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REACTION AND ACTIVATION VOLUMES FOR THE 1,4-CYCLOADDITION OF TETRACYANOETHYLENE TO α-METHYLSTYRENE IN 1,2-DICHLOROETHANE AT 25°C

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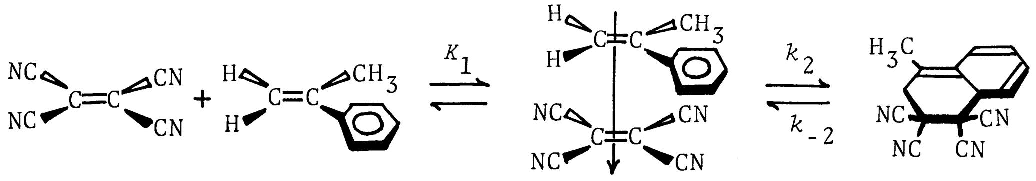
The charge-transfer spectrum of tetracyanoethylene with α-methylstyrene in 1,2-dichloroethane at 25°C has been measured at high pressures up to 1500 bar. Volume changes associated with the charge-transfer complex formation and the 1,4-cycloaddition at 1 bar are -6.9 ±0.6 and -29.2±0.7 $cm^3 mol^{-1}$, respectively.

Tetracyanoethylene (TCNE) causes the thermal 1,4-cycloaddition to various dienes and also 1,2-cycloaddition to electron-rich olefins, such as vinyl ethers and styrenes *para*-substituted by electron-donating groups.[1-4] Styrene (St) itself has been considered for a long while to be an electron donor too weak to make either a 1,2- or 1,4-cycloadduct with TCNE under a mild condition.[1] Recently, however, Nakahara and his coworkers have disclosed that a new species, 1,4-cycloadduct is formed reversibly besides the charge-transfer complex (C) in the solutions of TCNE and styrene or its derivatives.[5-7] In the present work, the authors have measured the charge-transfer spectrum (420-570 nm) in the solution of TCNE and α-methylstyrene (α-MeSt) in order to represent the large pressure effect on the 1,4-cycloaddition quantitatively in terms of the partial molal volume changes. Styrene is not so suitable for an equilibrium study of the 1,4-cycloaddition as α-MeSt because the former reqires an impractically long time for the completion of an equilibrium at any pressure, although its slow rate of the reversible 1,4-cycloaddition has made it possible to determine the structure of the product by means of the ^{13}C and ^1H spectra.[6]

The reactions involved in the solution of TCNE and α-MeSt are analyzed in detail by assuming the following reaction scheme;



A D C P (1)

The equilibrium constants K_1 and K_2 are, respectively, given by

$$K_1 = [C]/([D][A]), \tag{2}$$

and

$$K_2 = k_2/k_{-2} = [P]/[C], \tag{3}$$

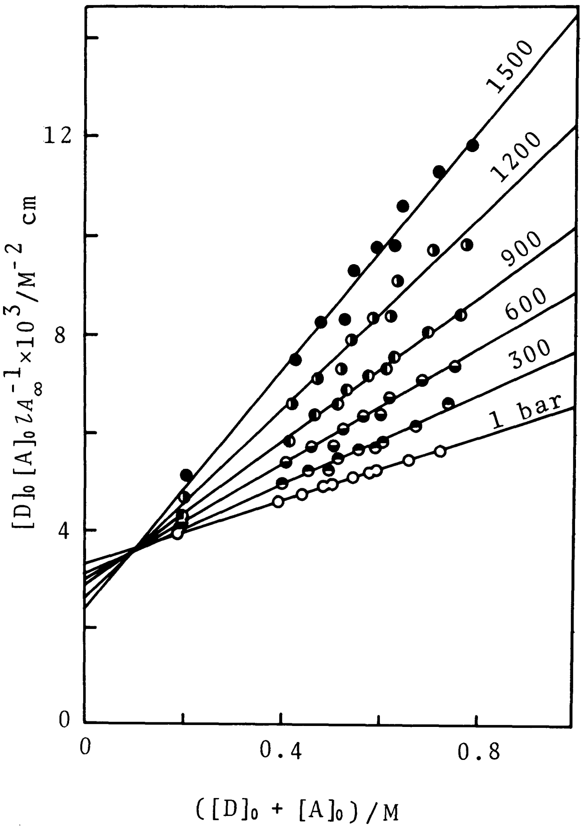


Fig.1 The plot of $[\mathrm{D}]_0[\mathrm{A}]_0 lA_\infty^{-1}$ against $([\mathrm{D}]_0+[\mathrm{A}]_0)$ at 25°C.

