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Pressure Effect on Reaction Rate of Cycloaddition of Tetracyanoethylene with α-Methylstyrene in Some Aprotic Solvents

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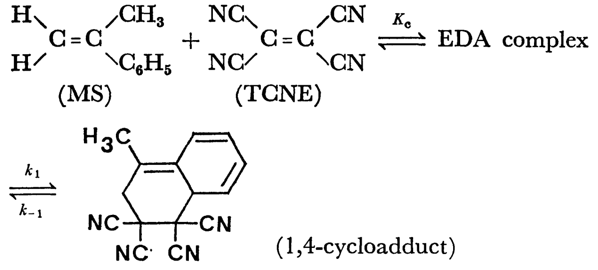
The high-pressure kinetic study of the title reaction was carried out at 25 °C up to 1500 bar in carbon tetrachloride, chloroform, 1,2-dichloroethane, and acetonitrile, taking into account the role of the EDA complex formation. The dipole moment at the transition state is as large as 8.5 ± 0.5 debye by Kirkwood's electrostatic model. The solvent effect is also ascribable to the polarity change upon activation. The intrinsic volume of activation is -27 ± 3 cm^3/mol for the cycloadding process and -3.3 ± 3 cm^3/mol for the reverse reaction.

Styrene was believed to give only the electron-donor-acceptor(EDA) complex with tetracyanoethylene (TCNE) in nonaqueous solvents at the ambient pressure and temperature.[1] Thereafter it was found[2] that a species other than the EDA complex was accumulated sufficiently at pressure as high as several kilobars and that its reversible decomposition after pressure withdrawal could be retarded at temperature as low as 0 °C. This species was identified as the 1,4-cycloadduct from the ^{13}C NMR and other spectra.[2] Careful examination confirmed that not only styrene but some of its derivatives gave the 1,4-cycloadduct with TCNE even at 1 bar, coexisting with the EDA complexes.[2—5] α-Methylstyrene(MS) reacts with TCNE more rapidly than styrene in some alkyl halides as solvent at room temperature to give the 1,4-cycloadduct.[3,4]



Scheme 1.

$$\text{EDA complex} \overset{K_c}{\rightleftharpoons} \text{MS} + \text{TCNE} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{1,4-cycloaddut}$$

Scheme 2.

Whether the EDA complex is an intermediate of the reaction (Scheme 1) or it is formed only in a dead-end equilibrium (Scheme 2) is of interest. However, it is impossible to distinguish the two schemes only by a simple kinetic study. We reported previously[5] that the second-order rate constant for the forward process being denoted by k_f, the reaction constant of its Hammett plot for the para-substituted styrenes was as negative as -5.5 ± 0.2. Moreover, a linear correlation was induced between $\log k_f$ and $\log K_c$; k_f increased with increasing equilibrium constant K_c for the EDA complex formation. The latter fact will support Scheme 1; otherwise the overall free energy of activation would not be correlated necessarily with the free energy change of the EDA complex formation. A similar scheme is presented for the reaction of TCNE with 9,10-dimethylanthracene,[6] in which the overall enthalpy of activation is negative. We have pointed out already the importance of the role of the EDA complex in the reaction between TCNE and enol ethers.[7]

Moreover the present reaction attracts much attention in a sense that unlike most [4+2] reactions the reaction rate depends significantly on solvent polarity.[3,4] This paper deals with the pressure and solvent effects on the reaction rate for the purpose of elucidating the transition state character. While a volume of activation, as a result of pressure effect on a reaction rate, is known to provide an important knowledge to understand a reaction mechanism,[8,9] the kinetic study on the thermal reaction faster than *ca.* half an hour has been hardly done at high pressure by a usual convenient method because it takes long time to attain the thermal equilibrium at a desired pressure after initiating the reaction. We could overcome the problem by developing a high pressure stopped-flow method.[10]

Experimental

Materials. All reagents were commercially obtained (Nakarai Chemicals Co. Ltd.). Tetracyanoethylene (TCNE) was sublimed three times *in vacuo* at 50—55 °C in the presence of active carbon, mp 200—201 °C. α-Methylstyrene (MS) was washed twice with slightly alkaline water and stored for 24 h over KOH. After being refluxed with CaH_2, it was distilled twice under a reduced pressure. Chloroform was treated with molecular sieves 5A, and then distilled twice just before use, bp 61—62 °C. Acetonitrile was refluxed with $NaHCO_3$ and P_2O_5, then distilled, bp 81—82 °C. Spectrograde 1,2-dichloroethane and carbon tetrachloride were used without further purification.

