Pressure and Solvent Effects on the Cycloaddition Reactions between Substituted Nitrosobenzenes and Butadiene Derivatives

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The cycloaddition reactions of 2,3-dimethylbutadiene with 4-chloro-1-nitrosobenzene and 4-ethoxy-1-nitrosobenzene and of cyclopentadiene with 4-chloro-1-nitrosobenzene were investigated as a function of temperature, solvent, and pressure. Rate constants, activation parameters, and volumes of reactions were evaluated. The data support a one-step mechanism for the cyclizations.

FOLLOWING the initial formulation of the synthetic principle describing the Diels–Alder reaction,[1] this method for ring formation has gained exceptional importance. Three possible mechanisms for these processes can be conceived, as shown in Figure 1. For the so-called (4 + 2) cycloadditions the reaction paths involve either two steps, *via* a biradical (A) or a zwitterionic intermediate (C), or synchronous ring formation (B). Woodward and Hoffmann[2] proposed orbital-symmetry rules according to which thermal (4 + 2) cycloadditions should proceed by synchronous bond formation.

Violations of the rules can be expected when the electron distribution creates substantial polarity as for instance in the (2 + 2) cycloaddition between tetracyanoethylene and enol ethers.[3] In case of (4 + 2) ring formation a deviation from the normal synchronous mechanism could perhaps be provoked by the introduction of heteroatoms into the dienophile supported by adequate substituents such as nitrosobenzenes.

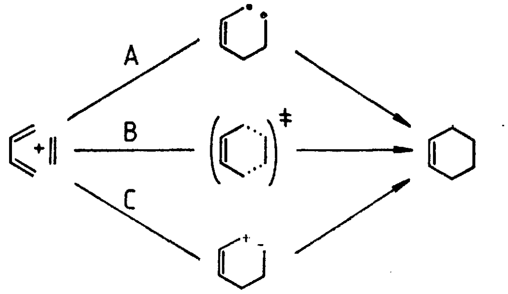
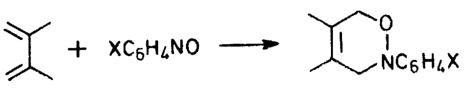


FIGURE 1 Possible reaction mechanisms for (4 + 2) cycloadditions



The determination of the volume of activation has been shown to be very useful during the elucidation of reaction mechanisms.[3-10] A combined study of the solvent and pressure dependence of cycloaddition reactions allows a distinction to be made between the three possible mechanisms indicated in Figure 1, especially when the volumes of activation are combined with the partial molar volumes of the starting materials and products.[11,12]

EXPERIMENTAL

Materials.—4-Chloro-1-nitrosobenzene was prepared by oxidation of commercial 4-chloroaniline by peroxysulphuric acid[13] or peroxyacetic acid.[14] After steam distillation and recrystallisation the product was identified by u.v.–visible and ^1H n.m.r. spectra (Found: C, 51.1; H, 2.8; Cl, 26.2; N, 9.9. Calc. for C_6H_4ClNO: C, 50.9; H, 2.8; Cl, 25.0; N, 9.9%). In order to prepare 4-ethoxy-1-nitrosobenzene phenol was converted into 4-nitrosophenol[15] and then into the final product[16] (Found: C, 63.0; H, 6.1; N, 9.3. Calc. for $C_8H_9NO_2$: C, 63.6; H, 6.0; N, 9.2%).

The dienes, 2,3-dimethylbutadiene, b.p. 69.2—69.5 °C, and cyclopentadiene (dimer), b.p. 40.8—41.0 °C, were obtained from Fluka and freshly distilled before use.

The cycloadducts of 4-chloro- and 4-ethoxy-1-nitrosobenzene with 2,3-dimethylbutadiene were obtained by mixing equimolar solutions of the substrates in carbon tetrachloride. After completion of the reaction the solution was evaporated to dryness and the crude product was then purified by column chromatography on aluminium oxide using light petroleum as eluant. The solid compounds were analysed and their constitution established by ^1H n.m.r. spectra.

The solvents ethanol, toluene, chlorobenzene, nitrobenzene, 1,2-dichloroethane, dichloromethane, and carbon tetrachloride were purchased in the highest quality available and dried and purified according to known procedures.[17]

Kinetic Experiments.—The cycloaddition reactions were followed spectrophotometrically by observing the time dependent change of the NO band at 720 nm with the knowledge that the nitroso compounds used are monomeric in solution. The products do not absorb at this wavelength. The use of u.v. spectra for rate measurements was not possible because the cycloadducts undergo photoinduced ring cleavage.

A Zeiss PMQ II single beam spectrophotometer, equipped with a transmission–extinction converter and recorder, and a Cary 15 spectrophotometer were used to monitor the absorbance changes. The latter instrument was attached to a high pressure apparatus consisting of a pressure generator, two manometers, a ' separator ', and a high pressure cuvette as described previously.[18] All reaction solutions were thermostatted to within ±0.1 °C.

