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THE RATES OF THE REVERSIBLE ELECTRON-TRANSFER REACTION BETWEEN 7,7,8,8-TETRACYANOQUINODIMETHANE ANION RADICAL AND 2,3-DICHLORO-5,6-DICYANO-P-BENZOQUINONE IN ACETONITRILE

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The rates of the electron-transfer reaction between 7,7,8,8-tetracyanoquinodimethane anion radical and 2,3-dichloro-5,6-dicyano-p-benzoquinone in acetonitrile have been determined with a temperature-jump apparatus. The forward and backward rate constants are (4 ± 1) x $10^9 M^{-1}s^{-1}$ and (1 ± 0.5) x $10^4 M^{-1}s^{-1}$ at 15°C, respectively. Addition of 10 per cent water to acetonitrile decreases the forward rate constant by a factor of 100.

In a previous communication, it was shown that the rates of the reversible electron-transfer involving aromatic p-diamine cation radicals in water were determined using the technique of the temperature-jump method.$^{1)}$ We now want to report on the temperature-jump study of the electron-transfer reaction between 7,7,8,8-tetracyanoquinodimethane anion radical ($\mathrm{TCNQ}^{\overline{\cdot}}$) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) in acetonitrile.

Materials and Apparatus. Anion radicals were prepared by reducing neutral molecules by tetraethylammonium iodide ($\mathrm{NEt_4I}$) in acetonitrile. A trace of $\mathrm{NEt_4I}$ left unreacted in radical salts caused a serious error in determining the equilibrium constants. Thus the reduction was performed under the condition of about 1.2 times excess of TCNQ or DDQ over $\mathrm{NEt_4I}$. Rates were determined with a Union-Giken temperature-jump apparatus. This apparatus uses a coaxial cable of 200m length as capacitor.$^{2)}$ The temperature-rise was attained within 2 μsec for an acetonitrile solution containing about 10^{-3}M $\mathrm{NEt_4ClO_4}$.$^{3)}$

Equilibrium Measurements. When DDQ is added to an acetonitrile solution of $\mathrm{NEt_4^+TCNQ^{\overline{\cdot}}}$ containing a large excess of TCNQ and $\mathrm{NEt_4^+DDQ^{\overline{\cdot}}}$, the concentration of $\mathrm{TCNQ^{\overline{\cdot}}}$ is decreased by reaction (1).

$$\mathrm{TCNQ}^{\overline{\cdot}} + \mathrm{DDQ} \rightleftharpoons \mathrm{TCNQ} + \mathrm{DDQ}^{\overline{\cdot}} \qquad (1)$$

In this expression, the ion-pair formation of ion radicals is neglected.$^{3)}$ The equilibrium constant, K, which is expressed as

$$K = [\mathrm{TCNQ}][\mathrm{DDQ}^{\overline{\cdot}}] \;/\; [\mathrm{TCNQ}^{\overline{\cdot}}][\mathrm{DDQ}] \quad ,$$

is obtained by determining the concentration of each species as follows ; $[\mathrm{TCNQ}^{\overline{\cdot}}]$

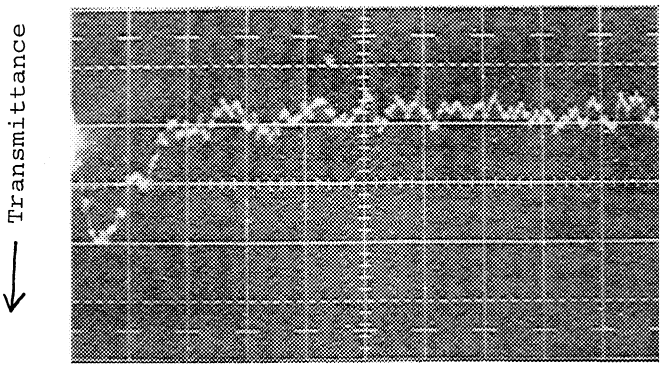

Fig. 1. The temperature-jump signal observed at 740nm in acetonitrile. [$\mathrm{TCNQ}^{\cdot-}$] 9.2×10^{-7}M, [DDQ] 1.5×10^{-5}M, [TCNQ] 3.84×10^{-3}M, [$\mathrm{DDQ}^{\cdot-}$] 1.73×10^{-3}M and [$\mathrm{NEt_4ClO_4}$] 4×10^{-3}M.

