The Effect of Pressure on the [2 + 2 → 4] Cycloaddition of Diphenylketen to Enol Ethers

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The volume profiles for the [2 + 2] cycloaddition reactions between diphenylketen and butyl vinyl ether, 2-methoxypropene, and 2,3-dihydro-4H-pyran, respectively, have been determined. For the first example a wide range of solvents was studied. The Kirkwood theory seems to be not fully adequate for the description of the solvent effects found for the rate constant and especially for the partial molar volumes. Solvent cohesive energy densities offer an alternative description. In most solvents the volumes of reaction and the volumes of activation are similar in magnitude and support a concerted mechanism for the cycloaddition.

The cycloadditions of ketens to olefins to give cyclobutanones were discovered by Staudinger and Suter.[1] The last twenty years have witnessed a renaissance of keten chemistry, concerning both preparative and mechanistic aspects.[2,3] The high stereospecificities in the additions of diphenyl- and dimethyl-keten to *cis,trans* isomeric enol ethers [4] suggest a concerted pathway. The structure–rate relationship on variation of the ketenophile and the medium-range influence of solvent polarity on the rate of diphenylketen cycloaddition [5] favour concerted, but not synchronous formation of the two new σ-bonds.

[2 + 2] Cycloadditions are forbidden to be concerted by orbital symmetry.[6] How is it possible to get round this obstacle? Ketens are heteroallenes and possess two π-bonds. A diagonal attack of the π-orbitals of the ketenophile onto the electron-deficient orbital of the carbonyl carbon atom as well as on the terminal carbon atom of the keten [4] would constitute a $[_\pi 2_s + _\pi 2_s + _\pi 2_s]$ process which is symmetry-allowed to be concerted. A second possibility is the allowed $[_\pi 2_s + _\pi 2_a]$ cycloaddition in which the CC double bond of the keten functions as an antarafacial unit and the electrophilic carbonyl orbital is engaged in a secondary orbital interaction in the transition state.[7]

These two concerted pathways are hard to distinguish. Both of them are in accord with unique features of keten cycloadditions. Ketens with two different substituents furnish the sterically less advantageous cyclopentadiene adduct.[8-10] Furthermore, *cis*-alk-1-enyl ethers add diphenylketen more than 100-fold faster than do the *trans*-isomers,[4,11] and the combination of rate and stereochemical data in the cycloadditions of alkylphenylketens to *cis,trans* isomeric enol ethers allows conclusions on the transition-state geometry.[12]

Keten cycloadditions to enamines, the most electron-rich alkenes, exceed all others in rate.[5] Two mechanistic pathways have been demonstrated for the reaction of N-isobutenyl-pyrrolidine and dimethylketen.[13a] The one with the higher effect of solvent polarity on the rate is the formation of a zwitterion. Highly electron deficient ketens like bis(trifluoro-methyl)keten afford methyleneoxetans with enol ethers, besides cyclobutanones; the addition to the C=O bond probably occurs *via* a zwitterionic intermediate.[13b]

SCF perturbation theory allowed a successful analysis of the concerted keten cycloadditions.[14] However, MO considerations also led to an alternative model which involves a zwitterionic intermediate with homoallyl resonance.[15] Thus, with various mechanisms under discussion, the application of new diagnostic criteria is highly desirable.

The present investigation of [2 + 2] cycloadditions of diphenylketen to enol ethers was undertaken to elucidate the volume profiles and their solvent dependences.

Experimental

Compounds.—Diphenylketen was prepared in good yield by a Wolff rearrangement of azibenzil [16] or from diphenylacetyl chloride and triethylamine.[17] Analytical and spectroscopic data ensured the structure and purity of the product (Found: C, 86.3; H, 5.3. Calc. for $C_{14}H_{10}O$: C, 86.6; H, 5.2%), b.p. 115 °C at 2 Torr. Under dry nitrogen diphenylketen can be stored in the refrigerator for several months, although some oligomerization takes place. Butyl vinyl ether, b.p. 94—95 °C, and 2,3-dihydro-4H-pyran, b.p. 85—86 °C, were purchased from Fluka and fractionally distilled over $LiAlH_4$ before use. 2-Methoxypropene, b.p. 34—35 °C, was prepared from acetone dimethyl acetal and purified by fractional distillation over $LiAlH_4$.

The cycloadducts, 3-butoxy- and 3-ethoxy-2,2-diphenyl-cyclobutanone as well as 8,8-diphenyl-2-oxabicyclo[4.2.0]-octan-7-one, closely corresponded to the description given elsewhere.[18] The cycloadduct of diphenylketen and 2-methoxypropene could not be isolated. A previous study of the reaction of 2-ethoxypropene and diphenylketen indicated that the cycloadduct is the primary product; however, ring opening to the β-diphenylacetylated enol ether is fast.[18]

The solvents used were of analytical grade (Fluka and Merck). In addition they were carefully purified because of the high reactivity of the keten towards various impurities. Dichloromethane and carbon tetrachloride were washed with aqueous H_2SO_4 and NaOH followed by pure water. Subsequently they were fractionated over P_2O_5. Chlorobenzene and benzonitrile were also distilled over P_2O_5, while $LiAlH_4$ was used for toluene, benzene, and n-hexane. After distillation all solvents were further purified by chromatography using Al_2O_3. Finally, all solvents were distilled from diphenylketen under nitrogen. The solutions were prepared and stored in a glove box.