Density Measurements.—These measurements were carried out at 25.0 ± 0.002 °C using a vibrating capillary apparatus (Parr DM 02).

RESULTS

The rates of reaction between 4-ethoxy- and 4-chloro-1-nitrosobenzene and 2,3-dimethylbutadiene were determined in seven solvents over a pressure range from 1 to

TABLE 1

Pressure and solvent dependence of the rate constants of three cycloaddition reactions at 25 °C

	Solvent						
p/bar	Toluene	Ethanol	Dichloromethane	Chlorobenzene	Nitrobenzene	1,2-Dichloroethane	Carbon tetrachloride
4-Ethoxy-1-nitrosobenzene + 2,3-dimethylbutadiene (10^4 k/l mol^{-1} s^{-1})							
1	1.04 ± 0.04	1.87 ± 0.04	1.36 ± 0.06	1.35 ± 0.08	1.40 ± 0.02	1.34 ± 0.02	1.36 ± 0.04
101	1.23 ± 0.02	2.09 ± 0.04	1.36 ± 0.07	1.53 ± 0.01	1.52 ± 0.01	1.47 ± 0.04	1.52 ± 0.02
202	1.40 ± 0.02	2.28 ± 0.07	1.68 ± 0.05	1.71 ± 0.01	1.73 ± 0.03	1.67 ± 0.04	1.70 ± 0.03
304	1.55 ± 0.06	2.51 ± 0.04	1.90 ± 0.01	1.86 ± 0.03	1.87 ± 0.02	1.82 ± 0.03	1.92 ± 0.04
507	1.97 ± 0.04	3.19 ± 0.02	2.17 ± 0.03	2.28 ± 0.01	2.27 ± 0.09	2.23 ± 0.06	2.36 ± 0.05
760	2.57 ± 0.04	4.00 ± 0.03	2.97 ± 0.04	2.63 ± 0.17	2.84 ± 0.02	2.89 ± 0.06	3.05 ± 0.04
1 013	3.09 ± 0.03	5.08 ± 0.06	3.64 ± 0.03	3.53 ± 0.03	3.50 ± 0.05	3.66 ± 0.07	3.82 ± 0.06
4-Chloro-1-nitrosobenzene + 2,3-dimethylbutadiene (10^3 k/l mol^{-1} s^{-1})							
1	4.06 ± 0.02	8.21 ± 0.12	5.49 ± 0.02	5.22 ± 0.17	8.91 ± 0.33	7.08 ± 0.05	4.33 ± 0.07
101	4.67 ± 0.05	9.32 ± 0.06	6.25 ± 0.13	6.66 ± 0.05	10.36 ± 0.26	7.62 ± 0.06	4.69 ± 0.04
202	5.26 ± 0.03	10.36 ± 0.02	6.92 ± 0.16	7.33 ± 0.03	11.46 ± 0.15	8.62 ± 0.07	5.34 ± 0.04
304	5.93 ± 0.15	11.76 ± 0.10	7.90 ± 0.04	8.11 ± 0.03	11.76 ± 0.06	11.19 ± 0.03	5.85 ± 0.12
507	7.17 ± 0.33	14.71 ± 0.14	9.28 ± 0.35	9.92 ± 0.22	13.95 ± 0.12	13.68 ± 0.98	7.41 ± 0.05
760	9.53 ± 0.09	18.62 ± 0.18	12.51 ± 0.17	12.53 ± 0.03	17.49 ± 0.22	18.59 ± 0.30	9.76 ± 0.36
1 013	10.21 ± 0.29	21.73 ± 1.18	16.83 ± 0.38	15.65 ± 0.12	21.70 ± 0.12	24.32 ± 0.25	13.02 ± 0.34
4-Chloro-1-nitrosobenzene + cyclopentadiene (10^2 k/l mol^{-1} s^{-1})							
1	4.01 ± 0.11	7.62 ± 0.07	5.85 ± 0.07	5.78 ± 0.26			
101	4.56 ± 0.45	8.13 ± 0.06	6.40 ± 0.23	6.17 ± 0.24			
202	5.18 ± 0.12	10.48 ± 0.29	7.05 ± 0.25	7.56 ± 0.03			
304	5.87 ± 0.06	11.64 ± 0.29	7.90 ± 0.08	8.43 ± 0.25			
507	7.25 ± 0.18	13.74 ± 0.05	9.25 ± 0.05	10.31 ± 0.03			
760	9.03 ± 0.12	17.95 ± 0.01	11.49 ± 0.27	12.93 ± 0.03			
1 013	11.69 ± 0.25	22.46 ± 0.15	14.15 ± 0.30	15.72 ± 0.06			

