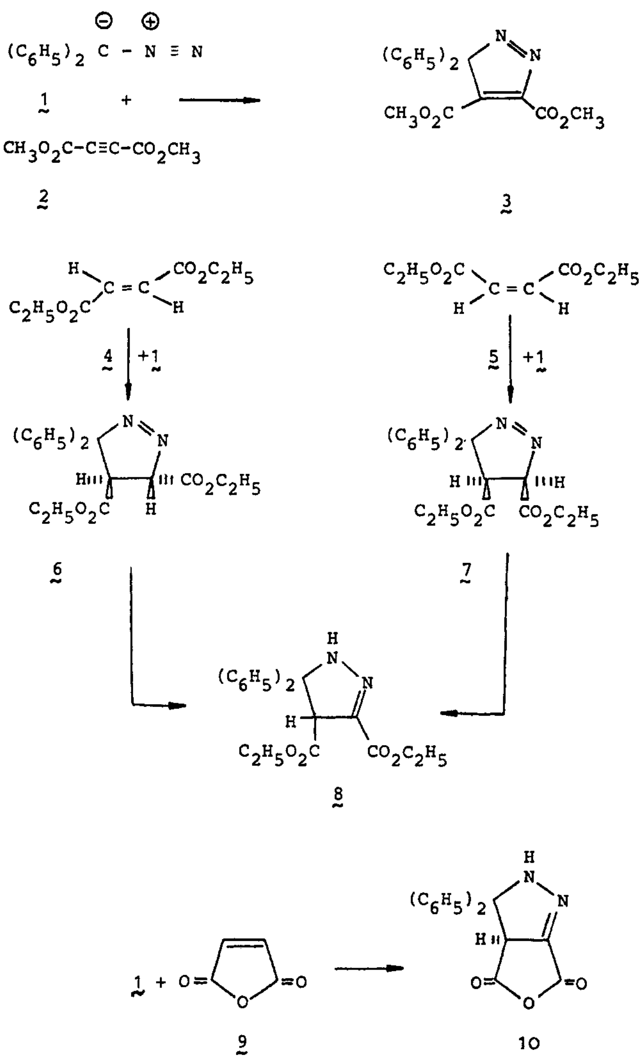
0022-3263/83/1948-1035$01.50/0

Scheme I



with the Diels–Alder reaction, and both thermal cycloadditions are allowed to be concerted by the Woodward–Hoffman rules. Some arguments in favor of a two-step mechanism via a diradical intermediate have been proposed[3] but found no support elsewhere.

Reaction kinetics under high pressure have turned out to be of great value in the elucidation of reaction mechanism.[4,5] In contrast to Diels–Alder reactions,[6] high-pressure data on 1,3-dipolar cycloadditions are scarce.[7] Therefore, we embarked in an investigation of the total volume profiles of typical examples and chose as the first ones the cycloadditions of diphenyldiazomethane (1) to dimethyl acetylenedicarboxylate (2), diethyl fumarate (4), diethyl maleate (5), and maleic anhydride (9) (see Scheme I) which had been preparatively studied by van Alphen.[8]

Experimental Section

Compounds. Diphenyldiazomethane (1) was prepared from benzophenone hydrazone with mercuric oxide.[9] The red needles of $(C_6H_5)_2CN_2$ [visible spectrum (hexane): λ_{max} = 523 nm (ϵ_{max} 160)] were stored at low temperatures. Commercial samples of dimethyl acetylenedicarboxylate (**2**), diethyl fumarate (**4**), and diethyl maleate (**5**) (Merck-Schuchardt) were purified by distillation under reduced pressure. Maleic anhydride (**9**) (Merck-Schuchardt) was sublimed before use.

Table I. Pressure and Solvent Dependence of the Rate Constants (*k*) of the 1,3-Dipolar Cycloaddition Reactions of Diphenyldiazomethane on Four Different Dipolarophiles Measured at 25 °C