Contrary to the behaviour in all other solvents used and despite intensive purification, soon after preparing a solution of diphenylketen in n-hexane a precipitate appeared, a phenomenon which has also been previously observed.[19] It is probably a mixture of oligomers and diphenylacetic anhydride; the highest mass peak, m/e 212, is that of diphenylacetic acid and the i.r. bands at 1 820 and 1 750 cm^{-1} are indicative of the anhydride. The low carbon content (Found: C, 75.8; H, 5.15%) suggests some autoxidation products.

Table 1. Partial molar volumes, $\bar{V}_i$, of reactants and products of three cycloaddition reactions at 25.0 °C

Solvent	Diphenylketen $\bar{V}$/cm³ mol⁻¹	Butyl vinyl ether $\bar{V}$/cm³ mol⁻¹	3-Butoxy-2,2-diphenyl-cyclobutanone $\bar{V}$/cm³ mol⁻¹	3-Ethoxy-2,2-diphenylcyclo-butanone $\bar{V}$/cm³ mol⁻¹	2,3-Dihydro-4H-pyran $\bar{V}$/cm³ mol⁻¹	8,8-Diphenyl-2-oxabicyclo-[4.2.0]octan-7-one $\bar{V}$/cm³ mol⁻¹	2-Methoxy-propene $\bar{V}$/cm³ mol⁻¹
n-Hexane		131.0 ± 0.4	271.8 ± 0.7				
Cyclohexane	180.2 ± 0.8	132.8 ± 0.1	281.7 ± 0.7				
Toluene	174.9 ± 0.8	128.5 ± 0.3	274.4 ± 0.1	238.4 ± 0.4	90.8 ± 0.3	234.6 ± 0.4	95.0 ± 0.5
Benzene	171.8 ± 0.6	129.4 ± 0.7	278.2 ± 3.2				
Dichloromethane	170.8 ± 1.2	129.6 ± 0.3	274.2 ± 0.1		92.1 ± 0.6	237.7 ± 0.5	
Chlorobenzene	175.1 ± 2.8	127.7 ± 0.4	276.4 ± 0.2	239.1 ± 0.3			
Benzonitrile	160.1 ± 0.9	125.7 ± 0.2	275.4 ± 0.2	239.8 ± 0.3			

After filtration the hexane solution could be used for kinetic runs; precision density measurements, however, were impossible.

Apparatus.—The u.v.–visible spectra of the compounds were recorded with a Zeiss DMR 10 spectrophotometer. I.r. and ¹H n.m.r. spectra were obtained by employing a Beckman IR 4240 or a Varian A 60 or XL 100 instrument, respectively. Precision densities of solutions were determined with a Paar DMA O2C system. The course of the reactions was followed spectrophotometrically with either a Cary 15 or a Zeiss PMQ II instrument, both being equipped with high-pressure attachments as described before.[20]

During kinetic runs the temperature was kept at 25.0 ± 0.1 °C. Density measurements at 25.0 °C, however, required a temperature constant to ±0.002 °C which was controlled by a Hewlett–Packard quartz thermometer 2801 A.

Results

Molar Volumes.—For solutions below 0.1M the apparent molar volumes of the reactants and products proved to be independent of the concentration. The partial molar volumes listed in Table 1 are therefore the average values of the low concentration apparent molar volumes.

Because of the unidentified precipitate in the hexane solution of diphenylketen and the instability of the diphenylketen–2-methoxypropene cycloadduct, the corresponding partial molar volumes could not be determined. Since the kinetics of formation of the latter compound show complex behaviour towards the end of the reaction, we failed to calculate the volume of reaction and thus the partial molar volume of the cycloadduct from the time-dependent density of the reacting solutions. As 3-butoxy-2,2-diphenylcyclobutanone could only be used as an oily raw material in the precision density measurements, it was desirable to check its partial molar volumes by comparison with a homologous pure compound. Therefore the partial molar volumes of the pure 3-ethoxy-derivative in three solvents are added to Table 1. The difference of 36.3 ± 0.7 cm³ mol⁻¹ is a typical incremental value when going from C_2H_5 to the homologous C_4H_9 derivative.[20]

Rate Constants.—The cycloaddition reactions of diphenyl-keten to the enol ethers are conveniently followed by monitoring the decrease of the keten absorption, A, at 400 nm. On using an at least ten-fold excess of the enol ether, one obtains linear plots of $\ln(A_t - A_\infty)$ versus time for three half-lives in the cases of butyl vinyl ether and 2,3-dihydro-4H-pyran. The pseudo-first-order rate constants were calculated by employing the Guggenheim method. Deviations from pseudo-first-order behaviour within the first half-life were observed only

for the reaction of 2-methoxypropene; thus, rate constants were calculated from initial slopes. It could be established by i.r. spectroscopy that here also the cyclobutanone is first formed and decomposes afterwards.

