BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (7), 2110—2113 (1979)

Chemical Reaction of Electron Donor-Acceptor System: Reaction Mechanism of the Tricyanovinylation Reaction of *N,N*-Dimethylaniline with Tetracyanoethylene

Takashi Nogami,* Yoshio Nakano, Yoshiki Hasegawa,
Yasuhiko Shirota, and Hiroshi Mikawa
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565

(Received August 28, 1978)

The decay of the charge-transfer (CT) absorption band in the tricyanovinylation reaction of *N,N*-dimethylaniline (DMA) with tetracyanoethylene (TCNE) in 1,2-dichloroethane was followed by the electronic absorption measurement. Primary hydrogen isotope effect was observed for the decay of the CT-band in line with the mechanism:

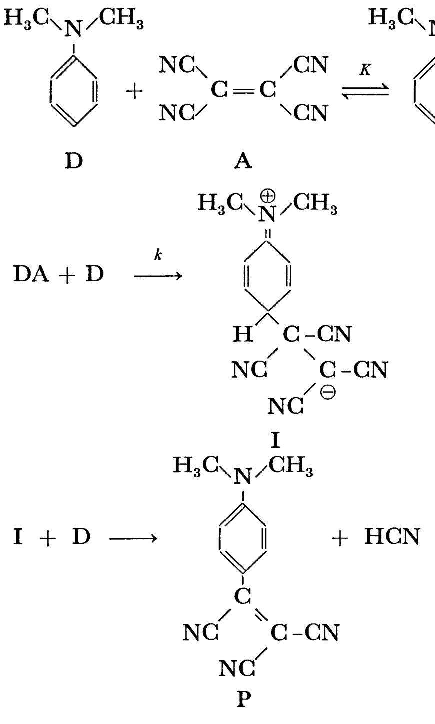
$$[\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{DA}] \longrightarrow \mathrm{I}$$
$$\mathrm{I} + \mathrm{D} \longrightarrow \mathrm{NA}$$
$$\mathrm{NA} + \mathrm{D} \xrightarrow[\text{slow}]{} \mathrm{P}$$

D: DMA; A: TCNE; DA: CT-complex; I: zwitterionic intermediate; NA: *p*-(1,1,2,2-tetracyanoethyl)-*N,N*-dimethylaniline; P: *p*-tricyanovinyl-*N,N*-dimethylaniline.

The tricyanovinylation reaction of several aromatic amines with tetracyanoethylene (TCNE) is a typical thermal reaction involving the formation of a charge-transfer (CT) complex.[1] The reaction proceeds in two steps, (1) formation of an accumulating intermediate, and (2) slow formation of the final product. Because of the large difference in reaction rate, the steps can be followed independently by an electronic absorption measurement. Rappoport measured the decay of the CT-absorption band for the *N,N*-dimethylaniline (DMA)–TCNE system in chloroform, and found that the pseudo first order rate constant for the decay of the CT-complex (k_{obsd}) obeys the relation[2]

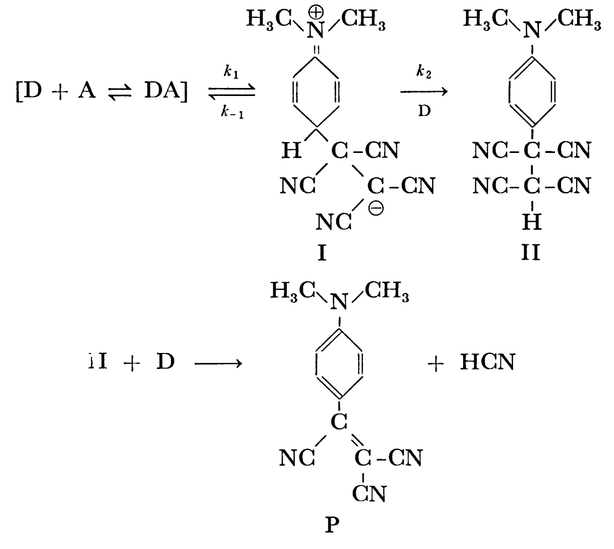
$$k_{\mathrm{obsd}} = \frac{kK[\mathrm{D}]^2}{1+K[\mathrm{D}]} . \tag{1}$$

Here, k, K, and $[D]$ denote the second order rate constant for transformation from the CT-complex into a zwitterionic intermediate (I), the association constant for the formation of the CT-complex, and the initial donor concentration, respectively. The following reaction (Scheme 1) has been proposed to explain the above kinetic result, which involves the bimolecular reaction of the CT-complex with another free donor (amine) molecule to give I.