TABLE 2

Pressure and solvent dependence of the equilibrium constant for the reaction 4-chloro-1-nitrosobenzene + cyclopentadiene $\rightleftharpoons$ cycloadduct at 25.0 °C (in l mol^{-1})

	Solvent			
p/bar	Ethanol	Dichloromethane	Toluene	Chlorobenzene
1	150 ± 24	74 ± 6	48 ± 4	60 ± 5
101	151 ± 6	98 ± 1	59 ± 2	63 ± 3
202	211 ± 6	111 ± 7	72 ± 3	93 ± 5
304	232 ± 16	128 ± 2	87 ± 3	118 ± 2
507	284 ± 6	145 ± 6	103 ± 3	150 ± 4
760	402 ± 11	182 ± 12	133 ± 7	204 ± 9
1 013	495 ± 7	231 ± 18	174 ± 2	290 ± 7

1 000 bar. In addition, the reaction between 4-chloro-1-nitrosobenzene and cyclopentadiene was studied in four solvents over the same pressure range. The rate constants obtained are listed in Table 1. For the latter reaction the equilibrium constant was investigated as a function of pressure (Table 2). The rate and equilibrium constants were also determined in three solvents as a function of temperature. The respective values are summarized in Tables 3 and 4. All tabulated data are mean values of at least three to four individual runs. As reported earlier,[19] cycloaddition reactions between aromatic nitroso compounds and dienes follow a second-order rate law. Only after about three half-lives can side reactions be observed.

The reaction with 4-ethoxy-1-nitrosobenzene was studied under pseudo-first-order conditions using the Guggenheim method for the evaluation of the rate constants, whereas second-order conditions were employed for the 4-chloro-1-nitrosobenzene reactions. In the latter case the second-order rate and equilibrium constants were calculated from the corresponding integral rate or equilibrium expressions assuming a second-order–first-order equilibrium.

Precision density measurements permit the apparent

TABLE 3

Temperature and solvent dependence of the rate constants of three cycloaddition reactions

t/°C	Ethanol	t/°C	Dichloromethane	t/°C	Toluene
4-Ethoxy-1-nitrosobenzene + 2,3-dimethylbutadiene (10^5 k/l mol^{-1} s^{-1})					
15.3	6.69 ± 0.76	15.2	5.67 ± 0.88		
20.1	9.60 ± 0.11	20.5	7.55 ± 0.05	20.0	6.65 ± 0.61
24.9	15.10 ± 0.77	25.2	11.12 ± 0.60	25.2	10.13 ± 0.25
30.0	24.50 ± 1.11	29.9	14.64 ± 0.24	29.7	11.43 ± 0.18
35.3	36.11 ± 0.01			35.0	17.90 ± 0.12
4-Chloro-1-nitrosobenzene + 2,3-dimethylbutadiene (10^3 k/l mol^{-1} s^{-1})					
10.7	2.15 ± 0.01	10.2	1.78 ± 0.08	9.8	1.14 ± 0.02
15.9	3.25 ± 0.01	15.2	2.60 ± 0.03	15.4	1.77 ± 0.01
20.2	4.67 ± 0.03	20.0	3.66 ± 0.01	20.1	2.44 ± 0.05
24.8	6.58 ± 0.18	24.7	5.03 ± 0.01	25.0	3.43 ± 0.01
30.0	9.45 ± 0.05	29.7	6.77 ± 0.04	30.1	4.84 ± 0.01
4-Chloro-1-nitrosobenzene + cyclopentadiene (10^3 k/l mol^{-1} s^{-1})					
6.3	26.60 ± 1.37			6.0	13.82 ± 0.21
10.9	34.41 ± 0.19	11.8	27.43 ± 0.30	12.6	20.91 ± 0.37
16.7	47.27 ± 1.77	15.6	33.67 ± 0.80	16.3	24.87 ± 0.49
21.0	62.26 ± 0.92	20.3	42.46 ± 0.38	20.5	32.81 ± 1.52
25.0	76.22 ± 0.74	25.5	58.49 ± 3.55	26.5	44.76 ± 1.60

TABLE 4

Temperature and solvent dependence of the equilibrium constant for the reaction 4-chloro-1-nitrosobenzene + cyclopentadiene $\rightleftharpoons$ cycloadduct (in l mol^{-1})

t/°C	Ethanol	t/°C	Dichloromethane	t/°C	Chlorobenzene
6.3	555			6.0	222
10.9	429	11.8	192	12.6	135
16.7	294	15.6	139	16.3	105
21.0	217	20.3	79	20.5	74
25.0	150	25.0	74	25.0	48

The average uncertainty in the equilibrium constants is ±5%.

molar volume ϕ_i to be determined according to the known equation (1) in which d_i and d_0 are the densities of the solution and the solvent, respectively, M is the molecular weight of the solute, and c_i its molar concentration.

$$\phi_i = M/d_0 - 1\,000(d_i - d_0)/d_0c_i \qquad (1)$$

Over the concentration range 10^{-2}—10^{-3}M, the apparent molar volumes were constant within experimental error so that the apparent molar volume was taken to be identical with the partial molar volume. The results are summarized in Table 5.

