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Chemical Reaction of Electron Donor-Acceptor System: A New Mechanism for the Tricyanovinylation Reaction of Some Aromatic Amines with Tetracyanoethylene

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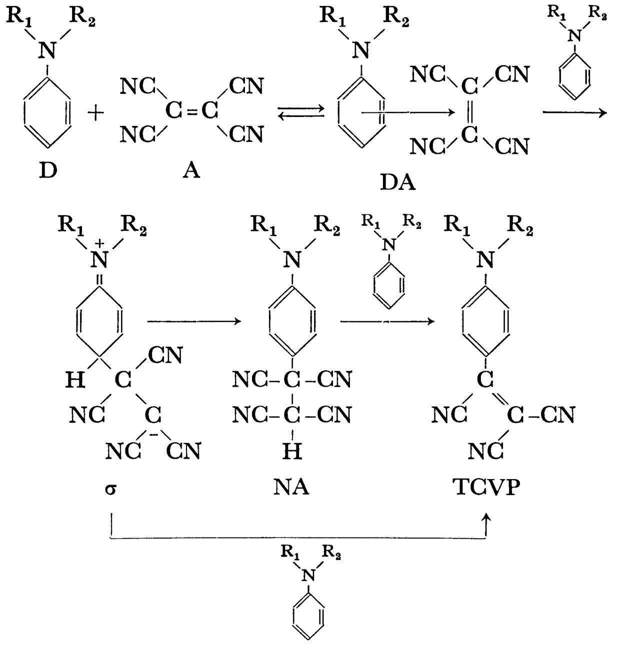
The tricyanovinylation reactions of several aromatic amines with tetracyanoethylene (TCNE) were investigated kinetically by observing the change of the absorbance of the charge-transfer (CT) band in 1,2-dichloroethane. The pseudo first order rate coefficient of the decay of the CT-complex (k_{obsd}) was found to obey the relation, $k_{\mathrm{obsd}}=kKD^n/(1+KD)$ (K: association constant of CT-complex; D: initial concentration of donor molecule), where $n=1$ in *N*,*N*-diethylaniline (DEA)–TCNE and *N*,*N*-di-*n*-butylaniline (DBA)–TCNE systems and $n=2$ in *N*-methyl-*N*-ethylaniline (MEA)–TCNE system. Since the currently accepted mechanism for the tricyanovinylation reaction cannot explain the case of $n=1$, we have proposed a new reaction mechanism which can explain all the kinetic data reported hitherto. Two characteristic points are involved in the new mechanism, *i.e.*, one is the unimolecular reaction of the CT-complex or the bimolecular reaction between reactants to form the σ-complex, and the other the decomposition of the σ-complex back to the component molecules. The reactions of MEA, DEA, and DBA with TCNE were discussed based on the new mechanism.

There have been extensive studies on the role of charge-transfer (CT) interaction in chemical reactions.[1] The tricyanovinylation (TCV) reactions of several aromatic amines with tetracyanoethylene (TCNE)[2–11] are the most typical reaction systems involving the formation of CT-complex. The clarification of the TCV reaction mechanism is very important, since it gives us fundamental information as to the role of the CT-complex to the reaction which has been left ambiguously yet.

Z. Rappoport studied systematically the TCV reactions of *N*,*N*-dimethylaniline (DMA) and *N*-methylaniline (MA) with TCNE for the first time,[2,3] and found that the 1:1 CT-complex (DA) formed between reactants gradually disappears to form the intermediate zwitterionic σ-complex (σ) or neutral adduct tetracyanoethane derivative (NA), and thereafter the final tricyanovinyl compound (TCVP) is slowly produced. The reaction scheme proposed by him is shown as Scheme 1. These two steps of reactions could be followed independently by an electronic absorption measurement because of the large difference in the reaction rates. In the first step, the decay of the CT-complex followed the rate equation (I-1),

$$-\frac{\mathrm{d[DA]}}{\mathrm{d}t}=k_{\mathrm{obsd}}[\mathrm{DA}]=\frac{kKD^2}{1+KD}[\mathrm{DA}] \qquad \text{(I-1)}$$

where [DA], D, K, k_{obsd}, and k denote the CT-complex, initial concentration of a donor molecule (D), association constant of the CT-complex, pseudo first order rate coefficient of the CT-complex and the coefficient for the process between the CT-complex and the σ-complex, respectively. This kinetic equation has to date been understood by the mechanism as described in Scheme 1. Namely, Z. Rappoport has postulated in this mechanism a bimolecular reaction between DA and D, which is considered to be inevitable in order to introduce D^2 term in the numerator of k_{obsd}, and he considered an exchange reaction of a complexed D and a free D in this process. The reactions of D with σ and NA have been considered as the proton abstraction reactions from σ and NA with D.