Despite the purification of reactants and solvents and careful handling a slow background loss of diphenylketen could not be totally suppressed. Fortunately, the background reaction(s) proved to be reproducible and the consumption of diphenylketen could be approximated by a first-order rate law. Assuming parallel reactions, the rate constants k' of cycloadditions are given by equation (1) where k_{obs} is the

$$k' = k_{obs} - k_b \qquad (1)$$

observed overall rate constant and k_b that of the background reaction. It is obvious that k_b has to be determined separately for all conditions (solvent, temperature, pressure). Normally k_b did not exceed 10% of k_{obs}, and only for the slow reaction with 2,3-dihydro-4H-pyran did k_b reach *ca.* 20% of k_{obs}. The second-order rate constants, k, of cycloaddition in different solvents at 25.0 ± 0.1 °C and within the pressure range 0.1—125 Mpa are compiled in Table 2.

The pressure dependence of k is given by equation (2) where

$$\partial \ln k / \partial P = -\Delta V^{\ddagger} / RT \qquad (2)$$

$\Delta V^{\ddagger}$ is the experimental volume of activation. The terms $n\kappa RT$ used in connection with equation (2) amount only to about half of the error in $\Delta V^{\ddagger}$. Thus no compressibility corrections were made.

For most of the reactions investigated the integrated form of equation (2) can be approximated by a linear function: $\ln(k_P/k_{P=1}) = a + bP$. In these cases $\Delta V^{\ddagger}$ was calculated for all possible pairs, k_{P_i}, P_i and k_{P_j}, P_j, and the average values of $\Delta V^{\ddagger}$ together with the average deviations $\sum_n |\Delta V^{\ddagger} - \Delta V_n^{\ddagger}|/n$ are given in Table 3. The only two reactions which show a marked curvature of their ln k *versus* P plots are those of 2,3-dihydro-4H-pyran and butyl vinyl ether in toluene. Here the functions $\ln(k_P/k_{P=1}) \equiv f_n(P)$ with $f_2(P) = a + bP + cP^2$, $f_3(P) = a + bP/(c + P)$, $f_4(P) = a + c(1 - e^{-Pb})$ were employed. Within experimental error identical results for $\Delta V^{\ddagger}$ were obtained from $f_2(P)$, $f_3(P)$, and $f_4(P)$. It is interesting to note that no curvature was detected when these two reactions were investigated in benzene which normally is expected to have similar solvation properties. For the reaction of 2-methoxypropene a linear relation of ln k *versus* P was found in toluene.

The unusual behaviour of the low-pressure rate constants for the reaction diphenylketen + butyl vinyl ether in chlorobenzene is probably due to unidentified background reactions. The upper errors limits given for $\Delta V^{\ddagger}$ in Table 3 are justified in view of the background reactions.

Table 2. Solvent- and pressure-dependences of rate constants of cycloaddition reactions of diphenylketen to three different enol ethers at 25.0 ± 0.1 °C

Diphenylketen + butyl vinyl ether

n-Hexane		Cyclohexane		Carbon tetrachloride	
P/MPa	$10^4 k$/l mol^{-1} s^{-1}	P/MPa	$10^4 k$/l mol^{-1} s^{-1}	P/MPa	$10^4 k$/l mol^{-1} s^{-1}
0.1	0.53 ± 0.07	0.1	0.37 ± 0.04	0.1	0.83 ± 0.07
20	0.61 ± 0.06	10	0.41 ± 0.04	15	0.97 ± 0.07
30	0.78 ± 0.12	20	0.46 ± 0.02	30	1.22 ± 0.04
50	0.94 ± 0.05	30	0.49 ± 0.03	50	1.53 ± 0.01
75	1.21 ± 0.30	50	0.66 ± 0.02	75	2.21 ± 0.04
100	1.45 ± 0.01			100	2.95 ± 0.28

Toluene		Benzene		Dichloromethane	
P/MPa	$10^4 k$/l mol^{-1} s^{-1}	P/MPa	$10^4 k$/l mol^{-1} s^{-1}	P/MPa	$10^4 k$/l mol^{-1} s^{-1}
0.1	1.86 ± 0.06	0.1	3.45 ± 0.24	0.1	15.88 ± 0.17
10	2.38 ± 0.03	10	3.76 ± 0.05	10	17.01 ± 0.54
20	2.83 ± 0.03	20	4.53 ± 0.26	20	21.70 ± 1.82
30	3.22 ± 0.10	30	5.59 ± 0.11	30	22.83 ± 1.21
50	4.48 ± 0.08	40	6.10 ± 0.14	50	29.68 ± 1.18
75	6.23 ± 0.23	50	8.66 ± 0.76	75	39.69 ± 0.80
100	7.61 ± 0.27	70	11.42 ± 0.07	100	51.05 ± 0.68
125	9.75 ± 0.42	100	20.02 ± 1.69	125	64.59 ± 0.24

