of hexane yielded (±)-D_2-bicyclo[8.8.0]octadec-1(10)-ene (**21**, 120 mg, 4% yield): bp 125-127 °C (0.1 mm); $n^{21}{}_D$ 1.5279; IR (film) 2925, 2850, 1460, 1450, 1264, 731, 705 cm^{-1}; NMR (CCl_4) δ 0.76-1.60 (m, 24 H), 1.60-1.83 (m, 2 H), 1.83-2.20 (m, 2 H), 2.25-2.90 (m, 4 H); UV and NMR spectra are tabulated in Table I and Figures 2 and 3; mass spectrum *m/e* 248 (M^+). Anal. ($C_{18}H_{32}$) C, H.

References and Notes

(1) Presented in part at the 36th Annual Meeting of the Chemical Society of Japan, Osaka, Japan, April 1, 1977, Abstracts II, p 582. A preliminary account of the synthesis of (±)-C_2-bicyclo[10.8.0]eicos-1(12)-ene has been published: M. Nakazaki, K. Yamamoto, and J. Yanagi, *J. Chem. Soc., Chem. Commun.*, 346–347 (1977).

(2) For a review of the stereochemistry of cis and trans cycloalkene, see J. Sicher, *Prog. Stereochem.*, **3**, 210–213 (1962).

(3) For fleeting existences of *trans*-cyclohexene and *trans*-cycloheptene, see E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934–935 (1965); K. Ziegler and H. Wilms, *Justus Liebigs Ann. Chem.*, **567**, 1–43 (1950); A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212–3215 (1953).

(4) Kinetics of racemization: A. C. Cope and B. W. Pawson, *J. Am. Chem. Soc.*, **87**, 3649–3651 (1965); A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *ibid.*, **87**, 3644–3649 (1965).

(5) Optical resolution: A. C. Cope, C. R. Gamellin, and H. W. Johnson, Jr., *J. Am. Chem. Soc.*, **84**, 3191–3192 (1962); A. C. Cope, C. R. Gamellin, H. W. Johnson, Jr., and T. V. van Auken, *ibid.*, **85**, 3276–3279 (1963).

(6) Absolute configuration: A. C. Cope and A. S. Metha, *J. Am. Chem. Soc.*, **86**, 1268–1269 (1964).

(7) Although the bicyclic olefins 14 and 19 can be conventionally called "cis–trans" (geometrical) isomers, the *E*, *Z* system fails to distinguish the "cis"–"trans" "cis"–"trans" pair of olefins **15** and **20**, having identical bridging chains. To circumvent this difficulty, we tentatively propose to use a "symmetry descriptor" in conjunction with Baeyer's system to specify these stereoisomers, e.g., **16** = D_{2h}-bicyclo[8.8.0]octadec-1(10)-ene, **21** = D_2-bicyclo[8.8.0]octadec-1(10)-ene. For the sake of nomenclature consistency in this paper, the convention of "symmetry descriptor" was further extended to distinguish the olefins **17** and **22** with different bridging chains, even through their stereochemistry can be fully specified by the conventional *E*, *Z* system, e.g., **18** = C_{2v}-bicyclo[10.8.0]eicos-1(12)-ene, **23** = C_2-bicyclo[10.8.0]eicos-1(12)-ene. Moreover, freely used in this paper were the more colloquial expressions such as "trans"-[8][8] doubly bridged ethylene for **21** and "cis"-[10][8] doubly bridged ethylene for **18** where the numbers in brackets indicate the numbers of carbon atoms in each of the bridges.

(8) M. Nakazaki, K. Naemura, and S. Harita, *Bull. Chem. Soc. Jpn.*, **48**, 1907–1913 (1975).

(9) M. Nakazaki, K. Yamamoto, and S. Tanaka, *J. Chem. Soc., Chem. Commun.*, 433 (1972); M. Nakazaki, K. Yamamoto, S. Tanaka, and H. Kametani, *J. Org. Chem.*, **42**, 287–291 (1977).

(10) M. Nakazaki, K. Yamamoto, and M. Itoh, *J. Chem. Soc., Chem. Commun.*, 433–434 (1972); M. Nakazaki, K. Yamamoto, and S. Tanaka, *J. Org. Chem.*, **41**, 4081–4086 (1976); M. Nakazaki, K. Yamamoto, M. Itoh, and S. Tanaka, *ibid.*, **42**, 3468–3473 (1977).

(11) Synthetic approaches from the precursors without a "ready-made" double bond confront with much divergent routes owing to the choice of the stage to introduce the double bond.

(12) J. A. Marshall and M. Lewellyn, *J. Am. Chem. Soc.*, **99**, 3508–3510 (1977).

(13) W. Brenner and P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, **5**, 961–962 (1966); *Justus Liebigs Ann. Chem.*, 660–671 (1975).

(14) I. Lalezari and A. Shafiee, *J. Heterocycl. Chem.*, **9**, 1411–1412 (1972).

(15) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677–2678 (1963); E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655–3657 (1968); J. N. Heines, M. J. Peagram, G. H. Whitham, and M. Wrigh, *Chem. Commun.*, 1593–1594 (1968).

(16) J. S. Swenton, *J. Org. Chem.* **34**, 3217–3218 (1969); J. A. Deyrup and M. Betkouski, *ibid.*, **37**, 3561–3562 (1972); Y. Inoue, S. Takamuku, and H. Sakurai, *Synthesis*, 111 (1977).

(17) This light source is reported to exhibit a characteristic energy distribution with maxima at 185 and 254 nm.

(18) G. C. Joshi, N. Singh, and L. M. Pande, *Tetrahedron Lett.*, 1461–1463 (1972).

(19) N. L. Allinger, *J. Am. Chem. Soc.*, **80**, 1953–1955 (1958).

Effect of Pressure on the [2 + 2 → 4] Cycloaddition Reaction of Tetracyanoethylene to Enol Ethers

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Abstract: The general volume profile of the cycloaddition reaction of tetracyanoethylene to different enol ethers was determined. It consists at 25 °C in CH_2Cl_2 solutions of a reaction volume of −30 mL/mol for the formation of the cycloadducts, a reaction volume of −4 mL/mol for the charge transfer complex formed between the educts, and a volume of activation of −36 mL/mol. A variation of the enol ether has no major effect on these volume data. This is in agreement with a mechanism which includes a zwitterionic intermediate and a "dead-end" charge transfer complex.

Introduction

Since their discovery[1] the thermal cycloaddition reactions between enol ethers and tetracyanoethylene (TCNE) have attracted much attention.[2-14] The mechanism of this type of ring formation, which in principle can proceed by three different pathways, was the subject of recent investigations. Several criteria like the steric course of the cycloadditions to cis-trans isomeric enol ethers,[4] the reversibility of the first step,[5] the solvent effect on the rate,[6] and the structure-rate relationship of the enol ether reactant[7] present strong evidence for an at least two-step mechanism involving a zwitterionic intermediate. The proposed intermediate could, in fact, be trapped with alcohols[8] and was amenable to 1,4-dipolar cycloadditions[9] to various heteromultiple bond systems to give six-membered rings.

A study of the pressure dependence of the reaction rate between TCNE and *n*-butyl vinyl ether[10] in different solvents showed that the experimentally observed volume of activation, $\Delta V^{\neq}_{\text{exp}}$, can be split into a part due to bond formation, $\Delta V^{\neq}_{\text{intr}}$, and a solvation term, $\Delta V^{\neq}_{\text{solv}}$. The latter proved to depend strongly on the electrostriction parameter

$$q_P = \frac{3}{(2D+1)^2}\frac{dD}{dP} \quad (D = \text{dielectric constant})$$

of the solvent. Within the Kirkwood formalism this agrees exactly with what one would expect for a highly polar transition state. The calculated dipole moment for the transition state, 15 ± 3 D, points to a zwitterionic structure in which, as opposed to the postulated intermediate, the charges are not yet fully developed.