$R_1=H$, $R_2=CH_3$: MA
$R_1=R_2=CH_3$: DMA
$R_1=CH_3$, $R_2=C_2H_5$: MEA
$R_1=R_2=C_2H_5$: DEA
$R_1=R_2=n\text{-}C_4H_9$: DBA

Scheme 1.

The kinetic studies on the cycloaddition reactions of electron-donating olefins with TCNE[12,13] and on the ionization reaction in *N*,*N*-diethyl-*p*-toluidine–TCNE system[14] have revealed that the reaction should be interpreted as either a unimolecular transformation of the CT-complex or a bimolecular reaction of D with A. Namely, the bimolecular reaction between CT-complex and D has not been involved in these reaction kinetics. We have had questions for a long time why a bimolecular reaction of CT-complex with free D must be involved only in the TCV reaction, and this question prompted us to study the TCV reactions of higher *N*-alkylanilines, *N*-methyl-*N*-ethylaniline (MEA), *N*,*N*-diethylaniline (DEA) and *N*,*N*-di-*n*-butylaniline (DBA), with TCNE in order to make clear the role of the CT-complex in the reaction. As the results, unimolecular reaction of the CT-complex or the bimolecular reaction between reactants were observed in DEA–TCNE and DBA–TCNE systems as shown later in this paper, being inconsistent with the currently accepted Rappoport mechanism. Therefore, we wish now to propose another mechanism for TCV reaction which can explain all the kinetic data reported hitherto and is considered to be more reasonable than the currently accepted one.

Experimental

Materials. DMA, DEA, and DBA were purchased from Tokyo Kasei Kogyo Co., Ltd. MEA was synthesized according to the literature.[15] All these amines were refluxed with sodium and thereafter distilled *in vacuo*. Special attention was made in the distillation of DBA to exclude *N*-monobutylaniline contained. The purity of the amines was confirmed by a gas chromatography. TCNE was purified by repeated sublimations. Commercially available 1,2-dichloroethane was shaken with KOH, washed with water, followed by extraction dried with $CaCl_2$ one day, refluxed with CaH_2, and finally distilled.

Measurements. The electronic absorption spectra and kinetic studies were made by a Hitachi 124 spectrophotometer. Thermostated water was circulated around the quartz observation-cell compartment (optical path length is 10 mm), and the donor and acceptor reservoirs. Donor and acceptor solutions were mixed directly in the observation cell. Initial absorption measurements could be made within 15 s after mixing.

Results and Discussion

Spectroscopic Course of the Reaction. The reactions in MEA–TCNE, DEA–TCNE, and DBA–TCNE systems were followed spectroscopically at a room temperature, using 1,2-dichloroethane as a solvent. Figure 1 shows the spectral change in MEA–TCNE system as a typical example. As the decrease of the CT-band at the long wavelength region, two new absorption bands, one locating at 440 nm with the vibrational structure and the other at 530 nm, increase gradually. The former band is assigned as a well-known TCNE anion radical[16] and the latter as tricyanovinylated product, *p*-tricyanovinyl-*N*-methyl-*N*-ethylaniline. The $TCNE^{\overline{\cdot}}$ band was observed for about one hour, and disappeared completely after all. The fate of $TCNE^{\overline{\cdot}}$ is unknown yet, but one possibility is that $TCNE^{\overline{\cdot}}$ is an intermediate for the formation of TCVP. Although we cannot answer to this possibility at present, independent study showed that TCVP is produced mostly through NA as shown below. The mixture of the equimolar ratio of MEA and TCNE showed the absorption band at 288 nm, and this band decreased gradually to produce TCVP. Although we could not isolate the species peaking at 288 nm because of its conversion into TCVP, it is safely assigned as NA in view of its quite similar absorption spectrum to that of the authentic NA in DMA–TCNE system.[5]

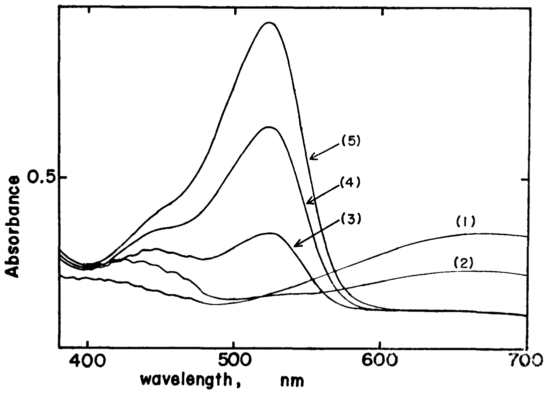
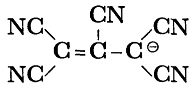


Fig. 1. Spectroscopic course of the reaction in MEA–TCNE system in 1,2-dichloroethane measured at a room temperature. [MEA]$=3.0\times10^{-2}$ M, [TCNE] $=3.0\times10^{-4}$ M. (1) 20 s, (2) 8 min, (3) 45 min, (4) 87 min, (5) 122 min after mixing.