Chlorobenzene		Benzonitrile	
P/MPa	$10^4 k$/l mol^{-1} s^{-1}	P/MPa	$10^4 k$/l mol^{-1} s^{-1}
0.1	4.91 ± 0.27	0.1	22.13 ± 1.50
10	4.87 ± 0.24	10	24.86 ± 1.59
20	5.60 ± 0.02	20	28.55 ± 1.67
30	5.63 ± 0.24	30	29.20 ± 0.32
50	7.77 ± 0.23	50	35.93 ± 0.35
75	11.63 ± 1.04	75	43.84 ± 0.25
100	15.14 ± 0.32	100	55.26 ± 0.48

Diphenylketen + 2,3-dihydro-4H-pyran

Toluene		Dichloromethane	
P/MPa	$10^4 k$/l mol^{-1} s^{-1}	P/MPa	$10^4 k$/l mol^{-1} s^{-1}
0.1	0.175 ± 0.021	0.1	0.85 ± 0.02
15	0.196 ± 0.028	20	1.19 ± 0.07
30	0.307 ± 0.012	30	1.49 ± 0.25
50	0.411 ± 0.016	50	1.66 ± 0.28
75	0.628 ± 0.021	75	2.46 ± 0.16
100	0.854 ± 0.022	100	3.13 ± 0.40
125	1.027 ± 0.014	125	4.28 ± 0.08

Diphenylketen + 2-methoxypropene

Toluene		Dichloromethane	
P/MPa	$10^4 k$/l mol^{-1} s^{-1}	P/MPa	$10^4 k$/l mol^{-1} s^{-1}
0.1	2.42 ± 0.09	0.1	31.0 ± 2.0
10	2.70 ± 0.11	10	35.6 ± 1.1
20	3.87 ± 0.35	20	39.7 ± 0.9
30	4.11 ± 0.34	30	44.7 ± 1.6
50	5.49 ± 0.41	50	58.6 ± 4.2
75	8.85 ± 0.71	75	76.8 ± 1.1
100	13.44 ± 0.78	100	118.8 ± 7.6

Table 3. Volumes of reaction, ΔV_R, and volumes of activation, $\Delta V^{\ddagger}$, measured at 25 °C for three diphenylketen + vinyl ether cycloadditions

Solvent	Butyl vinyl ether		2,3-Dihydro-4H-pyran		2-Methoxypropene
	ΔV_R/cm^3 mol^{-1}	$\Delta V^{\ddagger}$/m^3 mol^{-1}	ΔV_R/cm^3 mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
n-Hexane		-28 ± 6			
Cyclohexane	-31.3 ± 1.0	-26 ± 4			
Toluene	-29.0 ± 0.9	-52 ± 7	-31.1 ± 0.9	-50 ± 7	-43 ± 8
Benzene	-23.0 ± 3.3	-44 ± 7			
Dichloromethane	-26.2 ± 1.2	-29 ± 5	-25.2 ± 1.4	-32 ± 6	-31 ± 3
Chlorobenzene	-26.4 ± 2.8	-30 ± 6			
Carbon tetrachloride		-32 ± 2			
Benzonitrile	-10.4 ± 0.9	-22 ± 3			

Discussion

Solvent Dependence of Partial Molar Volumes.—The partial molar volumes, $\bar{V}_i$, of butyl vinyl ether, diphenylketen, and 3-butoxy-2,2-diphenylcyclobutanone were determined in various solvents convering a wide range of solvent properties. The values of $\bar{V}$ for butyl vinyl ether and 2,3-dihydro-4H-pyran agree with those previously reported.[21,22]

From the solvent dependence of the partial molar volumes, Grieger and Eckert calculated approximate dipole moments of the solutes employing Kirkwood's theory.[23] This theory predicts an electrostriction of the solvent due to the dipole moment of the solute molecule, with the consequence that its partial molar volume decreases with an increasing electrostriction parameter, $q_p = \partial[(\varepsilon - 1)/(2\varepsilon + 1)]/\partial P$, of the solvent. The opposite trend, however, is found within the partial molar volumes of both butyl vinyl ether and diphenylketen. The largest molar volumes are observed in hexane (q_p 24.3 × 10^{-12} cm^2 dyn^{-1}) and cyclohexane (q_p 16 × 10^{-12} cm^2 dyn^{-1}) whereas in benzonitrile (q_p 1.8 × 10^{-12} cm^2 dyn^{-1}) the smallest molar volumes are encountered. The partial molar volume of the cyclobutanone shows no systematic variation with the solvent. Obviously, the solvent dependences of the three molecules investigated cannot be determined by electrostatic (dipolar) solvent–solute interactions. This is quite remarkable in view of the small, but certainly not negligible, dipole moments of 1.76, 1.25, and 3.02 D (benzene; 25 °C) measured for the keten, butyl vinyl ether, and the cycloadduct, respectively.[5]

Dack has pointed out that the cohesive energy densities (c.e.d.), and internal pressure (P_i) of liquids can determine the solvent dependence of partial molar volumes, especially in the case of nonpolar solutes.[24] Calculations of Whalley also demonstrate the influence of internal pressures. Even for very polar molecules the contributions to $\bar{V}$ arising from electrostriction due to dipole as well as quadrupole moments and from the internal pressure of the solvent may be of the same order of magnitude.[25]

