Reaction Studies at High Pressure. Part I. Activation Volumes of Some [2 + 2] and Dipolar Cycloadditions

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Activation volumes have been determined over the pressure range 0—2 kbar for several [2 + 2] cycloadditions both with concerted and non-concerted mechanisms and also for a 1,3-dipolar cycloaddition. Values of $\Delta V^{\ddagger}$ are found to be large and negative there being little distinction between mechanistic types for the [2 + 2] reactions. The 1,3-dipolar cycloaddition and the dimerisation of dimethylketen show values comparable with those of Diels–Alder reactions. The implications of these findings are discussed.

THE effects of applied pressure on the rates of homogeneous reactions in solution have been extensively studied [1-4] with a view to obtaining the pressure coefficient of reaction velocity, $\partial \ln k/\partial P$ from which the volume change on activation $\Delta V^{\ddagger}$ may be deduced. The sign and magnitude of $\Delta V^{\ddagger}$ may be related to the mechanism of the rate-determining step. Thus, a homolytic bond fission contributes +5 to +10 cm^3 mol^{-1} and bond formation some −5 to −10 cm^3 mol^{-1}.[1] Heterolysis and charge separation in conjunction with solvent properties modify these figures.[5] Among the best data available for cycloaddition reactions are values of $\Delta V^{\ddagger}$ for some Diels–Alder reactions which lie in the range −25 to −35 cm^3 mol^{-1}.[6] This is consistent with a concerted mechanism requiring the simultaneous formation of two covalent bonds in the slow step and is at least twice the value expected for a stepwise reaction. Other evidence, of course, substantiates this interpretation.[7,8] We have now applied this mechanistic probe to the [2 + 2] cycloaddition reactions of diphenylketen, dimethylketen, tetracyanoethylene (TCNE), and diethyl diazodicarboxylate (DAzC) and to a typical 1,3-dipolar cycloaddition (a member of the [2 + 4] family). With one exception, pressure studies on these reactions have not previously been reported.

EXPERIMENTAL

The apparatus used for kinetic measurements at elevated pressures was modified from a design due to Bradley and Owen [9] and consisted of a two-stage vessel with a 50 : 1 intensification ratio between the large and small cylinders (Figure 1). Pressure was applied by a manual hydraulic pump. The reaction space in the small cylinder was provided with a quartz or sapphire window and an aluminised mirror permitting spectrophotometric examination of the cell contents while under pressure. Measurement of cell pressure was achieved by a manganin wire gauge calibrated against the solidification pressure of carbon tetrachloride. The temperature of the vessel was maintained at *ca.* 25 ± 0.5° and monitored by an internal thermocouple. In a typical experiment the reaction mixture, made up to known concentrations of reagents in toluene or dichloromethane, was inserted through the top plug which was closed. After being brought to the desired pressure, the vessel was allowed to stand for a few minutes to permit the dissipation of the heat of compression (not a severe problem in a metal vessel) and absorbance measurements were then taken as a function of time at the appropriate wavelength. Rate constants were calculated in the usual way using a least squares precision routine. Reactions **1**, **2**, and **4** were studied under pseudo-first-order conditions using at least a 10-fold excess of one reactant while observing the concentration of the other.

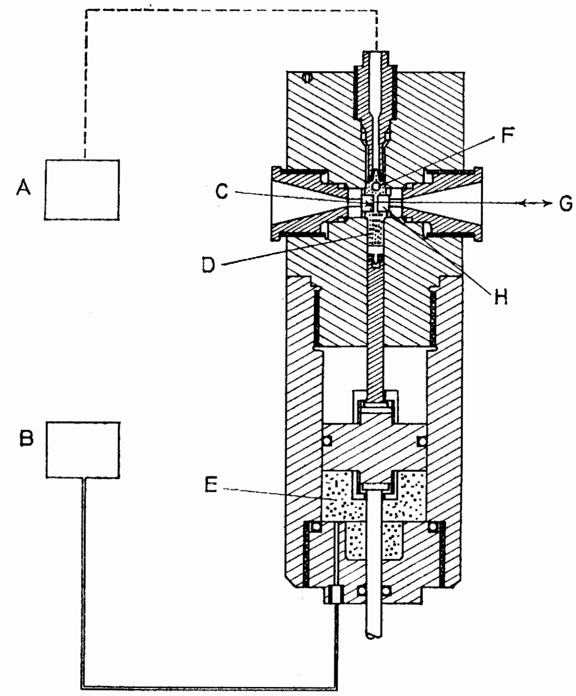

FIGURE 1 High pressure cell for kinetic and other studies: A, potentiometers; B, hydraulic pump; C, mirror; D, liquid at high pressure; E, low pressure oil; F, manganin gauge and thermocouple; G, to spectrophotomer; H, quartz window