and [$\mathrm{DDQ}^{\cdot-}$] are obtained spectrophotometrically using the molar extinction coefficients, $\varepsilon_{840}(\mathrm{TCNQ}^{\cdot-}) = 43300$ and $\varepsilon_{595}(\mathrm{DDQ}^{\cdot-}) = 6300$, respectively. [TCNQ] is equated to the initial concentration, since it is present in large excess over other species. [DDQ] is calculated according to the following equation.

$$[\mathrm{DDQ}] = [\mathrm{DDQ}]_0 - [\mathrm{TCNQ}^{\cdot-}]_0 + [\mathrm{TCNQ}^{\cdot-}] \quad ,$$

where $[\mathrm{DDQ}]_0$ and $[\mathrm{TCNQ}^{\cdot-}]_0$ are the added concentration of DDQ and the initial concentration of $\mathrm{TCNQ}^{\cdot-}$, respectively. In the concentration ranges of $(0.8 - 9.0) \times 10^{-6}$M[$\mathrm{TCNQ}^{\cdot-}$], $(0.5 - 6.0) \times 10^{-6}$M[DDQ] at 4.8×10^{-4}M[$\mathrm{DDQ}^{\cdot-}$] and 5.7×10^{-3}M[TCNQ], constant values are obtained for K, confirming the fact that the reversible one electron-transfer takes place between $\mathrm{TCNQ}^{\cdot-}$ and DDQ as expressed in eq. (1). The equilibrium constant for acetonitrile containing 10 per cent water is determined in a similar way. The results are

$$K(\text{acetonitrile}) = (4.7 \pm 1.0) \times 10^5 \quad \text{at } 15^\circ\text{C} \quad ,$$

and

$$K(\text{acetonitrile, 10\% water}) = (1.0 \pm 0.5) \times 10^4 \quad \text{at } 15^\circ\text{C} \quad .$$

Rate Measurements. Figure 1 shows the temperature-jump signal observed at 740nm. The initial rapid increase of transmittance is due to the dissociation reaction of $(\mathrm{DDQ}^{\cdot-})_2$, since the dimer form of $\mathrm{DDQ}^{\cdot-}$, $(\mathrm{DDQ}^{\cdot-})_2$, has an absorption at this wavelength.3)

$$2\mathrm{DDQ}^{\cdot-} \rightleftharpoons (\mathrm{DDQ}^{\cdot-})_2 \quad .$$

The slower change of transmittance in Fig. 1 corresponds to the increase of the concentration of $\mathrm{TCNQ}^{\cdot-}$ due to the electron-transfer reaction (1). Under the assumption that the monomer-dimer equilibrium of $\mathrm{DDQ}^{\cdot-}$ does not affect the electron-

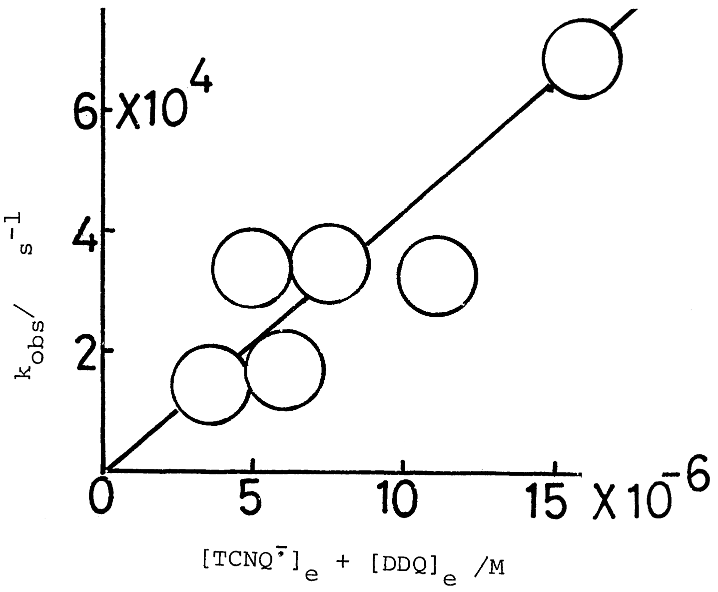

Fig. 2. The dependence of k_{obs} on the quantity, $[\text{TCNQ}^{\bar{\cdot}}]_e + [\text{DDQ}]_e$ in acetonitrile at 15 ± 2°C. [TCNQ] 1.66 - 5.84 x 10^{-3}M, $[\text{DDQ}^{\bar{\cdot}}]$ 1.73 - 0.33 x 10^{-3}M, and $[\text{NEt}_4\text{ClO}_4]$ 4 x 10^{-3}M.