Almost similar spectroscopic change was observed also in DEA–TCNE and DBA–TCNE systems, and TCVP was found to be produced mostly from NA. However, these systems produced also pentacyanopropenide anion (PCP)[17] (λ_{max}=410, 430 nm) as another reaction product. PCP is probably produced by the reaction of $TCNE^{\overline{\cdot}}$ with TCNE as evidenced previously.[17]



PCP

Yields of Reaction Products. The yields of TCVP and PCP under the kinetic work condition were estimated by measureing the electronic absorption spectra of the mixtures of the donor and acceptor solutions after keeping them for a few days at room temperature (Table 1). In these cases, the authentic extinction coefficients of PCP[17] and TCVP[18] were used. Each TCVP tends to increase slowly even several days after mixing the donor and acceptor solutions. Therefore, the yields of TCVP become higher than those in Table 1 day by day. This fact is due to the slow reaction rate from NA to TCVP. In other words, these reaction systems produce NA relatively fast, and it converts into TCVP very slowly. Therefore, the decrease in the CT-absorption does not correspond to the increase of TCVP. Furthermore, the correspondence between the decrease of the CT-complex and the increase of NA

Table 1. Yields of TCVP and PCP

	Yield of TCVP (%)	Yield of PCP (%)
[MEA]=0.4 M [TCNE]=1.0×10^{-3} M	90[a]	—
[DEA]=0.4 M [TCNE]=1.0×10^{-3} M	24[a]	23[a]
[DBA]=0.8 M [TCNE]=8.3×10^{-4} M	49[b]	9[b]

a) Measured two days after mixing. b) Measured six days after mixing.

could not be measured because of the overlap of the absorption band of NA with those of the component molecules. No noticeable reaction product other than TCVP and PCP was observed in these systems. Table 1 shows that the formation of TCVP is the main reaction at least in MEA–TCNE and DBA–TCNE systems.

Thermodynamic Parameters of the CT-complex. The association constant of the CT-complex was obtained from the extrapolation of the decay of the CT-complex to zero time to make Benesi-Hildebrand (B-H) plot by the least-squares method. Figures 2, 3, and 4 show the B-H plots of MEA–TCNE, DEA–TCNE, and DBA–TCNE systems, respectively, in 1,2-dichloroethane at several temperatures. Clearly 1 : 1 CT-complexes are formed in these systems. The Arrhenius plots of the association constants of the CT-complexes (K) in these systems give straight lines to obtain the standard enthalpy ($\Delta H°$) and the entropy ($\Delta S°$) changes. The values of K, $\Delta H°$, and $\Delta S°$ in these systems together with those in DMA–TCNE systems measured in 1,2-dichloroethane are summarized in Table 2. The value of K at each temperature is used in the analysis of the following decay kinetics of the CT-band.

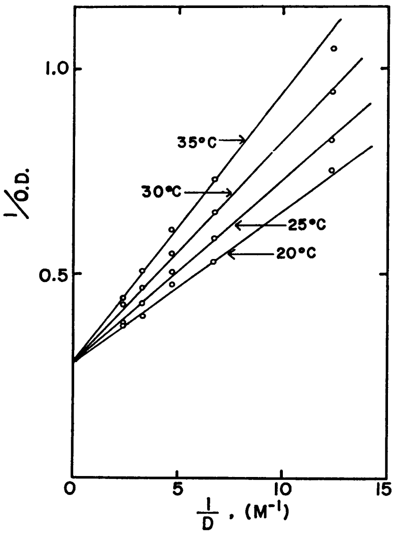


Fig. 2. Benesi-Hildebrand plot in MEA–TCNE system in 1,2-dichloroethane measured at the temperatures indicated. [TCNE]$=1.059\times10^{-3}$ M.

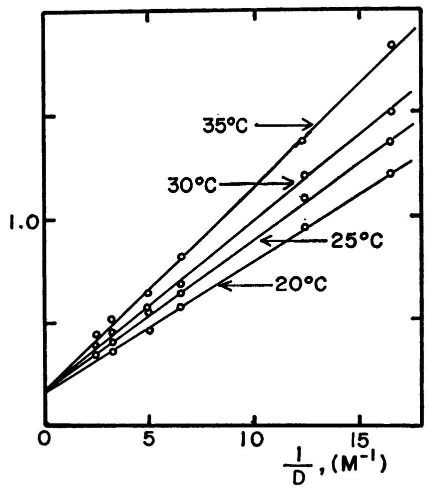


Fig. 3. Benesi-Hildebrand plot in DEA–TCNE system in 1,2-dichloroethane measured at the temperatures indicated. [TCNE]$=1.008\times10^{-3}$ M.