Figure 1 shows that there is indeed a good linear correlation between the c.e.d.s of the solvents [26] and the partial molar volumes of butyl vinyl ether and diphenylketen. An increase in c.e.d. from 216 (hexane) to ca. 500 MPa (benzonitrile) reduces $\bar{V}$ of butyl vinyl ether and diphenylketen by 6 and ca. 20 cm^3 mol^{-1}, respectively. The effect encountered here for diphenylketen is in the same order of magnitude (but reverse sign) as the one found for the solvent dependence of activation volumes of reactions passing highly polar transition states.[22,27] A simple qualitative explanation for such a decrease in $\bar{V}$ may be that the cavity for the solute collapses with increasing c.e.d. of the solvent. A more detailed explanation, however, cannot be given so far, since the constituents of c.e.d. and P_i of a solvent on a molecular basis are not sufficiently understood.[24] Moreover, the lack of data on intermolecular solvent–solute interactions as well as on the shape of dissolved molecules (intrinsic part in $\bar{V}$) prevent a calculation of partial molar volumes from first principles.

No systematic solvent dependence of $\bar{V}$ of 3-butoxy-2,2-diphenylcyclobutanone is observed. This may be the result of two opposing effects. Because this molecule has the highest dipole moment of those calculated, electrostriction of the solvent is expected to decrease $\bar{V}$ in the order benzonitrile $<$ ... $<$ hexane. In approximately the same order of solvents a decreasing c.e.d. allows for larger cavities. The subtle balance of different effects which determine $\bar{V}$ can be seen when the partial molar volumes of the cyclobutanone in hexane and cyclohexane are compared. Despite similar values of c.e.d., P_i, q_p, etc. of both solvents a difference of 10 cm^3 mol^{-1} in $\bar{V}$ is observed. Probably geometric factors, concerning the packing of open-chain and cyclic molecules, determine this difference.
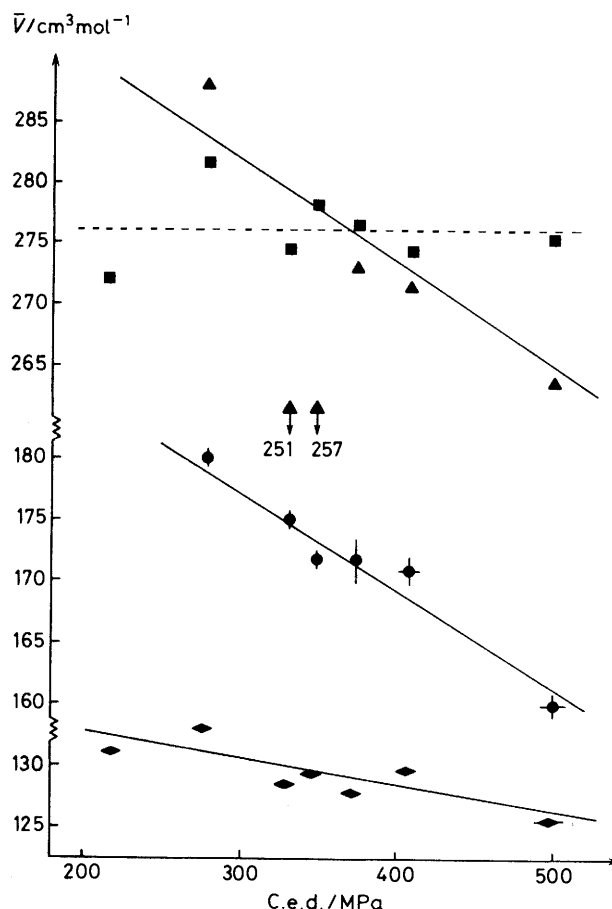

Figure 1. Dependence of the partial molar volumes of butyl vinyl ether (♦), diphenylketen (●), the transition state (▲), and 3-butoxy-2,2-diphenylcyclobutanone (■) on c.e.d.s of the solvent

Because of very similar P_i and c.e.d. values for the solvents used in the present study no experimental distinction can be made of which parameter allows a better description of the variation of the partial molar volumes. In protic solvents like H$_2$O and alcohols which have very different P_i and c.e.d. values, diphenylketen reacts very fast, with anhydride and ester formation.

Volumes of Reaction.—The volumes of reaction, $\Delta \bar{V}_R$, given in Table 3, are the differences between the partial molar volumes of the cycloadducts and those of the reactants. The solvent dependence of $\Delta \bar{V}_R$ for the cycloaddition of diphenylketen to butyl vinyl ether is thus determined by the solvent dependence of the appropriate $\bar{V}$ values. Therefore the remarkable increase of $\Delta \bar{V}_R$ from -31 cm^3 mol^{-1} in cyclohexane to -10 cm^3 mol^{-1} in benzonitrile is primarily the consequence of a 20 cm^3 mol^{-1} difference in $\bar{V}$ of diphenylketen in the two solvents. To our knowledge such a drastic solvent effect on the volume of reaction has not yet been reported for a cycloaddition reaction.

