Kinetics and Mechanism of 1,4-Cycloaddition between Tetracyanoethylene and Styrenes. III. Effects of Solvent Polarity and Temperature

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(Received April 24, 1981)

Experimental evaluation was made of rate constants for foward and backward steps of 1,4-cycloaddition between TCNE and α-methylstyrene and of constants for their complex formations in 1,2-dichloroethane, dichloromethane, chloroform, and carbon tetrachloride at a few temperatures around 25 °C. Kirkwood's dipole model for solvation is applied to analyzing kinetic data obtained. The dipole moment of the transition state is estimated to be 8.5±0.5 Debye, which is larger than either that of the complex (assumed as 1 Debye) or that of the cycloadduct (6±1 Debye). Major cause for the high dipole moment of the transition state is breakdown of the high molecular symmetry of TCNE and minor one is a certain contribution of a zwitterionic structure. The activation entropy for the cycloreversion is negative and in the range of −21 to −48 J K^{-1} mol^{-1}, corresponding to the high polarity of the transition state.

When a strong piezochromism was discovered in dichloromethane solution of tetracyanoethylene (TCNE) and styrene half a decade ago, marked solvent and temperature effects on the rate of color change in the solution were noticed in a qualitative manner.[1] Although the phenomenon was first ascribed to formation of a zwitterion because of the large solvent effect on the reaction, later structural studies on species found led to identification of 1,4-cycloadduct.[2,3] Kinetics and mechanism of the 1,4-cycloaddition were investigated with respect to α- and para-substituent effects in Parts I and II of the present series; large substituent effects were found, suggesting a participation of a polar transition state for the 1,4-cycloaddition.[4,5] The aim of the present paper is to elucidate in a quantitative way how much polar the rate-determining state is or whether or not it is similar in polarity to a zwitterion. Applying Kirkwood's dipole model for solvation[6] to kinetic data obtained in several solvents at various temperatures, it is made clear that although the transition state is polar, it is not so much polar as a zwitterion.

Experimental

α-Methylstyrene and TCNE were purified in the same way as in a previous paper.[3] The solvents, 1,2-dichloroethane, dichloromethane, chloroform, and carbon tetrachloride, were purified by the standard method and distilled over CaH$_2$ before use.

Two pycnometers of the Lipkin-Davison type (about 5 cm^3) were employed for measuring densities of 1,2-dichloroethane solutions of α-methylstyrene and of TCNE. They were calibrated by using distilled water for which very accurate density data are available.[7] Temperature was controlled to ±0.01 °C at 25 °C in density measurements, while it was kept to ±0.1 °C in spectrophotometric measurements of reaction rate. Concentrations of α-methylstyrene and TCNE solutions were in the ranges of 0.1 to 0.3 and 0.04 to 0.05 mol dm^{-3}, respectively. Partial molal volumes of the donor and the acceptor varied little with concentration within experimental error. The other apparatus and procedures in the present work are the same as those in Part I of this series.[4]

Analyses in the following section require some physical properties of the solvents listed in Table 1 where α is the thermal expansivity,[8] ε the dielectric constant,[9] and q equal to (ε−1)/(2ε+1).

Table 1. Properties of the used solvents at 25 °C

Solvent	$\alpha^{a)}$ / 10^{-3} K^{-1}	$\varepsilon^{b)}$	q	$\mathrm{d}q/\mathrm{d}T^{c)}$ / 10^{-4} K^{-1}
ClCH$_2$CH$_2$Cl	1.17$^{d)}$	10.36	0.431	3.7
CH$_2$Cl$_2$	1.37	8.93	0.421	2.5
CHCl$_3$	1.26	4.72	0.356	4.7
CCl$_4$	1.27	2.23	0.225	2.0

a) From Ref. 8. b) From Ref. 9. c) Estimated from the values of ε at 20 and 25 °C. d) Estimated from the densities at 25 and 30 °C.