Scheme 1.

The mechanism proposed by Rappoport indicates that the CT-complex is a true intermediate in the reaction. However, it is generally recognized that kinetic data alone cannot tell whether the CT-complex is a true intermediate in chemical reactions involving the formation of the CT-complex, *e.g.*, Diels-Alder and [2+2] cycloaddition reactions.[3] From the viewpoint that this may be the case also for the tricyanovinylation reaction of aromatic amines, we have proposed an alternative mechanism (Scheme 2) which can also explain the above kinetic data.[1,4] Either the monomolecular transformation of the CT-complex or the bimolecular reaction between the free donor and acceptor molecules produces a zwitterionic intermediate (I) which reversibly returns to either the CT-complex or the component molecules,[5] and then an accumulat-



Scheme 2.

ing intermediate, *p*-(1,1,2,2-tetracyanoethyl)-*N*,*N*-dimethylaniline (II) (neutral adduct), is produced.[7] The formation of II is induced by the deprotonation of I with another amine (donor) molecules, followed by back proton transfer from the quarternary amine to carbanion resulting from I. The neutral adduct (II, NA) then turns gradually to the final tricyanovinylated product by another free-amine catalysed dehydrocyanation.

The kinetic result alone cannot distinguish whether the CT-complex is a true intermediate in the reaction.[11] The decay of the CT-complex following the mechanism (Scheme 2) is expressed by Eqs. 2 and 3, which are kinetically indistinguishable from each other.

$$[\mathrm{DA}] = [\mathrm{DA}]_0 \exp(-k_{\mathrm{obsd}}t)$$

In the case of unimolecular transformation of the CT-complex:[12]

$$k_{\mathrm{obsd}} = \frac{(k_1k_2/k_{-1})K[\mathrm{D}]^2}{1+K[\mathrm{D}]} \tag{2}$$

In the case of bimolecular reaction between free donor and acceptor molecules:[12]

$$k_{\mathrm{obsd}} = \frac{(k'_1k_2/k'_{-1}K)K[\mathrm{D}]^2}{1+K[\mathrm{D}]} \tag{3}$$

In order to confirm which of Schemes 1 and 2 is more reasonable, we have carried out the measurement of the kinetic hydrogen isotope effect on the decay of the CT-complex for the DMA–TCNE and 4-deuterio-*N*,*N*-dimethylaniline (*d*-DMA)–TCNE systems in 1,2-dichloroethane. No primary hydrogen isotope effect will be observed for the mechanism shown in Scheme 1, since the decay process of the CT-complex involves only the exchange reaction of a complexed amine with a free amine, although a slight secondary hydrogen isotope effect might be observed. On the other hand, the primary hydrogen isotope effect will be observed for the mechanism shown in Scheme 2, since k_{obsd} involves the rate constant k_2 for the C–H and C–D bond breaking process.

Experimental

4-Deuterio-*N*,*N*-dimethylaniline (*d*-DMA) was synthesized according to the methods reported.[13] Purification of samples and solvents and the experimental procedures are described in a previous paper.[1]

Results and Discussion

Decay Kinetics of the CT-Band. The decay of the CT-absorption band at 675 nm was followed at 30, 35, and 40 °C for the DMA–TCNE and *d*-DMA–TCNE systems in 1,2-dichloroethane with a donor concentration much greater than that of TCNE. The measurement was made by varying the concentration of the donor (DMA and *d*-DMA), keeping that of TCNE constant. The plot of log I_{CT} (I_{CT}: absorbance of the CT-band at 675 nm) against time gave a straight line for each run. This shows that the decay of the CT-complex is of first order with respect to the concentration of the CT-complex. Typical plots of log I_{CT} against time for both DMA–TCNE and *d*-DMA–TCNE systems are shown in Fig. 1. A marked hydrogen isotope effect is observed for the decay of the CT-complex. The association constant for the formation of the CT-complex was obtained from the extrapolation of the decay of the CT-complex to time zero in order to get a Benesi-Hildebrand plot by the least squares method.[14] As expected from Eq. 1 for Scheme 1 or Eq. 2 or 3 for Scheme 2, the plot of $k_{\mathrm{obsd}}(1+K[\mathrm{D}])/[\mathrm{D}]$ against $K[\mathrm{D}]$ should give a straight line. Figures 2 and 3 show the plots of $k_{\mathrm{obsd}}(1+K[\mathrm{D}])/[\mathrm{D}]$ against $K[\mathrm{D}]$ by means of the least squares method for the DMA–TCNE and *d*-DMA–TCNE systems, respectively, both of which show a linear relation. The plots show two characteristics, *i.e.*, (1) a kinetic hydrogen isotope effect exists for the decay of the CT-complex as is evident from the marked decrease in the slope of the straight line in the *d*-DMA–TCNE system as compared with the DMA–TCNE system; (2) the plots do not pass through the origin, but have definite positive intercepts.