Apart from solvent effects, $\Delta \bar{V}_R$ is the sum of two contributions. Ca. -40 cm^3 mol^{-1} are due to the formation of two new carbon–carbon bonds. A positive term of ca. 10 cm^3 mol^{-1} originates from the displacement of solvent molecules from the inner region of the newly formed ring system.[28]

With one exception so far found for a [4 + 6] cycloaddition [29] the values of $\Delta \bar{V}_R$ for Diels–Alder reactions range from -30 to -38 cm^3 mol^{-1} and are essentially independent
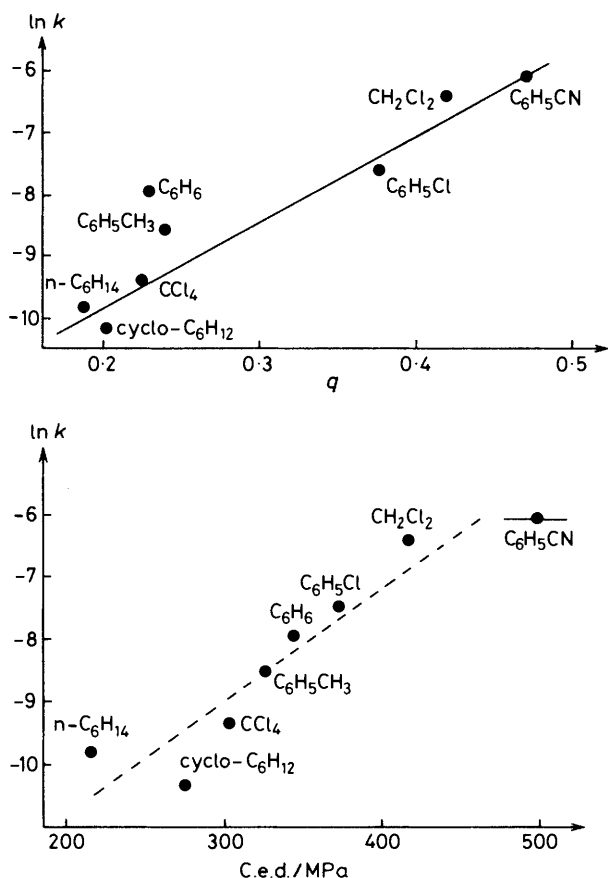
Figure 2. Dependence of rate constants for the cycloaddition of butyl vinyl ether to diphenylketen at 25.0 °C on the solvent polarity, $q = (\varepsilon - 1)/(2\varepsilon + 1)$ (top) and c.e.d.s (bottom)

of the solvent.[30,31] In dichloromethane solution the volume of reaction for the formation of 3,3,4,4-tetracyano-1-butoxycyclobutane from tetracyanoethylene (TCNE) and butyl vinyl ether amounts to -29 cm^3 mol^{-1}.[21] In most of the solvents listed in Table 3, a similar value is found for the formation of the butoxycyclobutanone derivative. Two representative values for the reaction of 2,3-dihydro-4H-pyran to diphenylketen suggest that the structure of the enol ether has no major effect on ΔV_R.

Solvent Dependence of Rate Constants at Ambient Pressure.
—The rate constants for the cycloaddition of diphenylketen to butyl vinyl ether given in Table 2 depend noticeably on the solvent. When cyclohexane is replaced by benzonitrile as solvent the rate constant measured at 1 bar increases by a factor of 60, in excellent agreement with the factor 63 reported previously for measurements at 31.4 °C.[5] According to Kirkwood theory a linear correlation between $\ln k$ and the solvent polarity, $q = (\varepsilon - 1)/(2\varepsilon + 1)$, is expected if the solvent dependence results from a polarity change during the formation of the transition state. Figure 2 shows that there is indeed a qualitative trend of this type. The quantitative correlation, however, is poor. On using the empirical E_T scale for solvent polarity,[32] one achieves a better correlation confirming the earlier report. However, the high reactivity in benzene and toluene as compared to the six other solvents is still found in the E_T correlation.

The log k values in four aromatic solvents fit a linear correlation (r^2 0.98) with Hammett's σ_p parameters. We wonder if

ρ $+0.78$ really means that the solvent acts as an electrophilic reaction partner. The relation based on four points may be coincidental.

When, according to Koppel and Palm,[33] the electrophilic solvation parameter, E, is introduced [equation (3) where E_T, $Y = q = (\varepsilon - 1)/(2\varepsilon + 1)$, $P = (n^2 - 1)/(n^2 + 1)$ are the Dimroth parameter, the solvent polarity, and the solvent pol-

$$E = E_T - 25.57 - 14.39\ Y - 9.08\ P \qquad (3)$$

arizibility, respectively], a better description of the solvent dependence of all rate constants is achieved. Neglecting the nucleophilic solvation parameter[33] for the solvents used and normalizing the experimental rate constants to the value measured in cyclohexane, equation (4) is obtained.

$$\ln(k/k_{C_6H_{12}}) = -3.06 + 4.27\ Y + 9.56\ P + 0.51\ E \qquad (4)$$

Table 4 demonstrates the excellent agreement between experimental and calculated rate constants. Despite its success we prefer to discuss equation (4) only in a qualitative manner because it is expected that the three-parameter equation (4) is superior to the linear correlations with q or E_T. The parameters E_T and Y indicate prevailing dipolar solvent–solute interactions and thus one can conclude that the transition state of the cycloaddition is more polar than the ground state. Further stabilization of the transition state may originate from induced dipole moments in the surrounding solvent molecules (P term).