Results and Discussion

Formation Constant of EDA Complex. α-Methylstyrene and TCNE form an EDA complex in solution. The formation constant (K_c) is defined as

$$K_c = [\mathrm{EDA}]/([\mathrm{D}][\mathrm{A}]), \qquad (1)$$

where EDA, D, and A denote the EDA complex, the donor, and the acceptor, respectively, and the brackets [ ] indicate the concentration of each species. The formation constant can be determined spectrophotometrically from the Scott equation under the condition of $[\mathrm{D}]_0 \gg [\mathrm{A}]_0$, as explained in detail elsewhere.[4] Values of K_c obtained in several solvents at various temperatures are summarized in Table 2, which includes also the wavelength ($\lambda_{\max}$) of the maximum absorption for the first charge-transfer band and the molar absorption coefficient ($\varepsilon_{\max}$) at $\lambda_{\max}$ utilized in the K_c determination. The higher the solvent polarity, the smaller the formation constant at any temperature. This trend is common to weak EDA complexes.[10] As a matter of fact, the complex studied here has been clarified to be weak from another criterion in a previous work.[4] Dipole moments of EDA complexes between TCNE and similar aromatic donors are reported to be approximately 1 Debye (Debye/C m=3.33×10^{-30}).[11] This kind of trend for weak complexes is usually interpreted in terms of desolvation of the donor and/or acceptor during the complex formation.[10] In the present case, desolvation of TCNE seems important for the following rea-

TABLE 2. FORMATION CONSTANTS OF THE EDA COMPLEX IN SEVERAL SOLVENTS AT VARIOUS TEMPERATURES AND RELEVANT SPECTROSCOPIC AND THERMODYNAMIC PARAMETERS

Solvent	$\lambda_{\max}$ nm	$\varepsilon_{\max}$ mol^{-1} dm^3 cm^{-1}	K_c/mol^{-1} dm^3 15 °C	20 °C	25 °C	30 °C	ΔH_c kJ mol^{-1}	ΔS_c J K^{-1} mol^{-1}
$ClCH_2CH_2Cl$	492	3330	0.092	0.088	0.084		−7.4	−45
CH_2Cl_2	495	2050	0.192	0.184	0.176		−7.2	−39
$CHCl_3$	504	1760	0.473	0.460	0.436		−6.7	−29
CCl_4	499	1510		1.49	1.39	1.31	−10.5	−32

son. Although TCNE itself has no dipole moment because of its high molecular symmetry, its CN groups have so large a bond dipole moment that they can interact strongly with polar solvent molecules. The role of higher moments like the quadrupole and octapole in TCNE is well reflected by strong dependences of its solubility[12] and heat of dissolution[13–15] on solvent polarity.

The enthalpy change (ΔH_c) and entropy change (ΔS_c) for the complex formation are obtained from the thermodynamic equations

$$\left(\frac{\partial \ln K_c}{\partial(1/T)}\right)_P = -\frac{\Delta H_c}{R} - \alpha T^2, \qquad (2)$$

and

$$\Delta S_c = \frac{\Delta H_c + RT\ln K_c}{T}, \qquad (3)$$

where T is the temperature, R the gas constant, and α the thermal expansivity of the solvent; values of these quantities in the temperature range studied here are given in Table 2. The negative sign of ΔH_c and ΔS_c is reasonable for the association reaction. The absolute value of ΔH_c also indicates that the complex is weak, and its decrease, though somewhat irregular, with increasing solvent polarity is compatible with the increase in solvation of TCNE mentioned above. However, the increase in magnitude of ΔS_c with increasing solvent polarity cannot be explained in terms of solvation, because the entropy loss due to the molecular association is canceled to some extent by the entropy gain due to liberation (desolvation) of polar solvent molecules on one side of the molecular plane of TCNE.

Reaction Rates and Activation Parameters. The 1,4-cycloaddition proceeds according to the scheme

$$\mathrm{D} + \mathrm{A} \overset{K_c}{\rightleftharpoons} \text{EDA Complex} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{P}, \qquad (4)$$

where k_1 and k_{-1} are the rate constants for the forward and backward cycloaddition processes, respectively, and P denotes the cycloaddition product.[5] The pseudo-first-order rate constant k_{obsd} for Reaction 4 is expressed as

$$k_{\mathrm{obsd}} = \frac{k_1 K_c[\mathrm{D}]_0}{1+K_c[\mathrm{D}]_0} + k_{-1}, \qquad (5)$$

where $[\mathrm{D}]_0$ denotes the initial concentration of the donor. The reaction is followed by observing the absorbance of the product at 325 nm,[3] and the value of k_{obsd} is determined from the Guggenheim plot. Figure 1 shows plots of k_{obsd} *vs.* $K_c[\mathrm{D}]_0/(1+K_c[\mathrm{D}]_0)$ in 1,2-dichloroethane at three different temperatures.

