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Kinetics and Mechanism of 1,4-Cycloaddition between Tetracyanoethylene and Styrenes. II.[1] Effect of Para Substituents

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The 1,4-cycloaddition of TCNE to *p*-methyl-, *p*-chloro-, and *p*-bromostyrenes by way of the EDA complex has been studied in chloroform at 25 °C by the spectrophotometric method. The Hammett correlation obtained from the kinetic data provides -5.5 ± 0.2 as the reaction constant ρ. The negative value is large in magnitude relative to other common 1,4-cycloadditions, suggesting some large partial charges in the rate-determining transition state. A linear correlation between the logarithmic forms of the reaction rate and the EDA-complex formation constant is in favor of the reaction scheme where the complex is on the pathway of the cycloaddition.

The 1,4-cycloadduct of tetracyanoethylene (TCNE) with styrene and its derivatives has been discovered in solution by the low-temperature ^{13}C NMR technique combined with a high-pressure quenching method.[2] The effect of α-substituents on the 1,4-cycloaddition has been discussed in detail in a previous paper; a polar transition state is suggested based on the α-substituent effect.[1] The electronic effect of α-substituents is coupled to some extent with the steric hindrance because of the small distance from the reaction sites. For this reason, para substitution is more desirable to see exclusively the electronic effect of substituents on the 1,4-cycloaddition. For this purpose *p*-methyl-, *p*-chloro-, and *p*-bromostyrenes are employed in the present work.

The 1,4-cycloaddition (so-called Diels-Alder reaction) is a typical cycloaddition reaction and of great interest from theoretical and synthetic points of view. A large number of kinetic studies have been done to get insight into the mechanism of this simple and useful reaction, as recently well reviewed.[3] Most of the kinetic data are in favor of the concerted mechanism ((a) in Fig. 1). In the 1,4-cycloaddition studied here, styrenes serve as a diene instead of a dienophile; one unsaturated bond comes from the vinyl group and the other from the phenyl group, and as a result, the aromaticity is lost in the product. The aim of the present investigation is to elucidate the reaction mechanism of this unique 1,4-cycloaddition from the point of view of kinetics.

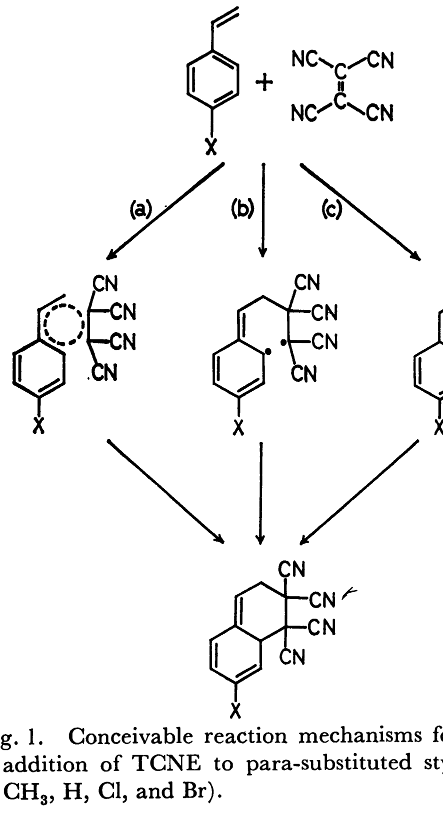

Fig. 1. Conceivable reaction mechanisms for 1,4-cycloaddition of TCNE to para-substituted styrenes (X= CH_3, H, Cl, and Br).

Experimental

p-Methyl-, *p*-chloro-, and *p*-bromostryenes were prepared by dehydrating the corresponding secondary alcohols with $KHSO_4$. The alcohols were synthesized by reducing the para-substituted acetophenones in ethanol with $NaBH_4$. All styrenes were repeatedly distilled at reduced pressure, stored in a refrigerator, and distilled again over CaH_2 before use. TCNE and chloroform were purified by repeated sublimation and distillation, respectively.