The present study was undertaken to examine whether $\Delta V^{\neq}_{\text{intr}}$ depends on the structure of the enol ether reactant, while the solvent, and thus to a first approximation $\Delta \bar{V}^{\ddagger}_{\text{solv}}$, is

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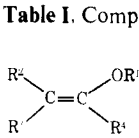
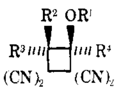
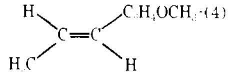
Table I. Compounds


1-8


9-16

	R^1	R^2	R^3	R^4	
1	C_2H_5	H	H	H	**9**
2	C_4H_9	H	H	H	**10**
3	C_6H_5	H	H	H	**11**
4	C_2H_5	CH_3	H	H	**12**
5	C_2H_5	H	CH_3	H	**13**
6	$-(CH_2)_3-$		H	H	**14**
7	C_2H_5	CH_3	CH_3	H	**15**
8	C_2H_5	CH_3	CH_3	C_6H_5	**16**


17

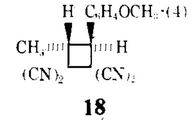
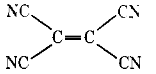
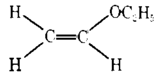
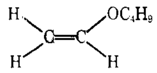
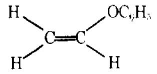
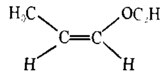
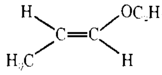
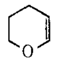
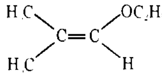
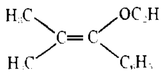
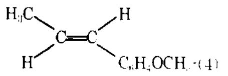
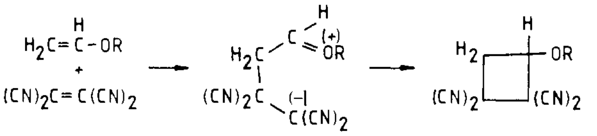

18

Table II. Partial Molar Volumes $\bar{V}_i$ of Compounds and Volumes of Reaction $\Delta\bar{V}_{cyc}$ for the [2 + 2 → 4] Cycloaddition of TCNE to Enol Ethers in CH_2Cl_2 at 25.0 °C

reactant	$\bar{V}_i$, mL/mol	cyclo-adduct	$\bar{V}_i$, mL/mol	$\Delta\bar{V}_{cyc}$, mL/mol
	107.5 ± 0.2			
1 	97.3 ± 0.8	**9**	172.9 ± 0.1	−31.9
2 	129.1 ± 0.4	**10**	207.4 ± 0.2	−29.2
3 	124.2 ± 0.3	**11**		
4 	112.9 ± 0.2	**12**	190.1 ± 0.3	−30.3
5 	115.5 ± 1.0	**13**	193.3 ± 0.1	−29.7
6 	93.1 ± 0.3	**14**	164.5 ± 0.3	−36.1
7 	130.6 ± 0.5	**15**	208.6 ± 0.2	−29.5
8 	189.0 ± 0.1		267.8 ± 0.2	−28.7
17 	151.9 ± 0.2	**18**	232.7 ± 0.4	−26.7

kept constant. With the help of additional data on the partial molar volumes of the compounds and the appropriate reaction



volumes it should be possible to establish the complete volume profile of the cycloaddition reaction.

Experimental Section

Materials. Commercial tetracyanoethylene (TCNE) from Fluka was sublimed at 125 °C and 10^{-3}-10^{-4} Torr before use. The enol ethers, ethyl vinyl ether (**1**), *n*-butyl vinyl ether (**2**), 2,3-dihydro-4*H*-pyrane (**6**), all from Fluka, and 4-*trans*-propenylanisole (anethole, **17**) from Schuchardt were fractionally distilled over $LiAlH_4$. The middle fractions of **1**, **2**, **6**, and **17** boiling at 35.5, 92.8, 84.7, and 113 °C (25 Torr), respectively, were used for all experiments. *cis*- and *trans*-1-ethoxypropene (**4**/**5**), 1-ethoxyisobutene (**7**), 1-ethoxy-1-phenylisobutene (**8**), and phenyl vinyl ether (**3**) were prepared as described elsewhere.[13,14] After fractionation their purity was checked by gas chromatography: **7**, 99.8%; **3**, 97%; **8**, 97%. The mixture of the isomers **4** and **5** was separated by preparative gas chromatography yielding samples of 98.4% (**4**) and 96.7% (**5**) purity (Table I).

The tetracyanocyclobutane derivatives were prepared by adding an excess of the corresponding enol ether to TCNE, in most cases without solvent. After the CT color of the solutions had faded, the excess enol ether was removed in vacuo and the residues were recrystallized from CCl_4-$CHCl_3$-CH_2Cl_2 mixtures. The purity and configuration of the cycloadducts were confirmed by melting points and 60-MHz ^1H NMR spectra.

Dichloromethane (Merck p.a.) was used as a solvent for all density measurements and kinetic runs. Traces of water and alcohol were removed from the solvent using standard procedures. As the density of freshly purified CH_2Cl_2 decreased from $d_{25°C}$ = 1.316 08 to 1.316 00 g/mL within a few days, small amounts of the solvent were purified repeatedly.

Apparatus. Densities of solvent and solutions were determined with the DMA 02C apparatus of the Anton Parr KG, Graz/Austria. A temperature control of ±0.001 °C at 25.0 °C allowed a resolution of $\pm 1 \times 10^{-5}$ g/mL. The temperature was measured with a Hewlett-Packard quartz thermometer 2801A.

The concentration measurements for the kinetic runs were performed on a Cary 15 spectrophotometer at 25.0 ± 0.1 °C. The 10-mm sample cuvette was part of a high-pressure apparatus described earlier.[15] The equilibrium studies were made on a Zeiss DMR 10 photometer using essentially the same pressure equipment.

Results

Molar Volumes. From precision density measurements the apparent molar volumes φ_i of solutes are determined according to

$$\varphi_i = \frac{M_i}{d_0}\frac{(d_i - d_0)}{c_i d_0}1000 \qquad (1)$$

M_i denotes the molecular weight of the solute, d_0 and d_i are the densities of the pure solvent and the solution, respectively, and c_i is the concentration (M). Extrapolating for $c \rightarrow 0$ the partial molar volumes, $\bar{V}_i$, are obtained.

Since the apparent molar volumes of TCNE, all the enol ethers (except **6**), and all the cycloadducts turned out to be independent of the concentration below 0.1 M, the partial molar volumes compiled in Table II are the average values of the apparent molar volumes at low concentrations. For the partial molar volume of **6** an extrapolation was made (0.1 M, φ = 91.7 mL/mol; 0.01 M, φ = 93.0 mL/mol). Above 0.1 M all apparent molar volumes decreased with increasing concentration. The difference between the partial molar volumes of the cycloadduct and the two reactants corresponds to the volume of reaction, $\Delta\bar{V}_{cyc}$, as listed in Table II.

The large decrease in molar volumes associated with the overall cycloaddition reaction permitted a study of the kinetics by following the change in density of the reaction mixture (Figure 1). The rate constants obtained under pseudo-first-order conditions are identical with those measured spectrophotometrically.