TABLE 3. RATE AND FORMATION CONSTANTS OF THE 1,4-CYCLOADDITION IN SEVERAL SOLVENTS AT VARIOUS TEMPERATURES

Solvent	Temperature/°C 15	20	25	30
	$10^2\,k_1$/s^{-1}			
$ClCH_2CH_2Cl$	6.64	8.58	12.4	—
CH_2Cl_2	3.46	4.77	6.13	—
$CHCl_3$	1.61	2.06	2.68	—
CCl_4	—	0.091	0.130	0.210
	$10^3\,k_{-1}$/s^{-1}			
$ClCH_2CH_2Cl$	3.89	6.50	10.7	—
CH_2Cl_2	3.39	5.78	9.90	—
$CHCl_3$	2.29	3.93	6.50	—
CCl_4	—	0.457	0.861	1.48
	K_1			
$ClCH_2CH_2Cl$	17.1 17.9[a]	13.2 13.8[a]	11.6 10.8[a]	— —
CH_2Cl_2	10.2 9.97[a]	8.25 7.90[a]	6.19 6.21[a]	— —
$CHCl_3$	7.03 6.64[a]	5.24 5.28[a]	4.12 4.29[a]	— —
CCl_4	—	1.99	1.51	1.42

a) Determined from equilibrium measurements.

Plots like these provides k_1 and k_{-1} as a slope and an intercept, respectively. Rate constants obtained in the four solvents by applying the least-squares method to plots like those in Fig. 1 are given in Table 3, together with adduct formation constants given by

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\mathrm{P}]}{[\mathrm{EDA}]}. \qquad (6)$$

When all the steps involved in Reaction 4 are at equilibrium, we can get K_1 independently by the method described in detail elsewhere (see Eq. 11 in Ref. 4). As seen in Table 3, the kinetically and thermodynamically determined values of K_1 are in good agreement. The activation enthalpies (ΔH_1^{*} for k_1 and ΔH_{-1}^{*} for k_{-1}) and entropies (ΔS_1^{*} and ΔS_{-1}^{*}) are obtained from the Eyring equation[16]

$$R\ln\frac{hk}{k_B T} = -\frac{\Delta G^{*}}{T} = -\frac{\Delta H^{*}}{T} + \Delta S^{*}, \qquad (7)$$

where h, k_B, and k are the Planck constant, the Boltzmann constant, and the rate constant (k_1 or k_{-1}), respectively. The activation parameters thus obtained are listed in Table 4; they will be discussed below.

Table 4. Activation parameters for the 1,4-cycloaddition in several solvents

Solvent	$\Delta H_1^{\ddagger}$ / kJ mol^{-1}	$\Delta H_{-1}^{\ddagger}$ / kJ mol^{-1}	$\Delta S_1^{\ddagger}$ / J K^{-1} mol^{-1}	$\Delta S_{-1}^{\ddagger}$ / J K^{-1} mol^{-1}
$ClCH_2CH_2Cl$	42	70	−121	−48
CH_2Cl_2	38	74	−139	−35
$CHCl_3$	34	72	−161	−45
CCl_4	59	84	−101	−21

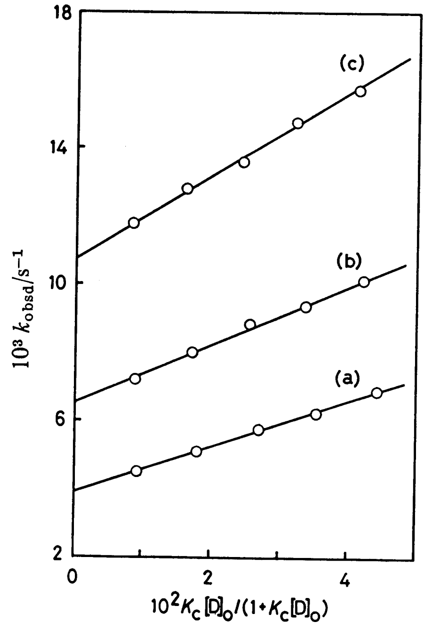

Fig. 1. Plots of k_{obsd} vs. $K_c[D]_0/(1+K_c[D]_0)$ in 1,2-dichloroethane.
(a): 15 °C, (b): 20 °C, (c): 25 °C.