DISCUSSION

Rates of Reaction.—Since a direct correlation exists between the electronic ground states of the reactants and products (4 + 2) cycloaddition reactions are thermally allowed. It is therefore assumed that the formation of cyclohexane derivatives occurs by a simultaneous formation of two carbon–carbon bonds (route B in Figure 1). However, the introduction of heteroatoms and substituents into both reactants may influence the electron distribution within the reactant molecules such that the two-step mechanisms (routes A and C) cannot be totally excluded.[20]

Methyl substitution in the 2,3-positions of the diene, *e.g.* butadiene, increases the reaction rates slightly. This is possibly the result of an ' allyl-type ' stabilization of a reactive radicaloid intermediate[21] or a conformational effect, dimethylbutadiene being a non-planar quasi-*cis* molecule. The large increase in rate when butadiene is replaced by cyclopentadiene is mainly due to the predetermined *cis*-form of the diene in the latter compound.

Substitution of the dienophile nitrosobenzene in the *para*-position by electron-withdrawing (Cl) or electron-donating (OC_2H_5) groups causes a substantial change in the rate of cyclisation.[22] Systematic variation of substituents leads to the conclusion that the nitroso compound acts as the electrophile with the nitrogen atom as electrophilic centre.[23] However, such studies do not provide sufficient evidence as to whether major changes in mechanism occur.

A more decisive indication of a possible polar two-step mechanism can be gained from a study of the solvent effect on cyclization. Assuming that in such a case electrostatic interactions play a major role, Kirkwood's theory[24] may be applied, which leads to equation (2).

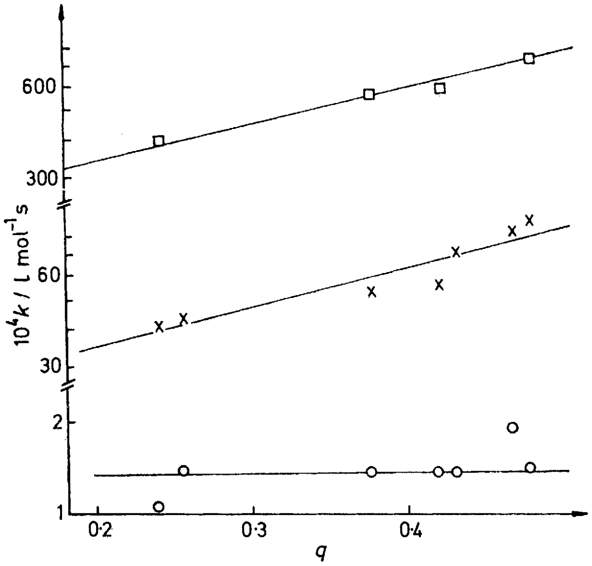


FIGURE 2 Plot of logarithm of rate constants *versus* solvent polarity parameter q for three cycloaddition reactions: □, 4-chloro-1-nitrosobenzene + cyclopentadiene; ×, 4-chloro-1-nitrosobenzene + 2,3-dimethylbutadiene; ○, 4-ethoxy-1-nitrosobenzene + 2,3-dimethylbutadiene

$$\ln k = \ln k_0 + \frac{N}{RT}\left(\frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} - \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^2}\right)\left(\frac{D-1}{2D+1}\right) + \frac{\Sigma\phi}{RT} \qquad (2)$$

Here N is Avogadro's number, μ_i and r_i are the respective dipole moments and radii of transition state and reactants, and D is the dielectric constant of the solvent used. The term $\Sigma\phi/RT$ summarizes all non-electrostatic interactions between the solute and solvent molecules. Figure 2 shows a plot of ln k *versus* $(D - 1)/(2D + 1)$, *i.e.* q, the solvent polarity parameter, for the three reactions investigated. None of the reactions are strongly dependent on solvent polarity and it remains in

TABLE 5

Partial molar volumes of reactants and products for the reactions 4-X-1-nitrosobenzene + 2,3-dimethylbutadiene $\longrightarrow$ cycloadduct at 25.000 ± 0.002 °C (in ml mol^{-1})