Materials.—Toluene and dichloromethane were purified by fractional distillation after drying. Butyl vinyl ether was commercial material distilled before use and kept under nitrogen and similarly for dihydropyran. Diphenylketen

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[2] S. D. Hamann, *Ann. Rev. Phys. Chem.*, 1964, **15**, 349.

[3] K. E. Weale, ' Chemical Reactions at High Pressures,' Spon, London, 1967.

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[6] R. A. Grieger and C. A. Eckert, *J. Amer. Chem. Soc.*, 1970, **92**, 7149; *Amer. Inst. Chem. Engineers J.*, 1970, 766.

[7] R. Huisgen, R. Grashey, and J. Sauer in ' The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, 739.

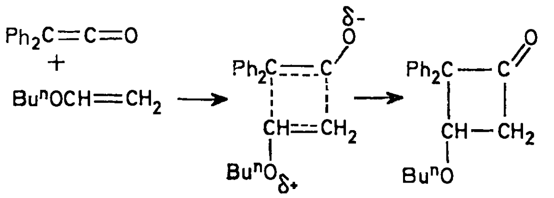
[8] R. B. Woodward and T. J. Katz, *Tetrahedron*, 1959, **5**, 70.

[9] R. S. Bradley, ' High Pressure Physics and Chemistry,' Academic Press, London, 1963; C. C. Bradley, ' High Pressure Methods in Solid State Research,' Butterworth, London, 1969.

was prepared by the method of Sandler and Karo,[10] b.p. 100—102° at 0.2 mmHg, $\lambda_{max.}$ 408 nm ($\varepsilon_{max.}$ 130.2). Dimethylketen was prepared as described previously and the purity determined by g.l.c. estimation of the ethyl isobutyrate formed by the addition of excess of ethanol. The purified material had $\lambda_{max.}$ 380 nm ($\varepsilon_{max.}$ 15.45) at 25° in toluene. Diethyl azodicarboxylate was prepared according to the procedure of Kauer [11] and purified by freezing, m.p. 6°. 5,6-Bisethoxycarbonyl-5,6-diazabicyclo[2.2.1.]-hept-2-ene (IV) was prepared by the reaction of DAzC with cyclopentadiene [12] and had b.p. 119—120° at 0.4 mmHg. After several months at 0° it crystallised and then had m.p. 29—32°. Solutions in toluene were found to be indefinitely stable. TCNE was resublimed before use. Ethoxydihydropyran (IX) was prepared by heating acrolein with a five-fold excess of ethyl vinyl ether in an autoclave at 140 for 12 h. After distillation under reduced pressure, the material was finally purified by preparative g.l.c. (2 m 8% Carbowax 20M on Chromosorb P at 160°).

RESULTS AND DISCUSSION

(i) *Diphenylketen and n-Butyl Vinyl Ether.*—This reaction was first studied by Staudinger and Suter [13] and



(I) (II)

later the identity of the product (II) was established by Hurd and Kimbrough and others.[14,15] The orientation of addition is in accordance with the results of our earlier studies [16] and those of Huisgen and his co-workers [17-21] who measured rates under second-order conditions. Dictated by limitations of pathlength and temperature, our measurements were made using a large excess (10-fold) of vinyl ether such that pseudo-first-order kinetics were observed. The progress of the reaction was followed by observing the disappearance of the colour of diphenylketen. A small correction for self reaction, amounting to *ca.* 5% of the total rate was necessary at the highest pressures.

The addition of ketens to vinyl ethers is believed to be a concerted process. Evidence supporting the mechanism as a $[_{\pi}2_s + _{\pi}2_a]$ cycloaddition [22] comes from the stereospecificity of addition of propenyl vinyl ethers [23-25] and the interpretation of steric factors on rates; [16] rates for addition of propenyl propyl ethers to diphenylketen show k_{cis}/k_{trans} 180.[16,17] This is supported, though the evidence is not unequivocal, by the activation parameters ($\Delta H^{\ddagger}$ 9.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ −40 cal K^{-1} mol^{-1} [17]). Furthermore, the sensitivity of this reaction to solvent change is quite small and comparable with that shown by some Diels–Alder reactions. Thus, $k_{cyclohexane}/k_{MeCN} = 0.006$.[17,26]

Consequently, while the transition state (I) may show some dipolar character it is reasonable to conclude that the two new bonds are formed synchronously. Measured rates are in Table 1.