When the kinetic runs were extrapolated toward the time of mixing the TCNE and enol ether solutions, no density effects could be detected which are associated with the instantaneous formation of the deeply colored charge transfer complexes between the educts. Even a large excess of the enol ether (in order to increase the CT complex concentration in the equilibrium) did not reveal any measurable volume of reaction. The system TCNE + **3** in CH_2Cl_2 showed the same phenomenon,

Table III. Pressure Dependence of Reaction Volumes $\Delta\overline{V}_{CT}$ for the Formation of Charge Transfer Complexes between TCNE and Enol Ethers in CH_2Cl_2 at 25.0 °C

pressure range, bar	2,3-dihydro-4*H*-pyrane $\Delta\overline{V}_{CT}$, mL/mol	phenyl vinyl ether $\Delta\overline{V}_{CT}$, mL/mol
1-100	−3.5 ± 0.3	−5.7 ± 0.1
100-200	−3.6 ± 0.5	−5.0 ± 0.4
200-300	−3.0 ± 0.3	−5.1 ± 0.3
300-400	−3.4 ± 0.1	−4.8 ± 0.5
400-500	−3.1 ± 0.1	−4.4 ± 0.1

here virtually undisturbed by the extremely slow cycloaddition.

When the cycloaddition was completed, the densities of the solutions corresponded to those calculated solely from the φ_i values of the cycloadduct and the excess enol ether. A complete conversion of the reactants is also observed spectrophotometrically.

CT Complexes. For all TCNE-enol ether reactions studied, the kinetics of the CT complex formation were too fast to be measured by stopped-flow techniques. Also the equilibrium constants of the CT complexes are not known. An attempt to determine K_{CT} and ϵ_{CT} from a Benesi-Hildebrand plot[16] for the CT complex from TCNE and **3** failed. For $[TCNE]_0 \sim 5 \times 10^{-2}$ M and 10^{-2} M $\leq$ [**3**] $\leq$ 0.15 M the CT extinctions were linearly related to the enol ether concentration and the Benesi-Hildebrand plot did not reveal any measurable intercept ($1/\epsilon$). Only for $[\mathbf{3}]_0 \geq 0.15$ M systematic deviations from linearity were observed which might indicate an intercept. However, under the assumptions, given below, the effect of pressure on the CT complex formation and the corresponding volumes of reaction, $\Delta\overline{V}_{CT}$, could be determined directly from the CT absorptions of two representative systems: TCNE + **3** and TCNE + **6**. The effect of pressure on the absorption of the CT complex from TCNE and **3** is solely due to the change of the equilibrium constant and the compressibility of the solution. For the CT complex from TCNE and **6** the decrease in absorption due to the slow cycloaddition was taken into account during the extinction measurement.

With the assumption of all activity coefficients being unity the ratio of equilibrium constants $K_{P(1)}$ and $K_{P(2)}$ of the CT complex at pressures $P(1)$ and $P(2)$ is given by

$$K_{P(1)}/K_P(2) = \frac{x_{P(1)}(a - x_{P(2)})(b - x_{P(2)})}{x_{P(2)}(a - x_{P(1)})(b - x_{P(1)})} \qquad (2)$$

$x_{P(1)}$ and $x_{P(2)}$ are the unknown concentrations of the CT complex at pressures $P(1)$ and $P(2)$, while a and b are the initial concentrations of TCNE and the enol ether. For low CT complex concentrations as compared to a and b eq 2 is converted to

$$\ln (K_{P(1)}/K_{P(2)}) = \ln (E_{P(1)}/E_{P(2)}) + 1/\epsilon_{CT}(1/a + 1/b)(E_{P(1)} - E_{P(2)}) \qquad (3)$$

where $E_{P(1)}$ and $E_{P(2)}$ are the optical densities at pressures $P(1)$ and $P(2)$, respectively, and ϵ_{CT} is the molar extinction coefficient of the CT complex. The optical densities have to be corrected for the compressibilities of the solutions.[17] For high values of ϵ_{CT} and small values of $(1/a + 1/b)$ $(E_{P(1)} - E_{P(2)})$ eq 3 reduces to

$$\ln (K_{P(1)}/K_{P(2)}) = \ln (E_{P(1)}/E_{P(2)}) \qquad (4)$$

from which the volume of reaction, $\Delta\overline{V}_{CT}$, of the CT complex formation is calculated by

$$\Delta\overline{V}_{CT} = RT\frac{\ln (K_{P(1)}/K_{P(2)})}{P(2) - P(1)} \qquad (5)$$

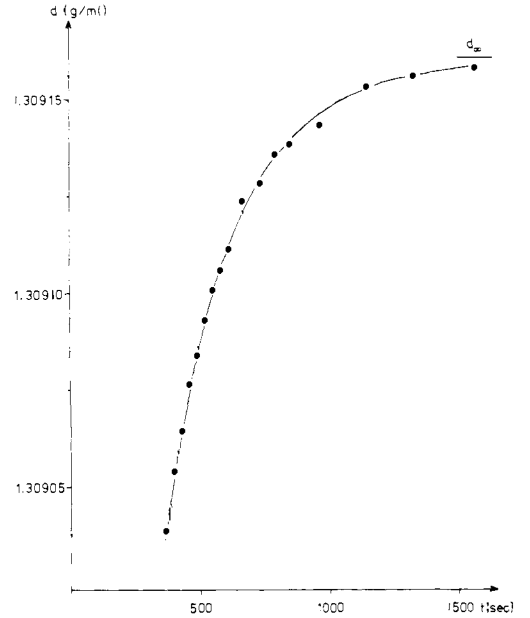


Figure 1. Change in CH_2Cl_2 solution density with time according to the cycloaddition reaction of TCNE ($[TCNE]_0$ = 0.009 496 M) to *n*-butyl vinyl ether ($[\mathbf{2}]_0$ = 0.103 34 M) at 25 °C (±0.001 °C). Calculated rate constant $k = 0.0358$ M^{-1} s^{-1}.

The results within the pressure range of 1-500 bar are listed in Table III.

The neglect of the second term of eq 3 seems to be justified because the experimental $\Delta\overline{V}_{CT}$ values did not depend on the initial TCNE and enol ether concentrations, the numerical value of the term being always less than 10^{-5} per bar if one assumes that $\epsilon_{CT} \geq 1000$ M^{-1} cm^{-1}.

It was noticed that the maximum of the broad and unsymmetrical CT absorption band is markedly red shifted with increasing pressure. An average value for the CT complexes from TCNE and **3** or **6** amounts to $\Delta\lambda_{max}/\Delta P = 1 \times 10^{-2}$ nm bar^{-1}.

Kinetic Measurements. Except for the system TCNE + **17**, which reacts too fast to be studied beyond 300 bar, the reaction rates of TCNE with six different enol ethers were investigated in CH_2Cl_2 solutions at 25.0 °C within the pressure range 1-1000 bar. While the reaction between TCNE and **8** is generally too fast for high-pressure studies at 25 °C with the equipment available, the mixture of TCNE and **3** only shows the fast formation of the intensely colored CT complex without noticeable reaction in 4 days.

The reactions of TCNE with **1**, **4**, **5**, and **7**, respectively, were followed spectrophotometrically at 273 nm, i.e., the change of the TCNE absorption. The cycloadditions of TCNE with **17** and with **6** were recorded at 660 and 485 nm, respectively, observing the decrease of the CT band; here overlapping absorptions prevented the use of the TCNE band. Either the CT absorption of the first four systems is too small or the necessary high concentrations of reactants accelerated the cycloaddition too much. When observing the TCNE absorption, typical educt concentrations were $[TCNE]_0$ = 0.0001-0.0003 M and $[ether]_0$ = 0.002-0.009 M. For TCNE + **17** $[TCNE]_0$ = 0.006-0.009 M and $[\mathbf{17}]_0$ = 0.05-0.08 M were used, while for TCNE + **6** the concentration ranges $[TCNE]_0$ = 0.02 M and $[\mathbf{6}]_0$ = 0.6-0.9 turned out to be advantageous.