Solvent	$\bar{V}$ (Dimethylbutadiene)	$\bar{V}$ (4-X-Nitrosobenzene)		$\bar{V}$ (Cycloadduct)	
		X = Cl	X = OC_2H_5	X = Cl	X = OC_2H_5
Carbon tetrachloride	114.2 ± 0.2	112.5 ± 0.3	135.3 ± 0.1	186.2 ± 0.4	216.0 ± 0.3
Dichloromethane	114.3 ± 0.5	111.1 ± 0.2	136.7 ± 0.2	188.7 ± 0.2	220.1 ± 0.1
1,2-Dichloroethane	114.9 ± 0.5	115.4 ± 0.1	137.8 ± 0.5	191.9 ± 0.3	220.1 ± 0.2
Nitrobenzene	111.0 ± 0.5	112.4 ± 0.3	137.0 ± 0.6	189.7 ± 0.3	216.8 ± 0.1
Chlorobenzene	112.6 ± 0.6	111.2 ± 0.8	136.3 ± 0.2	188.6 ± 0.1	218.3 ± 0.3
Toluene	113.7 ± 0.1	111.1 ± 0.1	136.1 ± 0.1	186.6 ± 0.1	217.3 ± 0.2
Ethanol	114.0 ± 0.1	111.0 ± 0.6	134.4 ± 0.7	184.2 ± 0.2	216.2 ± 0.1

doubt whether the effects seen are really due to polarity changes or merely result from more or less specific interactions.

Activation Parameters.—The temperature dependence studies, each performed in three solvents of differing polarity, result in the thermal activation parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ listed in Table 6. All enthalpies of activation, except that for the reaction between 4-ethoxy-1-nitrosobenzene and 2,3-dimethylbutadiene in ethanol range from *ca.* 40 to 50 kJ mol^{-1}. The entropies of activation lie between -130 and -170 J mol^{-1}, with the exception of the two reactions in ethanol. Such values are quite common for cycloaddition reactions and do not permit differentiation between the possible mechanisms.[25] The deviant behaviour found in ethanol may be due to specific interactions through hydrogen bonding.

TABLE 6

Solvent dependence of the thermal activation parameters of three cycloaddition reactions *

Solvent	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}	$\Delta G^\ddagger$/ kJ mol^{-1}
4-Ethoxy-1-nitrosobenzene + 3,3-dimethylbutadiene			
Ethanol	61.5 ± 1.7	−113 ± 8	94.6 ± 2.5
Dichloromethane	45.6 ± 2.9	−167 ± 13	95.8 ± 4.2
Toluene	44.8 ± 5.9	−172 ± 21	95.8 ± 8.4
4-Chloro-1-nitrosobenzene + 2,3-dimethylbutadiene			
Ethanol	52.7 ± 0.8	−109 ± 4	85.4 ± 0.8
Dichloromethane	46.4 ± 0.8	−134 ± 4	86.2 ± 1.3
Toluene	48.1 ± 0.4	−130 ± 4	87.0 ± 0.8
4-Chloro-1-nitrosobenzene + cyclopentadiene			
Ethanol	36.8 ± 0.8	−142 ± 4	79.5 ± 1.3
Dichloromethane	36.4 ± 1.7	−146 ± 4	80.3 ± 2.5
Toluene	37.2 ± 0.8	−146 ± 4	80.8 ± 1.3

* Values and errors resulted from linear least square fits.

TABLE 7

Solvent dependence of the thermodynamic parameters of the cycloaddition reaction 4-chloro-1-nitrosobenzene + cyclopentadiene $\rightleftharpoons$ cycloadduct

Solvent	ΔH/ kJ mol^{-1}	ΔS/ J K^{-1} mol^{-1}	ΔG/ kJ mol^{-1}
Ethanol	−47.7 ± 2.9	−117 ± 13	−13.0
Dichloromethane	−54.8 ± 10.5	−151 ± 38	−10.0
Toluene	−55.2 ± 2.9	−151 ± 13	−10.5

As already indicated in the Introduction, the volume of activation, $\Delta V^\ddagger_{\text{exp}}$, derived from the pressure dependence of the rate constant of a reaction according to equation (3), can play an important role in deciding the

$$d \ln(k_p/k_o) = -\Delta V^\ddagger_{\text{exp}}/RT \qquad (3)$$

kind of mechanism involved in cyclisation reactions. In equation (3) k_p and k_o are the rate constants determined at pressure P and 1 bar, respectively.

Following a simple model,[26] $\Delta V^\ddagger_{\text{exp}}$ can be considered to consist of two terms, $\Delta V^\ddagger_{\text{intr}}$, the change in volume due to changes in the nuclear positions of the reactants during the formation of the transition state, and $\Delta V^\ddagger_{\text{solv}}$, the volume effect derived from changes in solute–solvent interactions during the same process.

It is obvious that the term $\Delta V^\ddagger_{\text{solv}}$ should only contribute substantially to the overall volume of activation for path C, indicated in Figure 1, *i.e.* a distinct variation in $\Delta V^\ddagger_{\text{exp}}$ when varying the solvents should be observed. On the other hand, $\Delta V^\ddagger_{\text{intr}}$ should reflect bond making during the cyclization process. $\Delta V^\ddagger_{\text{intr}}$ is therefore expected to be negative with an approximate value of -15 ml mol^{-1} for single bond formation (routes A and C) and *ca.* -30 ml mol^{-1} for simultaneous formation of both bonds (route B).