pressure, MPa	10^3k, M^{-1} s^{-1}, for diphenyldiazomethane + dimethyl acetylenedicarboxylate			
	n *n*-hexane	toluene	chloro-benzene	aceto-nitrile
0.1	12.6 ± 0.6	17.3 ± 0.6	24.2 ± 0.9	42.3 ± 1.6
10	14.0 ± 2.0	19.2 ± 0.4	25.6 ± 1.1	45.9 ± 1.8
20	16.6 ± 0.8	21.0 ± 0.2	28.1 ± 1.2	48.5 ± 1.2
30	17.2 ± 0.2	23.0 ± 0.5	30.1 ± 1.8	52.7 ± 2.1
50	19.4 ± 0.9	26.6 ± 0.7	35.1 ± 2.1	58.1 ± 0.4
75	27.8 ± 1.3	31.8 ± 0.5	40.8 ± 2.9	67.4 ± 1.1
100	30.4 ± 2.1	38.1 ± 1.2	49.6 ± 2.7	78.9 ± 4.7

pressure, MPa	10^3k, M^{-1} s^{-1}		
	diethyl maleate (in chloro-benzene)	diethyl fumarate (in chloro-benzene)	maleic anhydride (in aceto-nitrile)
0.1	0.76 ± 0.12	5.11 ± 0.13	50.4 ± 5.0
10		5.64 ± 0.08	53.9 ± 7.4
20	0.92 ± 0.09	6.15 ± 0.06	
30		6.74 ± 0.05	65.0 ± 4.9
40	1.14 ± 0.02	7.22	
50	1.23 ± 0.11	7.87 ± 0.19	71.9 ± 5.4
70			79.3
75	1.57 ± 0.15	9.38 ± 0.49	
100	1.76	12.5 ± 1.1	101.6 ± 1.7

Dimethyl 3,3-diphenyl-3*H*-pyrrole-4,5-dicarboxylate (**3**) was prepared from **1** and **2** in ether. After recrystallization from methanol, the yellow adduct showed a melting point of 91–92 °C (lit.[8] mp 93 °C). Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.9; H, 4.8; N, 8.3. Found: C, 67.8; H, 4.8; N, 8.3.

The two diastereomeric 1-pyrazolines **6** and **7** are not isolable but tautomerize to one and the same racemate of diethyl 5,5-diphenyl-2-pyrazoline-3,4-dicarboxylate (**8**). Recrystallization from methanol afforded colorless needles, mp 67–68 °C. Anal. Calcd for $C_{21}H_{22}N_2O_4$: C, 68.83; H, 6.05; N, 7.65. Found: C, 69.0; H, 6.19; N, 7.60.

The IR and ^{1}H NMR spectra of **1**, **3**, and **8** proved the structure and purity of the compounds. No effort was made to prepare the cycloadduct **10** from **1** and maleic anhydride (**9**) because it decomposes at ambient temperatures.[8]

Apparatus. The kinetic runs were performed on a Cary-15 or a Zeiss PMQ II spectrophotometer. Both instruments are equipped with essentially the same high-pressure attachment.[10] IR and NMR spectra were recorded with Beckman IR-4240 and Varian A-60 and XL-100 instruments, respectively. Precision densities were measured with an A. Paar DMA 02 C apparatus, the constancy of temperature of the cell (±0.002 °C) being monitored by a Hewlett-Packard 2801 A quartz thermometer.

Results

The 1,3-dipolar cycloaddition of diphenyldiazomethane to the four dipolarophiles was conveniently observed by the decreasing diphenyldiazomethane absorption at 525 nm. With a 10–30-fold excess of the dipolarophile, the reactions follow a pseudo-first-order rate law. The second-order rate constants measured at 25.0 °C, at pressures ranging from 0.1 to 100 MPa (1–1000 bar), and in different

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Table II. Partial Molar Volumes of Reactants and Products of Some Diphenyldiazomethane + Dipolarophile Cycloaddition Reactions Measured at 25.0 °C

	$\bar{V}$, cm^3 mol^{-1}						
solvent	diphenyl-diazo-methane	dimethyl acetylene-dicarboxylate	dimethyl 3,3-diphenyl-3*H*-pyrazole-4,5-dicarboxylate	diethyl fumarate	diethyl maleate	diethyl 5,5-diphenyl-2-pyrazoline-3,3-dicarboxylate[a]	maleic anhydride
n-hexane	169.3 ± 1.6	129.7 ± 0.3	264.1 ± 0.2	167.0 ± 0.8	165.9 ± 0.6	307.3 ± 0.6	
toluene	173.3 ± 1.1	124.3 ± 0.1	270.8 ± 0.3	164.8 ± 0.4	161.3 ± 0.1	309.2 ± 0.2	
chlorobenzene	174.2 ± 0.1	124.3 ± 0.1	272.1 ± 0.4	164.1 ± 0.1	162.2 ± 0.2	311.3 ± 1.1	
acetonitrile	172.7 ± 0.2	120.5 ± 0.3	265.4 ± 0.6	163.0 ± 0.2	159.8 ± 0.1	304.3 ± 1.3	70.0 ± 0.6

[a] Measured instead of the unstable primary 1-pyrazolines.