Generally a tenfold excess of the enol ether was used in order to establish pseudo-first-order conditions. The corresponding rate constants were calculated using the Guggenheim method. The first 10 min of a run were omitted to allow the heat of compression to dissipate. The experimental second-order rate

Table IV. Pressure Dependence of Reaction Rates k of the [2 + 2 → 4] Cycloaddition of TCNE to Enol Ethers in CH_2Cl_2 at 25.0 °C

P, bar	k, $M^{-1}\,s^{-1}$	P, bar	k, $M^{-1}\,s^{-1}$
	Ethyl Vinyl Ether (**1**)[a]		*cis*-1-Ethoxypropene (**4**)[a]
1	0.0554 ± 0.001	1	0.170 ± 0.004
150	0.0773 ± 0.001	150	0.213 ± 0.011
250	0.0940 ± 0.002	250	0.271 ± 0.011
375	0.111 ± 0.002	375	0.324 ± 0.013
500	0.134 ± 0.003	500	0.425 ± 0.012
625	0.158 ± 0.005	625	0.517 ± 0.014
750	0.190 ± 0.004	750	0.621 ± 0.005
875	0.228 ± 0.008	875	0.767 ± 0.010
		1000	0.893 ± 0.010
	trans-1-Ethoxypropene (**5**)[a]		1-Ethoxyisobutene (**7**)[a]
1	0.145 ± 0.002	1	0.0596 ± 0.0019
100	0.176 ± 0.008	150	0.0848 ± 0.0022
150	0.202 ± 0.005	250	0.101 ± 0.004
250	0.240 ± 0.010	375	0.131 ± 0.004
300	0.260 ± 0.010	500	0.160 ± 0.005
375	0.286 ± 0.010	625	0.190 ± 0.001
500	0.342 ± 0.001	750	0.241 ± 0.009
625	0.421 ± 0.008	875	0.283 ± 0.007
750	0.470 ± 0.016	1000	0.343 ± 0.009
875	0.565 ± 0.012		
1000	0.728 ± 0.017		
	2,3-Dihydro-4*H*-pyrane (**6**)[b]		Anethole (**17**)[b]
1	$(2.40 \pm 0.05) \times 10^{-4}$	1	0.0251 ± 0.006
250	$(3.36 \pm 0.01) \times 10^{-4}$	100	0.0292 ± 0.0005
375	$(3.86 \pm 0.13) \times 10^{-4}$	150	0.0319 ± 0.0010
500	$(4.95 \pm 0.04) \times 10^{-4}$	200	0.0347 ± 0.0005
625	$(5.70 \pm 0.14) \times 10^{-4}$	250	0.0390 ± 0.0012
750	$(7.10 \pm 0.06) \times 10^{-4}$	300	0.0421 ± 0.0004
875	$(8.26 \pm 0.49) \times 10^{-4}$		
1000	$(9.94 \pm 0.08) \times 10^{-4}$		

[a] Change of TCNE absorption. [b] Change of CT complex absorption.

constants, k_{TCNE} and k_{CT}, according to

$$-d[TCNE]/dt = k_{TCNE}[TCNE][ether] \qquad (6a)$$

and

$$-d[CT]/dt = k_{CT}[TCNE][ether] \qquad (6b)$$

are listed in Table IV. The k values proved to be independent of $[ether]_0$ within the range of concentrations applied.

Activation Volumes. From the pressure dependence of the rate constants k_{TCNE}, k_{CT}

$$-RT\frac{\partial}{\partial P}\ln k = \Delta V^{\ddagger}_{exp} \qquad (7)$$

the volumes of activation, $\Delta V^{\ddagger}_{exp}$, were calculated. No effort was made to correct the $\Delta V^{\ddagger}_{exp}$ values for the compressibility of the solvent.

In Figure 2 the pressure dependence of ln k is plotted for three reactions. For TCNE + **6** a linear relation was observed. The results for TCNE + **17** indicate a linear dependence too; however, the pressure range covered in this study is too small to make a definite assignment. All other reactions follow a pattern which is characterized by a pronounced curvature at lower pressures and a linear dependence at higher pressures. None of the commonly used curve-fitting equations describes such a pattern satisfactory. Therefore, the activation volumes were calculated employing the secant method and Table V contains $\Delta V^{\ddagger}_{exp}(1)$ and $\Delta V^{\ddagger}_{exp}(P)$ values which correspond to activation volumes at 1 bar and at higher pressures (linear part). In the case of a curvature the actual $\Delta V^{\ddagger}_{exp}(1)$ values depend critically on the accuracy of the rate constants determined between 1 and 250 bar; a rather large error in $\Delta V^{\ddagger}_{exp}(1)$ is thus to be expected. Therefore, for the reactions TCNE + **1**, **5**, and **7**, which show very similar overall ln k vs. P plots, the same average value of $\Delta V^{\ddagger}_{exp}(1)$ is given.

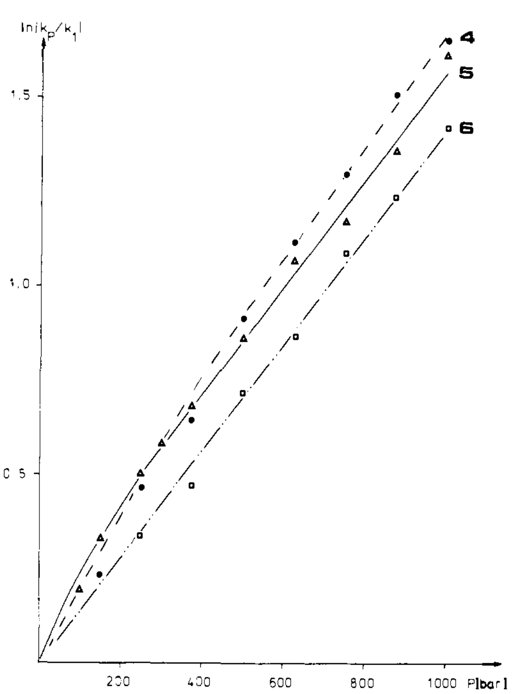


Figure 2. Pressure dependence of experimental rate constants (k_1 at 1 bar, k_P at higher pressures) for the cycloaddition of TCNE to three different enol ethers: - - - - - -, *cis*-1-ethoxypropene (**4**); ——, *trans*-1-ethoxypropene (**5**); - · · · -, 2,3-dihydro-4*H*-pyrane (**6**).

Table V. Experimental Volumes of Activation at 1 bar, $\Delta V^{\ddagger}_{exp}(1)$, and at High Pressures, $\Delta V^{\ddagger}_{exp}(P)$, for the [2 + 2 → 4] Cycloaddition of TCNE to Enol Ethers in CH_2Cl_2 at 25.0 °C

enol ether	$\Delta V^{\ddagger}_{exp}(1)$, mL/mol	$\Delta V^{\ddagger}_{exp}(P)$,[a,b] mL/mol
ethyl vinyl ether (**1**)	−55 ± 5	−35 ± 1 (250)
cis-1-ethoxypropene (**4**)	−50 ± 5	−37 ± 2 (500)
trans-1-ethoxypropene (**5**)	−55 ± 5	−35 ± 3 (250)
1-ethoxyisobutene (**7**)	−55 ± 5	−38 ± 2 (375)
2,3-dihydro-4*H*-pyrane (**6**)	−36 ± 3	−36 ± 3 (1)
anethole (**17**)	−44 ± 4	c

[a] Minimum pressure (in bar) for $\Delta V^{\ddagger}_{exp}(P)$ values in parentheses. [b] Average value for all possible secants within the pressure range and mean deviation. [c] No data available.

Discussion

Volumes of Cycloaddition. The partial molar volumes of the enol ethers and the corresponding cyclobutanes (Table II) confirm two well-known features. First, within a homologous series the addition of a CH_2 group is accompanied by an increase in molar volume of ca. 16 mL/mol. Second, molar volumes are relatively insensitive with respect to isomerism at double bonds.