Kinetic Measurement. The rate of the cycloaddition was spectrophotometrically determined by following the absorbance of the 1,4-cycloadduct. At 1 bar (1 bar=0.1 MPa) was used a Shimadzu UV-200S spectrophotometer equipped with a rapid mixing apparatus(Union Giken MX 703). At high pressure the kinetic measurement was done by using a high-pressure stopped-flow apparatus up to 1500 bar,[10] the absorbance change being traced in the whole course of the reaction. The weighed-in concentration of MS was less than 0.2 mol/dm^3 and that of TCNE was less than 1 mmol/dm^3. In all cases the former was *ca.* 100 fold over the latter. Temperature was maintained at 25 ± 0.2 °C by circulating the thermostated fluid around the high-pressure vessels.

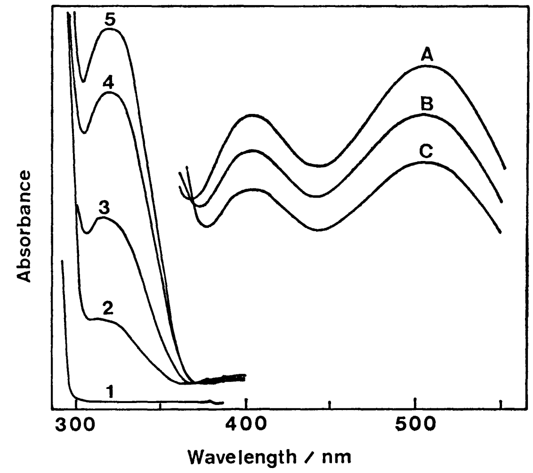


Fig. 1. Electronic spectra of the EDA complex (A—C, $[MS]_0=0.2$ mol/dm^3, $[TCNE]_0=5$ mmol/dm^3), and the 1,4-cycloadduct (2—5, $[MS]_0=0.1$ mol/dm^3, $[TCNE]_0=1$ mmol/dm^3) in chloroform at 1 bar at the following time/s after mixing.
A: 5, B: 90, C: 120, 1: TCNE, 2: 10, 3: 60, 4: 180, 5: 480.

Results and Discussion

The reaction mixture of TCNE and MS exhibited the increasing absorbance at 325 nm of the 1,4-cycloadduct with time, while the absorbances at 400 and 510 nm of the EDA complex decreased (Fig. 1); an isosbestic point appeared at 371 nm. When MS existed in large excess over TCNE, the rate of appearance of the adduct obeyed a first-order rate equation. Under the conditions that the EDA complex is always in equilibrium with TCNE and MS during the whole course of the reaction, we can represent the observed pseudo first-order rate constant k_{obsd} by Eq. 1 in terms of the rate and equilibrium constants as defined in Scheme 1:

$$k_{\mathrm{obsd}} = \frac{k_1K_c[D]_0}{1+K_c[D]_0} + k_{-1}, \tag{1}$$

where $[D]_0$ is the initial concentration of MS in molarity at a desired pressure. The correction of the weighed-in concentration for compression was made on the basis of the density data of Newitt *et al.*[11] for carbon tetrachloride, chloroform, and 1,2-dichloroethane, and of Srinivasan *et al.* for acetonitrile.[12] In chloroform and 1,2-dichloroethane where K_c was known even at high pressure,[13] the plot of k_{obsd} *vs.* $K_c[D]_0/(1+K_c[D]_0)$ was straight line to give k_1 and k_{-1} from the slope and the intercept, respectively (Fig. 2). In acetonitrile K_c being expected to be small enough, $1 \gg K_c[D]_0$, we obtain Eq. 2.