Dipole Moments of the Transition State and Product. The dipole moment of the transition state can be determined by applying Kirkwood's dipole model for solvation to the kinetic data in Table 3.[6] Kirkwood's model leads to the equations

$$\Delta G_1^{\ddagger} = (\Delta G_1^{\ddagger})_{\phi} - Lq\left(\frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} - \frac{\mu_{EDA}^2}{r_{EDA}^3}\right), \tag{8}$$

and

$$\Delta G_{-1}^{\ddagger} = (\Delta G_{-1}^{\ddagger})_{\phi} - Lq\left(\frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} - \frac{\mu_P^2}{r_P^3}\right), \tag{9}$$

where

$$q = \frac{\varepsilon - 1}{2\varepsilon + 1}. \tag{10}$$

Here, $\Delta G_1^{\ddagger}$ and $\Delta G_{-1}^{\ddagger}$ are the activation free energies relating to the rate constants k_1 and k_{-1} through Eq. 7, respectively; $(\Delta G^{\ddagger})_{\phi}$ denotes the activation free energy which is not explicitly given by Kirkwood's model (*i.e.*, a term associated with activation free energy in the hypothetical gas phase and with solvations due to van der Waals interactions, *etc.*); L is the Avogadro constant; $r_{\ddagger}$, r_{EDA}, and r_p are the radii of the transition state, the EDA complex, and the adduct, respectively (spherical symmetry is assumed here); and μ denotes the dipole moment for the species indicated.

Plots of $\Delta G_1^{\ddagger}$ and $\Delta G_{-1}^{\ddagger}$ against q in Table 1 are shown in Fig. 2; they are linear as expected. If μ_{EDA} is taken to be 1 Debye and r_{EDA} and $r_{\ddagger} \approx r_p$ are approximated to 4.6 and 4.4 Å based on measured partial molal volumes,[17,18] respectively, the slopes in Fig. 2 corresponding to Eqs. 8 and 9 provide 8.5±0.5 and 6±1 Debye as $\mu_{\ddagger}$ and μ_p, respectively. Alternatively, the dipole moment of the adduct can roughly be estimated from the vector sum of dipole moments of the cyano and methyl groups; the estimated dipole moment is 7—8 Debye.[19] The fairly good agreement indicates that the present analysis is reasonable. Since the dipole moment of α-methylstyrene is 0.76 Debye,[20] we have the following polarity profile for Reaction 4:

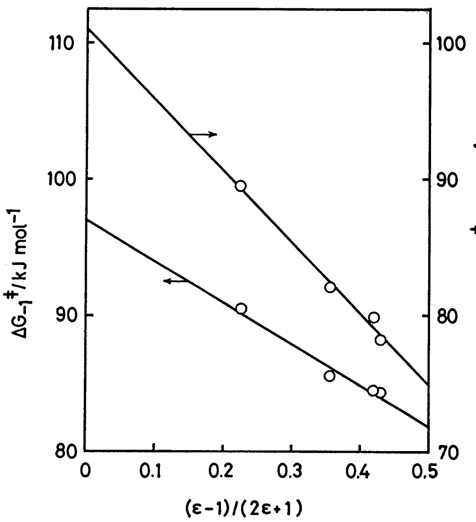

Fig. 2. Plots of $\Delta G_1^{\ddagger}$ and $\Delta G_{-1}^{\ddagger}$ vs. $(\varepsilon-1)/(2\varepsilon+1)$ at 25 °C.