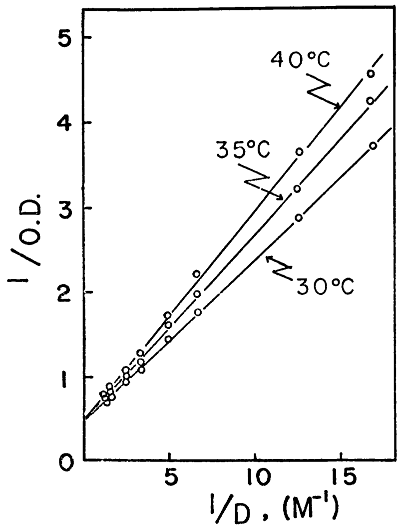


Fig. 4. Benesi-Hildebrand plot in DBA–TCNE system in 1,2-dichloroethane measured at the temperatures indicated. [TCNE]$=4.98\times10^{-4}$ M.

Table 2 THERMODYNAMIC PARAMETERS OF CT-COMPLEX IN 1,2-DICHLOROETHANE

	Temp. (°C)	K (M^{-1})	$\Delta H°$ (kcal/mol)	$\Delta S°$ (e.u.)
DMA–TCNE	30	5.04	−4.92	−12.5
	35	4.39		
	40	3.89		
MEA–TCNE	20	7.34	−5.72	−15.3
	25	6.24		
	30	5.42		
	35	4.55		
DEA–TCNE	20	2.64	−4.21	−14.3
	25	2.34		
	30	2.12		
	35	1.74		
DBA–TCNE	30	2.25	−4.75	−14.3
	35	1.98		
	40	1.75		

The Decay Kinetics of the CT-band. The decay of the CT-band was followed at the appropriate band positions (DMA–TCNE, 675 nm; MEA–TCNE, 750 nm; DEA–TCNE, 800 nm; DBA–TCNE, 800 nm) with the donors in large excess over TCNE. Varying the concentration of the donor keeping that of TCNE constant, plots of log I_{CT} (I_{CT}: the absorbance of the CT-complex at the wavelength measured) against time (t) give straight lines at several temperatures in all systems studied as shown for DBA–TCNE system as a typical example in Fig. 5, which shows that the decay rate of the CT-complex is of the first order with respect to the CT-complex. It was also found that the decay rate of the CT-complex is independent of the initial concentration of TCNE. Table 2 shows the values of the pseudo first order rate coefficients of the CT-complex

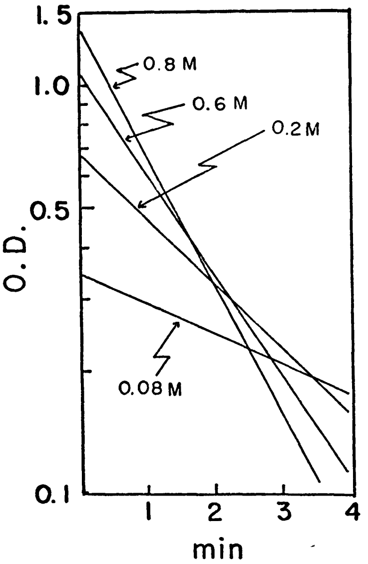


Fig. 5. The decay of the CT-band with time measured at 30 °C. [TCNE]=4.98×10^{-4} M. The concentration of DBA is indicated in the figure.

(k_{obsd}) in these systems, those of $k_{obsd}(1+KD)$ and of $k_{obsd}(1+KD)/D$ at various initial donor concentrations (D). The values of $k_{obsd}(1+KD)/D$ are almost constant irrespective of the initial donor concentrations within the experimental error in DMA–TCNE and MEA–TCNE systems but vary with the change of the donor concentrations in DEA–TCNE and DBA–TCNE systems. Fig. 6 shows the plot of $k_{obsd}(1+KD)/D$ against KD in MEA–TCNE system, and Figs. 7 and 8 those of $k_{obsd}(1+KD)$ against KD in DEA–TCNE and DBA–TCNE systems, these plots being obtained by the least squares method. The former and the latter plots are designated hereafter as "second order plot" and "first order plot," respectively, since $k_{obsd}(1+KD)$ is quadratic with D in the former plot and linear with D in the latter. One can see from Figs. 6, 7, and 8 that MEA–TCNE system gives straight lines in the second order plot and DEA–TCNE and DBA–TCNE systems in the first order plot at several temperatures measured. The kinetic studies on the TCV reactions of DMA–TCNE and *N*-methylaniline (MA)–TCNE systems have shown that the second order plots are linear in these systems,[2,3)] and this is also confirmed in the former system in this study. On the other hand, the values of $k_{obsd}(1+KD)$ was found to be proportional to D^3 in the *N*-tricyanovinylation reactions of aniline (A)–TCNE system[10)] (such a D^3 dependence is designated as "third order plot"). Therefore, the following results are derived from the kinetic studies on the TCV reactions carried out hitherto.

