September, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***54***, *2569—2572 (1981)*

Formation of Electron-Donor-Acceptor Complex and 1,4-Cycloadduct of Tetracyanoethylene with Styrene and Its α- or β-Substituted Derivatives

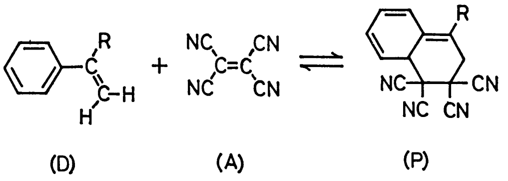
Yasuhiro Uosaki, Masaru Nakahara,* and Jiro Osugi
Department of Chemistry, Faculty of Science, Kyoto University,
Oiwake-cho, Kitashirakawa, Sakyo-ku, Kyoto 606

(Received February 9, 1981)

EDA-complex formation and 1,4-cycloaddition of tetracyanoethylene (TCNE) with styrene, α-methylstyrene, 1,1-diphenylethylene, *cis*-stilbene, and *trans*-stilbene were studied spectrophotometrically in chloroform at 25 °C. Formation constants of the EDA complexes were found to be in the order, *trans*-stilbene>styrene>α-methylstyrene>*cis*-stilbene>1,1-diphenylethylene. The difference in the formation constants was discussed in terms of both electronic and steric effects of the donors studied. α-Methylstyrene and 1,1-diphenylethylene underwent thermal cycloaddition to TCNE faster than styrene. It is suggested that some charge separation took place in the transition state. The fact that *trans*- and *cis*-stilbenes do not react with TCNE was explained in terms of the difference in stability of the 1,4-cycloadducts estimated from the 1,4-bislocalization energy obtained by Dewar's perturbation molecular orbital method.

The nature of tetracyanoethylene (TCNE) as a strong acceptor causes a few typical cycloaddition reactions with π-electron donors as well as the EDA (electron-donor-acceptor)-complex formation.[1] When TCNE is mixed with benzene derivatives, electron-rich olefins, and conjugated dienes, it usually yields the EDA complexes only, cyclobutane derivatives (1,2-cycloadducts), and cyclohexene derivatives (1,4-cycloadducts), respectively, under mild conditions.

Styrene has been considered to be nonreactive toward TCNE under mild conditions, although benzylidenemalononitrile and a cycloadduct consisting of two molecules of styrene and one molecule of TCNE were obtained by refluxing in xylene.[2] Recently, however, it was found by the high-pressure quenching method that styrene and its derivatives(D) undergo reversible cycloaddition to TCNE(A) to afford the 1,4-cycloadduct(P) besides the EDA complex.[3,4] The 1,4-cycloaddition reaction illustrated below is of interest. Styrenes serve as a diene, losing their aromaticity, while they act as a dienophile in the Diels-Alder reaction with anthracenes.[5] In order to get insight into the mechanism of the reaction, a detailed kinetic study has been carried out. It was not clarified in the previous work[4] why neither *cis*- nor *trans*-stilbene provides the 1,4-cycloadduct, despite the fact that ionization potentials of these molecules are lower than those of other styrenes which give the cycloadduct. An interpretation for the unexpected result is given herewith in view of the molecular orbital theory.



The formation constant and molar absorption coefficient of the EDA complex between TCNE and styrene were determined[6–9] without taking into consideration the coexistence of the 1,4-cycloadduct confirmed previously.[3,4] Reliable values of these parameters were obtained in the present study taking into account the 1,4-cycloadduct. Discussion is given on the factors determining the stability of the EDA complexes between TCNE and styrene and its derivatives.

Experimental

Electron donors and TCNE were purified by the method reported.[4] Chloroform as a solvent was purified by the standard method. The boiling points and melting points of all the reagents agree with the values reported.

