Electron Transfer Reaction between $\Delta^{2,2'}$-Bi-1,3-dithiole (TTF) and 7,7,8,8-Tetracyanoquinodimethane (TCNQ). Electron Donating Property of TTF

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The reaction between $\Delta^{2,2'}$-bi-1,3-dithiole (TTF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) in acetonitrile solution, $\mathrm{TTF}+\mathrm{TCNQ}\rightleftarrows\mathrm{TTF}^{+\cdot}+\mathrm{TCNQ}^{\cdot-}$, was analyzed spectrophotometrically. The thermodynamical data of chemical equilibrium were determined to be $K=(2.8\pm0.1)\times10^{-3}$ at 11 °C, $\Delta H=-6.7\pm1.3$ kJ mol^{-1} and $\Delta S=-72.8\pm17$ J K^{-1} mol^{-1}. The reaction-rate study of the equilibrium in several solvents was also made by temperature-jump technique. The difference in the electron-donating properties between TTF and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) is discussed by comparing the results with those of the reaction between TMPD and TCNQ.

Formation of charge-transfer complexes from electron donor and acceptor molecules is well-known. A combination of strong donor and acceptor molecules often gives rise to separated ions (a cation radical of the donor and an anion radical of the acceptor) in solution.[1)]

Attention has been paid to a charge-transfer complex of $\Delta^{2,2'}$-bi-1,3-dithiole (TTF)[2)] with 7,7,8,8-tetracyanoquinodimethane (TCNQ) because of its unusually high electric conductivity in solid state.[3)] TTF is a strong electron donor, and TCNQ a strong acceptor. In the solid complex, however, the charge transfer from TTF to TCNQ takes place incompletely, this being one cause for the TTF–TCNQ complex to show such high electric conduction. We have investigated the charge-transfer reaction from TTF to TCNQ in solution, only a few attempts having been made to study the behavior of the complex in solution. In order to clarify the charge-transfer interaction between TTF and TCNQ in solid state and in solution, we determined the thermodynamic equilibrium constants of reaction and also the kinetics of electron transfer in various solvents.

Experimental

Commercially available TTF (Aldrich Chem. Co.) and TCNQ (Kanto Chem. Co.) were purified by sublimation *in vacuo*. The temperature and concentration dependences of electronic absorption spectra of acetonitrile solutions containing TTF and TCNQ were measured with a Hitachi 808-Type spectrophotometer. The kinetic study of the electron transfer reaction in acetonitrile and dimethyl sulfoxide (DMSO) solution was made by the temperature-jump method, using a Union Giken temperature-jump apparatus. $\mathrm{NaClO_4}$ was used as a supporting electrolyte. The detail of temperature-jump method is similar to that described previously.[4)]

Results

Chemical Equilibrium of Electron Transfer Reaction. When TTF and TCNQ are mixed in acetonitrile, the observed electronic absorption spectrum almost comprises a superposition of the spectra of neutral TTF and TCNQ molecules. In addition, the spectra which are assigned to ionized TTF cation radical ($\mathrm{TTF}^{+\cdot}$) and TCNQ anion radical ($\mathrm{TCNQ}^{\cdot-}$) are observed faintly in the spectrum, no charge-transfer absorption due to TTF–TCNQ complex being detected. The observed absorptions around 700—900 nm are attributable to the absorptions of $\mathrm{TCNQ}^{\cdot-}$, the absorptions around 600 nm to those of $\mathrm{TTF}^{+\cdot}$.[5,6)] Thus, the reaction between TTF and TCNQ in acetonitrile solution can be expressed by

$$\mathrm{TTF}+\mathrm{TCNQ}\rightleftharpoons\mathrm{TTF}^{+\cdot}+\mathrm{TCNQ}^{\cdot-}. \tag{1}$$