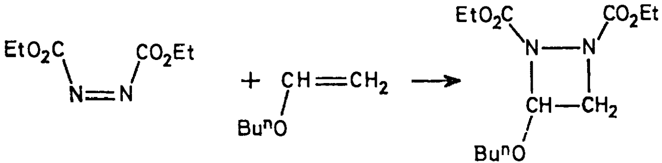
TABLE 1

Rates of reaction of diphenylketen with n-butyl vinyl ether in toluene at 25.5 ± 0.5°: $[Bu^nOCH{=}CH_2]_0 = 0.2145\text{M}$

	$10^3k_1/\text{min}^{-1}$			$10^3k_1/\text{min}^{-1}$	
P/ atm.	Experimental	Calculated *	P/ atm.	Experimental	Calculated
1	6.8 ± 0.3	6.9	780	27.0 ± 0.6	25.2
50	7.3 ± 0.3	7.7	990	31.0 ± 0.3	31.9
90	8.1 ± 0.1	8.3	1 680	47.0 ± 0.6	49.6
200	12.0 ± 0.1	12.3	1 720	53.0 ± 0.6	50.2
600	18.0 ± 0.1	19.8			

* From equation (2), parameters from Table 7.

(ii) *Diethyl Azodicarboxylate and n-Butyl Vinyl Ether.*—The structure of the diazetidine adduct (III) formed in good yield has been established by Koerner von Gustorf and his co-workers and by Firl and Sommer and



(III)

others.[27-29] Again, stereospecificity and activation parameters ($\Delta H^{\ddagger}$ 7—11 kcal mol^{-1}, $\Delta S^{\ddagger}$ −36 to −46 cal K^{-1} mol^{-1}) are those considered typical of concerted cycloadditions while inverse secondary isotope effects at both olefinic termini have been taken to indicate a change in hybridisation at each during progress to the transition state. Rates were measured using excess of vinyl ether and are shown in Table 2.

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[11] J. C. Kauer, *Org. Synth.*, Coll. Vol. IV, 411.

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[14] C. D. Hurd and R. D. Kimbrough, *J. Amer. Chem. Soc.*, 1960, **82**, 1373.

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[17] R. Huisgen, L. A. Feiler, and P. Otto, *Tetrahedron Letters*, 1968, 4485.

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[23] G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Letters*, 1968, 4497.

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[27] E. Koerner von Gustorf, D. V. White, J. Leitich, and D. Henneberg, *Tetrahedron Letters*, 1969, 3113.

[28] J. Firl and S. Sommer, *Tetrahedron Letters*, 1969, 1133, 1137; 1960, 1925, 1929.

[29] R. C. Kerber and T. J. Ryan, *Tetrahedron Letters*, 1970, 703.

(iii) *Dimerisation of Dimethylketen*.—Huisgen[30] has argued cogently as to the concerted nature of this symmetrical cycloaddition on the basis of activation parameters ($\Delta H^‡$ 10.8 kcal mol^{-1}, $\Delta S^‡$ −42 cal K^{-1} mol^{-1}), and lack of solvent sensitivity ($k_{\text{benzene}}/k_{\text{MeCN}}$ 0.066).

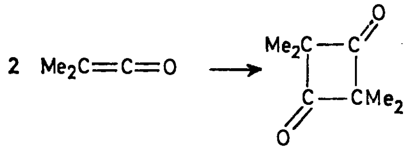


Table 2

Rates of reaction of diethyl azodicarboxylate with n-butyl vinyl ether in toluene at 24.5 ± 0.5°: [$\text{Bu}^n\text{OCH=CH}_2$]$_0$ = 0.4040M

P/atm.	10^4k_1/min^{-1}	
	Experimental	Calculated *
1	1.9 ± 0.03	1.92
180	2.8 ± 0.02	2.70
590	4.7 ± 0.09	5.14
1 320	14.9 ± 0.1	13.3
1 600	17.5 ± 0.2	15.6
2 520	23.2 ± 0.06	22.8

* From equation (2), parameters from Table 7.