$$k_{\mathrm{obsd}} = k_1K_c[D]_0 + k_{-1}. \tag{2}$$

Hence, by the k_{obsd} *vs.* $[D]_0$ plot, k_1K_c and k_{-1} can be readily determined. In carbon tetrachloride in which K_c was unknown at high pressure, we first estimated k_{-1} at the region of $K_c[D]_0 \ll 1$, then obtained k_1 by

$$\frac{1}{k_{\mathrm{obsd}}-k_{-1}} = \frac{1}{k_1K_c[D]_0} + \frac{1}{k_1}. \tag{3}$$

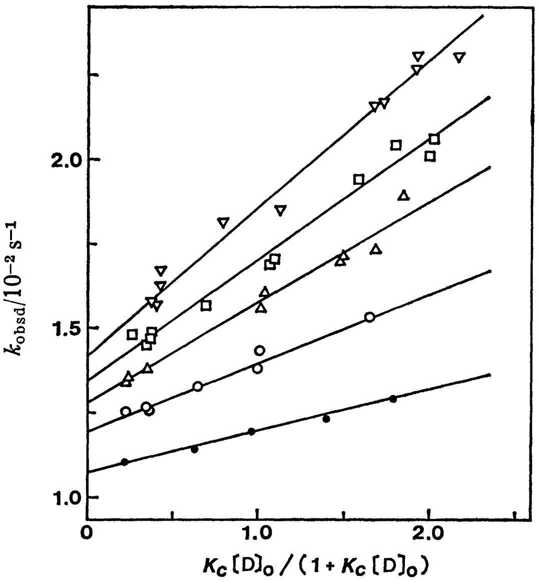


Fig. 2. Variation of k_{obsd} with $[D]_0$ according to Eq. 1 in chloroform at 25 °C.
●: 1 bar, ○: 250 bar, △: 500 bar, □: 750 bar, ▽: 1000 bar.

Table 1 shows the k_1 and k_{-1} values with K_c.

The volumes of activation $\Delta V_1^{\neq}$ for the step from the EDA complex to the 1,4-cycloadduct and $\Delta V_{-1}^{\neq}$ for the reverse one are calculated by the relation;

$$\Delta V^{\neq} = -RT\left(\frac{\partial \ln k}{\partial p}\right)_T, \tag{4}$$

where R, p, T, k, and $\Delta V^{\neq}$ are the gas constant, pressure, temperature, the rate constant(k_1 or k_{-1}) and the volume of activation($\Delta V_1^{\neq}$ or $\Delta V_{-1}^{\neq}$). The reaction volume ΔV_1 as calculated by $\Delta V_1^{\neq}-\Delta V_{-1}^{\neq}$ coincides with that by the equilibrium study.[13] In acetonitrile, K_c and k_1 are not reliable enough for the reaction volume associated with the EDA complex formation, ΔV_c, and $\Delta V_1^{\neq}$ to be recorded. If the volume of activation reflected only the structural change upon activation, the present value of $\Delta V_{-1}^{\neq}$ should be positive. It is worthy to note that $\Delta V_{-1}^{\neq}$ is negative in any solvent, since the volume decreases even for a bond-breaking process. As a consequence, in this case we are enforced to consider the electrostatic solvation in the transition state.

The solvent effect in which the electrostatic interaction plays an important role is sometimes successfully explained with Kirkwood's model,[14] which leads to Eq. 5 for the rate constants. Since the change of μ^2/r^3 terms with pressure is negligible up to a few kilobars compared to that of q, the volume of activation is represented by Eq. 6.

$$\ln k_1 = \ln k_{0(1)} + \frac{N}{RT}\left(\frac{\mu_{\neq}^2}{r_{\neq}^3} - \frac{\mu_{\mathrm{EDA}}^2}{r_{\mathrm{EDA}}^3}\right)q \tag{5a}$$

$$\ln k_{-1} = \ln k_{0(-1)} + \frac{N}{RT}\left(\frac{\mu_{\neq}^2}{r_{\neq}^3} - \frac{\mu_{\mathrm{P}}^2}{r_{\mathrm{P}}^3}\right)q \tag{5b}$$

$$\Delta V_1^{\neq} = \Delta V_{0(1)}^{\neq} - N\left(\frac{\mu^{\neq 2}}{r^{\neq 3}} - \frac{\mu_{\mathrm{EDA}}^2}{r_{\mathrm{EDA}}^3}\right)\left(\frac{\partial q}{\partial p}\right)_T \tag{6a}$$

$$\Delta V_{-1}^{\neq} = \Delta V_{0(-1)}^{\neq} - N\left(\frac{\mu_{\neq}^2}{r_{\neq}^3} - \frac{\mu_{\mathrm{P}}^2}{r_{\mathrm{P}}^3}\right)\left(\frac{\partial q}{\partial p}\right)_T \tag{6b}$$