First we obtained the chemical equilibrium data of this electron transfer (*i.e.*, oxidation-reduction) reaction spectrophotometrically. Since the absorption at 842 nm is entirely assigned to that of $\mathrm{TCNQ}^{\cdot-}$, the concentration of $\mathrm{TCNQ}^{\cdot-}$ in its equilibrium state, $[\mathrm{TCNQ}^{\cdot-}]$, was estimated by means of the optical density of the observed spectrum, together with the value of the molar extinction coefficient known for $\mathrm{TCNQ}^{\cdot-}$ ($\varepsilon_{\mathrm{TCNQ}^{\cdot-}}(842\ \mathrm{nm})=4.35\times10^4$). The equilibrium concentrations of the other molecular species in Eq. 1 were estimated by the relation, $[\mathrm{TTF}^{+\cdot}]=[\mathrm{TCNQ}^{\cdot-}]$, $[\mathrm{TTF}]=[\mathrm{TTF}]_0-[\mathrm{TCNQ}^{\cdot-}]$ and $[\mathrm{TCNQ}]=[\mathrm{TCNQ}]_0-[\mathrm{TCNQ}^{\cdot-}]$, where $[\mathrm{TTF}]_0$ and $[\mathrm{TCNQ}]_0$ indicate initial concentrations of TTF and TCNQ added, respectively. Assuming that the activity coefficients of these solutes are unity, the equilibrium constant of Eq. 1 is given by

$$K=\frac{[\mathrm{TTF}^{+\cdot}]\,[\mathrm{TCNQ}^{\cdot-}]}{[\mathrm{TTF}]\,[\mathrm{TCNQ}]}. \tag{2}$$

The K value thus estimated was found to be constant when $[\mathrm{TTF}]_0$ was in the range $(3-0.3)\times10^{-5}$ M and $[\mathrm{TCNQ}]_0$ in the range $(4-1)\times10^{-4}$ M, where 1 M $=$ 1 mol dm^{-3}.

Next, we examined the temperature dependence of the observed K value and found almost linear relationship between $\ln K$ and $1/T$ values in the temperature range 11—25 °C. The following thermodynamic data were obtained for the chemical equilibrium of Eq. 1 in acetonitrile solution:

$$K=(2.8\pm0.1)\times10^{-3}\ \text{at}\ 11\ ^\circ\mathrm{C},$$
$$\Delta H=-6.7\pm1.3\ \mathrm{kJ\ mol^{-1}},$$
$$\Delta S=-72.8\pm17\ \mathrm{J\ K^{-1}\ mol^{-1}}.$$

The K value agrees with $K=2.5\times10^{-3}$ obtained by Tomkiewicz *et al.*[7)] The large negative ΔS value indicates that the ordering of solvent molecules around $\mathrm{TTF}^{+\cdot}$ and $\mathrm{TCNQ}^{\cdot-}$ takes place upon ionization of TTF and TCNQ.

Kinetic Study of Electron Transfer Reaction. We measured the following forward, k_1, and backward, k_{-1}, rate constants by using temperature-jump technique,

$$\mathrm{TTF} + \mathrm{TCNQ} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{TTF}^{+\cdot} + \mathrm{TCNQ}^{-\cdot}. \qquad (3)$$

In pure acetonitrile solution, however, the equilibrium constant K is very small. Thus the signal due to $\mathrm{TCNQ}^{-\cdot}$ was so small that we could hardly detect any optical density change of $\mathrm{TCNQ}^{-\cdot}$ upon temperature jumping.