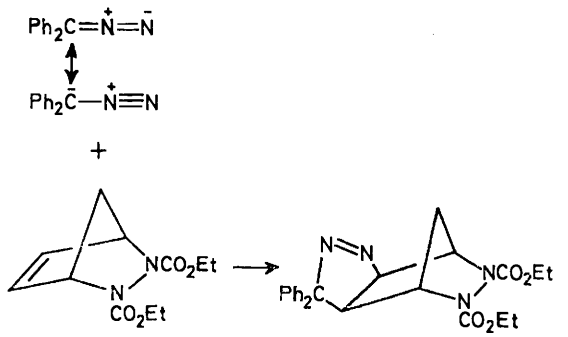
Table 3

Rates of dimerisation of dimethylketen in toluene at 25°

P/atm.	10^2k_2/l mol^{-1} min^{-1}	
	Experimental	Calculated *
1	1.80 ± 0.09	2.2
370	2.95 ± 0.10	3.5
745	6.0 ± 0.30	5.8
930	7.3 ± 0.25	7.4

* From equation (2), parameters from Table 7.

The slowness of the reaction resulted in some instrumental drift which adversely affected the precision of the data. The value of $\Delta V^‡$ (Table 7) is therefore of lower reliability than other data. The rates are given in Table 3.



(IV) (V)

(iv) *Diphenyldiazomethane and* 5,6-*Bisethoxycarbonyl*-5,6-*diazabicyclo*[2.2.1]*hept*-2-*ene* (IV).—This reaction is a typical 1,3-dipolar cycloaddition of the type described and studied by Huisgen and his co-workers[31-33] who have established the structure of the product (V). It was selected for study from many examples of this type of reaction by virtue of the stabilities of the reagents and convenience of rates of addition, determined by the disappearance of diphenyldiazomethane absorbance at 525 nm.

The entropy of activation for this reaction ($\Delta S^‡$ −34 cal K^{-1} mol in dimethylformamide) suggests a crowded transition state. There are many examples of stereospecificity in additions of olefins to 1,3-dipoles and sensitivity to steric hindrance is common (*e.g.* Ph_2CN_2 + acrylate : methacrylate : *trans*-crotonate; $k_{\text{rel}} = 1 : 0.07 : 3.6 \times 10^{-3}$). These factors and the low solvent sensitivity ($k_{\text{benzene}}/k_{\text{MeCN}}$ 0.93 for the above reaction) attest to a concerted mechanism. Pressure effects on rates measured with excess of (IV) are given in Table 4.

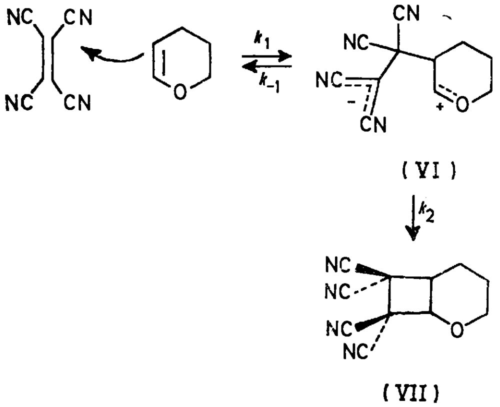
Table 4

Rates of reaction of diphenyldiazomethane with compound (IV) in toluene at 24.5 ± 0.5°: [(IV)]$_0$ 0.3985M

P/atm.	10^3k_1/min^{-1}	
	Experimental	Calculated *
1	2.12 ± 0.006	2.05
390	2.96 ± 0.08	3.26
840	5.56 ± 0.04	5.40
1 160	7.94 ± 0.16	7.46
1 360	9.44 ± 0.29	9.10
1 980	14.40 ± 0.22	14.78
3 040	34.77 ± 0.58	34.00

* From equation (2), parameters from Table 7.

(v) 2,3-*Dihydro*[4H]*pyran and Tetracyanoethylene*.—Vinyl ethers and other electron-rich olefins react with TCNE to give 1 : 1 adducts which have been shown to be cyclobutanes (VII).[34,35] Strong evidence is available indicating that this cycloaddition occurs *via* a zwitterionic intermediate (VI).[36] The system is very favourably disposed for stabilisation of both polar centres and the resulting large increase in dipole moment during the



(VI)

(VII)

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[30] R. Huisgen and P. Otto, *J. Amer. Chem. Soc.*, 1968, **90**, 5342.