First order plot (DEA–TCNE,[19)] DBA–TCNE[19)])

$$k_{obsd} = \frac{kKD}{1+KD}$$

Second order plot (MA–TCNE,[3)] DMA–TCNE,[2)] MEA–TCNE[19)])

$$k_{obsd} = \frac{kKD^2}{1+KD}$$

Third order plot (A–TCNE[10)])

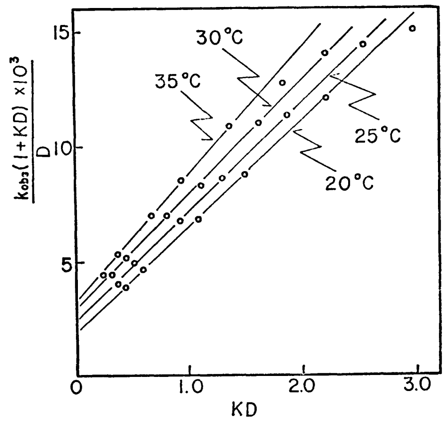


Fig. 6. Plots of $k_{obsd}(1+KD)/D$ against KD in MEA–TCNE system in 1,2-dichloroethane measured at the temperatures indicated. [TCNE]=1.059×10^{-3} M.

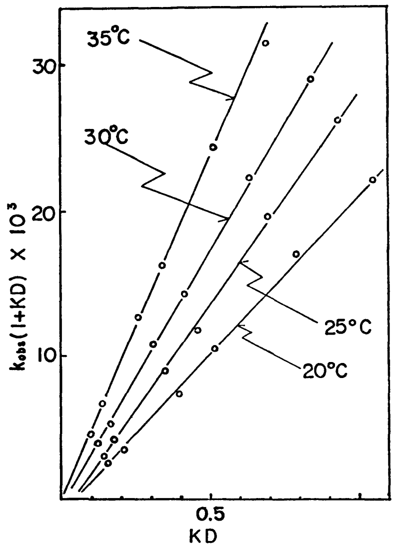


Fig. 7. Plots of $k_{obsd}(1+KD)$ against KD in DEA–TCNE system in 1,2-dichloroethane measured at the temperatures indicated. [TCNE]=1.008×10^{-3} M.

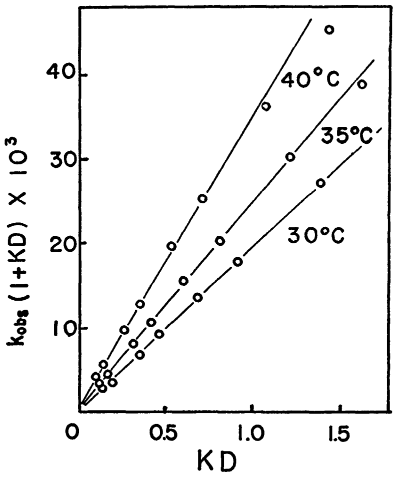


Fig. 8. Plots of $k_{obsd}(1+KD)$ against KD in DBA–TCNE system in 1,2-dichloroethane measured at the temperatures indicated. [TCNE]=4.98×10^{-4} M.

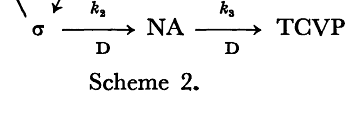
TABLE 3. VALUES OF PSEUDO FIRST-ORDER RATE COEFFICIENTS (k_{obsd}), $k_{\mathrm{obsd}}(1+KD)$, AND $k_{\mathrm{obsd}}(1+KD)/D$ IN 1,2-DICHLOROETHANE