Independently of the nature of the enol ether, nearly constant volumes of reaction of ca. −30 mL/mol are observed for the cycloadditions (Table II). Thus, one is led to interpret $\Delta\overline{V}_{cyc}$ as being the sum of nearly constant contributions, common to all reactions investigated. To a first approximation the volume of reaction results from the formation of two new carbon-carbon bonds and is influenced by volume effects associated with the ring formation and the changes in solvation due to differences in polarity between educts and product:

$$\Delta\overline{V}_{cyc} = 2\Delta\overline{V}(\text{C-C bond}) + \Delta\overline{V}(\text{ring}) + \Delta\overline{V}(\text{solvation}) \qquad (8)$$

There is indeed a change in polarity comparing the reactant TCNE with its four compensating partial dipole moments and the enol ethers with rather weak dipole moments on one side and the cyclobutane derivatives showing overall dipole moments of about 6 D[6] on the other side. Crude estimates of the upper and lower limits of the accompanying volume effects yield $\Delta\overline{V}$(solvation) = 0 to −5 mL/mol, depending on whether solvation is mostly influenced by the partial CN dipole moments or by the overall dipole moment of the molecule. The ring formation effect is attributed to the displacement of solvent molecules from the inner space of the cyclobutane ring which is too small to accommodate solvent molecules. Comparing the molar volumes of linear and cyclic hydrocarbons, a value of $\Delta\overline{V}$(ring) = +10 to +15 mL/mol is suggested. As a consequence, $\Delta\overline{V}$(C–C bond) amounts to −17 to −23 mL/mol, a range which agrees with a number of findings on C–C bond formation.[18]

Within this crude approximation one can even understand that increasing substitution at the cyclobutane ring with bulky groups causes a slight increase in $\Delta\overline{V}$(ring) and thus the slight increase in $\Delta\overline{V}_{cyc}$ observed experimentally. On the other hand, in a bicyclic compound the $\Delta\overline{V}$(ring) contribution has to be somewhat reduced giving rise to the most negative $\Delta\overline{V}_{cyc}$ value for the reaction TCNE + **6**.

Volume of Charge Transfer Complex Formation. The formation of CT complexes between TCNE and the enol ethers **6** and **3** is accompanied by reaction volumes, $\Delta\overline{V}_{CT}$, of −3.5 and −5.0 mL/mol, respectively (Table III). These values correspond to those measured by Ewald[19] and Nakayama and Osugi[20] for CT complexes of TCNE and various donors. The evaluation of $\Delta\overline{V}_{CT}$ was based on the assumptions that the equilibrium constant of the CT complex is small and that the molar extinction coefficient of the CT complex, ϵ_{CT}, is independent of pressure. According to Hamann and Linton[21] a neglect of pressure effects on ϵ_{CT} may give rise to only small errors within the range of 1–500 bar. Arimoto and Osugi[12] reported equilibrium constants for some TCNE–enol ether complexes with K_{CT} generally less than 1 M^{-1} and $\epsilon_{CT} \geq 2000$ M^{-1} cm^{-1}.

If high enol ether concentrations are used, small intercepts in the Benesi–Hildebrand–Scott plots can be found. However, in accordance with Steiner[13] we ascribe these effects to changes in polarity of the solution rather than to a shift of CT complex equilibrium. Thus, only the limits $K_{CT} \leq 0.3$ M^{-1} and $\epsilon_{CT} \geq$ 800 M^{-1} cm^{-1} for the CT complex of TCNE and **3** can be given; K_{CT} values for enol ethers without aryl substituents are probably smaller. Such K_{CT} and ϵ_{CT} data, however, justify the use of the simple eq 4 in the evaluation of the $\Delta\overline{V}_{CT}$ values. The small K_{CT} as well as $\Delta\overline{V}_{CT}$ values explain why during the precision density measurements no volume effects were found upon mixing the enol ether and TCNE solutions.

Overall Pressure Effects on Cycloaddition Rate Constants. For all reactions studied the rate constants at atmospheric pressure are in excellent agreement with those measured by Steiner and Huisgen.[5,7,13] In this study most of the reactions were followed by the decrease of the TCNE absorption, while Steiner and Huisgen determined the rate constant from the decreasing CT complex absorption. Under pseudo-first-order conditions the simple experimental rate laws given by eq 6a and 6b can be applied and the equivalence of k_{TCNE} and k_{CT} is confirmed.

The following features emerge from the study of the pressure dependence of the rate constants:

(1) Following the progress of the reaction by observing the CT band, ln k_{CT} depends linearly on pressure up to 1000 bar (class A: TCNE + **6**, **17** (?)).

(2) For ln k_{TCNE}, derived from the change of the TCNE absorption, a nonlinear dependence was found in the low pressure range and a linear one at high pressures, i.e., $P \geq 375$ bar (class B: TCNE + **1**, **4**, **5**, **7**).

(3) Except for the reaction TCNE + **17** (see below), both types of curves furnish volumes of activation from the linear portions which are approximately constant, $\Delta V^{\neq}_{exp} = -36 \pm 2$ mL/mol, independent of the enol ether variation. The value $\Delta V^{\neq}_{exp} = -37$ mL/mol found for TCNE + **2**[10] confirms the above average.

It is interesting to note that the reaction between TCNE and **6**, i.e., the reaction with the overall linear ln k_{CT} vs. P dependence, was already investigated. Isaacs and Rannala[22] studied the disappearance of TCNE via its CT complex absorption with added hexamethylbenzene. They observed a nonlinear pressure dependence of ln k. Although they used a quadratic equation for their curve-fitting procedure, resulting in $\Delta V^{\neq}_{P=1} = -43$ mL/mol, their data also permit the drawing of a function which is approximately linear at pressures above 480 bar and curved at lower pressures with volumes of activation which would correspond to class B systems.

Rate Laws. Two questions arise, the first for the origin of the different shapes of the ln k vs. P plots, and the second for the significance of the common value of $\Delta V^{\neq}_{exp} = -36$ mL/mol. Before discussing more complex mechanisms and rate laws as possible sources, it should be mentioned that the pressure-dependent compressibility of the CH_2Cl_2 solutions does not account for the strong curvature observed for class B systems.

Some conceivable mechanisms of cycloadditions are compiled in Table VI. The rate laws derived comply with the simple form of the experimentally observed eq 6a and 6b. In general, the expressions for −d[TCNE]/dt were based on the following assumptions: (a) no cycloreversion takes place, (b) steady-state condition holds for intermediates (Z) and the CT complex. −d[CT]/dt was obtained with the following assumptions: (c) no cycloreversion, (d) steady-state condition for (Z), (e) pseudo-first-order conditions, i.e., −d[E]/dt = 0. The assumptions agree with experimental conditions and observations.

It is tempting to describe the kinetics of the cycloaddition by the simple reaction schemes I and II given in Table VI. On studying the kinetics of the concerted [4 + 2] cycloadditions between various anthracene and maleic anhydride derivatives, Andrews and Keefer[23] pointed out that schemes I and II cannot be distinguished solely by kinetic data. For the case of the Diels–Alder reaction between TCNE and 9,10-dimethylanthracene Kiselev and Miller[24] interpreted apparent negative activation energies in favor of mechanism I ($|-\Delta\overline{H}_{CT}| > \Delta H^{\neq}_{k_2}$). The effect of pressure on the observed rate constants would either amount to $\Delta V^{\neq}_{k_2} + \Delta\overline{V}_{CT}$ or to $\Delta V^{\neq}_{k_2}$ of the cycloaddition step depending on the mechanistic scheme chosen. Apart from other objections, e.g., the neglect of a nonstereospecific path in the reaction of TCNE to enol ethers[4] and the interception of a zwitterionic intermediate,[8] both schemes I and II can be rejected on the basis of the volume data obtained. The reaction volumes for the CT complex formation, $\Delta\overline{V}_{CT}$, and their pressure dependencies are much too small to account for the different volumes of activation at 1 bar of class A and class B reactions, and they do not explain the strong curvature within class B.