Table 1. Rate and equilibrium constants at 25 °C

Solvent	Pressure bar	K_c $dm^3\,mol^{-1}$	k_1 $10^{-2}\,s^{-1}$	k_{-1} $10^{-3}\,s^{-1}$	k_ck_1 $10^{-2}\,dm^3\,mol^{-1}\,s^{-1}$
CCl_4	1	1.39	0.130	0.861	0.180
	200		0.172	1.03	0.245
	400		0.198	1.15	0.296
	600		0.252	1.24	0.408
	800		0.329	1.34	0.583
$CHCl_3$	1	0.422	2.80	6.50	1.18
	200	0.430	6.70	6.88	2.88
	400	0.435	8.32	7.30	3.17
	500	0.438	9.86	7.57	4.32
	600	0.441	10.8	8.00	4.76
	1000	0.452	14.6	8.86	6.60
	1500	0.466	21.4	9.88	9.97
$ClCH_2CH_2Cl$	1	0.094	12.5	10.7	1.19
	250	0.098	22.3	11.9	2.19
	500	0.100	30.0	12.8	3.00
	750	0.103	35.3	13.5	3.64
	1000	0.109	44.5	14.2	4.85
CH_3CN	1			37.5	0.7
	200			41.2	1.1
	400			43.4	2.0
	600			47.0	1.1
	800			49.7	1.4

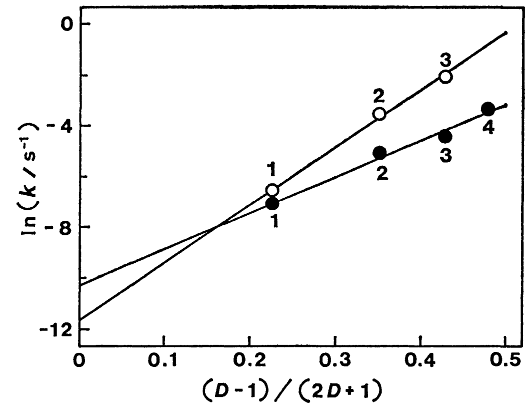


Fig. 3. Variation of k_1 (○) and k_{-1} (●) with the solvent dielectric constant parameter (Eq. 5).
1: Carbon tetrachloride, 2: chloroform, 3: 1,2-dichloroethane, 4: acetonitrile.

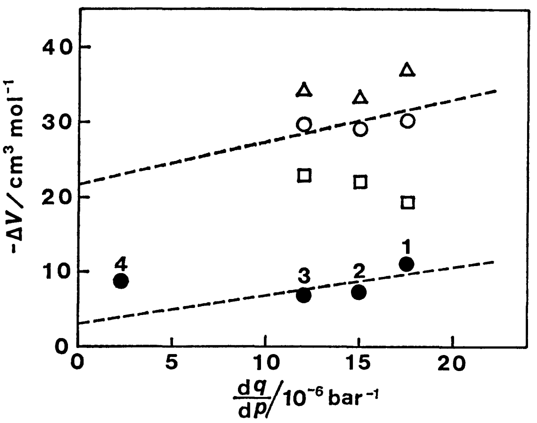


Fig. 4. Variation of the activation and the reaction volumes with solvent dielectric constant parameter (Eq. 6).
The number is the same as in Fig. 3. ○: ΔV_1^{*}, ●: ΔV_{-1}^{*}, □: ΔV_1, △: $\Delta V_c+\Delta V_1^{*}$.