Whenever the evidence is sufficiently strong that $\Delta V^\ddagger_{\text{solv}}$ is large an attempt to separate the two contributions by way of equation (2) may be useful. With the

$$\Delta V^\ddagger_{\text{exp}} = \Delta V_0^\ddagger - N\left(\frac{\mu_\ddagger^2}{r_\ddagger^3} - \frac{\mu_A^2}{r_A^2} - \frac{\mu_B^2}{r_B^2}\right)\frac{d}{dP}\left(\frac{D-1}{2D+1}\right) + \frac{d\Sigma\phi}{dP} \qquad (4)$$

assumption that electrostatic interactions again dominate, the pressure derivative of equation (2) yields (4).

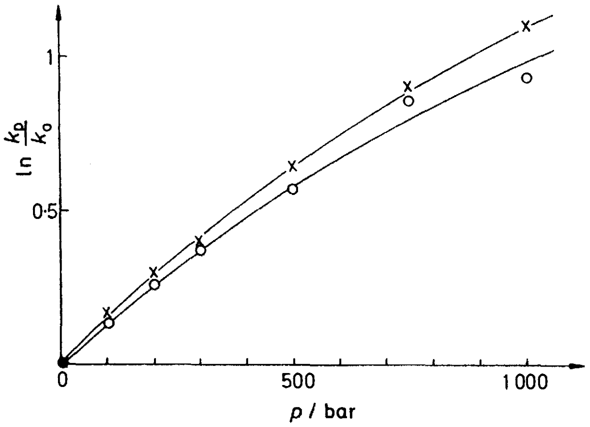


FIGURE 3 Plot of $\ln(k_p/k_o)$ *versus* pressure for the cycloaddition reaction between 4-X-1-nitrosobenzene and 2,3-dimethylbutadiene in toluene: ○, X = Cl; ×, X = OC_2H_5

Here the term $\Delta V_0^\ddagger$ is identical with $\Delta V^\ddagger_{\text{intr}}$ and $d[(D-1)/(2D+1)]/dP$ represents the pressure derivative of the solvent polarity parameter q, symbolized by q_p.[3] A plot of $\Delta V^\ddagger_{\text{exp}}$ *versus* q_p should yield a straight line with $\Delta V_0^\ddagger = \Delta V^\ddagger_{\text{intr}}$ as intercept, which in turn can be discussed in terms of one- or two-bond formation.

Since at least part of the $\ln(k_p/k_o)$ *versus* pressure plots show distinct curvature, the method of evaluation of volumes of activation at 1 bar, $\Delta V^\ddagger_{\text{exp,o}}$, is somewhat problematic. Besides graphical methods a number of mathematical functions $f(P) = \ln(k_p/k_o)$ have been proposed for curve fitting and are listed in Table 8. None of these functions are based on sound physical theory and their merits and shortcomings, together with those of a function proposed by Benson and Berson,[27] were recently discussed in detail.[28] The application of a particular function may influence the numerical value for $\Delta V^\ddagger_{\text{exp,o}}$ to some extent.

The reactions of two substituted nitrosobenzenes with 2,3-dimethylbutadiene in toluene can serve as examples. Figure 3 shows $\ln(k_p/k_o)$ *versus* pressure plots for these reactions, whereas Table 8 summarizes the best-fit values for $\Delta V^{\ddagger}_{\mathrm{exp,o}}$. Since most of the $\ln(k_{\mathrm{p}}/k_{\mathrm{o}})$ *versus* pressure relationships show almost linear behaviour at higher pressures, the average values of $\Delta V^{\ddagger}_{\mathrm{exp,p}}$ for these linear sections were determined graphically and are included in Table 8. Such values may serve as ' minimum values ' of $\Delta V^{\ddagger}_{\mathrm{exp}}$.

TABLE 8

Evaluation of $\Delta V^{\ddagger}_{\mathrm{exp}}$ for the reactions between 4-X-1-nitrosobenzene and 2,3-dimethylbutadiene in toluene at 25 °C ($\Delta V^{\ddagger}_{\mathrm{exp}}$ values in ml mol^{-1})

Function applied	X = Cl	X = OC_2H_5
$f_1(p) = a + bP$	-25.6 ± 1.8	-28.8 ± 1.2
$f_2(p) = a + bP + cP^2$	-38.6 ± 3.3	-38.2 ± 1.6
$f_3(p) = a + bP/(c + P)$	-40.8 ± 1.7	-40.0 ± 0.6
$f_4(p) = a + c(1 - e^{-bP})$	-40.0 ± 0.0	-39.3 ± 0.0
Graphical method [a]	-28.5 ± 3.5 [a]	-30.2 ± 3.4 [a]

[a] Average of all $\Delta V^{\ddagger}_{\mathrm{exp,p}}$ at higher pressures.