[31] R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 633.

[32] R. Huisgen, *Bull. Soc. chim. France*, 1965, 3431.

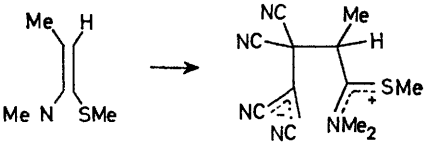
[33] R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, 1961, **73**, 170.

[34] J. D. Roberts and C. M. Sharts, *Org. Reactions*, 1962, **12**, 1.

[35] D. N. Dhar, *Chem. Rev.*, 1967, **67**, 611.

[36] R. Gompper, *Angew. Chem. Internat. Edn.*, 1969, **8**, 312.

initial step results in a high solvent sensitivity;[37,38] $k_{\text{cyclohexane}}/k_{\text{MeCN}} = 3.5 \times 10^{-5}$.[39,40] The addition of 1,2-disubstituted ethylenes such as alkyl *cis*- and *trans*-propenyl ethers to TCNE leads to products with variable loss of stereospecificity (5—15% depending on the solvent)[41] while the isomerisation of the *unchanged* propenyl ethers can only be explained by the assumption of some reversibility of the initial intermediate-forming step.[42] This appears to be important only in solvents of high polarity and we have assumed $k_2 \gg k_{-1}$ in our system. In related reactions, *e.g.* between TCNE and the *SN*-acetal (VIII), the dipolar intermediate (VIIIa) may be isolated at low temperatures.[43] Entropies of activation for these two-step cycloadditions are also strongly negative (—30 cal K^{-1} mol^{-1} for the above reaction) so it is evident that this provides no criterion of mechanism. The values typical of such reactions are evidently due to high ordering of solvent molecules. Pressure studies of the reaction between TCNE and n-butyl vinyl ether in several solvents have been reported by Fleischmann and Kelm and complement our measurements.[44] These are shown in Table 5, and obtained by following the disappearance of TCNE as its charge transfer complex with added hexamethylbenzene.



(VIII) (VIIIa)

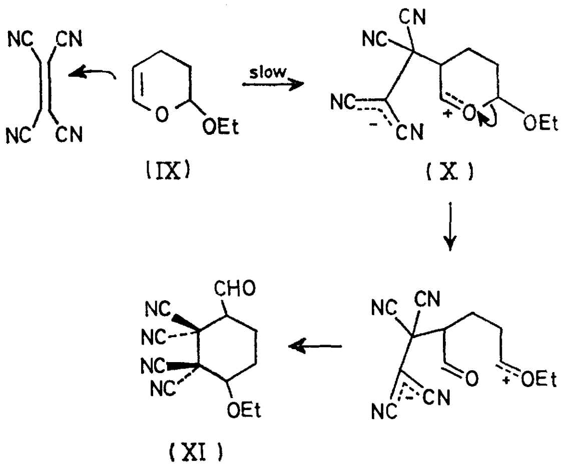
TABLE 5

Rates of reaction of dihydropyran with TCNE in dichloromethane at 27.5°

P/atm.	10^2k_2/mol^{-1} min^{-1} Experimental	Calculated *
1	1.51 ± 0.01	1.53
480	3.55 ± 0.07	3.40
760	5.27 ± 0.2	5.13
930	6.15 ± 0.15	6.51
1 060	7.77 ± 0.3	7.75

* From equation (2), parameters from Table 7.

(vi) 2-*Ethoxy*-2,3-*dihydro*(4H)*pyran and TCNE*.—This is believed to be a further example of a multi-step reaction both for the reasons discussed above and for the additional evidence that the product is not a simple adduct but is formed by rearrangement of the intermediate zwitterion (X) to an aldehyde (XI).[37] This could not arise in a single step. We determined rates of reaction by following the TCNE concentration using the charge-transfer absorption produced by added hexamethylbenzene. This evidently gives a measure of the slow step of the reaction for which there is no evidence as to reversibility. We also measured the rate of product formation using the carbonyl absorption at 1 720 cm^{-1} which was some 40% lower. Evidently the intermediate has a significant lifetime. Rates of reaction are set out in Table 6, and were measured under second-order conditions. Activation parameters for this reaction are $\Delta H^\ddagger$ 8.70 kcal mol^{-1}, $\Delta S^\ddagger$ —31 cal K^{-1} mol^{-1}.