Stock solutions of the donors and the acceptor were prepared immediately before use. Electronic absorption spectra and their time dependences for kinetic studies were measured with a Shimadzu UV-200S spectrophotometer. Thermostatted water (25 °C) was circulated around a quartz cell and donor and acceptor reservoirs. The temperature was regulated within ±0.1 °C. Under the conditions where the concentration (mol dm^{-3}) of the donor is in large excess, reaction rates were determined by following the increase in the absorbance around 320 nm due to the 1,4-cycloadduct, and equilibrium studies by observing the charge-transfer (CT) band at a longer wavelength. The absorbance due to the EDA complex decreased to a stationary value (not zero) with time except in the case of stilbenes. The time at half-mixing of donor and acceptor solutions was taken as time zero when we get an absorbance of the EDA complex at time zero by extrapolation.

Results and Discussion

EDA Complexes of TCNE with Various Styrene Derivatives. When α-methylstyrene is mixed with TCNE in chloroform, absorption bands due to the EDA complex instantaneously appear in the visible region (Fig. 1b). Similar absorption spectra can be observed in solutions of TCNE and other styrene derivatives. The donor and TCNE have no absorption in this region. The wavelength of the maximum absorption($\lambda_{\max}$) is slightly larger in chloroform than that in dichloromethane (Table 1).

The plot of transition energies ($h\nu_{\mathrm{CT}}$) of a series of EDA complexes with a fixed acceptor against ionization potential (I_{p}) of donors generally shows a

Table 1. Spectroscopic properties and formation constants of EDA complexes between TCNE and various styrene derivatives in $CHCl_3$ at 25 °C

Donor	I_p[a)] / eV	λ_{max}[b)] / nm	ε_{max} / $mol^{-1}\,dm^3\,cm^{-1}$	K_c / $mol^{-1}\,dm^3$
Styrene	8.50	486(480)	1960±30	0.467±0.010
α-Methylstyrene	8.50	504(495)	1760±50	0.436±0.013
1,1-Diphenylethylene	8.25	519(507)	1660±50	0.306±0.011
cis-Stilbene	8.20	541(528)	1950±110	0.415±0.023
trans-Stilbene	8.00	608(597)	1880±50	1.16±0.03

a) Ref. 13; 1 eV≈96.48456 kJ/mol. b) Values in parentheses were measured in CH_2Cl_2 from Ref. 4.

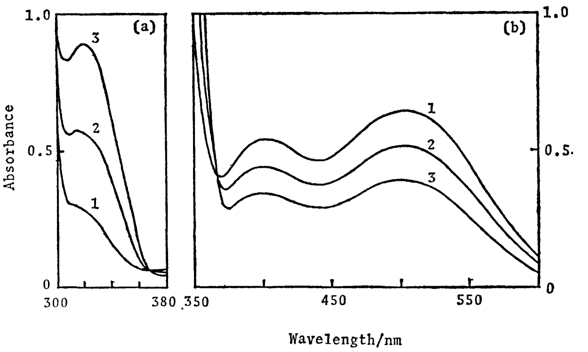


Fig. 1. Time dependence of the electronic spectrum of α-methylstyrene–TCNE system in $CHCl_3$ at 25 °C. (a) 1,4-Cycloadduct ($[D]_0=0.5$ mol dm^{-3}, $[A]_0=2\times10^{-4}$ mol dm^{-3}). (b) EDA complex ($[D]_0=0.5$ mol dm^{-3}, $[A]_0=2\times10^{-3}$ mol dm^{-3}). (1): 10 s after mixing, (2): 1 min, (3): stationary state.

linear relationship.[1b)] This was also found to be the case in this study:

$$h\nu_{CT}/\mathrm{eV} = 0.873(I_p/\mathrm{eV}) - 4.89 \quad (\text{in } CHCl_3) \quad (1)$$

$$h\nu_{CT}/\mathrm{eV} = 0.847(I_p/\mathrm{eV}) - 4.63 \quad (\text{in } CH_2Cl_2). \quad (2)$$

The gradients obtained for the TCNE–styrene derivative systems are nearly the same as those obtained for other TCNE–aromatic hydrocarbon systems in the corresponding solvents.[1b)] The fact that the gradient is not very far from unity suggests that the resonance interaction between the donors and acceptor is weak; the EDA complexes we have examined are weak ones.