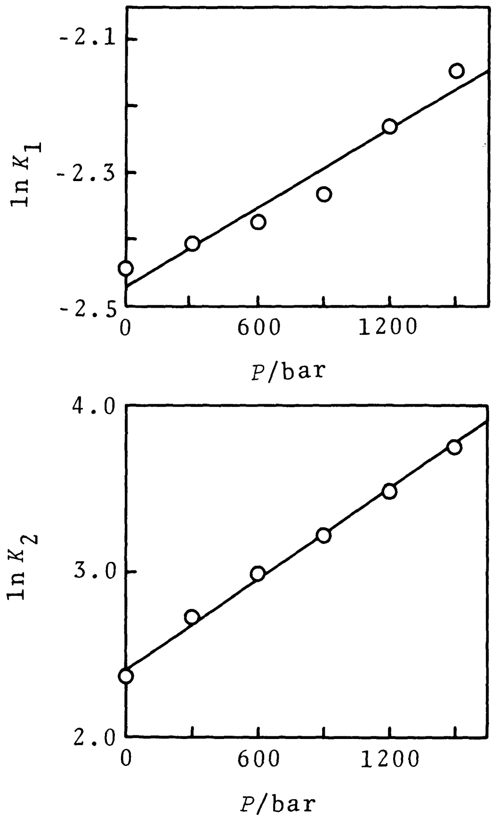


Fig.2 The plots of $\ln K_1$ and $\ln K_2$ against pressure at 25°C.

where [X] denotes the concentration (M = mol dm^{-3}) of a species X. Since the cycloaddition reaction is much slower than the charge-transfer complex formation, we can determine the absorbance (A) of the complex in equilibrium with only D and A by extrapolating the time (t) after mixing to zero. Hence, the absorption coefficient (ε) of the complex at the maximum absorption[8] is obtained from the Scott-type equation,[9]

$$[\mathrm{D}]_0[\mathrm{A}]_0\, l/A_0 = (K_1\varepsilon)^{-1} + \varepsilon^{-1}([\mathrm{D}]_0 + [\mathrm{A}]_0), \qquad (4)$$

where the subscript $_0$ indicates a quantity at t=0 and l the path length; ε is 3600±260 cm^{-1}M^{-1} at 1 bar. The absorbance of the complex at complete equilibrium (A_∞) is expressed by introducing K_2;

$$[\mathrm{D}]_0[\mathrm{A}]_0\, l/A_\infty = (K_1\varepsilon)^{-1} + \varepsilon^{-1}(1+K_2)([\mathrm{D}]_0 + [\mathrm{A}]_0) \qquad (5)$$

The plot of the left-hand side of Eq. (5) against $([\mathrm{D}]_0+[\mathrm{A}]_0)$ at each pressure in Fig. 1 provides $(1+K_2)\varepsilon^{-1}$ as a slope and $(K_1\varepsilon)^{-1}$ as an intercept. When we neglect the pressure dependence of ε, we can obtain K_1 and K_2 as a function of pressure. The values of $\ln K_1$ and $\ln K_2$ are plotted against pressure in Fig. 2. The partial molal volume changes ΔV_1 for K_1 and ΔV_2 for K_2 at 1 bar are, respectively, given by the thermodynamic relations,

$$\Delta V_1 = -RT(\partial \ln K_1/\partial P)_{P=1} - \kappa RT \quad (\kappa\text{, solvent compressibility}^{10)}), \qquad (6)$$

and

$$\Delta V_2 = -RT(\partial \ln K_2/\partial P)_{P=1}. \qquad (7)$$

The values of ΔV_1 and ΔV_2 obtained thus are -6.9±0.6 and -22.3±0.7 $cm^3\ mol^{-1}$, respectively, and the overall reaction volume for the 1,4-cycloaddition between TCNE and α-MeSt, expressed by

$$\Delta V_r = \Delta V_1 + \Delta V_2 \qquad (8)$$

is -29.2±0.7 $cm^3\ mol^{-1}$. These values are used in Fig. 3 to exhibit the partial molal volume of each state relative to that of the initial state, D + A. In the previous work,7) the reverse 1,4-cycloaddition was studied at high pressure from the decay of the absorbance of the adduct around 325 nm. The kinetic expression for the reaction is,

$$d\Delta[P]/dt = -\{k_2K_1[D]_0/(1+K_1[D]_0)+k_{-2}\}\Delta[P]$$
$$= -k_{obs}\Delta[P], \qquad (9)$$

where Δ[P] is the concentration deviation of the adduct from the final equilibrium state. In the previous analysis, the activation volume $\Delta V^{\ddagger}$ for k_{-2} was obtained from the approximation,