In order to increase the concentrations of $\mathrm{TTF}^{+\cdot}$ and $\mathrm{TCNQ}^{-\cdot}$, we examined the chemical equilibrium of Eq. 1 in several mixed solvents of acetonitrile and DMSO, in view of the report that TTF and TCNQ are mostly ionized in *N,N*-dimethylformamide, DMSO and pyridine solutions.[7] In 27 vol% DMSO–acetonitrile mixed solvent, the equilibrium constant K increased to $(12\pm2)\times10^{-3}$ at 11 °C. In 37 vol % DMSO–acetonitrile mixed solvent, we obtained $K=(22\pm4)\times10^{-3}$ at 11 °C, $\Delta H=-10.0\pm1.7$ kJ mol^{-1} and $\Delta S=-67.4\pm20.9$ J K^{-1} mol^{-1}. The values of both K and $-\Delta H$ increased with increase in the ratio of DMSO in mixed solvent. The increase facilitated our observation of the rate constants of Eq. 3 by temperature-jump method. Figure 1 shows the result of the temperature-jump experiment in 37 vol % DMSO–acetonitrile solution; initial and final temperatures were 9 and 12 °C, respectively. The reciprocal of observed relaxation time, τ^{-1}, of the signal due to $\mathrm{TCNQ}^{-\cdot}$ is plotted against the concentration of $[\mathrm{TCNQ}^{-\cdot}]+[\mathrm{TTF}^{+\cdot}]+K\{[\mathrm{TCNQ}]+[\mathrm{TTF}]\}$. In the reaction of Eq. 3, apparent relaxation time τ upon temperature jumping is given by

$$\begin{aligned}\tau^{-1} &= k_1([\mathrm{TTF}]+[\mathrm{TCNQ}])+k_{-1}([\mathrm{TTF}^{+\cdot}]+[\mathrm{TCNQ}^{-\cdot}])\\ &= k_{-1}\{[\mathrm{TTF}^{+\cdot}]+[\mathrm{TCNQ}^{-\cdot}]+K([\mathrm{TTF}]+[\mathrm{TCNQ}])\},\end{aligned} \qquad (4)$$

where we used the relation $K=k_1/k_{-1}$. Thus, we can obtain a linear relation between the τ^{-1} and $[\mathrm{TTF}^{+\cdot}]+[\mathrm{TCNQ}^{-\cdot}]+K([\mathrm{TTF}]+[\mathrm{TCNQ}])$ values, the slope giving k_{-1}. Our results almost agree with the linear relation. The backward rate constant, k_{-1}, was determined to be $k_{-1}=(5.3\pm1)\times10^8$ M^{-1} s^{-1} from the slope. The forward rate constant, k_1, was obtained as $k_1=k_{-1}K=(1.2\pm0.5)\times10^7$ M^{-1} s^{-1}.

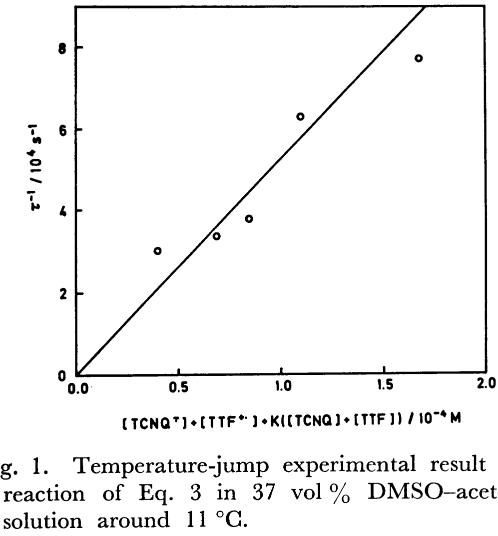

Fig. 1. Temperature-jump experimental result on the reaction of Eq. 3 in 37 vol % DMSO–acetonitrile solution around 11 °C.
Reciprocal of observed relaxation time of the signal due to $\mathrm{TCNQ}^{-\cdot}$, τ^{-1}, was plotted against concentration of $[\mathrm{TCNQ}^{-\cdot}]+[\mathrm{TTF}^{+\cdot}]+K([\mathrm{TCNQ}]+[\mathrm{TTF}])$. See text.

Discussion

First, let us discuss the experimental result on the chemical equilibrium data. It is of interest to compare the electron transfer reaction of Eq. 1 in acetonitrile with the reaction between *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) and TCNQ in the same solvent. Since TMPD is a strong electron donor, comparison of the electron donating strength between TTF and TMPD is significant. Yamagishi *et al.* examined the following electron transfer reaction between TMPD and TCNQ in acetonitrile:[8]

$$\mathrm{TMPD} + \mathrm{TCNQ} \rightleftharpoons \mathrm{TMPD}^{+\cdot} + \mathrm{TCNQ}^{-\cdot}, \qquad (5)$$

$$K' = \frac{[\mathrm{TMPD}^{+\cdot}]\,[\mathrm{TCNQ}^{-\cdot}]}{[\mathrm{TMPD}]\,[\mathrm{TCNQ}]}. \qquad (6)$$