The volumes of activation at 1 bar, calculated from $f_2(p)$, $f_3(p)$, and $f_4(p)$, are usually in close agreement. Average values were therefore taken for all the reactions investigated and are listed in Table 9. The corresponding values of $\Delta V^{\ddagger}_{\mathrm{exp,p}}$ are also included in Table 9. No definite trend of $\Delta V^{\ddagger}_{\mathrm{exp,o}}$ with solvent polarity, specifically in terms of the electrostriction parameter q_{p}, can be discovered for any of the three reactions. Thus a plot of $\Delta V^{\ddagger}_{\mathrm{exp,o}}$ *versus* q_{p} does not offer any advantages. One is rather inclined to take the observed scatter as an indication of a small $\Delta V^{\ddagger}_{\mathrm{solv,o}}$ contribution caused by non-electrostatic, specific interactions. The rather small individual error limits for the $\Delta V^{\ddagger}_{\mathrm{exp,o}}$ values listed in Table 9 are the result of the good fit obtained, using the functions mentioned.

TABLE 9

Solvent dependence of volume changes $\Delta V^{\ddagger}_{\mathrm{exp,o}}$, $\Delta V^{\ddagger}_{\mathrm{exp,p}}$, and $\Delta \bar{V}_{\mathrm{R}}$ for three cycloaddition reactions (in ml mol^{-1}) at 25 °C

	4-Chloro-1-nitrosobenzene + 2,3-dimethylbutadiene			4-Ethoxy-1-nitrosobenzene + 2,3-dimethylbutadiene			4-Chloro-1-nitrosobenzene + cyclopentadiene		
Solvent	$\Delta V^{\ddagger}_{\mathrm{exp,o}}$	$\Delta V^{\ddagger}_{\mathrm{exp,p}}$	$\Delta \bar{V}_{\mathrm{R}}$	$\Delta V^{\ddagger}_{\mathrm{exp,o}}$	$\Delta V^{\ddagger}_{\mathrm{exp,p}}$	$\Delta \bar{V}_{\mathrm{R}}$	$\Delta V^{\ddagger}_{\mathrm{exp,o}}$	$\Delta V^{\ddagger}_{\mathrm{exp,p}}$	$\Delta \bar{V}_{\mathrm{R}}$
Toluene	−39.2 ±1.0	−28.5 ±3.5	−38.2 ±0.2	−39.7 ±0.7	−30.2 ±3.4	−32.5 ±0.2	−33.9 ±0.6	−29 ±3	−41 ±6
Carbon tetrachloride	−32.0 ±0.5	−29.5 ±1.5	−40.5 ±0.5	−29.3 ±0.5	−28.7 ±1.8	−33.5 ±0.4			
Chlorobenzene	−26.7 ±0.5	−27.0 ±3.5	−35.3 ±1.0	−26.8 ±0.8	−26.3 ±3.0	−30.6 ±0.7	−37.1 ±0.8	−28 ±4	−52 ±10
Dichloromethane	−27.8 ±0.1	−29.5 ±2.8	−36.6 ±0.6	−28.8 ±0.7	−27.4 ±4.0	−30.9 ±0.5	−25.7 ±0.7	−25 ±2	−36 ±5
1,2-Dichloroethane	−27.5 ±0.2	−28.5 ±3.6	−38.4 ±0.6	−30.0 ±1.2	−26.0 ±1.1	−32.6 ±0.7			
Ethanol	−29.1 ±0.5	−29.0 ±3.2	−40.8 ±0.6	−37.0 ±0.4	−27.4 ±1.9	−32.2 ±0.7	−39.5 ±1.1	−29 ±4	−40 ±8
Nitrobenzene	−26.6 ±0.2	−22.2 ±3.2	−33.7 ±0.7	−22.8 ±0.1	−24.2 ±2.6	−31.2 ±0.8			
Average over all solvents	−29.8 ±0.5	−27.7 ±3.0	−37.6 ±0.5	−30.6 ±0.7	−27.2 ±2.7	−31.9 ±0.5	−34 ±5	−28 ±2	−42 ±8

It is generally assumed that the solvation contributions, $\Delta V^{\ddagger}_{\mathrm{solv}}$, are more or less pressure dependent whereas the $\Delta V^{\ddagger}_{\mathrm{intr}}$ parts are essentially pressure independent.[28] Therefore at higher pressures the solvation contribution may become small and negligible. In a rough approximation the average of the $\Delta V^{\ddagger}_{\mathrm{exp,p}}$ values for a reaction can be taken as a measure of $\Delta V^{\ddagger}_{\mathrm{intr}}$ and can then be compared with the expected value for an assumed mechanism. In fact, such comparisons are then valid not only for one reaction in different solvents but also for all reactions and solvents. The $\Delta V^{\ddagger}_{\mathrm{exp,p}}$ values centre around $-(28 \pm 1)$ ml mol^{-1} which indeed points towards a common mechanism in which two bonds are formed in the transition state.