In schemes III and IV the formation of one intermediate Z is introduced. Schemes V, VI, and VII account for the observed lack of stereospecificity of the reaction by the introduction of two conformationally different intermediates (Z1 and Z2). III and IV as well as V and VI place the CT complex either in a "dead-end" equilibrium or in an equilibrium preceding the cycloaddition step. Schemes III and V, in which the CT complex is an intermediate, both lead to the conclusion that k_{TCNE} differs from k_{CT}, and may therefore be ruled out as contradicting experiment. The reaction scheme VIII, which holds for

Table VI. Possible Reaction Schemes of Cycloadditions between TCNE and Enol Ethers, Rate Expressions, and Corresponding Experimental Volumes of Activation[a,b]

reaction scheme	$k_{\mathrm{TCNE}}/\Delta V^{\ddagger}_{\mathrm{exp}}$	$k_{\mathrm{CT}}/\Delta V^{\ddagger}_{\mathrm{exp}}$
I $\mathrm{T + E \underset{-1}{\overset{1}{\rightleftharpoons}} CT \underset{-2}{\overset{2}{\rightleftharpoons}} P}$	$\frac{k_1}{k_{-1}}k_2{}^{c}$ $\Delta V^{\ddagger}{}_{k_2} + \Delta\bar{V}_{\mathrm{CT}}{}^{c}$	$\frac{k_1}{k_{-1}}k_2$ $\Delta V^{\ddagger}{}_{k_2} + \Delta\bar{V}_{\mathrm{CT}}$
II $\mathrm{CT \underset{-1}{\overset{1}{\rightleftharpoons}} T + E \underset{-2}{\overset{2}{\rightleftharpoons}} P}$	k_2 $\Delta V^{\ddagger}{}_{k_2}$	k_2 $\Delta V^{\ddagger}{}_{k_2}$
III $\mathrm{T + E \underset{-1}{\overset{1}{\rightleftharpoons}} CT \underset{-2}{\overset{2}{\rightleftharpoons}} Z \underset{-3}{\overset{3}{\rightleftharpoons}} P}$	$k_1\left(1 - \frac{k_{-1}(k_{-2}+k_3)}{k_{-1}(k_{-2}+k_3)+k_2k_3}\right)$ $\Delta V^{\ddagger}{}_{k_1} + \frac{\mathrm{d}}{\mathrm{d}P}\ln f^1(k_i)$	$k_2\frac{k_1}{k_{-1}}\left(1 - \frac{k_{-2}}{k_{-2}+k_3}\right)$ $\Delta V^{\ddagger}{}_{k_2} + \Delta\bar{V}_{\mathrm{CT}} + \frac{\mathrm{d}}{\mathrm{d}P}\ln f^2(k_i)$
IV $\mathrm{CT \underset{-1}{\overset{1}{\rightleftharpoons}} T + E \underset{-2}{\overset{2}{\rightleftharpoons}} Z \underset{-3}{\overset{3}{\rightleftharpoons}} P}$	$k_{\mathrm{TCNE}} = k_{\mathrm{CT}} = k_2\left(1 - \frac{k_{-2}}{k_{-2}+k_3}\right)$ $\Delta V^{\ddagger}{}_{k_2} + \frac{\mathrm{d}}{\mathrm{d}P}\ln f^3(k_i)$	
V $\begin{array}{ccccccc} \mathrm{T+E} & \underset{-1}{\overset{1}{\rightleftharpoons}} & \mathrm{CT} & \underset{-2}{\overset{2}{\rightleftharpoons}} & \mathrm{Z1} & \underset{-3}{\overset{3}{\rightleftharpoons}} & \mathrm{P1} \\ & & & & {\scriptstyle 4}\Big\updownarrow{\scriptstyle -4} & & \\ & & & & \mathrm{Z2} & \underset{-5}{\overset{5}{\rightleftharpoons}} & \mathrm{P2} \end{array}$	$k_1\left(1 - \frac{k_{-1}(k_{-4}a+k_5b)}{k_{-1}(k_{-4}a+k_5b)+k_2(k_3c+k_4k_5)}\right)$ with $a = k_{-2}+k_3 \quad b = k_{-2}+k_3+k_4 \quad c = k_{-4}+k_5$ $\Delta V^{\ddagger}{}_{k_1} + \frac{\mathrm{d}}{\mathrm{d}P}\ln f^4(k_i)$	$k_2\frac{k_1}{k_{-1}}\left(1 - \frac{k_{-2}c}{k_{-4}a+k_5b}\right)$ $\Delta V^{\ddagger}{}_{k_2} + \Delta\bar{V}_{\mathrm{CT}} + \frac{\mathrm{d}}{\mathrm{d}P}\ln f^5(k_i)$
VI $\begin{array}{ccccccc} \mathrm{CT} & \underset{-1}{\overset{1}{\rightleftharpoons}} & \mathrm{T+E} & \underset{-2}{\overset{2}{\rightleftharpoons}} & \mathrm{Z1} & \underset{-4}{\overset{4}{\rightleftharpoons}} & \mathrm{P1} \\ & & & & {\scriptstyle 3}\Big\updownarrow{\scriptstyle -3} & & \\ & & & & \mathrm{Z2} & \underset{-5}{\overset{5}{\rightleftharpoons}} & \mathrm{P2} \end{array}$	$k_{\mathrm{TCNE}} = k_{\mathrm{CT}} = k_2\left(1 - \frac{k_{-2}(k_{-3}+k_5)}{k_{-2}(k_{-3}+k_5)+k_5(k_3+k_4)+k_{-3}k_4}\right)$ $\Delta V^{\ddagger}{}_{k_2} + \frac{\mathrm{d}}{\mathrm{d}P}\ln f^6(k_i)$	
VII $\begin{array}{ccccccc} \mathrm{CT1} & \underset{-1}{\overset{1}{\rightleftharpoons}} & \mathrm{T+E1} & \underset{-2}{\overset{2}{\rightleftharpoons}} & \mathrm{Z1} & \underset{-3}{\overset{3}{\rightleftharpoons}} & \mathrm{P1} \\ & & & & {\scriptstyle 4}\Big\updownarrow{\scriptstyle -4} & & \\ \mathrm{CT2} & \underset{-7}{\overset{7}{\rightleftharpoons}} & \mathrm{T+E2} & \underset{-6}{\overset{6}{\rightleftharpoons}} & \mathrm{Z2} & \underset{-5}{\overset{5}{\rightleftharpoons}} & \mathrm{P2} \end{array}$	$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{T}] = -\frac{\mathrm{d}}{\mathrm{d}T}[\mathrm{CT}] = k_2\left(1 - \frac{k_{-2}a+k_4k_{-6}}{ab-k_4k_{-4}}\right)[\mathrm{T}][\mathrm{E1}] + k_6\left(1 - \frac{k_{-6}b+k_{-2}k_{-4}}{ab-k_4k_{-4}}\right)[\mathrm{T}][\mathrm{E2}]$ with $a = k_{-4}+k_5+k_{-6} \quad b = k_{-2}+k_3+k_4$	

[a] T, E, CT, Z, and P stand for tetracyanoethylene, enol ether, charge transfer complex, zwitterionic intermediate, and cycloproduct, respectively. [b] For definitions of equations see text. [c] Derived from $k_1k_2/(k_{-1}+k_2)$; for the assumption $k_{-1} \ll k_2$ see ref 31.