	Temp (°C)	[D], (M)	[A]×10, (M)	$k_{\mathrm{obsd}}\times 10^2$, ($\mathrm{s}^{-1}$)	$k_{\mathrm{obsd}}\times$ $(1+KD)$	$k_{\mathrm{obsd}}\times$ $(1+KD)/D$
DMA–TCNE	30	0.059	0.975	0.089	0.00115	0.0195
		0.148		0.338	0.00591	0.0399
		0.295		0.769	0.01913	0.0648
	40	0.059	0.975	0.089	0.00109	0.0185
		0.148		0.350	0.00551	0.0372
		0.295		0.833	0.01789	0.0606
MEA–TCNE	20	0.060	1.059	0.164	0.00237	0.0394
		0.205		0.721	0.01806	0.0881
		0.405		1.535	0.06098	0.1506
	35	0.060	1.059	0.209	0.00266	0.0444
		0.205		0.911	0.01761	0.0859
		0.405		1.808	0.05319	0.1269
DEA–TCNE	20	0.197	1.008	0.685	0.01041	0.0529
		0.301		0.945	0.01696	0.0563
		0.400		1.068	0.02196	0.0549
	35	0.197	1.008	1.205	0.01331	0.0821
		0.301		1.587	0.02418	0.0803
		0.400		1.855	0.03146	0.0787
DBA–TCNE	30	0.149	0.498	0.494	0.00660	0.0443
		0.298		0.809	0.01351	0.0454
		0.599		1.128	0.02648	0.0442
	40	0.149	0.498	0.761	0.00959	0.0644
		0.298		1.273	0.01937	0.0650
		0.599		1.743	0.03570	0.0596

$$k_{\mathrm{obsd}} = \frac{kKD^3}{1+KD}$$

The first order plot obtained in this study is the first example for the TCV reaction, although the first order plot is rather general in many reaction systems involving CT-complex such as 2+2 and 4+2 cycloaddition reactions[12,13] and ionization reactions.[14] As stated previously, Z. Rappoport and P. G. Farrell explained the second order plot in the TCV reaction as resulting from the bimolecular exchange reaction between a complexed donor and a free donor, and this assumption has been accepted to be general for the TCV reaction (Scheme 1). By this currently accepted mechanism, however, the first order plots observed in DEA–TCNE and DBA–TCNE systems are difficult to understand. We considered, therefore, that a more general reaction scheme must exist for the TCV reaction, and the decay kinetics of the CT-complex obeys first order plot or second order plot, and sometimes third order plot, by applying the special conditions to the new reaction scheme.

New Mechanism for the TCV Reaction. We wish now to propose another mechanism which can also satisfy all the kinetic data reported hitherto as described in Scheme 2.



Scheme 2.

Two characteristic points are involved in the new mechanism, *i.e.*, (1) unimolecular reaction from CT-complex to zwitterionic σ-complex, and (2) dissociation reaction of zwitterionic σ-complex back to the component molecules. The other reaction steps (the reactions from σ to NA and from NA to TCVP) are the same as the currently accepted mechanism, and the introductions of D in these steps are due to the proton abstraction reactions from σ and NA with basic D molecule (see Scheme 4).

Applying the steady state approximations to the unstable σ-complex,[20] the decay of the CT-complex is derived as follows.

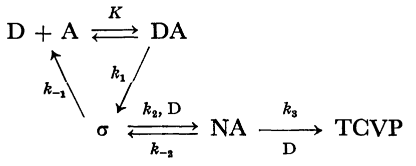
$$-\frac{\mathrm{d[DA]}}{\mathrm{d}t} = k_{\mathrm{obsd}}[\mathrm{DA}] = \frac{k_1k_2KD^2}{(1+KD)(k_{-1}+k_2D)}[\mathrm{DA}] \quad \text{(II-1)}$$

$$\approx \frac{(k_1k_2/k_{-1})KD^2}{1+KD}[\mathrm{DA}] \quad (k_{-1} \gg k_2D) \quad \text{(II-2)}$$

$$\approx \frac{k_1KD}{1+KD}[\mathrm{DA}] \quad (k_{-1} \ll k_2D) \quad \text{(II-3)}$$

The equation (II-1) reduces to (II-2) to give the second order plot if $k_{-1} \gg k_2D$ holds, and (II-2) is essentially identical with (I-1), *i.e.*, k in (I-1) is reinterpreted in the new mechanism as (k_1k_2/k_{-1}). That is to say, in the currently accepted mechanism the presence of DA+D reaction has been assumed in order to make the D term in the numerator of k_{obsd} quadratic, and in our new mechanism this is effected by introducing a back reaction from the σ-complex to the reactants. On the contrary, if $k_{-1} \ll k_2D$ holds, the equation (II-1) reduces to (II-3) to give the first order plot. In other words, in our new mechanism if the rate of the decomposition of the σ-complex to the component molecules (k_{-1}) is much faster than that of the conversion of the σ-complex to neutral adduct (k_2D), the second order plot is obtained and if in the reverse case, the first order plot is obtained.

We insist here that the former condition may hold in MA–TCNE and DMA–TCNE systems. Concerning the MEA–TCNE system, we observed the TCV reaction as well as the ionization reaction of the component molecules. The existence of the ionization process in this system is the characteristic point as compared with MA–TCNE and DMA–TCNE systems. The second order plot observed in MEA–TCNE system is considered to result from the fact that the TCV reaction occurs with the former condition ($k_{-1} \gg k_2D$), and that the TCV reaction dominates over the ionization reaction.[21] It cannot be necessarily said, however, that the latter condition ($k_{-1} \ll k_2D$) holds in DEA– and DBA–TCNE systems. The discussions on these two systems are shown later in this paper.