In this system, no absorption due to the charge-transfer complex of TMPD–TCNQ was detected. The thermodynamic data on the chemical equilibrium of Eq. 5 were obtained spectrophotometrically as follows:

$$K' = (7\pm2)\times10^{-2} \text{ at } 25\,°\text{C},$$
$$\Delta H' = -17\pm4 \text{ kJ mol}^{-1},$$
$$\Delta S' = -71\pm21 \text{ J K}^{-1}\text{ mol}^{-1}.$$

Let us combine these data with those of the reaction between TTF and TCNQ of Eq. 1, and consider the following oxidation-reduction reaction between TTF and TMPD in acetonitrile solution:

$$\mathrm{TTF}^{+\cdot} + \mathrm{TMPD} \rightleftharpoons \mathrm{TTF} + \mathrm{TMPD}^{+\cdot}. \qquad (7)$$

The equilibrium constant of this reaction, K'', can be derived from

$$K'' = \frac{[\mathrm{TTF}]\,[\mathrm{TMPD}^{+\cdot}]}{[\mathrm{TTF}^{+\cdot}]\,[\mathrm{TMPD}]} = \frac{K'}{K}, \qquad (8)$$

where the relations of Eqs. 2 and 6 are used. We can also estimate the enthalpy change, $\Delta H''$, and the entropy change, $\Delta S''$, of Eq. 7. The results are:

$$K'' = (3.6\pm1.2)\times10 \text{ at } 11\,°\text{C},$$
$$\Delta H'' = \Delta H' - \Delta H = -10.0\pm5.4 \text{ kJ mol}^{-1},$$
$$\Delta S'' = \Delta S' - \Delta S = +1.7\pm38 \text{ J K}^{-1}\text{ mol}^{-1}.$$

Let us consider the following equation in the chemical equilibrium of Eq. 7.

$$\begin{aligned}&E_0(\mathrm{TTF},\ \mathrm{TTF}^{+\cdot}) - \frac{RT}{F}\ln\frac{[\mathrm{TTF}^{+\cdot}]}{[\mathrm{TTF}]}\\ &\quad = E_0(\mathrm{TMPD},\ \mathrm{TMPD}^{+\cdot}) - \frac{RT}{F}\ln\frac{[\mathrm{TMPD}^{+\cdot}]}{[\mathrm{TMPD}]},\end{aligned} \qquad (9)$$

where R and F are gas constant and Faraday constant, respectively, and $E_0(\mathrm{TTF},\ \mathrm{TTF}^{+\cdot})$ and $E_0(\mathrm{TMPD},\ \mathrm{TMPD}^{+\cdot})$ represent the oxidation potentials in the formation of the cation radicals of $\mathrm{TTF} \rightleftharpoons \mathrm{TTF}^{+\cdot} +$

e and $TMPD \rightleftharpoons TMPD^{+\cdot} + e$, respectively. The reactions are assumed to be reversible electrode reactions in acetonitrile solution. By use of Eq. 8 together with the K'' value, we obtain

$$E_0(\mathrm{TTF},\ \mathrm{TTF}^{+\cdot}) = E_0(\mathrm{TMPD},\ \mathrm{TMPD}^{+\cdot}) - 0.086\pm0.008\ \mathrm{V}. \tag{10}$$