Table III. Volumes of Activation, $\Delta V^{\ddagger}$, and Volumes of Reaction, $\Delta \bar{V}_R$, of the 1,3-Dipolar Cycloaddition of Diphenyl Diazomethane to Four Different Dipolarophiles Measured at 25 °C

dipolarophile	dimethyl acetylenedicarboxylate		diethyl fumarate		diethyl maleate		maleic anhydride,
solvent	$\Delta V^{\ddagger}$, cm^3/mol	$\Delta \bar{V}_R$, cm^3/mol	$\Delta V^{\ddagger}$, cm^3/mol	$\Delta \bar{V}_R$,[a] cm^3/mol	$\Delta V^{\ddagger}$, cm^3/mol	$\Delta \bar{V}_R$,[a] cm^3/mol	$\Delta V^{\ddagger}$,[b] cm^3/mol
n-hexane	−24 ± 6	−34.9 ± 1.6		−29.0 ± 1.9		−27.9 ± 1.8	
toluene	−23.2 ± 1	−26.8 ± 1.1		−28.9 ± 1.2		−25.4 ± 1.1	
chlorobenzene	−17.8 ± 1.3	−26.4 ± 0.4	−20.9 ± 1.7	−27.0 ± 1.1	−23.6 ± 1.3	−25.1 ± 1.1	
acetonitrile	−15.3 ± 1.5	−27.8 ± 0.7		−31.4 ± 1.3		−28.2 ± 1.3	−16.7 ± 2.3

[a] Calculated from the partial molar volumes of the racemic mixture of the common Δ^2-pyrazoline. [b] No $\Delta \bar{V}_R$ data available.

solvents are compiled in Table I.

The pressure dependence of the rate constants, *k*, is given by eq 1, where $\Delta V^{\ddagger}$ denotes the volume of activation.

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

Except for one reaction, eq 1 was approximated by the linear dependence in eq 2 which allowed calculation of an

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

average value of $\Delta V^{\ddagger}$ from all pairs $\ln k_{P_i}/P_i$, $\ln k_{P_j}/P_j$. The only reaction which showed a definite curvature in its ln *k* vs. *P* plot was that of **1** + **2** in toluene. Here the experimental data were fitted to a quadratic equation (eq 3).

$$\ln k = a + bP + cP^2 \qquad (3)$$

The 100-MPa rate constant for the cycloaddtion of **1** + **5** is obviously too low and was neglected in the calculation of $\Delta V^{\ddagger}$. The *k* values for the reaction **1** + **2** in hexane show more scatter than usual.

The volumes of activation given in Table III are not corrected for the different compressibilities, κ, of the solvents since the second-order rate constants are based on molarity concentrations at ambient pressure.

The apparent molar volumes of reactants and adducts were calculated from precision density measurements and did not reveal any concentration dependence for solutions below ca. 0.1 M. The partial molar volumes, $\bar{V}$, listed in Table II are thus the average of the low-concentratioin apparent molar volumes.

The volumes of reaction, $\Delta \bar{V}_R$ (Table III), are the differences of the partial molar volumes of the cycloadducts and those of the reactants. The solvent dependence of $\Delta \bar{V}_R$ for the cycloaddition **1** + **2** thus results from the solvent-dependent $\bar{V}$ values of **1** and **2**. For the cycloadditions of **1** to **4** and **5** the $\Delta \bar{V}_R$ values listed in Table III correspond to the overall volume changes in the reaction sequences via **6** and **7** to give **8**; i.e., they receive contributions from the two steps, $\Delta \bar{V}_R = \Delta \bar{V}_1 + \Delta \bar{V}_2$. The second step, **6** → **8** and **7** → **8**, is merely a tautomerization; thus the $\Delta \bar{V}_2$ values are expected to be small. Experiments in our laboratory have confirmed this assumption.