$$q = \frac{D-1}{2D+1} \tag{7}$$

Here N is Avogadro's number, and r_{*}, r_{EDA}, and r_P are the radii of the transition state, the EDA complex and the 1,4-cycloadduct, respectively, and μ's denote the dipole moments. D is the dielectric constant of the solvent, and subscript 0 refers to the state free from the electrostatic interaction with the solvent. $\Delta V_{0(1)}^{*}$ and $\Delta V_{0(-1)}^{*}$ are the so-called intrinsic volumes of activation, and the second terms in Eq. 6 represent the volume contraction due to the solvation. The numerical values of q and $(\partial q/\partial p)_T$ are utilizable from the literatures.[12,15] The estimation of the radii was made on the assumption of the spherical model as follows:

$$r_{EDA}^3 = \frac{3}{4\pi N}\{\Delta V_c + V(\mathrm{TCNE}) + V(\mathrm{MS})\}, \tag{8a}$$

$$r_{*}^3 = \frac{3}{4\pi N}\{\Delta V_1^{*} + \Delta V_c + V(\mathrm{TCNE}) + V(\mathrm{MS})\}, \tag{8b}$$

$$r_P^3 = \frac{3}{4\pi N}\{\Delta V_1 + \Delta V_c + V(\mathrm{TCNE}) + V(\mathrm{MS})\}, \tag{8c}$$

and these approximated to be $r_{EDA}=4.6$, $r_{*}\approx r_P=4.4$ Å.[4,16]

The plot of ln k *vs.* q exhibits a good straight line

TABLE 2. REACTION AND ACTIVATION VOLUMES AT 25 °C

Solvent	ΔV_C / cm^3 mol^{-1}	ΔV_1 / cm^3 mol^{-1}	$\Delta V_1^{\ddagger}$ / cm^3 mol^{-1}	$\Delta V_{-1}^{\ddagger}$ / cm^3 mol^{-1}
CCl_4		−19±2	−30±1	−11±1
$CHCl_3$	−4.0±0.6[a]	−22±2 −20±1[a]	−29±1	−7±1
$ClCH_2CH_2Cl$	−6.9±0.6[a]	−23±2.4 −21±1[a]	−30±1.2	−7±1.2
CH_3CN				−9±1.2

a) Ref. 13.

for k_1 and k_{-1} as seen in Fig. 3; the slopes and r's provide the magnitudes of $\mu_{\ddagger}$ and μ_P to be 8.5±0.5 and 6±1 debye, respectively. Equation 6 is a severer test of this electrostatic model than Eq. 5. If not only the solvent effect on a reaction rate is expressed by Eq. 5 but also the volume of activation lies on a line of Eq. 6, the application of Kirkwood's theory is more justified, and the obtained value of $\mu_{\ddagger}$ becomes more reliable. That idea does not apply satisfactorily to the present results, as seen in Fig. 4. However, the relationship of Eq. 6 is useful to estimate the intrinsic volume terms. The slopes of the broken lines of Fig. 4 correspond to those of Fig. 3. The intercepts fall on −22±3 and −3±3 cm^3/mol for the cycloaddition and the reverse reaction, respectively. The volume changes for most EDA complex formations, arising mainly from the intrinsic contribution are around −5 cm^3/mol,[13,17] hence the intrinsic volume change from the reactants to the transition state results in about −27 cm^3/mol; this is larger than the values for many reactions of Diels-Alder type,[8,9] −35—−40 cm^3/mol. The fact that $\Delta V_{0(-1)}^{\ddagger}$, which should not be negative, is practically zero, suggests that the geometric structure at the transition state is not far from that of the cycloadduct. The apparent negative values for $\Delta V_{-1}^{\ddagger}$ must then be an indication of their difference in electronic character as reflected in the difference in their dipole moments.

The [2+2] cycloaddition of TCNE with a vinyl ether where the concerted mechanism is symmetrically forbidden by the Woodward-Hoffmann rule,[18] proceeds *via* a zwitterionic intermediate, and the dipole moment in the transition state is as large as 10—14 D.[19] Therefore, the volume contraction due to the electrostriction must be substantial in the transition state.[20,21] On the other hand, in many Diels-Alder reactions the dipole moment does not vary so much upon activation that the reaction rate cannot be affected by solvent and that the electrostriction hardly contributes to the volume of activation.

The present results that $\mu_{\ddagger}$ is large enough for the solvent polarity to affect the reaction rate remarkably and that $\Delta V_1^{\ddagger}$ is less negative than in usual Diels-Alder reactions strongly suggest that the 1,4-cycloaddition reaction undergoes a transition state of much higher polarity than do most [4+2] reactions.

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