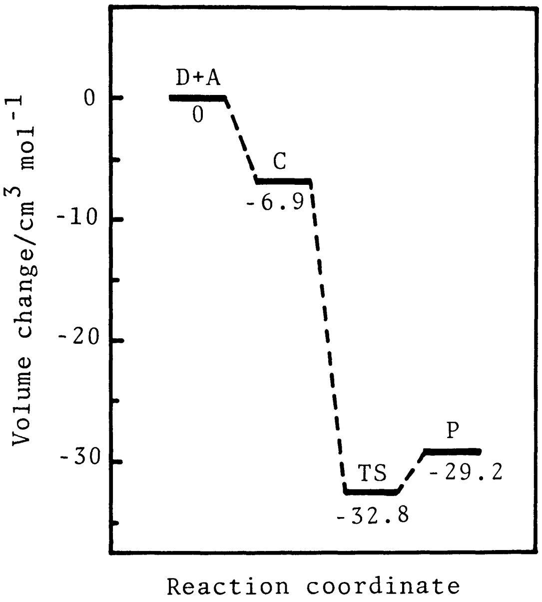


Fig.3 Volume profile for the reactions between TCNE and α-MeSt.

$$k_{obs} = k_2K_1[D]_0/(1+K_1[D]_0)+k_{-2} \approx k_{-2} \qquad (10)$$

because of no information about K_1 and K_2 at high pressure. Now we can compute k_{-2} as a function of pressure and hence, $\Delta V^{\ddagger}$ at 1 bar from the equation,

$$\Delta V^{\ddagger} = -RT(\partial \ln k_{-2}/\partial P)_{P=1}. \qquad (11)$$

The activation volume $\Delta V^{\ddagger}$ which is the difference in the partial molal volume between the transition state (TS) and the adduct (P) is -3.6±0.5 $cm^3\ mol^{-1}$, as shown in Fig. 3.

The volume profile shown in Fig. 3 is interpreted as follows. The volume changes associated with the formation of π-π charge-transfer complexes between neutral molecules in solution have been reported to be in the range of -2 to -12 $cm^3\ mol^{-1}$ at 1 bar at 25°C.11-13) The value of ΔV_1 for the present complex lies within this range; that is to say, the volume is slightly contracted during the formation of the charge-transfer complex. The reaction volumes for the 1,4-cycloadditions studied so far14-16) range from -30 to -40 $cm^3\ mol^{-1}$, irrespective of solvents used. Thus, the value of ΔV_r for this 1,4-cycloaddition is comparable with ones for other cycloadditions of the same type and supports the early considerration that 1,4-cycloadduct is produced in the solution of TCNE and α-MeSt as in that of TCNE and St. Two single bonds formed between the diene and the dienophile cause such a large volume contraction. It is very interesting that the partial molal volume of the transition state is smaller than that of the adduct in spite of the bond expansion or breakage during the course of the unimolecular decomposition of the 1,4-adduct. In general, the activation volume $\Delta V^{\ddagger}$ is composed of the bond term $\Delta_1V^{\ddagger}$ and the solvation term $\Delta_2V^{\ddagger}$. Since $\Delta_1V^{\ddagger}$ is positive in view of the bond expansion or breakage, the negative activation volume means that $\Delta_2V^{\ddagger}$ is negative with its maginitude in excess of $|\Delta_1V^{\ddagger}|$ and that the transition state is substantially solvated as a result of some charge production. The strong dependence of the 1,4-cycloaddition of TCNE to styrene and its derivatives upon the solvent polarity[5)] is in harmony with the idea that this 1,4-cycloaddition proceeds through a polar transition state or intermediate but neither by the concerted mechanism nor by the step-wise one *via* a diradical intermediate.

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