An alternative and independent way to describe the solvent dependence of the present rate constants is based on solvent c.e.d.s. Figure 2 shows that the correlation of $\ln k$ with c.e.d. is basically not worse than the correlation with q. The rate of cycloaddition is enhanced by increasing c.e.d.s. The ' pseudo volume of activation ', $\Delta V^{\ddagger}_{c.e.d.}$, which can be calculated from Figure 2 amounts to $ca.$ -45 cm^3 mol^{-1}. It is more negative than most of the volumes of activation obtained from applying external pressures (Table 3). Wong and Eckert have used c.e.d.s to predict the kinetic solvent effects on two Diels–Alder reactions within the framework of regular solution theory.[34] For these reactions which pass nonpolar transition states, $\Delta V^{\ddagger}_{c.e.d.}$ values of -20 to -25 cm^3 mol^{-1} are found. These values are more positive by $ca.$ $+10$ cm^3 mol^{-1} than the volumes of activation from high-pressure work.[23,35] In contrast to these data Neuman found no correlations between c.e.d.s and $\ln k$ values for decompositions of free-radical initiators.[36]

Does the concept of cohesive energy densities or that of equation (4) with basically electrostatic interactions adequately describe the solvent dependence of rates in the present system? The question is connected with the extent of polarity increase during the activation process of the reaction of diphenylketen and butyl vinyl ether. The [2 + 2] cycloadditions of TCNE to enol ethers pass a highly polar transition state, as rate ratios of k(benzonitrile)/k(cyclohexane) 1 800 for butyl vinyl ether, 4 900 for ethyl isobutenyl ether, and 9 100 for (E)-anethole testify.[37] The ratio of 60 observed for diphenylketen + butyl vinyl ether indicates a moderate solvent effect. Of course, the cycloaddition of diphenylketen (μ 1.76 D) starts at a slightly higher polarity level than that of TCNE (μ 0 D).

On the other hand, the rate constants of Diels–Alder reactions show solvent effects which rarely exceed a factor of 10;[38] this indicates little polarity difference between reactants and transition state. Amongst the Diels–Alder reactions, only those with TCNE or 4-phenyl-1,2,4-triazoline-3,5-dione as dienophiles reach a medium sized solvent effect;[38] however, for these electron-deficient dienophiles log k values do not give linear relations with E_T or other functions of solvent polarity.

Table 4. Comparison of experimental and calculated rate constants for the cycloaddition reaction of diphenylketen to butyl vinyl ether at 25.0 °C

| | $-\ln k$ | | | | |
Solvent	Found	Calculated	E^a	Y^a	P^a
Cyclohexane	10.20	9.72	0.00	0.254	0.257
n-Hexane	9.84	10.09	0.00	0.229	0.229
Carbon tetrachloride	9.39	9.40	0.00	0.291	0.274
Toluene	8.58	8.55	1.13	0.315	0.292
Benzene	7.97	8.18	1.93	0.299	0.295
Chlorobenzene	7.61	7.74	0.00	0.607	0.306
Dichloromethane	6.44	6.35	2.68	0.726	0.255
Benzonitrile	6.11	6.10	0.82	0.890	0.308

^{a} Parameters E, Y, and P according to equation (4), see text.

If within the concept of c.e.d.s about half of the $\Delta V^{\ddagger}_{c.e.d.}$ value of diphenylketen + butyl vinyl ether is due to nonpolar solvent–solute interactions only a solvent effect of ca. 5 would remain for electrostatic interactions. We must leave the question open.

Volumes of Activation.—Table 3 gives $\Delta V^{\ddagger}$ -29 ± 2 cm³ mol⁻¹ for the cycloaddition of diphenylketen to butyl vinyl ether in five (C_6H_{14}, C_6H_{12}, CH_2Cl_2, C_6H_5Cl, CCl_4) out of eight solvents. The more positive value in benzonitrile, $\Delta V^{\ddagger}$ -22 cm³ mol⁻¹, correlates with the small negative $\Delta \bar{V}_R$ in this solvent. The small volume of activation, $\Delta V^{\ddagger}$ -7.5 ± 1 cm³ mol⁻¹, for the [6 + 4] cycloaddition of tropone to cyclopentadiene was traced to the unusually small $\Delta \bar{V}_R$ of -4.3 ± 1 cm³ mol⁻¹.[29]

A closer inspection of Figure 1 suggests that the solvent dependence of $\bar{V}^{\ddagger}$ resembles much more that of the two reactants in the ground state, $\bar{V}$ of butyl vinyl ether and diphenylketen, than the solvent dependence of the product. Figure 1 uses the partial molar volumes rather than $\Delta V^{\ddagger}$ and $\Delta \bar{V}_R$. Admittedly, the $\bar{V}$ values of 3-butoxy-2,2-diphenylcyclobutanone don't provide a good linear relation with c.e.d.s of the solvents. Nevertheless, the parallel effects of solvent c.e.d. on $V^{\ddagger}$ and $\bar{V}$ (reactants) implies no major changes in the type of solvent–solute interaction during activation. The possibility that part of the solvent influence on the rate constants is nonpolar in nature cannot be excluded.