The apparatus and experimental procedures in the present work are the same as those described in detail in the previous paper.[1] Temperature was kept constant to ±0.1° C. The concentration of the donor was always much higher than that of the acceptor so as to simplify several equations utilized in the present analysis.

Results

Formation Constant of EDA Complex. When TCNE is mixed with each of the donors in chloroform, the electron-donor-acceptor (EDA) complex is formed instantaneously as a result of the diffusion-controlled reaction and exhibits two absorption maxima due to the first and second charge-transfer transitions in the visible region. All styrenes treated in this work and

Table 1. Spectroscopic parameters of EDA complexes in $CHCl_3$ at 25°C and some relevant properties of donors

X[a]	λ_{max} / nm	ε_{max} / $mol^{-1}\,dm^3\,cm^{-1}$	K_c / $mol^{-1}\,dm^3$	I_P / eV	σ_p^{+}[e]
CH_3	531	1330 ± 20	1.46 ± 0.03	8.38[d]	−0.311
H	486[b]	1960 ± 30[b]	0.467 ± 0.010[b]	8.50[c]	0
Cl	493	1970 ± 60	0.201 ± 0.007	8.48[d]	+0.114
Br	497	2390 ± 80	0.172 ± 0.006	8.47[d]	+0.150

a) X denotes the substituent at the para site of styrene (see Fig. 1). b) From Ref. 1. c) From Ref. 5. d) From Eq. 2. e) From Ref. 6.

TCNE have no absorption in this region. Spectroscopic parameters of the complexes are summarized in Table 1 together with some relevant properties of the donors.

The complex formation constant (K_c) and molar absorption coefficient (ε_{max}) of the first charge-transfer band, listed in Table 1, are determined from the Scott equation 1,[4]

$$\frac{[D]_0[A]_0 l}{A_0} = \frac{1}{K_c\varepsilon_{max}} + \frac{[D]_0}{\varepsilon_{max}}, \tag{1}$$

where $[D]_0$ and $[A]_0$ are the initial concentrations of the donor and the acceptor, respectively, l the path length (1 cm) and A_0 the absorbance of the complex before the 1,4-cycloadduct is formed. Figure 2 shows plots of the left-hand side of Eq. 1 against $[D]_0$, the slopes and intercepts of which provide K_c and ε_{max} simultaneously.

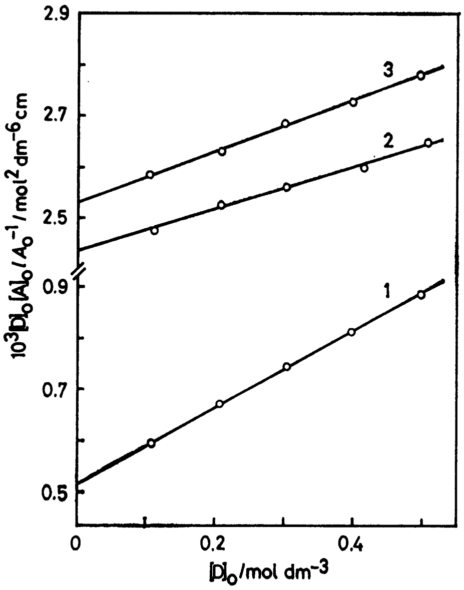

Fig. 2. Plots of $[D]_0[A]_0 l/A_0$ *vs.* $[D]_0$.
1: *p*-Methylstyrene, 2: *p*-bromostyrene, 3: *p*-chlorostyrene.