(IX) (X) (XI)

TABLE 6

Rates of reaction of ethoxydihydropyran with TCNE in dichloromethane at 25 ± 0.5°

P/atm.	10^2k_2/l mol^{-1} min^{-1} Experimental	Calculated *
1	3.10 ± 0.07	3.17
430	7.07 ± 0.18	6.65
900	10.1 ± 0.26	13.1
1 040	15.3 ± 0.18	15.3
1 115	17.8 ± 0.27	17.2
1 450	24.9 ± 1.0	24.6

* From equation (2), parameters from Table 7.

Determination of Activation Volumes.—While the concept of a volume of activation arises from transition state theory and is defined by equation (1) a plot of

$$[\partial \ln k/\partial P]_T = -\Delta V^\ddagger/RT \qquad (1)$$

ln k against P is usually strongly curved (Figures 2 and 3). This is because the second derivative, $[\partial^2 \ln k/\partial P^2]_T$, the ' compressibility of the transition state,' is by no means negligible as may usually be assumed for $\partial^2 \log k/\partial T^2 \equiv \Delta C_P$. Various methods for obtaining $\Delta V^\ddagger$ (referred to 1 atmosphere) have been proposed.[45,46]

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[46] J. W. Benson and J. A. Berson, *J. Amer. Chem. Soc.*, 1962, **84**, 152.

The most satisfactory, and simplest to apply which we have adopted throughout expresses the pressure–rate relationship by the power series (2) from which $B = -\Delta V^{\ddagger}/RT$.

$$\ln k = A + BP + CP^2 \qquad (2)$$

A least squares best fit of the data to a quadratic equation was computed and the coefficients A—C determined (Table 7), the activation volumes following from B directly. We have re-evaluated data of other workers shown in Table 7 by the same procedure for comparative purposes. The fitting of a quadratic equation is much more sensitive to experimental error than is a linear fit and consequently the value of $\Delta V^{\ddagger}$ varies somewhat depending on how much of the data is included in the computation. Contributions to the uncertainty of $\Delta V^{\ddagger}$ arise from the intrinsic limits of validity of the treatment given above, uncertainty in individual rate constants, and in the temperature of the pressure apparatus (±0.5°). With reasonable rate data there is probably an uncertainty of ± 5 cm^3 mol^{-1} and it is doubtful whether any significance may be attached to C, related to the compressibility of the transition state.

The most reliable quadratic fit of the data is obtained using measurements at frequent pressure intervals up to perhaps 3 kbar. It seems likely that significant deviations from equation (2) occur at higher pressures, the significance of which is uncertain. We have therefore with few exceptions restricted rate measurements to below 2.5 kbar in this work.

A further correction which has been noted by several authors concerns the fact that equation (1) is correct only if k is expressed in pressure-independent concentration units. No problem arises in first-order reactions but for those of higher order, the compression of the solution must be taken into account. This requires modification of equation (1) to (3), where $\Sigma\nu_i$ is the

$$\partial \ln k/\partial P = -\Delta V^{\ddagger}/RT + \Sigma\nu_i RT\beta \qquad (3)$$

algebraic sum of the coefficients in the stoichieometric equation and β, the compressibility of the medium = $[-\partial \ln V_0/\partial P]$. The correction for toluene and methylene chloride amounts to approximately -2 cm^3 mol^{-1} and so is less than the limits of accuracy in $\Delta V^{\ddagger}$ especially in view of the uncertainty in temperature. This correction is equivalent to calculating second-order rate constants on the basis of concentrations increased by compression of the solution.