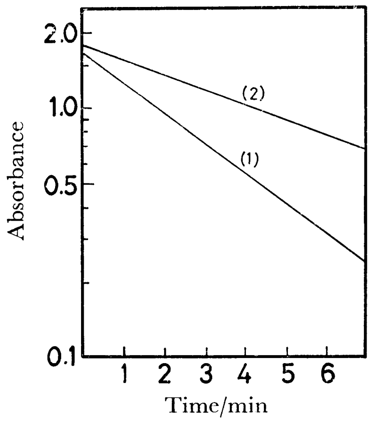


Fig. 1. The plot of log I_{CT} against *t*.
(1) DMA–TCNE system. [DMA]=0.2 M, [TCNE]=9.75×10^{-4} M. (2) *d*-DMA–TCNE system. [*d*-DMA]=0.2 M, [TCNE]=1.011×10^{-3} M.

Primary Hydrogen Isotope Effect. The slopes of the linear plots in Figs. 2 and 3 give the values of k (for Scheme 1) or k_1k_2/k_{-1} (for Scheme 2, in the case of monomolecular transformation of the CT-complex; hereafter, discussion will be made simply in terms of this mechanism for the sake of convenience). The ratio of the slopes of the straight lines (denoted by $s^{\mathrm{H}}/s^{\mathrm{D}}$)[15] in Figs. 2 and 3 is expressed as Eqs. 4 and 5 for the mechanism shown in Schemes 1 and 2, respectively. Since the substitution of hydrogen by deuterium at the *para*-position of DMA is assumed to give a minor effect on the rate constants k_1 and k_{-1} for the mechanism shown in Scheme 2, Eq. 5 can be approximated as Eq. 6.

$$s^{\mathrm{H}}/s^{\mathrm{D}} = k^{\mathrm{H}}/k^{\mathrm{D}} \quad \text{for Scheme 1} \tag{4}$$

$$s^{\mathrm{H}}/s^{\mathrm{D}} = (k_1^{\mathrm{H}}k_2^{\mathrm{H}}k_{-1}^{\mathrm{D}}/k_1^{\mathrm{D}}k_2^{\mathrm{D}}k_{-1}^{\mathrm{H}}) \quad \text{for Scheme 2} \tag{5}$$

$$s^{\mathrm{H}}/s^{\mathrm{D}} \approx k_2^{\mathrm{H}}/k_2^{\mathrm{D}} \quad \text{for Scheme 2} \tag{6}$$

The values of $s^{\mathrm{H}}/s^{\mathrm{D}}$ obtained from Figs. 2 and 3 are 3.35, 3.32, and 3.17 at 30, 35, and 40 °C, respectively, showing a large kinetic hydrogen isotope effect. The Arrhenius plot for the observed $s^{\mathrm{H}}/s^{\mathrm{D}}$ values gave an activation energy of about 1.04 kcal/mol,

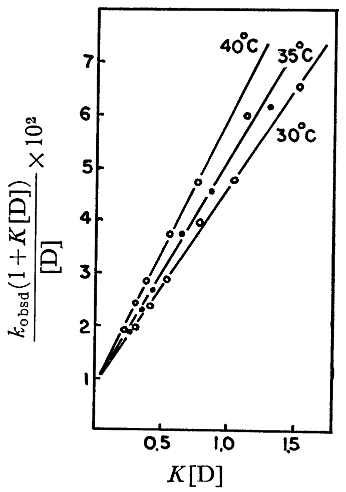


Fig. 2. The plot of k_{obsd} $(1+K[D])/[D]$ against K[D] in DMA–TCNE system in 1,2-dichloroethane measured at the temperatures indicated. [TCNE]$=9.75\times 10^{-4}$ M.