The formation constant(K_c) and molar absorption coefficient (ε_{max}) of the EDA complex at λ_{max} are determined by the Scott equation,[10)]

$$\frac{[D]_0[A]_0 l}{A_0} = \frac{1}{K_c\varepsilon_{max}} + \frac{[D]_0}{\varepsilon_{max}}, \quad (3)$$

where $[D]_0$ and $[A]_0$ are the initial concentrations of the donor and acceptor, respectively, A_0 is the absorbance of the EDA complex at λ_{max} at time zero, ε_{max} the molar absorption coefficient at λ_{max}, and l the path length (10 mm). Figure 2 shows a plot of the left-hand side of Eq. 3 against $[D]_0$ for α-methylstyrene–TCNE system. Applying the least-squares method to linear plots like this, we obtain values of K_c and ε_{max} of the complexes as in Table 1, the K_c values being in the sequence, *trans*-stilbene>styrene>α-methylstyrene > *cis*-stilbene > 1,1-diphenylethylene. The sequence of the TCNE complexes is similar to that of the 1,3,5-trinitrobenzene complexes, except for the case of *cis*-stilbene.[11)]

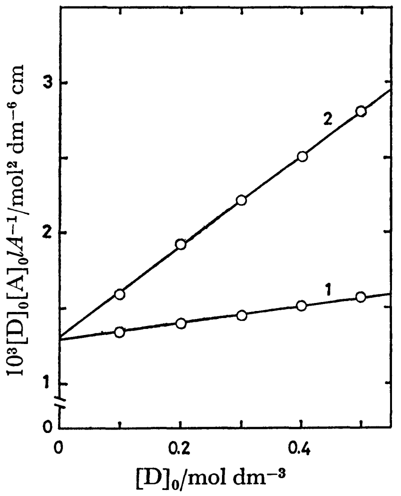


Fig. 2. Scott plots for α-methylstyrene–TCNE system in $CHCl_3$ at 25 °C.
1: $t=0$, 2: stationary state.

In the case of planar molecules like styrene and *trans*-stilbene, the sequence is in accord with the trend that the lower the ionization potential of the electron donors, the larger the formation constant. The trend has been derived theoretically by assuming that CT forces mainly contribute to the stabilization energy of the EDA complex.[9,12)] On the other hand, in the case of nonplanar molecules like α-methylstyrene, 1,1-diphenylethylene, and *cis*-stilbene, the result is not in accord with the general trend. Since these three nonplanar styrenes have dihedral angles, *ca.* 30—40°,[13,14)] the configuration of the complexes is considered to differ a great deal from that of planar-styrene complexes. The nonplanarity of the electron donors interferes approach of the planar TCNE molecule as a factor of steric hindrance, which is responsible for the formation constant smaller than that expected simply from the electronic effect.

Kinetics of 1,4-Cycloaddition. The absorption band around 320 nm due to the 1,4-cycloadduct increases and the CT-absorption band decreases with time, and finally, they reach stationary values (Fig. 1a). Since the EDA-complex formation and 1,4-cycloaddition take place reversibly, the following reaction scheme in which both reactions proceed successively can be assumed:[15)]

$$\mathrm{D} + \mathrm{A} \underset{}{\overset{K_c}{\rightleftharpoons}} \text{EDA complex} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{P} \tag{4}$$

where k_1 and k_{-1} are the rate constants of the forward and backward reactions, respectively. Let us carry out a kinetic analysis of the reaction according to Eq. 4. When $[\mathrm{D}]_0 \gg [\mathrm{A}]_0$, the rate equation for the increase of the 1,4-cycloadduct is