Scheme 3.

The cubic dependence of D in the numerator of k_{obsd} (third order plot) observed in aniline–TCNE system[10] is interpreted in our new mechanism in terms of the reversibility of both processes of the σ-complex and the neutral adduct formations probably due to the instability of the neutral adduct in this system. This is consistent with the fact that the absorption band of neutral adduct could not be detected by an electronic absorption spectra in this system. The reaction scheme for this system is given as Scheme 3. Applying the steady state approximations to the σ-complex and neutral adduct, the following kinetic equations are derived, where k_{-2} denote the reaction rate coefficient from neutral adduct to σ-complex.

$$-\frac{\mathrm{d}[\mathrm{DA}]}{\mathrm{d}t} = k_{\text{obsd}}[\mathrm{DA}]$$

$$= \frac{k_1k_2k_3KD^3}{(1+KD)(k_{-1}k_2+k_{-1}k_3D+k_2k_3D^2)}[\mathrm{DA}] \qquad \text{(III-2)}$$

$$\approx \frac{(k_1k_2k_3/k_{-1}k_{-2})KD^3}{1+KD}[\mathrm{DA}] \qquad \text{(III-2)}$$

$$(k_{-1} \gg k_2D,\ \text{and}\ k_{-2} \gg k_3D)$$

The rate equation (III-1) reduces to (III-2), the third order plot, if $k_{-1} \gg k_2D$ and $k_{-2} \gg k_3D$ hold simultaneously.

Discussions on the New Mechanism. At present, we have no direct evidence for the new mechanism, but we beleive that the new mechanism is more reasonable from the following reasons.

(1) The reaction of a complexed TCNE with a free donor, the currently accepted mechanism, is difficult to understand in such an electrophilic substitution reaction as TCV reaction, because the electron accepting property of the complexed TCNE may be sufficiently weakened. Furthermore, no experimental evidence has been found which shows the existence of the exchange reaction between a complexed donor and a free donor.

(2) The kinetic deuterium isotope effect was found to exist for the decay of the CT-complex between DMA–TCNE and 4-deuterio-*N,N*-dimethylaniline–TCNE systems.[7] The currently accepted mechanism cannot explain this result, since hydrogen abstraction reaction is not involved in the reaction of DA with D. On the other hand, the new mechanism can explain the isotope effect in view of the fact that the rate of hydrogen abstraction reaction from σ-complex (k_2) is involved in k_{obsd}, *viz.*,

$$k_{\text{obsd}} \approx \frac{(k_1k_2/k_{-1})KD^2}{1+KD}.$$

(3) The kinetic studies for the 2+2 and 4+2 cycloaddition reactions of electron donating olefins with TCNE[12,13] and ionization reaction in *N,N*-diethyl-*p*-toluidine–TCNE system[14,21] have revealed that the reaction should be understood as either unimolecular transformation of the CT-complex or bimolecular reaction between a free donor and an acceptor molecules. These results suggest that the unimolecular transformation of the CT-complex is favored over the bimolecular reaction between the CT-complex and a free donor. Thus, the primary process of the chemical reaction involving the formation of the CT-complex is systematically understood by the same mechanism.

(4) The assumption of back process of the zwitterionic σ-complex to the component molecules is reasonable, which has recently been evidenced in the 2+2 cycloaddition reaction of isomeric enol ethers with TCNE.[22]

(5) The new mechanism which involves σ-complex as an unstable intermediate and neutral adduct tetracyanoethane derivative as an accumulating intermediate is in accord with the fact that the latter has actually been isolated,[7,8] while the former cannot be detected even by the spectroscopic technique. The explanation in the literature[7] that the isolable neutral adduct may arise by rapid rearrangement of the σ-complex and may not be on the reaction path of the overall TCV reaction under the kinetic work conditions seems to be unattractive.

Discussions on the TCV Reaction in DEA–TCNE and DBA–TCNE Systems. As stated above, the decay of the CT-complex obeyed the first order plot in DEA–TCNE and DBA–TCNE systems. These results are now discussed based on the new mechanism. The following three cases can be considered as the reason of the first order plots in these systems.

(1) As stated in the description of the new mechanism, these systems are in the condition that the decomposition rate of σ-complex is much slower than the reaction rate from σ-complex to neutral adduct, *i.e.*, $k_{-1} \ll k_2D$. This may be rationalized by the stability of the σ-complexes in these systems because of the increasing donor properties of DEA and DBA as compared

with MA, DMA, and MEA, and the decomposition rate of the σ-complex back to the component molecules may be considerably reduced.