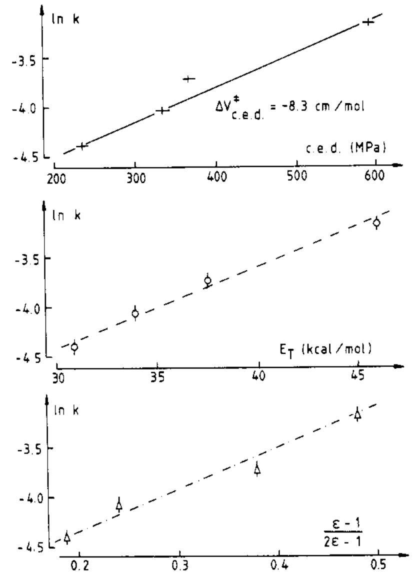

Figure 1. Solvent dependence of rate constants of the 1,3-dipolar cycloaddition of diphenyldiazomethane to dimethyl acetylenedicarboxylate. Solvent cohesive energies (top), the Dimroth parameter E_T (middle), and the solvent polarity (bottom) are used as solvent parameters.

The tendency of **10** to eliminate N_2[8] prevented the determination of $\Delta \bar{V}_R$ for **1** + **9**.

Discussion

Rate Constants of Cycloaddition at Ambient Pressures. The cycloadditions of diphenyldiazomethane (**1**) are slower than those of diazomethane by ~10^2.[11] The rate constants for the additions of **1** to olefinic and acetylenic dipolarophiles extend over four orders of magnitude, depending on the substituents.[11,12] In the framework of the MO perturbation theory, the HOMO(diazoal-

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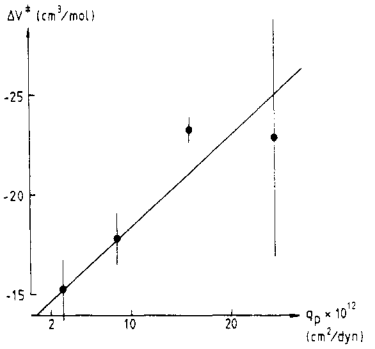

Figure 2. Dependence of volumes of activation, $\Delta V^{\ddagger}$, of the 1,3-dipolar cycloaddition of diphenyldiazomethane to dimethyl acetylenedicarboxylate on the solvent electrostriction parameter q_p.

kane)-LUMO(dipolarophile) interaction is the controlling factor for the variation of reactivity.[13,14]

When the cycloaddition of 1 to acetylenedicarboxylate (2) was carried out in solvents of increasing polarity, an increase of the rate constant was observed. For four solvents representative for the full range of solvent polarity Figure 1 reveals a fairly linear correlation between ln k and $q = (\epsilon - 1)/(2\epsilon + 1)$ (ϵ = dielectric constant of the solvent) as well as E_T, an empirical parameter of solvent polarity.[15,16]

Before these correlations are taken as evidence for an increase of polarity in the transition state, caution is advisable. First of all, the solvent effect in k is very small: k(acetonitrile)/k(hexane) = 3.4. The related cycloaddition of phenyldiazomethane to ethyl acrylate afforded k(methanol)/k(cyclohexane) = 5.3.[17] A small or sometimes negligible solvent dependence of rate constants is common to all 1,3-dipolar cycloadditions[1,12] and Diels–Alder reactions.[18] In contrast, the [2 + 2] cycloadditions of tetracyanoethylene (TCNE) to enol ethers, a prototype of the pathway via zwitterionic intermediates,[19] are accelerated by 10^4 when the solvent cyclohexane is replaced by acetonitrile.[20] Second, when ln k is plotted against the cohesive energy densities (ced's)[21] of the four solvents, an equally good correlation is found (Figure 1).

Apart from the conclusion that for the solvents studied q, E_T, and ced correlate, a different interpretation of the solvent effect on k is conceivable. Because the transition state of the cycloaddition 1 + 2 is smaller in volume than the initial state, an increasing ced of the solvent will accelerate the reaction. The volume of activation determined from the ln k vs. ced plot amounts to $\Delta V^{\ddagger}_{\text{ced}} = -8.3$ cm³/mol. This figure is only about half of the experimental volumes of activation, $\Delta V^{\ddagger}$, obtained from high-pressure kinetic data. When solvent internal pressures, P_i, are used to describe the solvent dependence of the present rate constants, an approximately parabolic correlation, $\ln k \approx a + bP_i + cP_i^2$, with b and $c > 0$ and $\Delta V^{\ddagger}_{P_i} \approx 0$ for $P_i \rightarrow 1$, is found. Thus, the solvent variation for the reaction 1 + 2 cannot be described by ced's and internal pressures, and one should rather fall back on high-pressure kinetics data.[4,22]