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = a - k_{\mathrm{obsd}}[\mathrm{P}], \tag{5}$$

where the square brackets denote the concentration, t time,

$$a = \frac{k_1 K_c[\mathrm{D}]_0[\mathrm{A}]_0}{1+K_c[\mathrm{D}]_0} = k_1[\mathrm{EDA}]_0, \tag{6}$$

and

$$k_{\mathrm{obsd}} = \frac{k_1 K_c[\mathrm{D}]_0}{1+K_c[\mathrm{D}]_0} + k_{-1}. \tag{7}$$

Integration of Eq. 5 gives the expression for [P] as

$$[\mathrm{P}] = \frac{k_1[\mathrm{EDA}]_0\{1-\exp(-k_{\mathrm{obsd}}t)\}}{k_{\mathrm{obsd}}}, \tag{8}$$

since [P]=0 at time zero. Pseudo-first-order rate constant, k_{obsd}, was determined by the Guggenheim plot. Plots of k_{obsd} *vs.* $K_c[\mathrm{D}]_0/(1+K_c[\mathrm{D}]_0)$ for the styrene– and α-methylstyrene–TCNE systems afford good straight lines as shown in Fig. 3. Values of k_1 and k_{-1} obtained from plots of this kind are given in Table 2, together with those of equilibrium constant between the 1,4-cycloadduct and EDA complex, $K_1(\equiv k_1/k_{-1})$, and overall equilibrium constant $K(\equiv K_c K_1)$. We see from Eq. 7 that the product $k_1 K_c$ is overall second-order rate constant from the reactants to the 1,4-cycloadduct. Table 2 shows that the effect of substitution at the α-position by methyl or phenyl group on $k_1 K_c$ is substantially large, the methyl or phenyl substitution enhancing the reactivity by factors of *ca.* 70 and *ca.* 50, respectively. Though most 1,4-cycloadditions are considered to proceed *via* concerted mechanism, the enhancement of the reaction is too large for a concerted mechanism.[16] Similar enhancement has been observed for 1,2-cycloaddition of TCNE to enol or enethiol ethers in which a dipolar intermediate is considered to be involved.[17,18] Thus the α-substitution effect suggests that some charge separation develops in the transition state of the 1,4-cycloaddition. The marked dependence of the rate on solvent polarity supports this idea.[19]

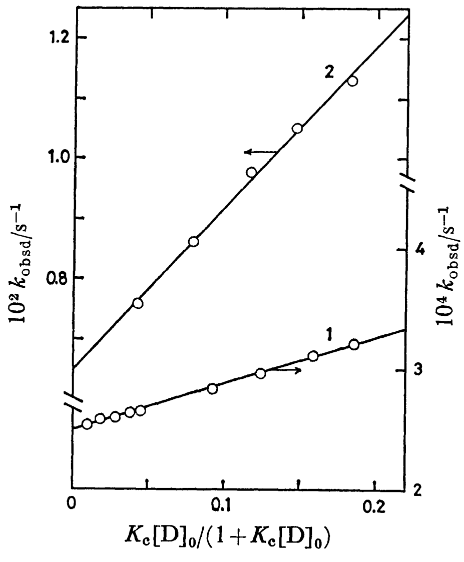


Fig. 3. Plots of k_{obsd} against $K_c[\mathrm{D}]_0/(1+K_c[\mathrm{D}]_0)$ in $\mathrm{CHCl_3}$ at 25 °C.
1: Styrene–TCNE, 2: α-methylstyrene–TCNE.