Since there is no photoelectron spectroscopic investigation on the para-substituted styrenes treated here, the ionization potentials (I_p) of these molecules in Table 1 are estimated by using the relation.

$$h\nu_{CT}/eV = 0.873(I_P/eV) - 4.89, \tag{2}$$

which is obtained on the basis of reported ionization potentials of some other styrene derivatives[5] and first charge-transfer transition energies ($h\nu_{CT}$) of their EDA complexes with TCNE.[1]

Reaction Rate of 1,4-Cycloaddition. Since the EDA-complex formation and 1,4-cycloaddition are reversible reactions, the following reaction scheme is assumed:

$$D + A \overset{K_C}{\rightleftharpoons} \text{EDA Complex} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P, \tag{3}$$

where k_1 and k_{-1} are the rate constants of the forward and backward reactions, respectively and P denotes the cycloaddition product. The rate equation for the reaction 3 is easily solved and affords the expression for [P] as a function of time (t):[1]

$$[P] = \frac{k_1[EDA]_0\{1-\exp(-k_{obsd}t)\}}{k_{obsd}}, \tag{4}$$

where

$$k_{obsd} = \frac{k_1K_c[D]_0}{1+K_c[D]_0} + k_{-1}. \tag{5}$$

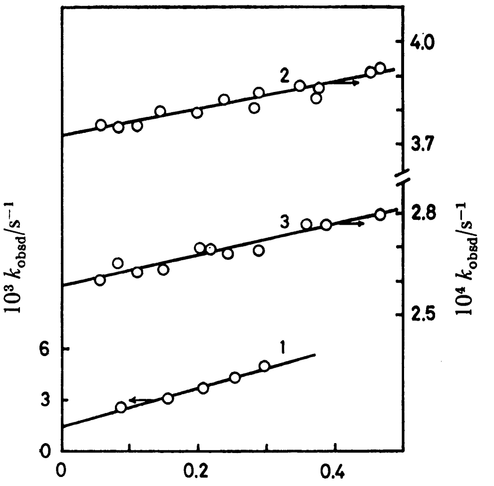

Fig. 3. Plots of k_{obsd} *vs.* $[D]_0/(1+K_c[D])$.
1: *p*-Methylstyrene, 2: *p*-chlorostyrene, 3: *p*-bromostyrene.

The pseudo-first-order rate constant, k_{obsd} was determined by the Guggenheim plot. As shown in Fig. 3, plots of k_{obsd} *vs.* $[D]_0/(1+K_c[D]_0)$ are linear, and from these slopes and intercepts we can get the values of k_1K_c and k_{-1}. The overall formation constant for the 1,4-cycloadduct K_p expressed as

$$K_P = \frac{[P]}{[D][A]} \tag{6}$$

$$= \frac{[EDA][P]}{[D][A][EDA]} \tag{7}$$

$$= K_cK_1 \tag{8}$$

$$= K_ck_1/k_{-1} \tag{9}$$

$$= k_f/k_{-1} \tag{10}$$

is given in Table 2 together with $k_f(=K_ck_1)$ and k_{-1}.

TABLE 2. KINETIC AND THERMODYNAMIC PARAMETERS OF 1,4-CYCLOADDUCTS IN $CHCl_3$ AT 25°C

X[a]	$10^4 k_f$ / $mol^{-1}\,dm^3\,s^{-1}$	$10^4 k_{-1}$ / s^{-1}	K_P / $mol^{-1}\,dm^3$
CH_3	115±4	14.5 ±0.09	7.93 ±0.33
H	1.77 ±0.05[b]	2.50±0.01[b]	0.708±0.023[b]
Cl	0.400±0.040	3.72±0.01	0.108±0.011
Br	0.454±0.049	2.59±0.01	0.175±0.020

a) X denotes the substituent at the para site of styrene.
b) From Ref. 1.

Discussion

The Hammett Correlation. The electronic effect of the para substitution (X in Table 1) on the formation of the 1,4-cycloadduct is expressed in terms of the

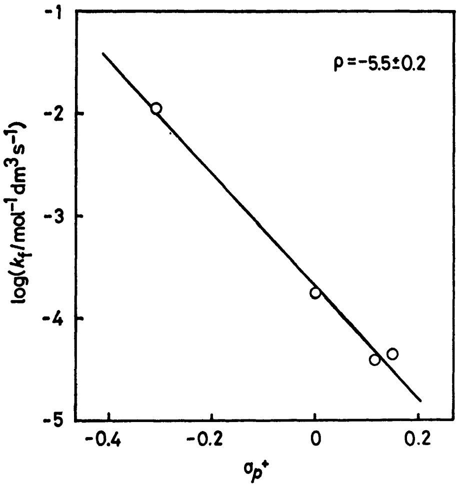

Fig. 4. A Hammett plot of log k_f vs. σ_p^+.