Volumes of Activation. The volumes of activation determined for the cycloaddition 1 + 2 in four different solvents range from −15 to −24 cm³/mol (Table III). Figures 2 demonstrates that the electrostriction parameter (eq 4) allows a semiquantitative description of the solvent

$$q_p = \frac{3}{(2\epsilon + 1)^2} \frac{\partial \epsilon}{\partial P} \tag{4}$$

dependence of $\Delta V^{\ddagger}$. According to the underlying Kirkwood theory—a purely electrostatic approach which neglects specific solvent interactions—the slope of the $\Delta V^{\ddagger}$ vs. q_p plot is connected with the change in dipole moment during the formation of the transition state. From the intercept ($q_p = 0$) the intrinsic part, $\Delta V^{\ddagger}_{\text{intr}}$, of the volume of activation is obtained. The correlation of Figure 2 provides $\Delta V^{\ddagger}_{\text{intr}} = 14$ cm³/mol with a decrease in $\Delta V^{\ddagger}$ of 8 cm³/mol on going from acetonitrile to toluene. For the [2 + 2] cycloaddition of TCNE to butyl vinyl ether the same value of $\Delta V^{\ddagger}_{\text{intr}}$ was found, whereas $\Delta V^{\ddagger}$ was diminished by 14 cm³/mol for a similar variation in q_p (acetonitrile → benzene).[23]

The rash conclusion that the 1,3-dipolar cycloaddition 1 + 2 has transition-state properties similar to those of the [2 + 2] cycloaddition of TCNE and, therefore, that the reaction is a two-step process via a zwitterion with one bond formed in the first step ($\Delta V^{\ddagger}_{\text{intr}} = 14$ cm³/mol is a typical value for a one-bond formation) and a highly polar transition state is misleading, however. Within the framework of the Kirkwood theory the *small* solvent dependence of the rate constants is caused by a negligible increase in the purity during activation excluding a zwitterionic two-step process. Thus the apparent solvent dependence of $\Delta V^{\ddagger}$ must be of a different origin.

Before some reasons for the solvent dependence of $\Delta V^{\ddagger}$ and its size are discussed we point out that, according to the scanty data of Table III, $\Delta V^{\ddagger}$ is probably not too much affected by the nature of the dipolarophile. The addition of 1 to dimethyl acetylenedicarboxylate and maleic anhydride in acetonitrile are accompanied by virtually the same volume of activation. The decrease of $\Delta V^{\ddagger}$ from −17.8 to −23.6 cm³/mol observed for the series dimethyl acetylenedicarboxylate, diethyl fumarate, and diethyl maleate in chlorobenzene can be rationalized by steric effects. For maleic ester, the squeeze of the cis ester groups during the hybridization from sp² to sp³ causes a smaller rate constant as compared to the fumarate[24] and a more densely packed transition state. The variations in k and $\Delta V^{\ddagger}$ are in line with the Hammond postulate. Finally, a more negative value, $\Delta V^{\ddagger} = -30$ cm³/mol, was reported for the addition of 1 to a diazanorbornene derivative.[7]

Partial Molar Volumes. The partial molar volumes of dimethyl acetylenedicarboxylate range from 120 to 130 cm³/mol (Table II). The fact that the highest value of $\bar{V}$ is observed in hexane and the lowest in acetonitrile indicates that electrostriction cannot be responsible for the solvent variation in $\bar{V}$; prevailing electrostatic interactions should effect a decrease in $\bar{V}$ with increasing q_p values of the solvent. For 2, however, the opposite trend is true. Figure 3 (bottom) demonstrates that the solvent dependence of $\bar{V}$ is reasonably well explained by the variation in solvent ced's. An increasing ced of the solvent allows a smaller cavity for the solute. It is noteworthy that the

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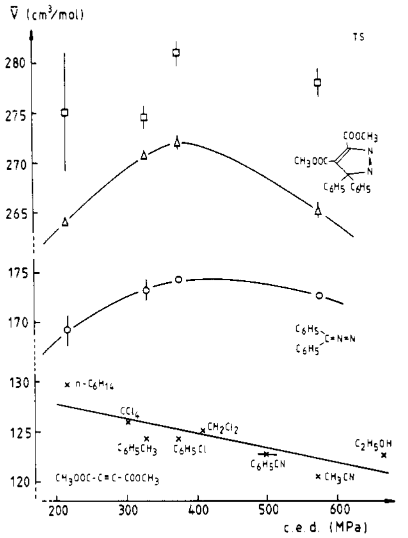

Figure 3. Dependence of partial molar volumes on solvent cohesive energy densities: ×, dimethyl acetylenedicarboxylate; ○, diphenyldiazomethane; △, cyclo product; □, transition state.