TABLE 7

Volumes of activation and related data for cycloaddition reactions

	Reaction	Temp. (°C)	Solvent	A	10^3B	10^7C	$\Delta V^{\ddagger}$/ cm^3 mol^{-1}	s(%)	M.c.c.[a]	Ref.
(i)	$Ph_2C{=}C{=}O + Bu^nOCH{=}CH_2$	25	Toluene	-4.97	2.072	-5.36	-50.7	5.1	0.9952	This work
(ii)	$DAzC + Bu^nOCH{=}CH_2$	25	Toluene	-8.557	1.879	-9.40	-45.9	6.5	0.9934	This work
(iii)	Ph_2CN_2 + (IV)	24.5	Toluene	-6.19	1.231	-1.01	-30.0	9.5	0.9977	This work
(iv)	$Me_2C{=}C{=}O$ dimerisation	25	Toluene	-3.82	1.31	-0.80	-32	5.2	0.9946	This work
(v)	Dihydropyran + TCNE	27.5	CH_2Cl_2	-4.18	1.743	-1.98	-43.0	7.8	0.9363	This work
(vi)	Ethoxydihydropyran + TCNE	25	CH_2Cl_2	-3.452	1.854	-3.03	-45.3	1.9	0.9983	This work
(vii)	Cyclopentadiene + acetylenedicarboxylate	10	EtOAc	1.018	1.214	-1.460	$-28.2(-30.2)$		0.9996	6
(viii)	Isoprene + MA	35	Acetone	1.826	1.448	-1.457	$-36.6(-39)$		0.9998	49
(ix)	1-Methoxybutadiene + MA	35	MeCN	5.287	1.256	-0.086	$-32.6(-32)$		0.9983	47
(x)	2,3-Dimethylbutadiene + butyl acrylate	70	Butyl acrylate	-4.61	1.076	-1.08	$-30.3(-28.6)$		0.9972	48
(xi)	Cyclopentadiene dimerisation	30	BuCl	4.55	0.998	-0.557	$-24.8(-22.2)$		0.9995	50
(xii)	Butyl vinyl ether + TCNE	30	CCl_4	-9.03	1.646	-3.178	$-40.9(-50)$			44
		30	CH_2Cl_2	-2.82	1.566	-1.559	$-39.0(-37)$			44
		30	MeCN	-7.678	1.18	-1.185	$-29.5(-29)$			44

[a] M.c.c. = multiple correlation coefficient, P and P^2 as dependent variables.

This work was in part carried out with the purpose of examining the proposition that volumes of activation may be used as additional criteria of mechanisms for these cycloadditions. The abundance of data for Diels–Alder reactions, (vii)—(xi) (see Table 7) [47–50] leads to the conclusion that the concurrent formation of two bonds in an essentially apolar transition state is accompanied by an activation volume of -25 to -35 cm^3 mol^{-1} or *ca.* -15 cm^3 mol^{-1} per bond. This value is a little larger than previous estimates.[1] We would therefore predict that $\Delta V^{\ddagger}$ for multi-step cycloadditions should be significantly lower than that for concerted reactions, perhaps of the order 15—20 cm^3 mol^{-1}. This is clearly not the case; reactions (v), (vi), and (xii) have activation volumes which are much greater (negative) than the Diels–Alder values. The explanation must therefore lie in contributions from other factors, in particular the effect of solvent organisation or electrostriction by an increasingly dipolar transition state. This is a well known phenomenon and one may, for

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[47] R. A. Grieger and C. A. Eckert, *Ind. and Eng. Chem.* (*Fundamentals*),1971, **10**, 369.

[48] B. E. Poling and C. A. Eckert, *Ind. and Eng. Chem.* (*Fundamentals*), 1972, **11**, 451.

[49] R. A. Grieger and C. A. Eckert, *J. Amer. Chem. Soc.*, 1970, **92**, 2918; *Trans. Faraday Soc.*, 1970, **66**, 2579.

[50] C. Walling and H. J. Schugar, *J. Amer. Chem. Soc.*, 1963, **85**, 607.

example, compare volumes of activation for a ' neutral ' S_N2 displacement such as (4)[51] with a dipole-forming

$$\mathrm{Pr^nI} + {}^{131}\mathrm{I}^- \xrightarrow{\mathrm{MeOH}} \mathrm{Pr^{n131}I} + \mathrm{I}^- \qquad (4)$$
$$\Delta V^\ddagger\ -10\ \mathrm{cm^3\ mol^{-1}}$$

version (5) of the same reaction.[52] Clearly, the high

$$\mathrm{Pr^nI} + \mathrm{NEt_3} \xrightarrow{\mathrm{MeOH}} \mathrm{Pr^n\overset{+}{N}Et_3I^-} \qquad (5)$$
$$\Delta V^\ddagger\ -24\ \mathrm{cm^3\ mol^{-1}}$$