Volumes of Reaction.—The volumes of reaction, $\Delta \bar{V}_{\mathrm{R}}$ were determined from the partial molar volumes of the reactants and products for two systems. Because the cycloadduct formed in the reaction between 4-chloro-1-nitrosobenzene and cyclopentadiene is unstable, $\Delta \bar{V}_{\mathrm{R}}$ values were determined from the pressure dependence of the equilibrium constants in this case and, as a consequence, are less accurate. These $\Delta \bar{V}_{\mathrm{R}}$ values are included in Table 9. They are comparable in magnitude with those for Diels–Alder adducts.

Normally $\Delta \bar{V}_{\mathrm{R}}$ values for cycloaddition reactions can be considered to consist of three contributions, the volume change resulting from the formation of two bonds, $2\Delta \bar{V}(\mathrm{bond})$, a ring effect, $\Delta \bar{V}(\mathrm{ring})$, and a change in solvation associated with the ring formation $\Delta \bar{V}(\mathrm{solv})$ [equation (5)]. The term $\Delta \bar{V}(\mathrm{ring})$ originates from the displacement of solvent molecules from the inner part of the ring-shaped product. Its magnitude is assumed

$$\Delta \bar{V}_{\mathrm{R}} = 2\Delta \bar{V}(\mathrm{bond}) + \Delta \bar{V}(\mathrm{ring}) + \Delta \bar{V}(\mathrm{solv}) \quad (5)$$

to be *ca.* +10 ml mol^{-1} for the formation of a six-membered ring. $\Delta \bar{V}(\mathrm{solv})$ can only be estimated from a solvent dependence study. As expected from the preceding discussion of the activation parameters, the volumes of reaction also show little variation with solvent. Nevertheless, the accuracy of the data obtained from partial molar volumes *via* precision density measurements is sufficient such that a correlation of $\Delta \bar{V}_{\mathrm{R}}$ with the parameter q_{p} may be justified in order to separate electrostriction effects. A plot of $\Delta \bar{V}_{\mathrm{R}}$ *versus* q_{p} is shown in Figure 4 for the two reactions involving

2,3-dimethylbutadiene as reactant. Neglecting the exceptional value of $\Delta\bar{V}_R$ for the reaction between 4-chloro-1-nitrosobenzene and 2,3-dimethylbutadiene in ethanol, the extrapolation towards $q_p \longrightarrow 0$, *i.e.* $\Delta\bar{V}(\text{solv}) \longrightarrow 0$, presents a common intercept of $-(32 \pm 1)$ ml mol^{-1}. From these estimates for $\Delta\bar{V}_R$ −32, $\Delta\bar{V}(\text{ring})$ +10, and $\Delta\bar{V}(\text{solv})$ 0 ml mol^{-1}, a value of $\Delta\bar{V}(\text{bond})$ of *ca.* −20 ml mol^{-1} emerges, which is indeed reasonable.

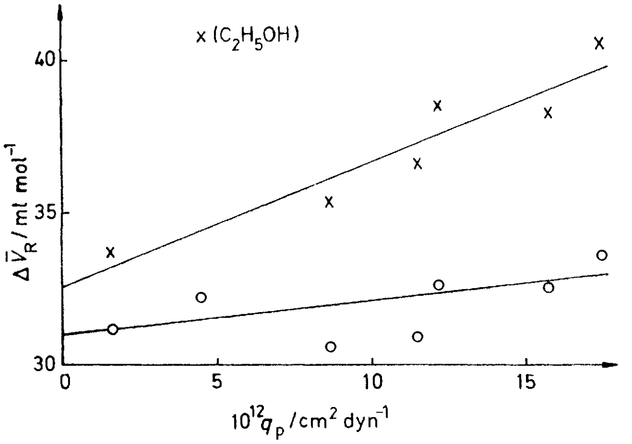


FIGURE 4 Plot of volumes of reaction $\Delta\bar{V}_R$ *versus* solvent polarity parameter q_p for the cycloaddition reaction between 4-X-1-nitrosobenzene and 2,3-dimethylbutadiene: ○, X = OC_2H_5; ×, X = Cl

A final comparison of $\Delta\bar{V}_{\text{exp},0}$ and $\Delta\bar{V}_R$ values underlines the conclusion derived so far that the cycloaddition reactions investigated here follow a mechanism according to route B in Figure 1 involving little or no polarity change.

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