$\bar{V}$ data of **2** show no obvious correlation with the internal pressures, P_i, of the solvents.

Both diethyl fumarate (**4**) and diethyl maleate (**5**) exhibit the same trend in their partial molar volumes as **2**, i.e., a decrease in $\bar{V}$ with increasing ced of the solvent. The total spread in $\bar{V}$, however, is somewhat smaller than that for **2**.

The partial molar volumes of diphenyldiazomethane in toluene and chlorobenzene are about 1 cm^3/mol smaller than the partial molar volumes of diphenylketene.[25] This similarity can be anticipated from the bond lengths of the >C=C=O and >C=N=N group. The solvent dependences of both $\bar{V}$ values, however, differ markedly although both molecules have similar dipole moments (diphenylketene, μ = 1.76 D; diphenyldiazomethane, μ = 1.42 D). While the partial molar volume of diphenylketene decreases linearly with the ced of the solvents, opposing effects are suggested by the four $\bar{V}$ values of diphenyldiazomethane; a maximum seems to occur in the plot of Figure 3. The increase in $\bar{V}$ with decreasing q_p (increasing ced) could be due to decreasing electrostriction effects in the solvation shell of **1**. At higher ced values of the solvent (low q_p) a further expansion of the solvent cage of **1** is reversed by the cohesion of the solvent. Why diphenylketene as compared to **1** shows a different solvent dependence of $\bar{V}$ is not clear. Unfortunately, no theory is available which connects the macroscopic solvent parameters $_p$ and ced with microscopic properties of the solvent molecules and their appropriate interactions.

The partial molar volumes of the cycloadducts **3** and **8** show a solvent dependence analogous to that of diphenyldiazomethane, the maximum being somewhat more pronounced. Due to the different solvent dependencies of **2**, **4**, and **5** on one side and **1** and the cycloadducts on the other side, the volumes of reaction, $\bar{V}_R$, have the smallest negative values at intermediate values of the solvent parameters q_p and ced (toluene, chlorobenzene). The small absolute values of $\Delta\bar{V}_R$ measured for three reactions in chlorobenzene are the result of high $\bar{V}$ values of **1** and the cycloadducts in this solvent.

Apart from the solvent effects mentioned above, the average value of $\Delta\bar{V}_R$ = −28 cm^3/mol is close to the volumes of reaction found for two types of [2 + 2] cycloadditions[25,26] while Diels–Alder reactions normally show slightly more negative values ($\Delta\bar{V}_R$ = −30 to −36 cm^3/mol[4]). Thus, the formation of four-, five-, and six-membered cyclic compounds appears to be accompanied by similar volume effects. On this basis $\Delta\bar{V}_R$ for the formation of the cycloadducts **3** and **8** can be split into two terms. About −40 cm^3/mol are due to the formation of the two new σ bonds, whereas a positive contribution of +12 cm^3/mol results from the displacement of solvent molecules from the center of the cyclic compound.

With the aid of the appropriate $\bar{V}$ and ΔV^* values partial molar volumes, $\bar{V}_{TS}$, can be ascribed to the transition states of the 1,3-dipolar cycloadditions of **1** to **2**, **4**, and **5**. The solvent dependence of $\bar{V}_{TS}$ for the reaction **1** + **2** shown in Figure 2 is, admittedly, not a well-defined function of ced. This graph suggests for $\bar{V}_{TS}$ a similar solvent dependence as that observed for the partial molar volumes of **1** and the cycloadduct **3** and which is different from the solvent dependence of $\bar{V}$ of **2**. The solvation of the transition state seems to be governed by the forces that act already on the diphenyldiazomethane molecule in the ground state, but a reorientation in the solvation shell of dimethyl acetylenedicarboxylate must occur when the transition state is reached. The idea that this change of solvation is responsible for the solvent dependence of the rate constant and the volume of activation for the 1,3-dipolar cycloaddition of **1** + **2** is supported by similar volume effects in the above quantities. When the solvent hexane is replaced by acetonitrile the partial molar volume of **2** is diminished by 9.2 cm^3/mol, the rate constant increases with ΔV^*_{ced} = −8.4 cm^3/mol, and the volume of activation ΔV^* increases by 8.7 cm^3/mol. Thus, not an increase in polarity during the activation process with contradictory consequences on k and ΔV^* but rather changes in the partial molar volumes of the reactants allow a satisfactory description of the solvent dependence of k and ΔV^*.