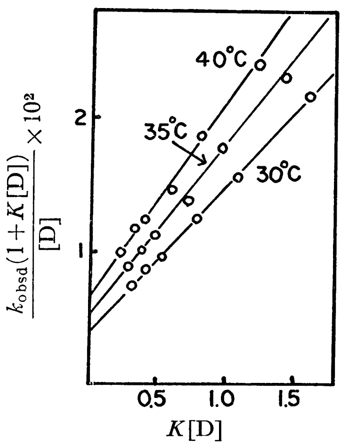


Fig. 3. The plot of k_{obsd} $(1+K[D])/[D]$ against K[D] in d-DMA–TCNE system in 1,2-dichloroethane measured at the temperatures indicated. [TCNE]$=1.011\times 10^{-3}$ M.

which is roughly equal to the zero point energy difference between the C–H and C–D stretching vibrations. The results are attributed to the primary hydrogen isotope effect. They can be explained more satisfactorily in terms of Scheme 2, since s^H/s^D roughly represents k_2^H/k_2^D,[15] the ratio of the rate constants for the C–H and C–D bond breakage.[16]

On the Positive Intercept of the Linear Plot of $k_{obsd}(1+K[D])/[D]$ *against* K[D]. The fact that the linear plot of $k_{obsd}(1+K[D])/[D]$ against K[D] has an intercept has not so far been discussed as regards reaction mechanism. Experimental results show that the plots have negative intercepts for *e.g.*, the indole–TCNE system in dichloromethane,[17] and DMA–TCNE system in dichloromethane.[18] The present study of the DMA–TCNE system in 1,2-dichloroethane gives definite values of positive intercepts (Figs. 2 and 3), indicating that k_{obsd} is more rigorously given by Eq. 7. The k_3 term in Eq. 7 will probably arise from the following reactions: (1) the formation of unknown species X from the initial equilibrium between the CT-complex and free donor and acceptor molecules, (2) the monomolecular reaction of I to give probably NA and/or another unknown species X (Scheme 3).

$$\begin{tikzcd}
{[D + A \rightleftarrows DA]} \arrow[r, "(1)"] \arrow[dr] & X \\
 & I \arrow[u] \arrow[r, "(2)"] & NA
\end{tikzcd}$$

$$k_{obsd} = \frac{(k_1/k_{-1})K[D]}{1+K[D]}(k_2[D]+k_3) \tag{7}$$

Scheme 3. Conceivable reactions which contribute to the k_3 term in Eq. 7.

Table 1 gives the values of k_{obsd} obtained from Fig. 1 (three plots are chosen for the sake of simplicity), and $(k_1k_2/k_{-1})K[D]^2/(1+K[D])$ (denoted by $k_{obsd(bi)}$) calculated by using the values of the slopes of the linear plots in Figs. 2 and 3. Calculation using the values of intercepts of the linear plots in Figs. 2 and 3, or substraction of $k_{obsd(bi)}$ from k_{obsd} will give $(k_1k_3/k_{-1})K[D]/(1+K[D])$ (denoted by $k_{obsd(mono)}$). It should be noted that the values of the intercepts are much less reliable than those of the slopes in Figs. 2 and 3; the values of $k_{obsd(mono)}$ are much less reliable than those of $k_{obsd(bi)}$.[19] Although no quantitative discussion on the k_3 process can be made, it is shown that the k_3 process contributes significantly under the reaction conditions of a low donor concentration ($[D]\approx 0.06$ mol dm^{-3} with constant [TCNE]$\approx 10^{-3}$ mol dm^{-3}). Under the reaction conditions of a high donor concentration ($[D]>0.1$ mol dm^{-3} with constant [TCNE]$\approx 10^{-3}$ mol dm^{-3}), however, the contribution of the k_2 process is dominant as shown in the values of $k_{obsd(bi)}/k_{obsd}$ in Table 1, the main reaction mechanism being explained in terms of the mechanism shown in Scheme 2.

Summary. The primary kinetic hydrogen isotope effect observed for the decay of the CT-complex in the tricyanovinylation reaction of the DMA–TCNE system in 1,2-dichloroethane is explained by Scheme 2.

We are grateful to Dr. Takashi Ando, The Institute of Scientific and Industrial Research, Osaka University, for his helpful discussion.

References

1) T. Nogami, Y. Hasegawa, Y. Shirota, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **48**, 3048 (1975), and references cited therein.

2) Z. Rappoport, *J. Chem. Soc.*, **1963**, 4438.

3) Y. Shirota, J. Nagata, Y. Nakano, T. Nogami, and H. Mikawa, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 14; T. Arimoto and J. Osugi, *Chem. Lett.*, **1974**, 271.

4) Y. Shirota, T. Nogami, Y. Hasegawa, and H. Mikawa, *Chem. Lett.*, **1974**, 1009.

5) The reversibility of a zwitterionic intermediate has been evidenced for the [2+2] cycloaddition reaction.[6]

6) R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95**, 5055 (1973).