negative values of $\Delta V^\ddagger$ for the polar cycloadditions derives largely from the attractive forces between the transition state and neighbouring solvent molecules. This effect is larger the less polar the solvent[1] as can be seen in the effects of solvent change in reaction (xii). It has been argued that values of $\Delta V^\ddagger$ for these reactions are in fact composite due to the reversibility of the slow step. This is probably true in highly polar solvents but in media which are poorly ion-supporting the amount of regression seems to be negligible. In any event, if k_{-1} were kinetically significant, it would make a positive contribution to $\Delta V^\ddagger$ which would not affect the above argument. The activation volumes of reactions (1) and (2) are notably highly negative, considerably more so than the Diels–Alder reactions. We may postulate that these values arise from the much tighter transition state geometry imposed by the requirement of orthogonal approach of the reagents in order to undergo the symmetry-permitted $[_\pi2_s + {}_\pi2_a]$ addition[22] which is supported on other experimental grounds.[16] In part it may also be due to some dipolar character in the respective transition states (I) and concomitant solvent electrostriction. The value for dimethylketen dimerisation is apparently lower than those for reactions (i) and (ii) and this reaction would be accompanied by a diminution of dipole moment and, presumably, solvation.

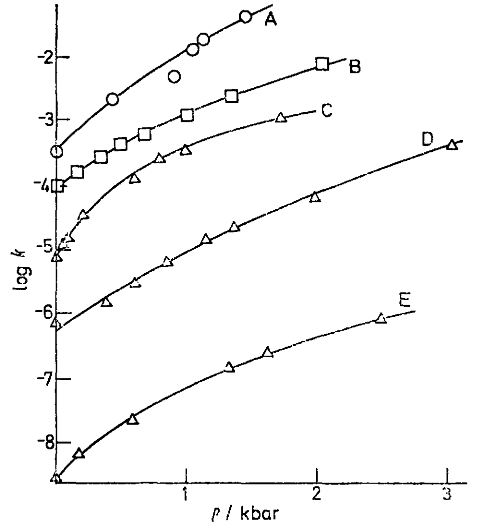

FIGURE 2 Pressure–rate curves for some cycloadditions: A, reaction (vi); B, ref. 48; C, reaction (i); D, reaction (iv); E, reaction (ii)

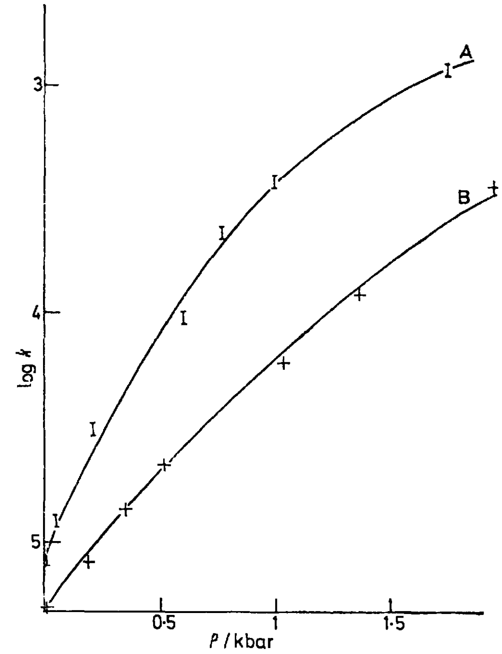

FIGURE 3 Precision of curve-fitting: A, reaction (i); B, ref. 49, reaction (x). Lines defined by equation (2), values of A—C from Table 7

The 1,3-dipolar cycloaddition with $\Delta V^\ddagger$ -30 cm^3 mol^{-1} appears to be similar in nature to a Diels–Alder reaction. The name is misleading in that neither reagents nor products are highly dipolar and the reaction behaves like a neutral $[_\pi2_s + {}_\pi4_s]$ process.

In conclusion, while values of the activation volumes may be plausibly rationalised, they do not appear to yield a clear guide for the assignment of mechanism in the cases considered. It may, indeed, be unsafe to conclude that the same mechanisms operate for the $\mathrm{AlCl_3}$-catalysed and the uncatalysed Diels–Alder reactions, deduced on the basis of the identity of activation volumes.[48] It is possible that this could arise by a fortuitous cancellation of effects, the former being non-concerted. This question might be resolved by variation of the solvent.

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[51] Y. A. Ershov, V. B. Miller, M. B. Neiman, F. S. D'yachkovsky, G. I. Likhtenshtein, and A. A. Opekunov, *Zhur. fiz. Khim.*, 1956, **30**, 784.

[52] A. P. Harris and K. E. Weale, *J. Chem. Soc.*, 1961, 146.