The two extremely negative $\Delta V^{\ddagger}$ values found in benzene and toluene (Figure 1), -44 and -52 cm³ mol⁻¹, respectively, are the result of extraordinarily low partial molar volumes in the transition state; the $\bar{V}$ values of reactants and cycloadduct are normal in these solvents. The reason for this drastic lowering of $\Delta V^{\ddagger}$ in benzene and toluene is not known, and it offers little consolation that the data agree well with $\Delta V^{\ddagger}$ -50.7 cm³ mol⁻¹ reported earlier by Isaacs and Rannala[39] for the same reaction in toluene. The assumption of a charge transfer complex of the aromatic hydrocarbons with the transition state is somewhat arbitrary and an extra contribution to $\Delta V^{\ddagger}$ of -20 cm³ mol⁻¹ would be unreasonably large for charge transfer complexation.[40] It should be emphasized, however, that the rate constants in benzene and toluene are unusually high and constitute the largest deviation from the linear relation of $\ln k$ and q in Figure 2.

Some $\Delta V^{\ddagger}$ values for the reactions of diphenylketen with 2,3-dihydro-4H-pyran and 2-methoxypropene in Table 3 suggest that the structure of the enol ether has no major effect on the $\Delta V^{\ddagger}$ data. Values in toluene of -50 and -43 cm³ mol⁻¹ underline the special role of the aromatic solvent.

Mechanism of Cycloaddition.—The general pathways conceivable for cycloadditions are the two-step reactions *via* a diradical or zwitterionic intermediate and the one-step

mechanism in which the formation of the two new σ bonds is concerted, but not necessarily synchronous. In the transition state of the two-step process *via* zwitterion the full charge separation has not yet been achieved. On the other hand, unequal bond formation in the transition state of the concerted mechanism may also change the extent of charge separation. The key feature is the location of the transition state on the reaction co-ordinate. According to often confirmed expectations, the late transition state of the two-step process is structurally related to the high-energy intermediate, whereas the generally early transition state of the concerted process is more reactant-like. An especially lucid example of [2 + 2] and [4 + 2] cycloadditions of polycyanoethylenes[41] may be quoted here.

For a diradical pathway a modest solvent dependence (the polarity of the reactants may have changed somewhat in the late transition state) and $\Delta V^{\ddagger}$ ca. -15 to -20 cm³ mol⁻¹ are anticipated. In our opinion the solvent effect and the size of the negative $\Delta V^{\ddagger}$ values of the diphenylketen reaction are too large.

Reactions with a large increase of polarity in the activation process are characterized by a large influence of the solvent on the rate constant as well as on $\Delta V^{\ddagger}$. The highly polar transition states of the [2 + 2] cycloadditions of TCNE to enol ethers and of the Menschutkin reaction belong to this class. The moderate influence of solvent polarity and a $\Delta V^{\ddagger}$ value which is for the majority of solvents almost constant are hardly compatible with a zwitterionic intermediate in the present [2 + 2] cycloaddition. There are even hints that the exceptional $\Delta V^{\ddagger}$ values in two aromatic hydrocarbons and the solvent dependence of the rate constant stem partially from nonpolar solute–solvent interactions.

The Koppel–Palm treatment of the high solvent dependence found for the [2 + 2] cycloaddition of TCNE + divinyl ether revealed a negligible influence of the electrophilic solvation power E and of the polarizability P; the purely electrostatic effect $Y = (\varepsilon - 1)/(2\varepsilon + 1)$ is controlling.[42] In the present case the influence of P matches that of Y and that of E is noticeable.

The comparison of the rate and volume data with those of the Diels–Alder reaction as the prototype of concerted cycloaddition is useful. Both negative and solvent-independent $\Delta V^{\ddagger}$ values are a common feature; generally the $\Delta V^{\ddagger}$ of Diels–Alder reactions are -33 to -38 cm³ mol⁻¹[30] more negative than those of the present investigation (-29 cm³ mol⁻¹). On the other hand, the solvent effects of most Diels–Alder reactions are smaller and can hardly be correlated with solvent polarity. A novel feature of our reaction is the strong solvent dependence of the partial molar volumes of diphenylketen itself and its transition state.

In conclusion, despite some anomalies, the volume and rate data are consistent with a concerted, but not synchronous,

pathway for the diphenylketen cycloadditions. Of course, our results do not help in the subtle distinction between the $[_\pi 2_a + _\pi 2_s]$ mechanism with its orthogonal arrangement of the reactant π-systems in the orientation complex[7] and the $[_\pi 2_s + _\pi 2_s + _\pi 2_s]$ pathway with its diagonal attack on the ketenophilic π-system.[4]

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