7) The intermediate NA was actually isolated after complete disappearence of the CT-complex in the tricyanovinylation reactions of a few aromatic amines.[8–10]

TABLE 1. TYPICAL KINETIC DATA FOR THE DECAY OF THE CT-COMPLEX IN 1,2-DICHLOROETHANE

	Temp (°C)	[D] (mol dm^{-3})	$k_{\mathrm{obsd}} \times 10^3$ (s^{-1})	$k_{\mathrm{obsd(bi)}} \times 10^3$ [a]	$k_{\mathrm{obsd(bi)}}/k_{\mathrm{obsd}}$
DMA-TCNE[b]	30	0.295	7.69	6.87	0.89
		0.2	4.74	3.91	0.82
		0.059	0.88	0.52	0.59
	35	0.295	7.98	6.99	0.87
		0.2	4.89	3.93	0.80
		0.059	0.89	0.51	0.57
	40	0.295	8.33	7.88	0.94
		0.2	5.37	4.37	0.81
		0.059	0.88	0.55	0.62
d-DMA-TCNE[c]	30	0.3	2.52	2.08	0.82
		0.2	1.53	1.17	0.76
		0.06	0.33	0.16	0.48
	35	0.3	2.85	2.22	0.77
		0.2	1.83	1.24	0.67
		0.06	0.41	0.16	0.39
	40	0.3	3.25	2.37	0.72
		0.2	2.08	1.30	0.62
		0.06	0.47	0.16	0.34

a) s^{-1}; $k_{\mathrm{obsd(bi)}} = (k_1k_2/k_{-1})K[\mathrm{D}]^2/(1+K[\mathrm{D}])$. b) [TCNE] $= 9.75 \times 10^{-4}$ mol dm^{-3}. c) [TCNE] $= 1.011 \times 10^{-3}$ mol dm^{-3}.

8) Z. Rappoport and E. Shohamy, *J. Chem. Soc., B*, **1969**, 77.

9) P. G. Farrell and R. K. Wojtowski, *J. Chem. Soc., B*, **1970**, 1390.

10) Y. Shirota, S. Ezaki, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **45**, 836 (1972).

11) I is produced from the initial equilibrium state between D+A and DA shown symbolically as $[\mathrm{D}+\mathrm{A} \rightleftharpoons \mathrm{DA}] \rightleftharpoons \mathrm{I}$. In deriving the kinetic equation, however, it is assumed that the reaction proceeds either by the monomolecular transformation of the CT-complex or by the bimolecular reaction of the free donor and acceptor molecules.

12) Unimolecular transformation of the CT-complex.

$$\mathrm{D} + \mathrm{A} \overset{K}{\rightleftharpoons} \mathrm{DA}$$

$$\mathrm{DA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow[k_2]{\mathrm{D}} \mathrm{NA} \xrightarrow[\text{slow}]{\mathrm{D}} \mathrm{P}$$

Bimolecular reaction between the free donor and acceptor molecules.

$$\mathrm{D} + \mathrm{A} \overset{K}{\rightleftharpoons} \mathrm{DA}$$

$$\mathrm{D} + \mathrm{A} \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow[k_2]{\mathrm{D}} \mathrm{NA} \xrightarrow[\text{slow}]{\mathrm{D}} \mathrm{P}$$

13) J. H. Billman, A. R. Radike, and B. W. Mundy, *J. Am. Chem. Soc.*, **64**, 2977 (1942); D. G. Thomas, J. H. Billman, and C. E. Davis, *ibid.*, **68**, 895 (1946); S. Baba, *Yakugaku Zasshi*, **89**, 1158 (1969).

14) Observed association constants of the CT-complex in 1,2-dichloroethane. DMA–TCNE system: K (dm^3 mol^{-1}) 5.04 (30 °C), 4.39 (35 °C), 3.89 (40 °C). *d*-DMA–TCNE system: K (dm^3 mol^{-1}) 5.31 (30 °C), 4.79 (35 °C), 4.06 (40 °C).

15) Superscripts H and D denote the rate constants for DMA–TCNE and *d*-DMA–TCNE systems, respectively.

16) P. G. Farrell and J. Newton, *J. Chem. Soc., C*, **1970**, 1630. They also observed the kinetic hydrogen isotope effect for the decay of the CT-complex in the tricyanovinylation reaction of DMA–TCNE system in chloroform.

17) R. Foster and P. Hanson, *Tetrahedron*, **21**, 255 (1965).

18) S. Garbutt and D. L. Gerrand, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 782.

19) A small variation in the values of the slopes yields a large variation in the values of intercepts. This arises from the fact that the values of $k_{\mathrm{obsd(bi)}}$ are much greater than those of $k_{\mathrm{obsd(mono)}}$.