transfer reaction (1), the pseudo first order rate constant, k_{obs}, for the slower relaxation,

$$-d\Delta[\text{TCNQ}^{\bar{\cdot}}]/dt = k_{obs}\Delta[\text{TCNQ}^{\bar{\cdot}}]$$

is expressed as below in terms of the forward and backward rate constants of reaction (1), $\overrightarrow{k}$ and $\overleftarrow{k}$, respectively.

$$k_{obs} = \overrightarrow{k}\left\{[\text{TCNQ}^{\bar{\cdot}}]_e + [\text{DDQ}]_e\right\} + \overleftarrow{k}\left\{[\text{TCNQ}]_e + [\text{DDQ}^{\bar{\cdot}}]_e\right\} \quad , \qquad (2)$$

where $[\ \ ]_e$ denotes the equilibrium concentration of each species after the rise of temperature. In the present system the equilibrium constant is so large that the second term in eq. (2) is negligible. The dependence of k_{obs} on the quantity, $[\text{TCNQ}^{\bar{\cdot}}]_e + [\text{DDQ}]_e$, is shown in Fig. 2. As expected from eq. (2), k_{obs} increases linearly with $[\text{TCNQ}^{\bar{\cdot}}]_e+[\text{DDQ}]_e$. $\overrightarrow{k}$ is obtained from the slope of the straight line in Fig. 2. $\overrightarrow{k}$ for acetonitrile containing 10 per cent water is determined in a similar way. The results are

$$\overrightarrow{k}(\text{acetonitrile}) = (4 \pm 1) \times 10^9 M^{-1}s^{-1} \qquad \text{at } 15 \pm 2°C \quad ,$$

and $\overrightarrow{k}$(acetonitrile, 10% water)

$$= (4.4 \pm 0.4) \times 10^7 M^{-1}s^{-1} \qquad \text{at } 15 \pm 2°C \quad .$$

The backward rate constants, $\overleftarrow{k}$, are calculated using the relation, $K = \overrightarrow{k}/\overleftarrow{k}$. The results are

$$\overleftarrow{k}(\text{acetonitrile}) = (1 \pm 0.5) \times 10^4 M^{-1}s^{-1} \qquad \text{at } 15 \pm 2°C \quad ,$$

and $\overleftarrow{k}$(acetonitrile, 10% water)

$$= (4 \pm 2) \times 10^{3} M^{-1} s^{-1} \quad \text{at } 15 \pm 2^{\circ}C \quad .$$

The rate constant of the electron exchange between TCNQ and $\text{TCNQ}^{\dot{-}}$ in acetonitrile, k_{ex}, has been recently determined by the ESR line-shape measurements.[4)]

$$\text{TCNQ}^{-} + \text{TCNQ}^{*} \rightleftharpoons \text{TCNQ} + \text{TCNQ}^{*-} \quad ,$$

$$k_{ex} = 3.3 \times 10^{9} M^{-1} s^{-1} \quad \text{at } 25^{\circ}C \quad .$$

Comparing $\overrightarrow{k}$(acetonitrile) obtained in the present work with k_{ex}, it is concluded that the electron-transfer from $\text{TCNQ}^{\dot{-}}$ to a neutral organic acceptor proceeds with nearly a diffusion-controlled rate constant as far as the free energy change of the reaction is less than zero.

On the other hand, the addition of 10 per cent water to acetonitrile decreases the forward rate constant by a factor of 100. Presumably, the formation of the hydrogen-bonding of $\text{DDQ}^{\dot{-}}$ with water molecules causes an additional energy barrier to the electron-transfer processes. A similar effect of water was previously observed for the electron exchange reaction between p-benzoquinone anion and its parent molecule in dimethylformamide. The present results demonstrate that the energy barrier due to the specific solvation like hydrogen-bonding is not lowered by the decrease of the free energy of the reaction.

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