Mechanism of Cycloaddition. Concertedness does not require a precisely synchronous formation of the two new σ bonds; one bond may be established in the transition state to a greater extent than the second bond. The extreme of unequal bond formation would be the two-step process which is characterized by a minimum in the energy profile and thus an intermediate. Numerous mechanistic criteria including stereospecificity, regioselectivity, structure–rate relationships, etc. have been applied to 1,3-dipolar cycloadditions.

Recently, quantum chemical calculations have been used to shed light on the structure of transition states (TS) of cycloadditions. MINDO/3 favors a highly asymmetric TS of the Diels–Alder reaction and a "biradicaloid" intermediate[27] whereas ab initio methods provide a symmetric TS for butadiene + ethylene.[28,29] According to Houk et al.,[30] semiempirical techniques invariably favor the asymmetric TS and ab initio methods the symmetric TS. This dichotomy pertains also to 1,3-dipolar cycloadditions. That of fulminic acid (formonitrile oxide) to acetylene served as a test: MNDO predicts a greatly asymmetric TS on the way to a zwitterionic intermediate;[27] ab initio techniques, up to highly sophisticated ones, indicate the slightly as-

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ynchronous TS (one C–C and one C–O being formed) of a concerted cycloaddition.[31,32] Likewise, the system carbonyl ylide + ethylene passes an asymmetric TS according to MNDO calculations[33] and a fully symmetric one with ab initio calculations.[34] Related to the subject of our study, ab initio calculations furnished for diazomethane cycloadditions to ethylene and acrylonitrile an "early" TS (still weak bonds) of a concerted process.[35]

Thus, it is desirable to employ further *experimental* criteria to the mechanism of 1,3-dipolar cycloadditions. The entropies of activation have often been used, but unfortunately, $\Delta S^{\ddagger}$ amounts to –30 to –40 eu for nearly all types of cycloadditions, concerted or stepwise. A somewhat better situation is encountered with the volume profiles.

Diels–Alder reactions are the best studied examples of concerted $[_{\pi}4_{s} + {}_{\pi}2_{s}]$ cycloadditions.[4,6] Normally their volumes of activation are very close to the volumes of reaction, and both are found to be within the range –30 to –40 cm^3/mol. For most reactions studied these volume data are not too much influenced by the solvent. Only a few examples are known with a wide solvent-induced variation of $\Delta V^{\ddagger}$ (but still fairly constant $\Delta \bar{V}_R$ values.[36,37] For these cases, however, the solvent effects in $\Delta V^{\ddagger}$ do not correlate with any known solvent parameter, especially any polarity parameter.

The concerted $[_{\pi}2_{s} + {}_{\pi}2_{a}]$ cycloaddition of diphenylketene to butyl vinyl ether shares with the Diels–Alder reaction the feature that in most solvents $\Delta V^{\ddagger}$ and $\Delta \bar{V}_R$ are very similar and close to –30 cm^3/mol. In some solvents, however, also some exceptional volume data have been measured.[25] In the best investigated cycloaddition via a zwitterionic intermediate, the reaction of TCNE with enol ethers, $\Delta V^{\ddagger}$ depends highly and regularly on solvent polarity; due to electrostriction of solvent molecules, $\Delta V^{\ddagger}$ shows substantially greater negative values than $\Delta \bar{V}_R$.[23,26]

The 1,3-dipolar cycloadditions **1** + **2**, **4**, **5**, and **9** present novel features. While the average value of $\Delta \bar{V}_R = -28$ cm^3/mol is close to the expected value for the formation of a five-membered ring, the volumes of activation are definitely more positive with an average value of $\Delta V^{\ddagger} = -20$ cm^3/mol. Thus the $\Delta V^{\ddagger}$ values of 1,3-dipolar cycloadditions differ from those of typical volume profiles of [2 + 2] and [2 + 4] cycloadditions.