$$\begin{array}{ccccccc} \mathrm{T+E1} & \rightleftharpoons & \mathrm{CT1} & \rightleftharpoons & \mathrm{Z1} & \rightleftharpoons & \mathrm{P1} \\ & & & & \updownarrow & & \\ \mathrm{T+E2} & \rightleftharpoons & \mathrm{CT2} & \rightleftharpoons & \mathrm{Z2} & \rightleftharpoons & \mathrm{P2} \end{array} \qquad \mathrm{VIII}$$

isomeric cis and trans enol ethers E1 and E2, likewise leads to $k_{\mathrm{TCNE}} \neq k_{\mathrm{CT}}$ and may be ruled out (it was omitted from Table VI because it leads to very complex equations). Moreover, these schemes cannot account for the pressure effects (cf. Table VI). We are therefore left with schemes IV, VI, and VII, in all of which the CT complex is not an intermediate but a "dead end". On considering the effect of pressure, one obtains for all these schemes

$$\Delta V^{\ddagger}{}_{\mathrm{exp}} = \Delta V^{\ddagger}{}_{k_2} + \frac{\partial}{\partial P}\ln f^j(k_i)$$

where $\Delta V^{\ddagger}{}_{k_2}$ is connected with the formation of the intermediate (Z) from the reactants (TCNE and E). $f^j(k_i)$ is an algebraic function of rate constants depending on the mechanistic scheme. Unfortunately, the contribution of $\partial/\partial P$ ln $f^j(k_i)$ to $\Delta V^{\ddagger}{}_{\mathrm{exp}}$ cannot be calculated explicitly. Even for the most simple case,

$$k_2 f^3(k_i) = k_2\left(1 - \frac{k_{-2}}{k_{-2} + k_3}\right) \text{ (scheme IV)}$$

model calculations show that experimental volumes of activation at 1 bar, $\Delta V^{\neq}_{\text{exp}}(1)$, and the curvature of the ln k vs. P plot depend crucially on both the relative values of the rate constants, k_2, k_{-2}, and k_3 at 1 bar and the corresponding pressure dependencies.

If we suppose that the constancy of the volumes of activation which were calculated from the linear portions of the ln k vs. P plots (Table V, third column) is not merely accidental, then we must conclude that for most of the reactions studied the functions $\partial/\partial P \ln f^j(k_i)$ depend strongly on pressure between 1 and ca. 375 bar and reach a constant (or zero) value at higher pressures. Such a pattern is compatible with the complex rate expression for scheme VII, which describes best all experimental facts so far collected for the cycloadditions between TCNE and enol ethers. One also can expect that the individual k_i values within $f^j(k_i)$ depend on the nature of the enol ether with a limiting case $f^j(k_i) = 1$ and $\partial/\partial P \ln f^j(k_i) = 0$ which is probably reached for **6**. Of the cis,trans isomeric enol ethers **4** and **5** the cis isomer **4** shows the smoothest curvature. This fact supports the speculation that the linear pressure dependence of ln k_{CT} for **5** results from the fixed cis configuration.

Experimental Volumes of Activation. It was suggested above that the linear portion of the experimental ln k vs. P plot is associated with the volume of activation, $\Delta V^{\neq}_{\text{exp}}$, for the formation of the intermediate Z (characterized by k_2), this linear dependence being found either at 1 bar or at higher pressures. Such an assignment of a volume of activation to a specific step within a complex mechanism calls for justification and comparison with the expected quantity of $\Delta V^{\neq}_{k_2}$.

The transition states of zwitterion formation involving TCNE and enol ethers generally have large dipole moments (~10 D) as can be deduced from the solvent dependence of these cycloaddition reactions.[6] Thus the overall volume of activation consists of two major contributions.

$$\Delta V^{\neq}_{\text{cyc}} = \Delta V^{\neq}_{k_2} = \Delta V^{\neq}(\text{C-C bond}) + \Delta V^{\neq}(\text{solvation})$$

Herein $\Delta V^{\neq}$(C-C bond) represents the volume effect connected with the formation of the first carbon-carbon bond, while $\Delta V^{\neq}$(solution) originates from the electrostriction of the solvent during the development of the strong dipole of the zwitterion.

The limits of $\Delta V^{\neq}$(C-C bond)[18] are given by ca. −14 and ca. −20 mL/mol, as can be deduced from previous high-pressure studies on the solvent dependence of the reaction TCNE + **2**[10] and the value of $\Delta \bar{V}$(C-C bond) discussed above, respectively. Thus, assuming that all other steps involved in scheme VII contribute only negligible amounts to $\Delta V^{\neq}_{\text{exp}} = -36$ mL/mol, about −20 mL/mol are left for the contribution of electrostriction. Such a value for $\Delta V^{\neq}$(solution) agrees well with corresponding contributions to the volume of activation of Menschutkin reactions,[25] where similar, highly polar transition states are formed.

The large, negative values of −55 mL/mol for $\Delta V^{\neq}(1)$ found for some reactions of Table V are difficult to rationalize. As proposed in scheme VII the interplay of several rate and equilibrium constants may be responsible for these effects.

The constancy of all the $\Delta V^{\neq}_{\text{exp}}(P)$ values of Table V emphasizes the similarity of the transition state properties. Alkyl substitution at the β carbon of the enol ether—the reaction center of the first step of cyclization—neither changes the position of TS_{cyc} on the reaction coordinate nor has any detectable influence on its polarity. Only during the reaction of **17** with TCNE the greater charge separation in the transition state causes a higher dipole moment (14 D)[6] and consequently a more negative $\Delta V^{\neq}$(solvation) contribution.

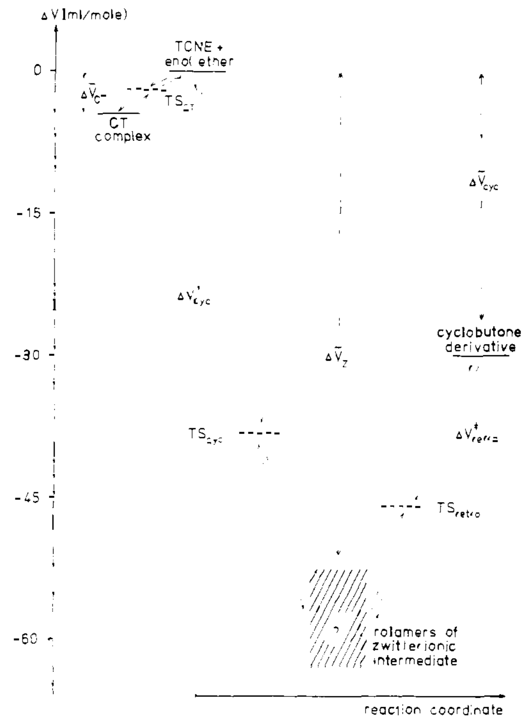


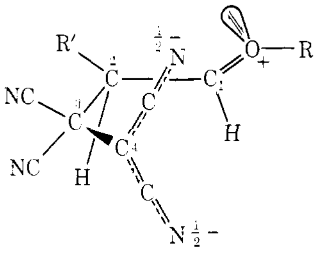
Figure 3. Volume profile for the cycloaddition of TCNE to enol ethers.