As regards the oxidation potentials, the following results were reported for acetonitrile solution.[9]

$$E_0(\mathrm{TMB},\ \mathrm{TMB}^{+\cdot}) = E_0(\mathrm{TMPD},\ \mathrm{TMPD}^{+\cdot}) - 0.28\ \mathrm{V}, \tag{11}$$

$$E_0(\mathrm{DMPD},\ \mathrm{DMPD}^{+\cdot}) = E_0(\mathrm{TMPD},\ \mathrm{TMPD}^{+\cdot}) - 0.078\ \mathrm{V}, \tag{12}$$

where TMB and DMPD denote *N,N,N',N'*-tetramethylbenzidine and *N,N*-dimethyl-*p*-phenylenediamine, respectively, and $E_0(\mathrm{TMB},\ \mathrm{TMB}^{+\cdot})$ and $E_0(\mathrm{DMPD},\ \mathrm{DMPD}^{+\cdot})$ refer to the reversible oxidation potentials in the formation of the cation radicals, $TMB \rightleftharpoons TMB^{+\cdot} + e$ and $DMPD \rightleftharpoons DMPD^{+\cdot} + e$, in acetonitrile solution, respectively. Comparison of Eqs. 10—12 reveals that one-electron donating power of TTF is a little weaker than that of TMPD and is nearly equal to that of DMPD; the order of electron donating strengths is expressed by $\mathrm{TMPD} > \mathrm{DMPD} \gtrsim \mathrm{TTF} > \mathrm{TMB}$ in acetonitrile solution.

Let us discuss the ionization potential of TTF. In the oxidation-reduction equilibrium of Eq. 7, the observed enthalpy change, $\Delta H''$, is given by

$$\Delta H'' = I_\mathrm{p}(\mathrm{TMPD}) - I_\mathrm{p}(\mathrm{TTF}) + \Delta\Delta H_\mathrm{solv}(\mathrm{TMPD}^{+\cdot},\ \mathrm{TMPD}) - \Delta\Delta H_\mathrm{solv}(\mathrm{TTF}^{+\cdot},\ \mathrm{TTF}), \tag{13}$$

where $I_\mathrm{p}(\mathrm{M})$ is the ionization energy of the neutral molecule, (M=TMPD or TTF), in gas phase, and $\Delta\Delta H_\mathrm{solv}(\mathrm{M}^{+\cdot},\ \mathrm{M})$ is the difference of solvation energy between $\mathrm{M}^{+\cdot}$ and M in acetonitrile solution. Note that $I_\mathrm{p}(\mathrm{M})$ corresponds to an adiabatic ionization potential, since the reaction of Eq. 7 involves thermodynamic equilibrium. Thus, if we assume that the solvation energy, $\Delta\Delta H_\mathrm{solv}(\mathrm{TMPD}^{+\cdot},\ \mathrm{TMPD})$, is similar to $\Delta\Delta H_\mathrm{solv}(\mathrm{TTF}^{+\cdot},\ \mathrm{TTF})$, the difference of the ionization potentials between TMPD and TTF can be determined by means of Eq. 13. $I_\mathrm{p}(\mathrm{TMPD}) = 6.20$ eV was chosen as a standard value for the adiabatic ionization potential of TMPD.[9] By use of the value, $\Delta H'' = -10.0\pm5.4\ \mathrm{kJ\ mol^{-1}}$, the adiabatic ionization potential of TTF was estimated to be $I_\mathrm{p}(\mathrm{TTF}) = 6.30\pm0.06$ eV, which is a little larger than that of TMPD, but almost the same as that of $I_\mathrm{p}(\mathrm{DMPD}) = 6.28$ eV.[9] On the other hand, the vertical ionization potential of TTF has been determined to be 6.86 eV by photoionization method in gas phase.[10] The vertical energy of TTF exceeds the adiabatic energy by 0.56 eV. The vertical ionization potential of TMPD was found to be 6.75 eV by Nakato *et al.*[11] This is less than the 6.86 eV value of TTF by 0.11 eV, being in line with our finding that the adiabatic ionization potential of TMPD is also less than that of TTF by 0.1 eV.

The entropy change, $\Delta S''$, of the equilibrium of Eq. 7 is small. The reason for this is as follows. Although there is a significant entropy effect upon solvation of ion radicals in acetonitrile solution, the entropies due to the solvation of $\mathrm{TMPD}^{+\cdot}$ and $\mathrm{TTF}^{+\cdot}$ ions are almost the same and cancel each other, resulting in a small entropy change for the equilibrium of Eq. 7. There is some uncertainty in the value of $\Delta S'' = +1.7\pm38\ \mathrm{J\ K^{-1}\ mol^{-1}}$ obtained from $\Delta S' - \Delta S$ because of the accumulation of errors of $\Delta S'$ and ΔS. Thus, direct measurement of the equilibrium constant of Eq. 7 is desirable in order to obtain a more reliable value of $\Delta S''$ for the sake of confirmation.