$$\begin{array}{ccccccc} 0.8 & & 1 & & 8.5 & & 6 \text{ Debye} \\ D + A & \rightleftharpoons & \text{EDA Complex} & \rightleftharpoons & \text{TS} & \rightleftharpoons & P, \end{array} \tag{11}$$

where TS denotes the transition state. Although these absolute values have uncertainties as indicated above, their differences are more reliable. There is a large difference between the EDA complex and the transition state and a small difference between the adduct and the transition state. This corresponds to the fact that the forward reaction depends on solvent polarity more strongly than the backward one (see Table 3). The found polarity difference of 2.5 Debye for the backward step is very important since it suggests that a zwitterionic structure contributes to the transition state to some extent (see Fig. 1 in Ref. 5). The conclusion that the transition state is more polar than the cycloadduct, is strongly supported by the negative activation volume for the same step as determined by rapid-reaction techniques at high pressures.[21,22] A much larger dipole moment of 14 Debye is reported for the transition state in the 1,2-cycloaddition of TCNE to *trans*-anethole where a zwitterionic intermediate is considered to exist.[23,24] Major factor for the high polarity of the transition state studied here is breakdown of the molecular symmetry of TCNE in the transition state. The symmetry breakdown is also responsible for the relatively large dipole moment for the adduct where the CN bond dipoles are not fully canceled. The large difference of 7.7 Debye between the reactants and the transition state clearly explains why the formation reaction ($k_f = K_c k_1$) has a large negative reaction constant, $\rho = -5.5 \pm 0.2$, for para-substituted styrenes.[5]

Effect of Solvent Polarity on Activation Entropies. To get insight into the mechanism of the cycloaddition, the cycloreversion process which is unimolecular is most important and thus, mainly the activation entropy for this process is discussed here. The negative values of $\Delta S^{\neq}_{-1}$ (-21 to -48 J mol^{-1}) correspond to the negative activation volume for the process mentioned above, and tell us that the transition state is more polar than the adduct. More negative values of $\Delta S^{\neq}_{-1}$ in the range of -40 to -100 J K^{-1} mol^{-1} have been reported for 1,2-cycloadditions in various solvents where a zwitterionic intermediate is considered to exist.[25]

By differentiating Eq. 9 with respect to temperature and neglecting temperature dependences of μ's and r's, we get the equation

$$\Delta S^{\neq}_{-1} = (\Delta S^{\neq}_{-1})_{\phi} + L\left(\frac{\mu^2_{\neq}}{r^3_{\neq}} - \frac{\mu^2_{\mathrm{P}}}{r^3_{\mathrm{P}}}\right)\frac{\mathrm{d}q}{\mathrm{d}T}. \qquad (12)$$

Inserting $\Delta S^{\neq}_{-1}$ in Table 4, $\mathrm{d}q/\mathrm{d}T$ in Table 1, and the corresponding slope in Fig. 2 into Eq. 12, we obtain -20 to -40 J K^{-1} mol^{-1} as $(\Delta S^{\neq}_{-1})_{\phi}$. These negative values indicate that some solvations not explicitly represented by Kirkwood's dipole model play a role, because $(\Delta S^{\neq}_{-1})_{\phi}$ in the hypothetical gas phase is expected to be somewhat positive from the bond loosening involved in the transition state. If we plot $\Delta S^{\neq}_{-1}$ in Table 4 against $\mathrm{d}q/\mathrm{d}T$ in Table 1, the slope obtained gives a larger dipole moment for the transition state. However, the differentiated form of Kirkwood's relation (Eq. 12) is no doubt less reliable than Eq. 9. Thus, the solvent effect on $\Delta S^{\neq}_{-1}$ can qualitatively be understood in terms of Kirkwood's dipole model. Influences of solvent polarity on $\Delta S^{\neq}_{1}$, $\Delta H^{\neq}_{1}$, and $\Delta H^{\neq}_{-1}$ may be explained in a similar manner.

Some other thermodynamic quantities relating to the reaction are to be mentioned in brief. The reaction enthalpy ($\Delta H_1 = \Delta H^{\neq}_{1} - \Delta H^{\neq}_{-1}$) and entropy ($\Delta S_1 = \Delta S^{\neq}_{1} - \Delta S^{\neq}_{-1}$) for the cycloaddition from the complex are in the ranges of -25 to -38 kJ mol^{-1} and -70 to -116 J K^{-1} mol^{-1}, respectively. Neither is unusual, telling us that the adduct is stabler and more rigid than the complex. In the literature, the activation entropy, $\Delta S^{\neq}_{f} = \Delta S_c + \Delta S^{\neq}_{1}$, from reactants is compiled for many other 1,4-cycloadditions where TCNE is involved.[26] The present values are in the range of -133 to -190 J K^{-1} mol^{-1}, comparable with those in the literature (-120 to -200 J K^{-1} mol^{-1}).