Adopting the arguments that $\Delta V^{\neq}(P)$ equals essentially $\Delta V^{\neq}_{k_2}$, these volumes of activation underline that the mechanism of the cycloaddition reactions studied here can only be a two-step process involving a zwitterionic intermediate. For a two-step mechanism with a biradical intermediate definitely smaller values of activation (ca. −15 to −20 mL/mol) are expected. A synchronous formation of both carbon-carbon bonds usually leads to $\Delta V^{\neq}_{\text{exp}}$ being very close to $\Delta \bar{V}_{\text{cyc}}$, although in a few cases more negative values of activation than volumes of reaction were found.[26] In addition, the $\Delta V^{\neq}_{\text{exp}}$ values of concerted processes should be almost independent of the solvent polarity contrary to the experimental findings for the type of cycloaddition studied here.[10]

Volume Profile of the Cycloaddition. Besides the reaction volumes for the overall cycloaddition $\Delta \bar{V}_{\text{cyc}}$, that of CT complex formation, $\Delta \bar{V}_{\text{CT}}$, and the volume of activation for the formation of the intermediate, $\Delta V^{\neq}_{\text{cyc}}$, three quantities are left to establish the complete volume profile of the cycloaddition: the volumes of activation of CT complex formation, $\Delta V^{\neq}_{\text{CT}}$, that of cycloreversion, $\Delta V^{\neq}_{\text{retro}}$, and the reaction volume for the formation of the intermediate, $\Delta \bar{V}_{\text{Z}}$. Accurate data on pressure kinetics for CT complex formation are not known because of the high reaction rate. The limits for $\Delta V^{\neq}_{\text{CT}}$ (0 to −4 mL/mol) can be estimated from $\Delta \bar{V}_{\text{CT}}$ (Figure 3).

Le Noble and Mukhtar[27] have shown that the rate of the reaction between 2-*r*-methyl-3,3,4,4-tetracyano-1-*t*-ethoxycyclobutane and CH_3OH is enhanced by pressure with $\Delta V^{\neq}_{\text{retro}} = -16.7$ mL/mol. If one assumes that during this reaction the opening of the cyclobutane ring is rate determining, the observed overall volume of activation includes at least two major effects. The cleavage of the C-C bond leads to a positive contribution of about +10 to +20 mL/mol depending on how much the transition state TS_{retro} resembles the open-chain zwitterionic intermediate. Obviously, TS_{retro} has such a strong dipolar character that negative volume contributions due to electrostriction predominate. It is most probable that the molar volume of the transition state, TS_{retro}, is considerably smaller than the partial molar volume of the cyclobutane derivative.

The zwitterion from TCNE and enol ethers can be described by formula **19**. The stereochemistry of the trapping reaction with alcohols[8] established the cis or gauche conformation with respect to the 2,3 bond. The gauche conformation would be free of conformational strain at the 2,3 bond; the distance of the charge centers is not noticeably reduced compared with the cisoid conformation. A recent claim to have observed a zwitterion from TCNE and styrene by its UV spectrum[28] was abandoned after studying the ^{1}H and ^{13}C NMR spectra.[29] An X-ray analysis of the stable crystalline zwitterion **20** from benzenesulfonyl isothiocyanate and *N*-isobutenyldimethylamine[30] revealed a structure which likewise demonstrates the strength of intramolecular Coulombic attraction of charge centers.



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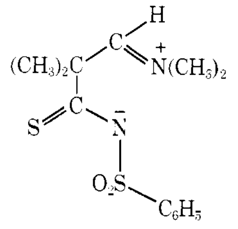

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Starting from the educts the volume of reaction, $\Delta\bar{V}_Z$, for the 1,4-dipolar intermediate can be estimated using an expression analogous to eq 8. According to the preceding discussion $\Delta\bar{V}_Z$(C–C bond) amounts to ca. -20 mL/mol. Based on the proposed structure **19** for Z, Steiner and Huisgen[6] have estimated dipole moments of 17–21 D for the zwitterion. When the value of $\Delta V^{\ddagger}_{k_2}$(solvation) is taken as a reference, the very high dipole moments of the zwitterions lead according to the Kirkwood formalism to $\Delta\bar{V}_Z$(solvation) ≤ -40 mL/mol in CH_2Cl_2 solution. Since the conformation of Z resembles a cyclic structure, a positive contribution of $\Delta\bar{V}_Z$(ring) is possible. However, in toto $\Delta\bar{V}_Z$ can be as low as -60 mL/mol. Osugi et al.[28] deduced also such extremely negative reaction volumes from the pressure dependence of the visible spectra of the TCNE–styrene system. It is worth mentioning that the zwitterion has no fixed conformation. Though for electrostatic reasons the structure **19** is the preferred one, rotations about the C–C bonds are feasible and lead to the reduced stereospecificity of the overall reaction. Different charge separations (dipole moments) of the rotamers of Z can change $\Delta\bar{V}_Z$(solvation) considerably.

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References and Notes

(1) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962); T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961).
(2) R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **8**, 312 (1969).
(3) R. Huisgen, *Acc. Chem. Res.*, **10**, 117, 199 (1977).
(4) R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95**, 5054 (1973).
(5) R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95**, 5055 (1973).
(6) G. Steiner and R. Huisgen, *J. Am. Chem. Soc.*, **95**, 5056 (1973).
(7) R. Huisgen and G. Steiner, *Tetrahedron Lett.*, 3763 (1973).
(8) R. Huisgen, R. Schug, and G. Steiner, *Angew. Chem., Int. Ed. Engl.*, **13**, 80, 81 (1974).
(9) R. Schug and R. Huisgen, *J. Chem. Soc., Chem. Commun.*, 60 (1975).
(10) F. K. Fleischmann and H. Kelm, *Tetrahedron Lett.*, 3733 (1973).
(11) G. Swieton, J. v. Jouanne, and H. Kelm, *Proc. 4th Int. Conf. High Pressure Kyoto*, 652 (1974).
(12) T. Arimoto and J. Osugi, *Rev. Phys. Chem. Jpn.*, **44**, 25 (1974).
(13) G. Steiner, Ph.D. Thesis, University of Munich, 1972.
(14) R. Schug, Ph.D. Thesis, University of Munich, 1976.
(15) F. K. Fleischmann, E. G. Conze, D. R. Stranks, and H. Kelm, *Rev. Sci. Instrum.*, **40**, 1427 (1974).
(16) G. Briegleb, "Elektronen-Donator-Acceptor Komplexe", Springer-Verlag, West Berlin.
(17) Landolt-Börnstein, "Zahlenwerte und Funktionen", Vol. II/1, Springer-Verlag, West Berlin, 1971.
(18) W. J. le Noble, *Prog. Phys. Org. Chem.*, **5**, 207 (1967).
(19) A. H. Ewald, *Trans. Faraday Soc.*, **64**, 733 (1968).
(20) T. Nakayama and J. Osugi, *Rev. Phys. Chem. Jpn.*, **45**, 79 (1975).
(21) S. D. Hamann and M. Linton, *Aust. J. Chem.*, **28**, 701 (1975).
(22) N. S. Isaacs and E. Rannala, *J. Chem. Soc., Perkin Trans. 2*, 1555 (1975).
(23) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 6284 (1955).
(24) V. D. Kiselev and J. G. Miller, *J. Am. Chem. Soc.*, **97**, 4036 (1975).
(25) H. Hartmann, H. Kelm, and G. Rinck, *Z. Phys. Chem. (Frankfurt am Main)*, 44, 335 (1965).
(26) R. A. Grieger and C. A. Eckert, *Trans. Faraday Soc.*, **66**, 2579 (1970).
(27) W. J. le Noble and R. Mukhtar, *J. Am. Chem. Soc.*, **97**, 5938 (1975).
(28) M. Nakahara, Y. Tsuda, M. Sasaki, and J. Osugi, *Chem. Lett.*, 732 (1976).
(29) M. Nakahara, Y. Uosaki, M. Sasaki, and J. Osugi, in press.
(30) E. Schaumann, A. Röhr, S. Sieveking, and W. Walter, *Angew. Chem., Int. Ed. Engl.*, **14**, 493 (1975).
(31) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).