The observed k_{-1} value of Eq. 3 in 37 vol% DMSO–acetonitrile solution is smaller than the $k_{-1} = (6\pm2)\times10^9\ \mathrm{M^{-1}\ s^{-1}}$ value for the reaction of $\mathrm{TMPD}^{+\cdot} + \mathrm{TCNQ}^{-\cdot} \rightarrow \mathrm{TMPD} + \mathrm{TCNQ}$ in acetonitrile solution.[8] This might be explained in terms of the difference in the solvents used. Ionic species such as $\mathrm{TTF}^{+\cdot}$ are solvated more strongly in DMSO than in acetonitrile. Since k_{-1} is for the electron transfer from ionic species to neutral molecules, the process involves release of solvation of the ionic species. Thus, the reaction in DMSO/acetonitrile requires more activation energy for k_{-1} than the reaction in pure acetonitrile, and the k_{-1} rate constant in the former solvent may be smaller than that in the latter. Except for this solvation effect, the reaction rates in the TTF/TCNQ system are almost of the same magnitude as those in the TMPD/TCNQ system. The difference in the molecular structures of TTF and TMPD may make a minor contribution to the kinetic difference.

Concluding Remarks

Let us consider the electronic states of solid TTF–TCNQ and TMPD–TCNQ complexes on the basis of the above discussions. In the TTF–TCNQ complex, there have been evidences for incomplete charge transfer, where 0.59 electron is transferred from TTF to TCNQ. Segregated columns composed of partially ionized TTF and TCNQ exist, giving rise to metallic properties in the TTF–TCNQ complex.[3] On the other hand, the TMPD–TCNQ complex shows almost ionic character of TMPD cation radical and TCNQ anion radical in the solid state. The X-ray analysis by Hanson,[12] ESR study by Kinoshita and Akamatu,[13] and measurement of the crystal spectra by Kuroda *et al.*[14] provide evidences for almost one electron transfer from TMPD to TCNQ. If the complete charge transfer occurs in the solid TMPD–TCNQ complex, the complex would show semiconductive properties of a Mott-Hubbard-type insulator. Actually, its electric conductivity has been reported to be as low as 10^{-6}—$10^{-8}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.[5]

Since the acceptor TCNQ is common, the difference between incomplete charge transfer in the TTF–TCNQ complex and almost complete charge transfer in the TMPD–TCNQ complex might depend mostly on the difference in adiabatic ionization potentials between TTF and TMPD. In view of the magnitude of the estimated adiabatic ionization potentials of $I_\mathrm{p}(\mathrm{TMPD}) = 6.20$ eV and $I_\mathrm{p}(\mathrm{TTF}) = 6.30\pm0.06$ eV, the TMPD–TCNQ complex might undergo ionization more easily in the solid state than the TTF–TCNQ complex.

McConnell *et al.* showed that, under certain conditions, a slight change in the ionization potential of donor or the electron affinity of acceptor might sharply discriminate ionic state from non-ionic state in solid charge-transfer complex.[15] Recently, Soos reexamined their argument to improve crystal binding energy and found that the $TTF^{+\gamma}$ $TCNQ^{-\gamma}$ complex might be charged with $\gamma \approx 0.35$, the $TMPD^{+\gamma}TCNQ^{-\gamma}$ complex, with $\gamma \approx 0.6$—0.7.[16] Although the estimated $\gamma \approx 0.35$ value in the TTF–TCNQ complex is lower than the experimental $\gamma \approx 0.59$ value, the slight difference in the ionization potentials between TMPD and TTF causes considerable difference in the degree of charge transfer between TMPD–TCNQ and TTF–TCNQ complexes.

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