(2) The steric effect of the bulky alkyl groups attached to the amino nitrogens of DEA and DBA hinder the proton abstraction reaction of these amines from the σ-complex, and the conversion of the σ-complex into the neutral adduct is a unimolecular reaction.[23] Thus, in this case k_2D in equation (II-1) must be replaced by k_2 to give

$$k_{\text{obsd}} = \frac{(k_1k_2/(k_{-1}+k_2))KD}{1+KD}.$$

(3) The ionization reaction dominates over TCV reaction.[21] Which of these three cases actually holds is now under investigation.

Concerning the ionization reaction, three mechanisms are conceivable, *i.e.*, ionization from (1) component molecules, (2) CT-complex, and (3) σ-complex. In order to know the ionization mechanism, the ESR studies are now under investigation.[14]

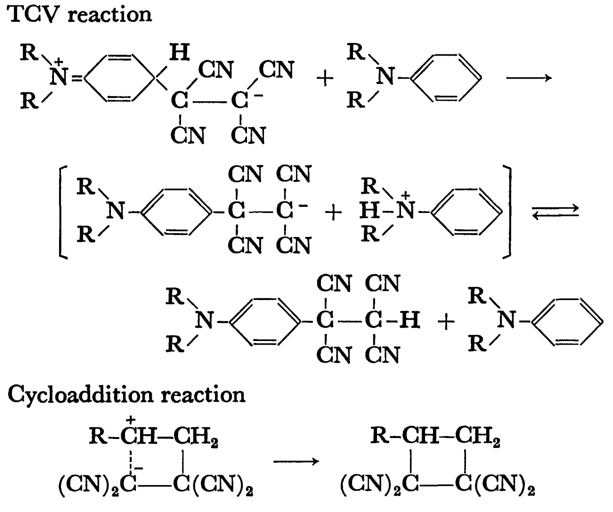
Comments. The followings are the additional comments to be noted. (1) We have discussed the mechanism based on the unimolecular transformation of CT-complex to the σ-complex (Scheme 2). However, another mechanism is also possible in which σ-complex is produced from the component free molecules and the CT-complex exists in a side reaction as shown in Scheme 2′. The reaction scheme and rate equation are as follows.

$$\begin{tikzcd}
D + A \arrow[r, shift left, "K"] \arrow[d, shift left, "k_1'"] & DA \arrow[l, shift left] & \\
\sigma \arrow[u, shift left, "k_{-1}"] \arrow[r, "k_2", "D"'] & NA \arrow[r, "k_3", "D"'] & TCVP
\end{tikzcd}$$

$$-\frac{d[DA]}{dt} = \frac{k_1'k_2D^2}{(1+KD)(k_{-1}+k_2D)}[DA] \qquad \text{(II}'\text{-1)}$$

Scheme 2′.

Where, k_1' is the rate coefficient from the component molecules to the σ-complex. The two mechanisms, Schemes 2 and 2′, are indistinguishable kinetically. The detailed discussions will be reported in the near future.



Scheme 4.

(2) It has been reported that the decay of the CT-complex obeys the first order plot in many cycloaddition reactions of electron rich olefins with TCNE.[12,13] The apparent difference in the rate equations for the decay of the CT-complex between the TCV reaction and the cycloaddition reaction is understandable as resulting from the fact that in the TCV reaction one more donor molecule participates in abstracting a proton from the σ-complex in the neutral adduct formation process, while in the cycloaddition reaction such a process is not involved (Scheme 4).[24]

(3) It has been to date insisted that the CT-complex is the essential intermediate in the TCV reaction based on the mechanism of the bimolecular reaction of the complexed donor and a free donor. In the new mechanism, however, the kinetic data alone cannot tell whether or not the CT-complex is the true intermediate in the TCV reaction.[24]

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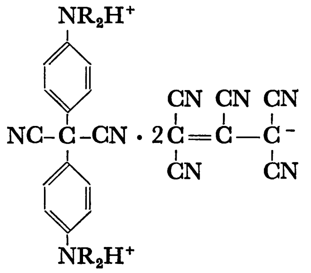

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19) Present study.

20) The change of the [σ] with time is assumed to be negligibly small as compared with those of the other reaction species.

21) Concerning the ionization reaction involving the CT-complex, we have carried out kinetic studies on *N*,*N*-diethyl-*p*-toluidine–TCNE system in which no TCV reaction is expected to occur, and found that the decay of the CT-complex obeys the first order plot.[14] We think that the ionization reactions involving the CT-complex may be generalized as the first order plot.

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24) The isolable neutral adduct tetracyanoethane derivative might exist as a carbanion species (see Scheme 4).