Equilibria Including 1,4-Cycloadduct. At the stationary state, *i.e.*, $t=\infty$, we obtain

$$[\mathrm{P}]_e = \frac{k_1[\mathrm{EDA}]_0}{k_{\mathrm{obsd}}}, \tag{9}$$

where $[\mathrm{P}]_e$ is the concentration of the 1,4-cycloadduct at the stationary state. By means of the definition $K_1=[\mathrm{P}]_e/[\mathrm{EDA}]_e$ and Eqs. 6, 7, and 9, we have

$$[\mathrm{EDA}]_e = \frac{K_c[\mathrm{D}]_0[\mathrm{A}]_0}{1+(1+K_1)K_c[\mathrm{D}]_0}. \tag{10}$$

This can be rewritten as

$$\frac{[\mathrm{D}]_0[\mathrm{A}]_0 l}{A_e} = \frac{1}{K_c\varepsilon_{\max}} + \frac{(1+K_1)[\mathrm{D}]_0}{\varepsilon_{\max}}, \tag{11}$$

by means of Beer's relation $[\mathrm{EDA}]_e = A_e/\varepsilon_{\max}\, l$, where A_e is the absorbance of the EDA complex at $\lambda_{\max}$ at the stationary state. A plot of the left-hand side of Eq. 11 against $[\mathrm{D}]_0$ in the α-methylstyrene–TCNE system is also shown in Fig. 2. The two kinds of plots corresponding to Eqs. 3 and 11 should have the same intercept; this is actually the case. The equilibrium constant K_1 is determined from Eq. 11 and the slope of the line 2 in Fig. 2. The value of K_1 obtained from the equilibrium measurement is in accord with that obtained kinetically ($K_1 \equiv k_1/k_{-1}$) within experimental error (Table 2). The agreement indicates that the present analysis is self-consistent.

We can obtain from Eq. 8 a reliable value of the molar absorption coefficient (ε_{320}) of the 1,4-cycloadduct at 320 nm. The values of $\varepsilon_{320}/\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ are $(7.7\pm0.1)\times10^3$, $(5.1\pm0.3)\times10^3$, and $(4.0\pm0.2)\times$

Table 2. Rate and equilibrium constants of the 1,4-cycloaddition between TCNE and various styrene derivatives in $\mathrm{CHCl_3}$ at 25 °C

Donor	$10^3 k_1/\mathrm{s^{-1}}$	$10^3 k_{-1}/\mathrm{s^{-1}}$	K_1	$K/\mathrm{mol^{-1}\,dm^3}$
Styrene	0.380±0.012	0.250±0.001	1.52±0.05	0.71±0.04
α-Methylstyrene	26.8±0.6	6.50±0.09	4.12±0.15 (4.29±0.15)[a]	1.80±0.12
1,1-Diphenylethylene	28.9±2.5	8.21±0.12	3.51±0.35	1.07±0.15

a) From the equilibrium measurement.

10^3 for the styrene, α-methylstyrene, and 1,1-diphenylethylene adducts, respectively. The value of ε_{320} for the styrene adduct is slightly larger than that obtained in dichloromethane ($(5.5\pm0.1)\times10^3$).[4)] The difference arises from the change of solvents and the neglect of the presence of the EDA complex in the previous treatment.

Tonchéva *et al.* determined K_c and ε_{max} of the TCNE complexes with styrene and α-methylstyrene in 1,2-dichloroethane at 20 °C without noticing the 1,4-cycloadduct, and reported 645 as ε_{max} for styrene and 200 for α-methylstyrene.[7)] These values are too small for the TCNE complexes with aromatic hydrocarbons.[1b)] The stationary state reaches within 10 minutes in the case of α-methylstyrene–TCNE in chloroform (Table 2). In a more polar solvent, 1,2-dichloroethane, the stationary state is attained faster. The ε_{max} is considered to be $\varepsilon_{max}/(1+K_1)$; ε_{max} and K_1 are shown to be $(3.33\pm0.16)\times10^3$ mol^{-1} dm^3 cm^{-1} and 13.8 under the same condition.[19)]

Reactivity of Styrenes. The reactivity of dienes toward TCNE generally increases with the decrease in its ionization potentials, though it is not the diene having lower ionization potential that shows high reactivity in the Diels-Alder reaction. This is also the case for the reaction we examined. Although *trans-* and *cis*-stilbenes have lower ionization potentials than other styrene derivatives, the stilbenes react with TCNE to form only the EDA complex, showing no further reaction such as 1,4-cycloaddition.