References

1) M. Nakahara, Y. Tsuda, M. Sasaki, and J. Osugi, *Chem. Lett.*, **1976**, 731.

2) M. Nakahara, Y. Uosaki, M. Sasaki, and J. Osugi, *Rev. Phys. Chem. Jpn.*, **47**, 119 (1977).

3) M. Nakahara, Y. Uosaki, M. Sasaki, and J. Osugi, *Bull. Chem. Soc. Jpn.*, **53**, 3395 (1980).

4) Y. Uosaki, M. Nakahara, and J. Osugi, *Bull. Chem. Soc. Jpn.*, **54**, 2569 (1981).

5) Y. Uosaki, M. Nakahara, and J. Osugi, *Bull. Chem. Soc. Jpn.*, **54**, 3681 (1981).

6) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

7) G. S. Kell, *J. Chem. Eng. Data*, **12**, 66 (1967).

8) J. A. Riddick and W. B. Bunger, "Organic Solvents," in "Techniques of Chemistry," 3rd ed, ed by A. Weissberger Wiley-Interscience, New York (1970).

9) M. H. Abraham, "Progress in Physical Organic Chemistry," ed by A. Streitwieser, Jr., and R. W. Taft, Interscience, New York (1974), Vol. 11, p. 1.

10) R. Foster, "Organic Charge-transfer Complexes," Academic Press, London (1969).

11) N. Kulevski, "Molecular Association," ed by R. Foster, Academic Press, London (1975), Vol. 1, Chap. 2.

12) M. Lotfi and R. M. G. Roberts, *Tetrahedron*, **35**, 2137 (1979).

13) F. E. Rogers, *J. Phys. Chem.*, **75**, 1734 (1971).

14) A. I. Konovalov, V. D. Kiselev, A. N. Ustyugov, and N. G. Gess, *Zh. Org. Khim.*, **12**, 2541 (1976).

15) B. N. Solomonov, I. S. Antipin, and A. I. Konovalov, *Zh. Org. Khim.*, **13**, 2491 (1977).

16) S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill, New York (1941).

17) Y. Uosaki, M. Nakahara, M. Sasaki, and J. Osugi, *Chem. Lett.*, **1979**, 727.

18) The radius r is calculated from the partial molal volume V by; $r = \{3V/(4\pi N)\}^{1/3}$. Values of V for D, A, and P in 1,2-dichloroethane are 132.5 ± 0.3, 107.0 ± 1.0, and *ca.* 210[17] cm^3 mol^{-1}, respectively.

19) The dipole moments of CN and CH$_3$ groups are 3.5—4 and 0.3 Debye, respectively.[8]

20) M. Charton, *J. Org. Chem.*, **30**, 552 (1965).

21) J. Osugi, M. Sasaki, H. Tsuzuki, Y. Uosaki, and M. Nakahara, "High-pressure Science and Technology," ed by K. D. Timmerhaus and M. S. Barber, Plenum (1979), Vol. 1, p. 651.

22) H. Tsuzuki, Y. Uosaki, M. Nakahara, M. Sasaki, and J. Osugi, *Bull. Chem. Soc. Jpn.*, submitted.

23) R. Huisgen, *Acc. Chem. Res.*, **10**, 117 (1977).

24) The reported dipole moment is based on kinetic data for $k_f = K_c k_1$. As pointed out in the text, however, not only k_1 but also K_c depend on solvent polarity. Since K_c decreases with increasing solvent polarity, a value larger than 14 Debye is to be obtained.

25) B. N. Solomonov, I. S. Antipin, A. I. Konovalov, and V. B. Novikov, *Zh. Org. Khim.*, **15**, 2466 (1979).

26) J. Sauer and R. Sustmann, *Angew. Chem. Int. Ed. Engl.*, **19**, 779 (1980).