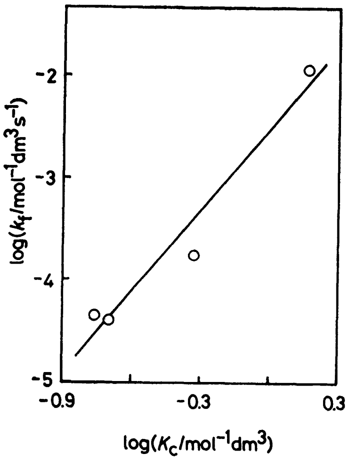

Fig. 5. A Plot of log k_f vs. log K_c.

reaction constant ρ, which is determined as -5.5 ± 0.2 from the Hammett plot of log k_f (in Table 2) vs. σ_p^{+}[6] (in Table 1) in Fig. 4. The ρ value obtained here is negative and considerably large in magnitude. Actually, ρ values are in the range of -1.8 to $+2.6$ for many other 1,4-cycloaddition reactions where CC-, NN-, and NO-double and CC-triplet bonds act as dienophiles.[3] The small ρ values found so far are considered to support the concerted mechanism (a) in Fig. 1. A large negative ρ value of -7.1 ± 0.5 has been reported for the 1,2-cycloaddition of TCNE to styrene derivatives having a strong electron-releasing substituent at the para site according to the Yukawa-Tsuno equation.[7] The large negative value for this 1,2-cycloaddition is regarded as an indication of a zwitterionic intermediate which is recognized in a similar 1,2-cycloaddition by various methods.[8] The large negative value found for the present reaction suggests some large partial charges in the rate-determining transition state. The following paper clarifies that the transition state has a dipole moment which is considerable but not so large as in a zwitterion existing in the 1,2-cycloaddition reaction.[9] Thus, the zwitterionic structure (c) in Fig. 1 contributes to the transition state of the 1,4-cycloaddition studied here to some extent. At the present time, however, we can not argue whether this 1,4-cycloaddition proceeds by one step or by two steps, because our attempt to trap any probable polar intermediate by using ice-cold methanol was unsuccessful.[10]

There is a frontier molecular orbital approach to the interpretation of the Hammett correlation.[11] It is not useful, however, in the present reaction because the ionization potential of the donor used as a measure of the HOMO energy (E_{HOMO}) does not correlate with the obtained k_f (see Table 1). In other words, the substituent constants σ_p^+ are not linearly correlated with ($E_{\mathrm{HOMO}}-E_{\mathrm{LUMO}}$) in the present series of the donors.

A Correlation of the Rate Constant k_f with the Complex Formation Constant K_c. In Fig. 5, the values of log k_f in Table 2 are plotted against log K_c. There exists a linear correlation, the correlation coefficient of which is 0.976. The linear correlation between log k_f and log K_c somehow supports the assumed reaction scheme shown by Eq. 3 because the free energy of the transition state of the 1,4-cycloaddition and the free energy of the complex are not necessarily expected to be linearly correlated in a reaction system where the complex formation is merely a side reaction. Similar correlations are reported in the 1,4-cycloaddition of TCNE to anthracenes[12] and some other kind of reactions.[13] In the former case, a negative activation enthalpy has been found, which is considered to support the scheme shown by Eq. 3 where the complex is on the pathway of the 1,4-cycloaddition reaction.[14] These linear correlations are often taken as evidence for the intermediacy of the EDA complex. The linear correlation found here between log k_f and log K_c suggests that the charge-transfer interaction between the donor and the acceptor is somehow important among interactions in the transition state.

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