When the volume profile of the 1,3-dipolar cycloaddition is discussed with the background of all conceivable reaction mechanisms for cycloadditions, i.e., one-step or two-step processes with "early" or "late" transition states, most of the possibilities can be excluded very soon.

Considering the two-step processes first, no experimental support is given for a zwitterionic pathway because even the apparent solvent dependence of $\Delta V^{\ddagger}$ can be traced back to solvent-dependent initial-state partial molar volumes as has been discussed before. With regard to a diradical two-step process, both a very early and a late transition state do not agree with the present data. The experimental value of $\Delta V^{\ddagger} = -20$ cm^3/mol is too negative for a transition state in which the early formation of the first C–C bond occurs. For such a case one expects $\Delta H^{\ddagger} \geq -10$ cm^3/mol.[4,38] If the transition state for the rate-determining elementary step is reached as late as the formation of the second bond, one should find $\Delta V^{\ddagger} \approx \Delta \bar{V}_R$ for all reactions and solvents.

Because $\Delta V^{\ddagger} > \Delta \bar{V}_R$ it is also very unlikely that the present data indicate a transition state which occurs very late during a concerted pathway. Thus a distinction has to be made only between two possibilities: (i) a diradical pathway with a transition state close to the diradical intermediate; (ii) a concerted mechanism with an "early" transition state.

Arguing further solely on the basis of volume profiles, it looks as if two observations support the first possibility. First, in the dimerization of chloroprene the Diels–Alder reaction competes with radical pathways resulting in [4 + 2] and [2 + 2] products. The $\Delta V^{\ddagger}$ values of the diradical processes are more positive by ~9 cm^3/mol than $\Delta V^{\ddagger}$ of the concerted reaction.[39] Because a value of $\Delta V^{\ddagger} = -30$ cm^3/mol is a typical one for Diels–Alder reactions the difference, i.e., ~(–20) cm^3/mol, would justify a diradical pathway for the 1,3-dipolar cycloadditions. Second, experience has shown that the volume of reaction for the formation of one carbon–carbon σ bond, $\Delta \bar{V}_R$(CC), amounts to values between –20 and –15 cm^3/mol. If the transition state of pathway i resembles the diradical intermediate, one could assume $\Delta V^{\ddagger} \approx \Delta \bar{V}_R$(CC).

However, the second possibility of interpretation ii also gains substantial support in this volume based discussion. It had been argued in favor of i, that $\Delta V^{\ddagger}$ receives its main contribution from the formation of *one* carbon-carbon bond. An equally large effect should arise from the initial formation of *two* bonds during a concerted process. In this context one can argue that the formation of each initial bonding gives a contribution of –10 cm^3/mol in $\Delta V^{\ddagger}$.[4] It is therefore not possible to decide between the two alternatives solely on the basis of volume profile considerations.

It has already been mentioned that apart from volume profiles there is overwhelming experimental and theoretical evidence in favor of ii. It is thus reasonable to adopt pathway ii and interpret the obtained volume data.

The average $\Delta V^{\ddagger} = -20$ cm^3/mol for the reaction of diphenyldiazomethane with dimethyl acetylenedicarboxylate could well be the result of an early transition states on the reaction coordinate. It was proposed for Diels–Alder reactions and 1,3-dipolar cycloadditions that the concerted bond-making starts from an orientation complex in which the σ frames of the two reactants occupy parallel planes. A volume of activation of –20 cm^3/mol for the 1,3-dipolar cycloaddition instead of –30 cm^3/mol for a Diels–Alder reaction would correspond to a more loosely bound TS and an increase in the radius of an assumed spherical transition-state complex of $\bar{V}_{TS} = 280$ cm^3/mol by only 0.06 Å. Thus, we regard the concerted mechanism as the one which is in harmony with the volume data as well as with the additional evidence. However, in order to declare this as a rule for 1,3-dipolar cycloaddition reactions, more experimental material on the pressure dependence of this type of reaction is desirable.

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Registry No. **1**, 883-40-9; **2**, 762-42-5; **3**, 31419-01-9; **4**, 623-91-6; **5**, 141-05-9; **6**, 84695-52-3; **7**, 84695-53-4; **8**, 84695-54-5; **9**, 108-31-6; benzophenone hydrazone, 5350-57-2.

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