The reactivity of styrenes toward TCNE can be examined by the method described by Mok and Nye;[20)] the energy of the transition state is considered to depend on the FMO (frontier molecular orbital) interaction energy between reactants and on the stability of the product. The FMO treatment predicts that a diene of lower ionization potential is more reactive on the assumption that other interactions (*e.g.*, van der Waals interactions) are constant within a series of dienes. Since this is contradictory to the experimental results, we should examine the stability of the product. The 1,4-bislocalization energy calculated from Dewar's perturbation molecular orbital method is of great use for a comparison of the stability of the adducts.[21)] The 1,4-bislocalization energies computed for three styrenes are given in Table 3, where *para*-localization energies by Brown[22)] are included for comparison. It turns out that both parameters have nearly the same value for the donors. We see from the definition of localization energy that a diene of a smaller localization energy, *i.e.*, smaller coefficient of the localization energy, reacts with TCNE to form a stable adduct. For the discussion of reactive sites,[22)] the critical value of the localization energy divided by the resonance integral (β) is taken as 3.6 below which reaction takes place. Stilbenes have a larger value than this corresponding to the fact that they are nonreactive toward TCNE (Table 3).

TABLE 3. 1,4-BISLOCALIZATION AND *para*-LOCALIZATION ENERGIES OF THREE STYRENES

Donor	1,4-Bislocalization energy/β	*Para*-localization energy[a)]/β
Styrene	3.51	3.44
1,1-Diphenylethylene	3.26	3.34
Stilbene	3.84	3.89

a) Ref. 22.

References

1) For recent reviews see: a) E. M. Kosower, "Progress in Physical Organic Chemistry," ed by S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Interscience Publishers, New York (1965), Vol. 3, p. 81; b) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London (1969); c) A. K. Colter and M. R. J. Dack, "Molecular Complexes," ed by R. Foster, Elek Science, London (1974), Vol. 2, p. 1.

2) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962).

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

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

5) J. Sauer, *Angew. Chem. Int. Ed. Engl.*, **6**, 16 (1967).

6) A. R. Cooper, C. W. P. Crowne, and P. G. Farrell, *Trans. Faraday Soc.*, **62**, 18 (1966).

7) B. Tonchéva, R. Vélichkova, and I. M. Panayotov, *Bull. Soc. Chim. Fr.*, **1974**, 1033.

8) K. Hayashi, P. A. Marchese, S. Munari, and S. Russo, *Chim. Ind. (Milan)*, **56**, 187 (1974).

9) T. Arimoto and J. Osugi, *Rev. Phys. Chem. Jpn.*, **44**, 25 (1974).

10) R. L. Scott, *Recl. Trav. Chim. Pays-Bas*, **75**, 787 (1956).

11) P. H. Emsile, R. Foster, I. Horman, J. W. Morris, and D. W. Twiselton, *J. Chem. Soc., B*, **1969**, 1162.

12) M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron, Suppl.*, **7**, 97 (1966).

13) J. P. Maier and D. W. Turner, *J. Chem. Soc., Faraday Trans. 2*, **69**, 196 (1973).

14) H. Suzuki, *Bull. Chem. Soc. Jpn.*, **33**, 619 (1960).

15) For example, there is another scheme in which the complex formation competes with cycloaddition. However, both schemes are indistinguishable kinetically, no means being found for distinction.

16) For a recent review see: J. Sauer and R. Sustmann, *Angew. Chem. Int. Ed. Engl.*, **19**, 779 (1980).

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

18) T. Okuyama, M. Nakada, K. Toyoshima, and T. Fueno, *J. Org. Chem.*, **43**, 4546 (1978).

19) Y. Uosaki, M. Nakahara, and J. Osugi, unpublished.

20) K. Mok and M. J. Nye, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1811.

21) M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry," Plenum, New York (1975).

22) R. D. Brown, *J. Chem. Soc.*, **1950**, 2730.